Micro-mechanism study on synergistic degradation of the oil-paper insulation with dibenzyl disulfide, hexadecyl mercaptan and benzo thiophene

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Abstract
In recent years, there have been many cases of transformer failures caused by corrosive sulfides. At present, research mainly focuses on the single sulfide dibenzyl disulfide, but few research on multiple sulphur or the oil-paper hybrid insulation. In this study, three typical sulfides dibenzyl disulfide, hexadecyl mercaptan and benzo thiophene were selected to form seven sulfide-oil-paper models. Then relaxation calculations were carried out, and through molecular dynamics simulation, the synergistic effect of different sulfides on the properties of insulating paper and insulating oil was discussed. Results show that the coexistence of the three sulfides has the most severe weakening on the mechanical properties of cellulose, and it also causes great damage to hydrogen bonds. Hexadecyl mercaptan has a weaker effect on hydrogen bond destruction, but it will greatly aggravate the cellulose chain movement. The viscosity of insulating oil is generally increased by the influence of sulfide. Hexadecyl mercaptan is the main factor affecting the viscosity. Thiophene has little effect on the viscosity, active protection technology on sulphur corrosion.

1 INTRODUCTION

Transformers are the key equipment for energy transmission and conversion in power systems, and are of great significance for the safe and stable operation of the entire power grid. Mineral insulating oil is commonly used in transformer oil, which is mainly refined from petroleum. In addition to carbon and hydrogen, it also contains sulphur, nitrogen, oxygen and metal elements. The sulphur element mainly exists in the form of mercaptan, thioether, sulphur, thiophene and disulfide [1, 2]. In recent years, there have been many transformer insulation failures caused by corrosive sulfides in many countries. The insulation failures caused by sulphur corrosion have seriously affected the safe and stable operation of oil-immersed power transformers [3, 4]. With the increasing accidents of transformer insulation failure caused by sulphur corrosion, how to effectively reveal the internal mechanism of sulphur corrosion phenomenon, and then to put forward a technology to prevent sulphur corrosion failure has become one of the key issues urgently to be resolved in the power sector.

At present, it is generally believed that dibenzyl disulfide (DBDS) is the most important corrosive sulfide. Scholars have conducted a lot of experimental studies around the influence of DBDS on oil-paper insulation. The corrosion mechanism of DBDS was first proposed in the literature [5]. This result was verified by others, and the above-mentioned reaction mechanism was analysed during thermal ageing [6]. Literature [7] further tested the concentration changes of DBDS, dibenzyl sulfide (DBS) and diphenylethane (BiBZ) in oil before and after ageing through gas chromatography–mass spectrometry (GC-MS) and solid-phase extraction (SPE) technology. They verified the aforementioned research results and found that DBDS can react completely in different oxygen concentration, as well as the reaction process does not need oxygen to participate. Regarding the concentration of sulphur corrosion, experiments also have shown that even the DBDS concentration as low as 1 mg/L will cause sulphur corrosion, and the content of most dissolved gases in the oil and the acid value in the oil would increase [8]. Scholars have also carried out a lot of research work on the influencing factors of corrosive
sulfides [9–11], and find that the external conditions such as electric field [9], oxygen [10], temperature [11] and other factors also have an important influence on the formation of sulfides. Besides DBDS, mercaptan, thiophene and other substances are also found to be corrosive. Literature [12] tested the corrosiveness of various sulfides in transformer oil and found that the sulphur-containing components such as mercaptans, sulfides, thioether, and sulfone compounds all have a certain degree of corrosion. Moreover, different sulfides may transform into each other under certain conditions, among which DBDS has a more diffuse nature and may decompose to another corrosive disulfide [13]. The study in literature [14] produce other types of sulfides under certain conditions. Captans, sulfides, thioether, and sulfone compounds all have a way as first oxidised in oil to form cuprous oxide (Cu$_2$O) and dissolved in insulating oil, and then Cu$_2$O would react with mercaptans (RSH) to produce copper mercaptanate (CuSH) which could be dissolved in oil [16]. Some scholars have analysed the ageing samples of transformer oil by using gas chromatography-sulphur chemiluminescence detector [17]. The results showed that the reaction mechanism in the presence of a single mercaptan and multiple mercaptans is different, and different mercaptans will have cross-linking reaction. Literature [18] tested the influence of thiophene on thermal ageing of transformer oil-paper insulation system, and found that although thiophene is relatively stable, it may be converted to other corrosive sulphide in the late ageing period under long-term high temperature environment, resulting in a sharp increase in the acid value in the oil and thus causing corrosion of the copper sheet. However, the micro-level explanation of the thiophene mechanism still need further exploration. For the impact of sulphur on oil-paper insulation, literature [19] tested the influence of DBDS on the insulation performance of transformer oil-paper. Based on the dielectric response of oil-paper insulation at high temperature by using frequency-domain spectroscopy as well as the measurement of polarisation and depolarisation current, the following conclusion was drawn. In the process of forming Cu$_2$S, the polarisation current amplitude increased significantly, and the thermal breakdown of insulating paper occurred. Experiments also showed that during the thermal ageing of paper-covered copper wires and bare copper wires in insulating oil, the dielectric properties of oil-paper insulation were changed due to copper sulphur corrosion, and the electrical breakdown strength of oil-paper insulators was greatly reduced due to copper sulphide deposition [20]. Literature [21, 22] tested the influence of DBDS, dibenzyl sulfide (DBS) and dodecyl mercaptan (DDM) on the oil-paper insulation, and found that the increase of sulphur compounds would lead to a significant decrease in the polymerisation degree of insulating paper, and the corrosive sulphur addition will accelerate the cellulose pyrolysis process of insulation paper. What's more, the effect of DBDS and DDM on thermal ageing of oil-paper insulation system is the strongest. The ageing characteristic parameters such as furfural, moisture content, acid value has obvious changes, and the copper corrosion degree is more serious.

