Aging Simulation of Epoxy Resin Based on Molecular Dynamics Analysis

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Abstract. Epoxy resin is the main insulation material for dry-type insulation equipment and is widely used in power systems. To explore the insulation aging process and detection method of insulation aging at the molecular level, molecular dynamics modelling and simulation of epoxy resin is needed. This paper studies the model construction method and model optimization processing method of epoxy resin, and based on this, a simulation study of epoxy resin aging based on molecular dynamics simulation is carried out.

1. Introduction

Dry-type insulation equipment is a common device in the power grid, and generally includes dry-type transformers, dry-type reactors, and dry-type transformers. As the main insulation of dry-type insulation equipment, epoxy resin directly determines whether the dry-type equipment can operate normally. Although there is sufficient margin for mechanical and electrical characteristics in the design of epoxy resin insulation, some congenital local defects such as bubbles, cracks, and electrode burrs will always form during the manufacturing process due to accidental factors. Accelerated insulation aging affects the service life of dry-type insulation equipment. Therefore, it is necessary to monitor and evaluate the insulation status of dry-type insulation equipment in order to timely maintain dry-type insulation equipment and ensure that the power grid can operate safely and reliably. [1]

At present, the insulation state detection methods of epoxy resin mainly include traditional measurement methods such as partial discharge, electrical and dielectric properties. These detection methods are mostly indirect reflections of the insulation state. It is impossible to establish a direct relationship between the state characteristic parameters and the degradation process of the epoxy resin, leading to the unclear mechanism of the degradation process of dry-type insulation equipment and the failure of unknown causes. Hidden defects in discharge, inaccurate remaining life assessment, etc. [2]
The aging process of the insulating material is actually a slow chemical reaction process. In the chemical reaction process, the change of the reactant can often be reflected by the change of energy. The parameter of activation energy represents the energy barrier to be overcome by the chemical reaction. It directly reflects the difficulty of the insulation material cracking and can characterize the essential properties of the insulation aging process. Therefore, it is necessary to explore the aging process of epoxy resin insulation and its detection method at the molecular level.

From the micro perspective, this project explores the aging process of dry insulation equipment / epoxy resin systems under the combined thermal, electric, and electrical and thermal effects based on molecular dynamics simulation methods, and obtains electrical and thermal conditions for the environment. The effect of the oxygen resin system is used to calculate its energy change. Based on the element tracer method, quantitatively study the defect detection and aging assessment technology of dry insulation equipment from a micro perspective, which not only helps to further reveal the aging process and degradation mechanism of dry insulation equipment, but also reliably evaluates its operating status it has important practical guiding significance and engineering application value.

2. Molecular dynamics simulation principle

The reaction force field used in this research project is ReaxFF. The ReaxFF reaction force field introduces the interaction between Van der Waals force \( E_{vdw} \) and Coulomb force \( E_{coul} \). The current moment is determined by calculating the relationship between bond orders (BO), bond energy, and bond distance. The connectivity between any two atoms, which characterizes the breaking and generation of chemical bonds between atoms. [3, 4]

In the model of the ReaxFF reaction force field, the concept of atom type in the classical field does not exist, and there is no connectivity between the atoms in the system. Assuming the distance between atom \( i \) and atom \( j \) at the current moment is \( r_{ij} \), the \( BO_{ij} \) between these two atoms can be expressed as:

\[
BO_{ij} = \exp \left[ p_{bo1} \cdot \left( \frac{r_{ij}}{r_0^\sigma} \right)^{p_{bo2}} \right] + \exp \left[ p_{bo3} \cdot \left( \frac{r_{ij}}{r_0^\sigma} \right)^{p_{bo4}} \right] + \exp \left[ p_{bo5} \cdot \left( \frac{r_{ij}}{r_0^\sigma} \right)^{p_{bo6}} \right]
\]  

(1)

Where \( r_0^\sigma \) is the atomic parameter and \( p_{bo} \) is the bond parameter.

Therefore, the ReaxFF reaction position is based on the expression of BO. Based on this, the interaction between atoms is expressed as a function of BO, and the distinction is calculated based on complex functions such as bond, angle, dihedral angle, common Yoke, Coulomb, Van der Waals, and adjustment terms, etc., the system interaction energy expression is:

\[
E_{system} = E_{bond} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{tor} + E_{con} + E_{vdw} + E_{coul}
\]  

(2)

The energy in the formula are respectively the bond energy term, the valence angle energy term, the overcoordinated energy correction amount, the twist energy term, the penalty energy term, the non-bonded Van der Waals force action term, the molecular energy binding action term, and the Coulomb action term.[5]

Based on the above ReaxFF force field theory, the reaction molecular dynamics simulation process is shown in Figure 1. The main process is:

