Research on Aging Dielectric Properties and Physical Testing of Electric Vehicle Insulating Silicone Rubber under First Principles

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Abstract. Aiming at the aging problem of insulating silicone rubber for new energy vehicles, this paper studies the equations of the aging of silicone rubber and its dielectric properties based on first-principles calculations. First, through the analysis of the microscopic mechanism of silicone rubber aging, the equations of the aging of silicone rubber and the rupture of the molecular main chain is obtained. Then the equations of silicone rubber molecular length and dielectric constant are solved by density functional theory. Ultimate, a molecular chain scission model of silicone rubber was built, and the micro-dielectric relationship was extended to the macroscopic level. The equation of the norm molecular length of silicone rubber and the dielectric constant is obtained. It provides an important theoretical basis for the aging detection of insulating silicone rubber for new energy vehicles based on electromagnetic waves.

Keywords: New energy vehicles, aging of insulating silicone rubber, first principles, dielectric constant, molecular chain rupture.

1. Introduction
The layout of the new energy vehicle industry is becoming more and more complete, and the service life of electric vehicles has also become longer. This has led to the problems caused by the aging of the silicone rubber insulation materials used for the insulation of electric vehicles. Aging will reduce the insulation resistance, and there may be breakdown in rainy weather, which is not conducive to the healthy and stable operation of new energy vehicles [1-3].

As an insulating material, silicone rubber has been widely used in the field of electric power. Therefore, domestic and foreign electric power researchers have conducted a lot of research on the aging properties of silicone rubber. Literature [4] measured the hydrophobicity of silicone rubber by contact angle method and water spray method, and aging it Degree classification. The equations of the hydrophobicity and microstructure of the aging surface of silicone rubber are found by using infrared spectroscopy and energy dispersion analysis. Literature [5] analyzed the surface of corona-aged silicone rubber and concluded that the aging of silicone rubber would cause the breakage of the molecular backbone and branch chains. Literature [6] further explored the aging characteristics of silicone rubber...
by studying the conductivity-temperature characteristics of silicone rubber and its breakdown strength. Literature [7] studied the influence of electric field on the aging characteristics of silicone rubber through the mechanism of microstructure evolution at the atomic level. The above-mentioned scholars have studied the aging characteristics of silicone rubber from many aspects and angles, but the above methods all require silicone rubber aging detection under laboratory conditions, which cannot better adapt to the real-time sensing needs of new energy vehicles. The existing online non-contact The most direct method of detection is the wave method, and the most direct effect of dielectric materials on electromagnetic waves is the change of electromagnetic wave propagation loss caused by the change of the material's dielectric constant. Therefore, it is of great significance to study the change trend of the dielectric constant of silicone rubber materials with aging.

In response to this problem, this paper proposes to use first principles to study the equations of the aging of silicone rubber and its dielectric constant from the atomic level.

2.  Theory
Methyl vinyl silicone rubber (PDMS) is the base material that constitutes the silicone rubber composite insulating medium. Because it needs to be connected to the network for a long time in an outdoor environment, it will be affected by many factors, such as strong winds, ultraviolet rays, pollution, and high-voltage electric fields. Corona arc etc. [8]. These factors will have a certain impact on the microstructure of PDMS. For example, the high temperature environment will cause the material to undergo thermal cracking, thereby cutting the main chain; The main chain will also be cut, because substances such as acid, alkali and ozone have a certain probability of causing the Si-O bond to break; The molecular backbone is often directly cut off due to the impact of high-energy charged particles generated by electric sparks or discharges [9]. In summary, microscopically, PDMS's response to environmental aging is mainly manifested as molecular chain scission. As the working hours increase, the insulation performance and mechanical strength of PDMS will decrease due to the breakage of the molecular chain, which will bring great harm. However, due to the changes of microscopic molecules, some macroscopic electromagnetic parameters of PDMS have also changed, such as the increase of dielectric constant and so on. Therefore, the aging degree of PDMS can be accurately measured by electromagnetic waves according to the changes of these parameters.

Based on the above problems, this paper constructs a PDMS molecular model, uses density functional theory to solve the molecular dipole moment and polarizability, and then obtains the molecular permittivity. At the same-molecular chain length is used as an indicator of PDMS aging. Finally, the equation of the dielectric constant and molecular length of PDMS macroscopic materials was explored.