Due to the limitations of the macro experimental technology, it is difficult to explore the energy changes of micro-chemical bonds inside the oil-paper insulation system with experimental methods. The computer simulation methods based on molecular dynamics and quantum mechanics which have emerged in recent years, which can measure microscopic mechanical modulus and explain the deterioration of oil-paper insulation system on a microscopic scale. Literature [23] first proposed a model of cellulose and other isomers that is similar to the experimental data and can be applied to molecular simulations. Literature [24] calculated the density, lattice parameters and chain conformation parameters of cellulose crystals under the conditions of 300 K through simulation, and found that when the calculation range was small, the radial distribution function (RDF) of cellulose $\beta$ crystals and amorphous regions was relatively close. Glass transition temperature is an important parameter in the amorphous region of cellulose. Subsequently, the molecular simulation technology was used to obtain a glass transition temperature of 500 K [25], and some scholars studied on the bending and the winding of cellulose molecular chains at different temperatures. It was found that the relaxation rate of cellulose molecular bending was closely related to temperature [26]. Some researchers simulated the behaviour of the microcellulose structure at 500 K and found significant differences from the traditional hydrogen bond structure of cellulose [27]. Literature [28] studied on the migration process of water molecules in the oil-paper insulating system, and obtained the interaction energy between the water molecules and the oil-paper insulating medium. The multiple sulfide model of DBDS and hexadecyl mercaptan was used to conduct molecular dynamics simulations, exploring on the mechanical properties and energy changes of cellulose. It was found that when the same proportion of DBDS and hexadecyl mercaptan were added, the tensile strength and the polymerisation degree of insulating paper decreased significantly more than a single sulfide [29, 30], indicating that the synergistic degradation effect of multiple sulfides on insulation paper was greater than the same amount of single sulfides. However, most of the current research work only considers the effects of DBDS and mercaptan, and the analysis of the effects of thiophene and other sulfides on the oil-paper insulation properties has not been carried out. In addition, the existing simulation model only incorporates the effect of insulating paper and does not consider the effect of insulating oil. The actual transformer is an oil-paper hybrid insulation system, therefore it is necessary to establish an oil-paper hybrid model to analyse the mechanism of sulfide impact on the entire oil-paper insulation system.

In this study, seven sulfide-oil-paper models composed of three typical sulfides (DBDS, hexadecyl mercaptan and benzo-thiophene) were established by using the Materials Studio software to explore the synergistic mechanism of sulfide on oil-
paper insulation system. By analysing the molecular dynamics characteristics, the energy and hydrogen bonding at different sulfide concentrations, the effect of sulfides on oil-paper insulation performance and the law of energy change were revealed from the molecular level.