1. Enter the initial configuration of the molecular simulation system, and set the simulation temperature \( T \), the total simulation time \( t_s \) and the simulation step \( \Delta t \);
2. Calculate the distance \( r_{ij} \) between any two atoms by the coordinate position of each atom \( (X_{i}, Y_{i}, Z_{i}) \) at time \( t_i \), and the ReaxFF reaction force field;
3. Calculate the inter-atomic bond order function BO at time \( t_i \) according to formula (1). This simulation refers to the literature and selects BO=0.3 as the criterion for chemical bond rupture and generation (when \( BO_{ij} \geq 0.3 \), chemical bond formation is considered);

4. \( \text{ReaxFF} \) calculates the system material distribution at time \( t_i \) and calculates the system energy \( E_{\text{system}} \);

5. Judge whether \( t_i = t_s \) is satisfied. If it is satisfied, end and output the simulation result; otherwise, calculate the coordinate of each atom \((X_{i+1}, Y_{i+1}, Z_{i+1})\), repeat the above calculation until \( t_i = t_s \), and end the simulation calculation.

Figure 1. Molecular dynamics simulation flow chart of the reaction.

Compared with classical molecular mechanics and quantum chemistry methods, \( \text{ReaxFF} \)-based reaction molecular dynamics simulation does not need to fix the connectivity between atoms in the molecule. The chemical bonds between atoms in the simulation can be freely broken and generated, so it can handle dynamic chemical reaction processes; The simulation speed is fast, which can handle the chemical reaction process in larger systems and condensed phases. In addition, the parameters of the \( \text{ReaxFF} \) reaction position are derived from a large amount of quantum mechanical training data, and have very high accuracy.

3. Model Construction of Epoxy Resin Crosslinking System

Epoxy resin molecular model for dry-type insulation equipment. Diglycidyl Ether of Bisphenol a (DGEBA) was used as the epoxy resin monomer, and 3, 3’-diaminodisulfone (33DDS) was used as the curing agent. The structure and molecular model are shown in Figure 2 and Figure 3, respectively. [6]
In the figure, $n$ is the polymerization degree. In order to simplify the calculation process, the polymerization degree of the epoxy resin monomer is set to 0 when the model is built.

The software commonly used in molecular dynamics simulation includes: NAMD, GROMA CS, CHARMM, AMBER, LAMMPS, etc. These molecular dynamics software have their own characteristics and have a wide range of applications. The simulation software used in this research project is AMS. As the world's earliest density functional software, since its birth in the early 1970s, AMS has been developing rapidly in terms of computing theory, methods, computational analysis tools, and graphical user interfaces.

In the AMS environment and the ReaxFF reaction force field, the optimized parameter settings for the molecular structure of the epoxy resin and the structure of the curing agent are shown in Figures 4 and 5.
Figure 4. Molecular structure optimization parameters of epoxy resin

Figure 5. Molecular structure optimization parameters of 33DDS

4. Epoxy Insulation Model Processing Method
Based on the microstructure simulation software of Amsterdam Density Functional (ADF), based on the molecular structure of monomer and curing agent, and referring to the cross-linking curing method proposed by Wu C., 50 DGEBA and 25 33DDS were established at 31.28Å×31.28Å×31.28Å. In the periodic cubic unit cell, a molecular model of cross-linked epoxy resin was constructed.

Figure 6 shows the general structure of a common cured epoxy resin. Undertake the curing simulation results, remove the free small molecules and the combination of hydroxyl radicals and hydrogen bonds in the reaction system, and further obtain a cross-linked cured epoxy resin model, as shown in Figure 7, for the micro-dynamic simulation of the subsequent degradation process.

Figure 6. General structure of common cured epoxy resin
In order to make the model fit the actual situation better, the density of the model needs to be optimized. The built model is imported into simulation software such as \textit{ADF}, \textit{LAMMPS} and the \textit{ReaxFF} is selected as the force field for molecular simulation. It is widely used in carbon-based systems and can accurately describe material properties. First, the energy is minimized using the conjugate gradient method. Second, the pressure is set to 1 standard atmospheric pressure and the temperature is 300K under the NVT system, which simulates 200,000 steps, that is, 50ps.

Subsequently, the energy is minimized using the conjugate gradient method under the NVT ensemble of constant particle number ($N$), constant volume ($V$) and constant temperature ($T$). And constant temperature ($T$) under the NPT ensemble to optimize the model density to ensure its structural stability.

In practice, the density of epoxy resin after curing is generally 1.1~1.2g/cm$^3$, and the final density of epoxy resin curing system after energy minimization is 1.2935g/cm$^3$. There is a certain error compared with empirical data, which is mainly due to curing. The degree is different, the error is within the allowable range.

5. Conclusion
This paper analyzes the molecular dynamics simulation principle, and proposes a molecular dynamic modeling method of epoxy resin insulation material based on AMS environment and \textit{ReaxFF} reaction force field. Furthermore, the optimized processing method of the model is analyzed, and the validity of this method in analyzing the insulation aging of dry equipment is verified.

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