3.  Calculation and result analysis
By performing first-principles calculations on the molecular and atomic structure of PDMS, the microscopic mechanism of PDMS aging has been explored, and the relationship between the microscopic molecular structure of PDMS and material properties has been constructed. The calculation of the molecular model uses the DMol3 package in the MATERIAL STUDIO software. In order to explore the influence of PDMS chain length on electromagnetic performance, PDMS with various chain lengths was established. The unsaturated C atoms in the molecular model are all filled with methyl groups. In order to determine a reasonable molecular chain structure, the molecular structure was optimized after fixing the distance between the carbon atoms at both ends of the PDMS. By traversing all lengths, a stable structure with the lowest molecular potential energy is found. The B3LYP basis set is selected to describe the electronic interactions in PDMS molecules. Kohn-Sham wave function and Grimme correction are also used. At the microscopic level, the law between the change of PMVS molecular structure and the dielectric properties during the aging process was discussed. Then establish the equations of PMVS molecular microscopic parameters and material macroscopic parameters.
3.1. Model

PDMS is a high molecular weight polymer of methyl vinyl siloxane chain link and dimethyl siloxane chain link [10], and its molecular structure is shown in Figure 1.

![Figure 1. PMVS molecular structure.](image)

The methyl group contained in the PDMS molecular chain accounts for the majority, and the Vinyl group only accounts for 0.1%-0.3%. And the molecular weight of PDMS is about 700,000. The change of Vinyl group mainly affects the mechanical properties of PDMS, and has almost no effect on the dielectric constant [11]. Therefore, in order to facilitate the calculation of the simplified model, only the methyl group on the side chain is considered when the PDMS model is established.

Next, we will build a model based on DFT molecular calculations. The construction of the PDMS model is based on the short chain model of dimethylsiloxane. The price drop of multiple dimethylsiloxanes is used to simulate the electromagnetic performance effects of different molecular chain lengths. In the end, a total of 13 PDMS molecular models were built. They are 1-8, 10, 12, 14, 16, and 18 dimethylsiloxane chain segments, respectively. The PDMS model with 18 chain links is shown in Figure 2.

![Figure 2. The PDMS model with 18 chain links.](image)

3.2. Calculation of the equations of the PDMS molecular length and the dielectric constant

Materials Studio software is used to calculate the molecular chain dipole moment and polarizability, the set temperature is 298K, and the electric field is 0.001 a.u. After the first-principles calculation is completed, the dielectric constant is calculated by the Clausius-Mosotti method [12,13], the Relational equation is shown in equation (1), (2)

\[
\varepsilon_r = \frac{1 + 2K\rho}{1 - K\rho} \quad (1)
\]

\[
K = \frac{4\pi N_s \alpha'}{3M_w} \quad (2)
\]

Among them, \( \rho \) is the density of the material, \( M_w \) is the molar mass of the molecule, \( N_s \) is the Avogadro constant, \( \alpha' \) is the volume of the polarizability, and the equations of \( \alpha' \) and the polarizability \( \alpha \) is \( \alpha' = \alpha / 4\pi\varepsilon_0 \).

The finally obtained and fitted PDMS molecular length and dielectric constant trendline are shown in Figure 3.
As can be seen from the figure above, for PDMS molecular chain monomers, the relative dielectric constant of PDMS is very high when the molecular chain is very small, as the molecular chain length increases, the relative permittivity of PDMS gradually decreases, and finally tends to converge almost unchanged. It can be seen from the fitting function that when the molecular chain is infinitely long, the relative dielectric constant is stable at about 2.1.

3.3. Calculation of the equations of norm molecular length and dielectric constant

PDMS molecular length and dielectric constant trend lines need to be applied to macroscopic PDMS materials. After the PDMS material ages due to environmental factors, the molecular chain is randomly broken under the influence of compound factors, and its distribution is more complicated. Therefore, a solution model of molecular chain length distribution based on normal distribution is proposed. This model builds a large number of molecular chains through programs, and performs random chain scission based on normal distribution. Finally, the distribution of molecular chain length is obtained, and then the norm molecular length and dielectric constant equation of PDMS material are obtained through the trend obtained in Chapter 2.