2 | SIMULATION MODEL AND CALCULATION PROCESS

2.1 | Model building process

2.1.1 | Sulfide model

DBDS is currently recognised as the most corrosive sulfide, consisting of two sulphur atoms connecting two benzyl groups, with the molecular formula \( C_{13}H_{14}S_2 \). Hexadecyl mercaptan, also known as 1-hexadecyl mercaptan, has a molecular formula of \( C_{16}H_{34}S \), and its sulphur atom at the end of the chain leads to higher activity. Since the mercaptan group has a lone pair of electrons, it could easily interact with the empty orbits of copper atoms to corrode the copper sheet [31]. Benzothiophene is formed by the condensation of thiophene and benzene ring, and its molecular formula is \( C_9H_8S \). It usually has low activity, however literature [18] have shown that long-term high temperature conditions would cause it to undergo chemical changes and become corrosive. Therefore, the three typical sulfides, DBDS, hexadecyl mercaptan and thiophene were included in the simulation model. The sulfide model is shown in Figure 1 below, where the black is carbon atoms, the yellow is sulphur atoms and the white is hydrogen atoms. In the model, the net mass (relative atomic mass) of DBDS is 246.4, the net mass of hexadecyl mercaptan is 258.5, and the net mass of benzothiophene is 134.2. The length of the carbon-carbon single bond or double bond is 1.54 Å, the carbon-hydrogen bond length is 1.14 Å, the carbon–sulphur bond length is 1.81 Å, and the sulphur–sulphur length is 2.08 Å.

2.1.2 | Sulfide-oil model

The mineral oil is a mixture composed of 60% alkane, 10%~40% cycloalkane and 5%~15% aromatic hydrocarbon. The average number of carbon atoms of hydrocarbon molecules is between 15 and 23. Therefore this simulation included an oil model composed of 60 \( C_{20}H_{42} \) molecules, 30 \( C_{20}H_{38} \) molecules and 10 \( C_{20}H_{36} \) molecules. The oil density was set to 0.9 g/cm³.

Subsequently, the ‘Amorphous cell’ module was used to add different concentrations of different sulfides into the established oil model. At the same time, the periodic boundary conditions (PBC) was adopted in the construction process. As this can ensure that the atoms at the boundary are evenly stressed, so the influence of the boundary effect can be ignored. Each of the seven groups of models was divided into three groups according to the number of sulphur atoms. When the concentrations are 2.58%, 5.15% and 7.73%, the total number of sulphur atoms in the control model is 6, 12 and 18 respectively. According to this method, 22 sulfide-oil models were constructed, and then geometric optimisation was performed to find the lowest point of the energy of the system. The addition of sulfides is shown in Table 1 below, and the model after geometric optimisation is shown in Figure 2. The model has a density of 0.9 g/cm³ and contains 100 hydrocarbon molecules, a total of 2000 carbon atoms and 3920 hydrogen atoms. The unit cell size is 37.23 × 37.23 × 37.23 Å³.

2.1.3 | Cellulose model

The basic unit of insulating paper is cellulose molecules, and cellulose is a linear natural macromolecular polysaccharide formed by \( \beta-1,4 \)-glycosidic linkages of glucose, the chemical formula is \((C_6H_{10}O_5)_n\) where \( n \) represents the degree of polymerisation (DP) and the DP of the cellulose molecule represents the number of glucose monomers in the molecule. The tensile strength of the paper has a good correlation with the DP, so the DP can be used to accurately and reliably reflect the ageing degree of cellulose. The structure of cellulose glucoclobiose monomer is shown in Figure 3 below.

The interior of cellulose is divided into 30% amorphous area and 70% crystalline area. The cellulose molecules in the
TABLE 1 Sulfide content addition in different oil-paper models

| Models                  | Sulfide Content 2.58% | Sulfide Content 5.15% | Sulfide Content 7.73% |
|-------------------------|------------------------|------------------------|------------------------|
|                         | DBDS       | Mercaptan | Thiophene | DBDS       | Mercaptan | Thiophene | DBDS       | Mercaptan | Thiophene |
| DBDS                    | 3          | –         | –         | 6          | –         | –         | 9          | –         | –         |
| Mercaptan               | –          | 6         | –         | –          | 12        | –         | –          | 18        | –         |
| Thiophene               | –          | –         | 6         | –          | –         | 12        | –          | –         | 18        |
| DBDS + mercaptan        | 2          | 2         | –         | 4          | 4         | –         | 6          | 6         | –         |
| DBDS + thiophene        | 2          | –         | 2         | 4          | –         | 4         | 6          | –         | 6         |
| Mercaptan + thiophene   | –          | 3         | 3         | –          | 6         | 6         | –          | 9         | 9         |
| DBDS + Mercaptan + thiophene | 1  | 2     | 2         | 2          | 4         | 4         | 3          | 6         | 6         |
| Control group           | –          | –         | –         | –          | –         | –         | –          | –         | –         |

Abbreviation: DBDS, dibenzyl disulfide.

FIGURE 2 Sulfide-oil model

crystalline area are closely arranged, and the properties and structure are relatively stable, it will not be easily changed by external influences. However, the amorphous region has disordered structure, the chemical bonds are easy to break and mechanical properties are easy to change. Therefore, the ageing research was generally concentrated in amorphous region. Literature [32] used a box with periodic boundaries to construct a cellulose long chain with a DP of 10, 20 and 40 to perform molecular dynamics simulations on the amorphous region of cellulose. The study found that the cellulose chains of different lengths had similar physical and chemical properties and were not affected by the DP in the model. At the same time, they can successfully measure the parameters such as cellulose energy and density. Some scholars constructed a cellulose chain with a DP of 20 to simulate the amorphous region of cellulose. After the mechanical simulation analysis, the results were found basically consistent with the experimental results [17, 33]. Therefore, the molecular simulation in this study adopted 10 cellulose chains with a DP of 20 to form the cellulose model.

First, the glucobiose monomer was built, as shown in Figure 4, where the black is carbon atoms, the red is oxygen atoms, and white is hydrogen atoms. Then the building polymer function was used to splice and form the cellulose chains, where the torsion is the default 180°, the chain length is 10, the number of chain is 10. Then the amorphous cell module was used to build its amorphous model, using the tetragonal method when building to maximise the contact area with the oil model under the same volume. The cellulose density was set 1.5 g/cm³. After the construction was completed, the energy minimisation step was performed. The resulting cellulose model is shown in Figure 5, and the repeating part of the carbon chain is marked pink. The model has a density of 1.5 g/cm³, which contains 1200 carbon atoms, 2020 hydrogen atoms, and 1000 oxygen atoms. The unit cell specification is 39.52 × 39.52 × 23 Å³, and the net mass is 3244.84.

2.1.4 Sulfide-oil-paper model

Scholars have used the build layer module to construct the oil-paper model, and obtained the experimental data in line with expectations [34]. Therefore, the oil-sulfide model shown in Figure 2 and the cellulose model shown in Figure 5 were constructed into the sulfide-oil-paper mixed model using the build layer module, as shown in Figure 6. Then the model was chosen with crystal for the construction method, default for the section property, and a fixed volume for the construction method. The average value of the original lattice was adopted
2.2 Calculation process

The basic method of molecular dynamics is to solve the Newton's second law for each particle:

\[ \vec{F}_i = m_i \vec{a}_i = m_i \frac{d^2 \vec{r}_i}{dt^2} = -\frac{\partial V}{\partial \vec{r}_i} \quad i = 1, 2, 3, \ldots, N \quad (1) \]

In the formula, \( m_i \) is the particle mass, \( \vec{a}_i \) is the particle acceleration, and \( \vec{r}_i \) is the particle displacement. In order to prevent the occurrence of very large mechanical effects in the early stage of the simulation, the starting position of the atom should be kept as low as possible. Therefore, for the complex systems composed of large molecules appear in this simulation, the energy minimisation steps are required to keep the system energy at the lowest point. The relaxation is a process in which the system is kept under certain conditions, allowing the particles in it to move sufficiently to maintain a relatively balanced state in the system. The spatial coordinates of a given molecule are not necessarily at the most stable position of the molecular force field. Therefore, each atom is not in an equilibrium state, which causes the energy of the system to be relatively high, so the model is subjected to a relaxation process of 20 ps.

The more commonly used ensembles in simulation process are isothermal–isobaric ensemble (NPT) and canonical ensemble (NVT). The NPT ensemble can control the pressure (P) and temperature (T) unchanged. It is allowed to change the unit cell vector and adjust the pressure by changing the volume, and the characteristic of the NVT ensemble is that the volume (V) and temperature (T) of the system remains unchanged. Since the side length of the lattice can be changed under the NPT ensemble, the position of the atom can be better relaxed. Therefore, here the relaxation calculations were performed under the NPT ensemble to obtain a stable state. After obtaining the volume under a given temperature and pressure environment, the NVT ensemble under this volume was used to perform molecular dynamics calculations at 100 ps. The NVT ensemble could provide advantage of less perturbation of the trajectory, due to the absence of coupling to a pressure bath.

In the above steps, the Andersen method was selected in the temperature control process, which can randomise the velocities of all atoms during a predefined collision period, and couple the system to the thermal bath by changing the random force of the kinetic energy of atoms or molecules. As for the pressure control method of NPT ensemble, the Berendsen pressure control method can obtain good results in isotropic system and can independently change the parameters of cell in three directions. Therefore, the Berendsen method was chosen, which is to couple the system to the virtual pressure bath to maintain the pressure at a specific target.
According to the standards IEEE Std 1276-2020, the top oil temperature should not exceed 105°C (378 K) during normal loading. In addition, according to another relevant standard DL/T 572-95, the upper oil temperature of the natural circulation self-and air cooling transformers shall not exceed 85°C, and the top oil temperature shall not exceed 95°C. For the forced circulation of water-cooling transformers, the top oil temperature should not exceed 70°C (343 K). In order to ensure the simulation efficiency at the same time within the specified temperature, 70°C (343 K) was then selected as the simulation temperature. The pressure was set to $1 \times 10^{-4}$ Pa, the pcf force field suitable for carbohydrates was used, the electrostatic interaction method was the Ewald method. The step size of each step was set to 1 fs, where a trajectory was output every 5000 steps and each model finally obtained a 21-frame molecular trajectory file. The simulation process is shown in Figure 7 below.