First, the model molecular chain length is calculated by calculating the ratio of each chain link to the atomic mass and the PDMS molecular weight. The molecular weight of PDMS is greater than 700,000, and the molecular weight of a single link is 74, so the number of PDMS links is set to 10,000. The model initially generates 10,000 molecular chains. By default, there is no bond break in the side chain of the model during the simulation. At the same time, the norm numerator length is used to measure the degree of aging. Taken from 4000-10000, the step size is 500, that is, a total of 13 calculations have been performed. The aging factor of PDMS is diversified and random. This makes the fragmentation of PDMS molecules very random. And because the aging factors are relatively independent, the noise between the molecular chains has little effect. Therefore, approximately PDMS molecular chain breaks obey a normal distribution in position. At the same time, considering that too short chains are volatile and difficult to stay in the material, small molecules with chain lengths below ten are automatically eliminated during the model operation. The solution process of the molecular chain length distribution solution model is shown in Figure 4.
Figure 4. Molecular chain break model solution flowchart.

Solve the molecular chain length distribution solution model, and get the PDMS molecular chain length distribution under different \( L_u \) is shown in Figure 5.

![Molecular chain length distribution](image)

Figure 5. Molecular chain length distribution.

Some characteristics can be seen in Figure 5. When the norm molecular length is lower, the ratio of molecular chain lengths between 0-9900 is greater, and the proportion of molecular chain lengths between 9900-10000 is smaller, and vice versa. Among them, the number of molecular chains with a length of 5000, that is, about half of the total length, is the largest, and the proportion of the number will gradually decrease as the length increases and decreases.

Substitute each curve in Figure 5 into the equation of PDMS molecular length and dielectric constant obtained by the equation shown in Figure 3. Obtain the respective dielectric constants of different molecular chain lengths, and combine their respective quantities to illustrate the relative dielectric
constants. After the averaging length obtained by adding the standard molecular and macroscopic dielectric constant PDMS regular curve as shown in Figure 6.

![Figure 6. Relationship between norm molecular length and dielectric constant.](image)

By observing Figure 6, it can be concluded that as the aging degree of PDMS is proportional to the breakage of the molecular chain chemical bonds, the overall relative permittivity changes. As the length of the norm molecule becomes smaller and smaller, the rate of change of the dielectric constant gradually increases. This is because there are more and more small molecular chains in PDMS. According to the previously fitted PDMS molecular length and relative permittivity changes, the fewer molecular chains, the greater the change in permittivity. Therefore, when the entire molecular chain of PDMS is less than a certain length, the relative permittivity change rate is higher. However, from the perspective of the entire curve, the overall change of PDMS is also within a limited range. This is because the chemical bonds of the overall PDMS molecules are also within a limited range under the influence of aging factors.

It is worth noting that the relative permittivity calculated by molecular simulation technology in this article will deviate from the true relative permittivity of PDMS molecules in actual conditions. In the simulation calculations in this article, the calculation and multi-scale problems will cause deviations. Errors, and the construction of molecular chain models is mainly based on the increase of molecular chain links, that is, the main observation is the influence of the change of length on the relative dielectric constant, and the deformation of the molecular chain, bending and other shape changes are not considered for the time being. In reality, the entire PDMS is made of tens of thousands of molecular chains that are entangled and cross-linked. During the aging process, the PDMS will be subject to some electric field, temperature, mechanical stress and other factors, which will induce some bending of the molecular chain, Not just a simple straight chain. Although there is a gap between the dielectric constant simulated by computer theory and the actual one, the equation trend of the relative dielectric constant and the norm molecule length is basically the same. Based on this, the change in the relative permittivity of the PDMS as a whole can be used as a characteristic quantity to establish the equations of the microscopic molecular chain breakage and the macroscopic relative permittivity of the PDMS during the aging process. Contribute to the follow-up research progress of PDMS non-contact detection based on electromagnetic waves.
4. Conclusions
(1) Through the microscopic analysis of PDMS aging, it is found that the broken link will change the
dielectric constant of the PDMS material.
(2) Perform molecular simulation calculations on methyl vinyl PDMS to obtain the molecular dipole
moment and polarizability, then obtain the molecular dielectric constant, and finally through the solution
of molecular chains of different lengths, the relative dielectric constant and The equations of the length
of the molecular chain shows that for a single molecule, with the growth of the molecular chain, its
relative permittivity begins to gradually decrease in the form of a power series, and finally tends to
converge.
(3) A simulation model of molecular length distribution based on normal distribution is proposed.
The calculation shows that the dielectric constant of PDMS gradually increases with the decrease of the
standard molecular length, and the growth rate of the dielectric constant gradually increases.
This paper has obtained the equations of the average analytical chain length of PDMS and the
dielectric constant through research, which can provide important basis and guidance for the subsequent
detection of the aging of PDMS for new energy vehicles based on electromagnetic waves.

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