For the 21-frame model file obtained after the molecular dynamics calculation, the last frame was selected as its final calculated model. The Cleave surface function was used to divide the oil and cellulose into the cellulose model as well as the oil-sulfide model on the intersection surface to ensure that the analysis was not affected by other parts of the model. Among them, the Cleave rule was selected Default, and subsequent analysis was then performed on the segmented model.

### 3 | PROPERTY ANALYSIS OF CELLULOSE RESULTS

#### 3.1 Cellulose mechanical properties

The decrease occurring in mechanical strength of cellulose can be found in the many literature. For instance, literature [14] find that the more probable cause of failure may be associated with the particulate semiconducting copper sulphide, Cu2S, contaminants that diffuse into the porous kraft paper fibre structure and thereby render it more conductive. The resulting elevated dielectric losses lead to thermal degradation of the kraft paper, which is manifest by its reduced dielectric breakdown strength. Literature [22] find that the results of increased duration of diffusion experiments at higher concentration of Cu2S leads to degradation of paper and transfer of corrosion by-products to paper as seen in the photograph. Moreover, literature [35] puts forward through experimental results that the greater the concentration of added sulfide, the greater the degradation rate of insulation paper. However, there are some difference in other literature [36], in which the insulation paper did not degrade significantly in the experiment. It may be possibly because the ageing time was not long enough or the ageing temperature was not high enough. Therefore, the effect of sulfide on cellulose is simulated. The relationship between stress and strain of solid materials can be derived from the generalised Hooke's law, and the relationship is listed as follows, where $\sigma$ is normal stress, $\varepsilon$ is normal strain, $\tau$ is shear stress, $\gamma$ is shear strain.

$$\begin{bmatrix}
\sigma_x \\
\sigma_y \\
\sigma_z \\
\tau_{yz} \\
\tau_{zx} \\
\tau_{xy}
\end{bmatrix} =
\begin{bmatrix}
C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\
C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\
C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\
C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\
C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\
C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66}
\end{bmatrix}
\begin{bmatrix}
\varepsilon_x \\
\varepsilon_y \\
\varepsilon_z \\
\gamma_{yz} \\
\gamma_{zx} \\
\gamma_{xy}
\end{bmatrix}$$

Through the mechanical properties function of the Forcite module, the $C_{ij}$ elastic coefficient matrix is obtained, and then various mechanical parameters of cellulose can be derived. This article aims at its Young's modulus, shear modulus, Poisson's ratio and bulk modulus to analyse its mechanical properties. For the isotropic elastic rigid bodies, the Young's modulus is used to measure its stiffness and the Young's modulus is defined as the ratio of uniaxial stress to uniaxial deformation (within the scope of Hooke’s law). If the rigidity of the solid material is stronger, its ability to resist the external force deformation is stronger and its Young's modulus value is larger. The insulation paper of the transformer oil-paper insulation system is a non-ideal plastomer, so the magnitude of the Young's modulus in the simulation is closely related to its tensile strength [37]. The shear modulus characterises the ratio of shear stress to shear strain (within the limit of elastic deformation ratio). Its value is closely related to the material’s ability to resist the shear strain. The greater the shear modulus, the stronger the material's ability to resist shear strain. The Poisson's ratio can be used to reflect the magnitude of the lateral deformation of the material. It refers to the absolute
value of the transverse normal strain compared to the absolute value of the axial normal strain after the material is unidirectionally tensioned or compressed. After the Young's modulus and shear modulus are obtained, the Poisson's ratio can be calculated by the following formula

\[ G = \frac{E}{2(1 + \mu)} \]  

(3)

In the formula, \( E \) is the Young's modulus, \( G \) is the shear modulus, and \( \mu \) is the Poisson's ratio.

The macroscopic properties of the material can be reflected by the bulk modulus. It is used to characterise the amount of deformation of the material against the pressure around the surface. It is defined as the pressure required to produce a unit of relative volume shrinkage, which can be derived from Young's modulus and Poisson's ratio.

\[ K = \frac{E}{3(1 - 2\mu)} \]  

(4)

In Equation (4), \( K \) is the bulk modulus, \( E \) is the Young's modulus, and \( \mu \) is the Poisson's ratio. The Young's modulus, shear modulus, Poisson's ratio and bulk modulus under the influence of different sulfides is shown in Figure 8.

As shown in Figure 8a, with the sulphur content increasing, the Young's modulus of each model shows a downward trend. Literature [30] conducted tensile strength experiments on the DBDS, hexadecyl mercaptan, and DBDS + hexadecyl mercaptan groups in Section 1.3.2, and found that the tensile strength of each experimental group decreased to varying degrees. Moreover, the influence of DBDS + hexadecyl mercaptan on the mechanical properties of insulating paper is greater than that of single sulphide. The simulation results in this study is roughly the same as the effect trend of sulphide on the insulating paper in literature [30]. Among them, thiophene has a lower activity, so the downward trend of its modulus is not obvious. The modulus of the hexadecyl mercaptan group decreases slightly when the sulphur content is low, and the change of the modulus become relatively gentle when the sulphur content increases. The DBDS group decreases more when the sulphur content is higher, and the thiophene group enters the late ageing stage earlier when the sulphur content is higher, causing its ring opened and converted into corrosive sulphide. As can be seen from the data in Figure 8b and Figure 8d, the shear modulus and bulk modulus have a similar rule to the Young's modulus. The effect of sulphide on the Poisson's ratio is shown in Figure 8c. Most sulphide models show a downward trend, however some models with hexadecyl mercaptan have an upward trend at high concentrations. The three sulphide mixed group has the largest decrease in modulus. For a single sulphide, the degree of decrease in modulus ranges from large to small, and the trend is DBDS > hexadecyl mercaptan > thiophene. The effect of the DBDS + hexadecyl mercaptan group is greater than that of the single

**FIGURE 8** Young's modulus, shear modulus, Poisson's ratio and bulk modulus under the influence of different sulfides (a) Young's modulus, (b) Shear modulus, (c) Poisson's ratio, (d) Bulk modulus
DBDS. The DBDS + hexadecyl mercaptan group has the strongest corrosion effect at the intermediate concentration, and this conclusion can also be well verified in the following literatures. Literature [29] conducted a tensile strength experiment on DBDS and hexadecyl mercaptan and found that at low sulphide concentration, the hexadecyl mercaptan group sample decreased more than the DBDS group sample. In addition, literature [38] found that the mechanical strength of the insulating paper added with the hexadecyl mercaptan group is lower than the value of the DBDS group at the same temperature and concentration and it keeps decreasing with the increase of the sulphide concentration. The above phenomenon obtained from experiment is similar to the simulation results on mechanical performance. At the same time, the modulus decreases most significantly under the synergistic effect of the three at high concentration. It can be speculated that the corrosion effects of different sulfides would promote each other.

3.2 Hydrogen bond in cellulose

The hydrogen bonds in cellulose are shown in Figure 9. Since the electronegativity of oxygen is greater than sulphur, most of the intramolecular and intermolecular hydrogen bonds are O-H...O bonds. Figure 10 statistics the different changes in the number of hydrogen bonds with the addition of sulfides.

As can be seen from the figure, with the increase of sulphide content, due to the damage caused by the corrosive sulphur, the number of hydrogen bonds generally decreases. It can be also seen that the corrosive sulfides have a strong effect on hydrogen bond destruction when added with DBDS. Mercaptans have a weaker effect on hydrogen bond destruction, and the one with the greatest effect on hydrogen bond destruction is the DBDS + hexadecyl mercaptan group. When the three sulphur compounds coexist under the condition of high sulphur concentration, the hydrogen bonds will also be greatly damaged. It is also note that in the benzothiophene group, the number of hydrogen bonds increases abnormally with the increase in the concentration of sulfide added. It is presumably because the low thiophene activity is not sufficient to damage the hydrogen bonds of cellulose, and the number of thiophene molecules increases in the model. Therefore the thiophene forms more sulphur–hydrogen intermolecular hydrogen bonds with cellulose. As the hydrogen bond is destroyed, the mechanical strength of cellulose is also weakened, which thereby exacerbating the ageing phenomenon.

3.3 Cellulose molecular chain motion

The size of the cellulose chain motion can reflect the heat capacity of the cellulose chain in the insulating paper. The stronger the chain motion of cellulose, the worse its mechanical properties and thermal stability [39]. The strength of the chain motion can be analysed by mean square displacement (MSD). In this simulation, the various sulfide models are compared longitudinally with different sulfide concentrations, as shown in Figure 11 below.

As shown in Figure 11a, thiophene has a greater weakening effect on the cellulose chain at low concentrations, but its destructive effect at high concentrations is much lower than the synergistic effect of DBDS and hexadecyl mercaptan. The effect of DBDS alone is not as good as that of its combined action with hexadecyl mercaptan, as shown in Figure 11bc. It can be inferred that due to the characteristics of its long chain molecules, the hexadecyl mercaptan has a larger single molecule size than DBDS and thiophene, and also a larger number of atoms per molecule. Therefore it is easier to cause the geometrical structure of the cellulose in the amorphous region to be unstable. It can be seen from Figure 11c that under the three groups of concentrations, the hexadecyl mercaptan group has a larger MSD value, followed by the DBDS + hexadecyl mercaptan group. It can be also obtained that these two sulfides have a greater weakening effect on the stability of cellulose chain, reducing its mechanical properties and deformation resistance, thus leading to the ageing breakdown of insulating medium.
3.4 | Electrostatic energy of cellulose

The electrostatic energy of different sulfide models is shown in Figure 12. The electrostatic energy is derived from the external force overcoming the electric field force to do work. The total electrostatic energy is obtained by adding the self-energy of each charge and the mutual energy between other charges. For most models, due to the presence of sulphur atoms, the polarisability of the molecule is increased, which leads to a slight increase in the electrostatic energy of the cellulose as the sulfide concentration increases. Among them, the DBDS + thiophene + hexadecyl mercaptan group increases significantly, followed by the DBDS + hexadecyl mercaptan group, and the thiophene group is relatively stable. For the hexadecyl mercaptan group, due to the characteristics of its long chain molecules, the charge of the tail functional group will be reduced [40]. Therefore, compared with other groups, the molecular electrostatic energy would decrease while the remaining groups generally shows an upward trend.

4 | PROPERTY ANALYSIS OF INSULATING OIL

4.1 | Van der Waals energy of insulating oil

Van der Waals force, also known as intermolecular force, is a weak mutual attraction between molecules composed of orientation force, inducing force and dispersion force. The van der Waals energy of different sulfide models is shown in Figure 13.

It can be seen that the Van der Waals energy generally decreases with increasing sulphur concentration. However, when the three sulfides act synergistically, the van der Waals energy decrease is small at high sulphur concentrations. It is speculated that there is no orientation force between the sulfide molecules and the non-polar alkane molecules in the oil at low concentrations. However, at higher concentrations, the orientation force between different sulfide molecules begins to become prominent, reducing the decrease in van der Waals energy. The synergistic effect of DBDS + hexadecyl mercaptan group on van der Waals energy is significantly greater than that of DBDS and hexadecyl mercaptan alone. Moreover, under the synergistic effect of DBDS and thiophene, the weakening of the insulating oil van der Waals energy is also greater than the two alone. It is speculated that when the total number of sulphur atoms is the same. Among DBDS, hexadecyl mercaptan and benzo thiophene, the hexadecyl mercaptan group has more molecules and the molecular weight of its single molecule is also larger, which makes it easier to deform and thus has higher dispersion force. DBDS and thiophene have higher induction force due to their stronger polarity, which also slowed the decline of Van der Waals energy. Although the carbon atom of hexadecyl mercaptan uses the less polar sp³ hybrid method to form bonds, its longer chain weakens the effect of the terminal sulphhydryl group on the
molecular polarity, making its molecular polarity lower and resulting in lower induction force than the DBDS + thiophene group. However, as the dispersion force occupies the main position in Van der Waals force, the Van der Waals energy of DBDS and thiophene group is still lower than that of hexadecane group.

4.2 Shear viscosity of insulating oil

Viscosity can be expressed as the ability of the fluid to impede its relative flow. The electrical insulating oil needs to conduct the heat dissipation by itself, so the viscosity should be kept as moderate as possible to ensure the effective flow and heat dissipation of transformer oil. At the same time, the flash point of the oil will not be reduced as the viscosity is too small. When the flash point is sufficiently high, the smaller the viscosity, the more favorable the transformer operation.

As shown in Figure 14, the viscosity of insulating oil generally increases with the addition of sulfide. Among them, the synergistic effect of DBDS and hexadecyl mercaptan greatly increases the viscosity of insulating oil. Literature [41] found through experiments that the kinematic viscosity of oil samples added with DBDS would be increased compared with ordinary oil samples, which is similar to the above simulation results. It can be also seen that the hexadecyl mercaptan has a great influence on the viscosity of insulating oil. It is speculated that the large molecular weight of hexadecyl mercaptan and the large carbon-hydrogen combination in the molecule may lead to a large internal friction force, resulting in a large increase in the viscosity of insulating oil.

5 PRACTICAL APPLICATION OF THE SULPHIDE EFFECTS ON OIL-INSULATION SYSTEM

As is known, the power transformer is the most important equipment in the power system, and the protection of its insulation system is the top priority. The impact mechanism of sulphur corrosion of power transformers is an urgent problem to be solved at present, which has good value for extending the service life of transformers and improving the insulation capacity of equipment. Exploring the micro-mechanism of sulphur corrosion is able to understand the problems which need to be solved from the molecular field in detail, and the molecular dynamics simulation is currently a common method. This article discusses the effects of DBDS, hexadecyl mercaptan and benzothiophene on the performance of oil-paper insulation system based on molecular dynamics simulation, and fills the gaps on the basis of existing research.

According to the above results, the degradation effects of different kinds of sulfides on insulation paper were promoted each other. Therefore, in order to reduce the effect of sulphur corrosion, the species of sulfide should be controlled. For example, the use of additives containing sulphur should be reduced. Though the benzothiophene at low concentration is not enough to break the hydrogen bond, it will increase the number of hydrogen bonds, therefore the concentration of benzothiophene should be strictly controlled. Low concentration of benzothiophene can help to maintain the stability of insulation paper, but the sulphur corrosion caused by high concentration of benzothiophene could also aggravate the damage of oil-paper insulation system. According to the strength of the chain motion reflected by MSD, when the concentration of sulfide exceeds 5.15%, the MSD has reached more than 8 Å². The hexadecyl mercaptan molecule could weaken the stability of cellulose chain, so it is necessary to reduce the concentration of hexadecyl mercaptan in the insulating oil. At the concentration of 7.73%, it has a strong weakening effect, therefore it is
suggested that the concentration should not exceed 5.15%. Due to the increase of sulfide, the viscosity of insulating oil will also increase. When the viscosity of insulating oil is measured, the concentration of sulfide in insulating oil can be preliminarily determined. According to this phenomenon, a new test method can be provided for the determination of sulfide concentration in the insulating oil.

Through the analysis of the mechanical properties, as well as the energy and hydrogen bonds at different sulfide concentrations, the molecular level reveals the influence of different combinations of three sulfides on the insulation properties of oil-paper insulation, and explores the influence of concentration changes on the deterioration of oil-paper insulation system. The above results can provide a reference for evaluating the damage degree of insulation caused by multiple sulphur corrosion, as well as practical application to effectively prevent the deterioration of oil-paper insulation system.

6 CONCLUSIONS

In this study, three typical sulfides, DBDS, hexadecyl mercaptan and benzothiophene were selected and combined to form seven groups of models. The molecular dynamics simulation analysis was carried out on various microscopic characteristics of insulating paper and insulating oil. The main conclusions are as follows.

(1) For the mechanical properties such as shear modulus, bulk modulus and Young’s modulus, the three sulfides have the greatest decrease in modulus under the synergistic effect. For a single sulfide, the degree of decrease in modulus ranges from large to small: DBDS > hexadecyl mercaptan > thiophene, and the effect of DBDS + hexadecyl mercaptan group is greater than that of DBDS alone. Under the synergistic effect of the three, the modulus decreases most obviously, and the degradation effects of different kinds of sulfides will promote each other.

(2) With the increase of sulfide content, the number of hydrogen bonds generally decreases. When DBDS is added to the model, the damage to the hydrogen bond is strong, and the hexadecyl mercaptan has a weak effect on the hydrogen bond. The largest bond breaking effect is the DBDS + hexadecyl mercaptan group. Under the combined action of the three sulfides, when the sulphur concentration is relatively high, the hydrogen bond will also be greatly destroyed. With the addition of benzothiophene, the number of hydrogen bonds increased abnormally and it is speculated that the lower thiophene activity is not enough to damage the hydrogen bonds of cellulose. As the number of thiophene molecules increases, thiophene forms more sulphur–hydrogen intermolecular hydrogen bonds with cellulose.

(3) The MSD of hexadecyl mercaptan group and DBDS + hexadecyl mercaptan group are generally larger, while DBDS acting alone has less influence on cellulose chain movement. It can be inferred that the hexadecyl mercaptan molecules have a greater weakening effect on the stability of cellulose chain. However, at high concentrations, the thiophene group, the thiophene + hexadecyl mercaptan group and the DBDS + thiophene + hexadecyl mercaptan group, which contain benzothiophene molecules, are far less damaging to cellulose than the DBDS + hexadecyl mercaptan group.

(4) The van der Waals energy of the insulating oil is more affected by the synergistic sulfide than the sulfide acting alone. At high concentration, different sulfide molecules produce orientation force due to their polarity, which reduces the van der Waals energy decline. The viscosity of insulating oil is generally increased by the influence of sulfide. Due to its large molecular weight, the hexadecyl mercaptan increases the internal friction of insulating oil and becomes the main factor affecting the viscosity. Therefore, the DBDS + hexadecyl mercaptan group has greater influence on the viscosity under high sulphur concentration than under DBDS alone.

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