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Study on the Enhancement of Interaction between Surface Groups Modified Nanoparticles and Natural Ester Insulating Oil

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Abstract. Power transformers in high-voltage power grids are among the most critical components, and insulating oil serves as the most important liquid dielectric medium inside high-voltage power transformers, playing key roles in insulation, heat dissipation, and monitoring transformer operating conditions. In recent years, considering environmental protection and the application of nanotechnology, researchers have explored the use of nanomodified natural ester insulating oil as a substitute for traditional mineral insulating oil. However, the interfacial compatibility between nanoparticles and insulating oil has not yet been properly addressed. In this work, natural ester insulating oils modified with SiO_2 nanoparticles functionalized with four different groups were prepared, and their key physicochemical properties were tested. Meanwhile, molecular dynamics simulations were employed to investigate the surface interactions between triglycerides and the nanoparticles. The results indicate that SiO_2 nanoparticles modified with functional groups all enhance the thermal conductivity of the insulating oil, with the APTES-SiO_2 exhibiting the most pronounced effect. The molecular simulation results suggest that functionalized nanoparticles improve compatibility with the insulating oil, inhibit the generation and development of streamers within the oil, and thereby prevent macroscopic breakdown of the insulating oil. This work can provide a solid theoretical foundation for the application of nanotechnology in liquid dielectric media.

Keywords: Interaction; Thermal conductivity; Surface modifier; Molecular dynamics

1. Introduction

For a long time, mineral oil has been the dominant product for transformer insulating oil, owing to its excellent electrical properties and low cost. However, mineral oil has two inherent drawbacks that are difficult to overcome: first, it is non-renewable, and its resources are increasingly depleted; second, it has poor biodegradability, and once a leak occurs, it can cause severe environmental pollution to soil and water sources.[5, 8, 9] Natural ester insulating oil has gradually come into researchers' view due to its outstanding fire safety performance, excellent biodegradability, and good insulation characteristics, and is considered one of the most promising alternatives to mineral oil. [1-2] Natural esters offer advantages such as a high flash point (>300 °C), renewability, non-toxicity, and complete biodegradability in the natural environment, aligning with the United Nations Sustainable Development Goals. [3, 4, 7]

Despite these numerous advantages, natural esters face a series of technical challenges in practical applications. First, the high viscosity of natural esters affects their heat dissipation performance and impregnation capacity. [6, 10] The emergence of nanomodification technology offers a novel approach to overcoming these performance bottlenecks. Research shows that doping natural ester insulating oil with nanoparticles (such as Al_2O_3, TiO_2, SiO_2, and SiC) can significantly improve its thermal conductivity and dielectric properties.[11] For example, adding an appropriate amount of nano-modifiers can increase the breakdown strength of natural esters by 32%, reduce viscosity by 40%, and enhance thermal conductivity by 27.9%. Nanoparticles act as "charge traps" to capture free electrons in the oil, inhibiting the generation and development of streamers while improving the thermal conduction network at the solid-liquid interface. [12]

In recent years, surface modification technology has further advanced the development of nanomodified insulating oils. By introducing functional groups (such as $-NH_2$, $-CH_3$) onto the nanoparticle surface using silane coupling agents (such as APTES, KH550), the interfacial

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compatibility between the nanoparticles and the natural ester base oil can be significantly enhanced, nanoparticle agglomeration can be suppressed, and dispersion stability can be improved. [13]

Considerable research achievements have been made regarding nanomodified natural ester insulating oil and its enhancement mechanisms. However, the correlation mechanism between the macroscopic parameter variations of surface-modified nanoparticles and the insulating oil, and their microscopic interactions, has remained unclear. In view of this, this work prepared nano-insulating oil fluids using SiO_2 nanoparticles modified with several different surface groups, tested their key electrical and physicochemical properties, and simultaneously employed molecular dynamics simulations to explore the interactions between nanoparticles and the insulating oil under typical thermal fields. The conclusions of this paper can provide an important theoretical reference for understanding the mechanisms behind the performance enhancement of nano-insulating oil fluids and can also help promote the application of environmentally friendly liquids in power equipment.

2. Materials and Methods

2.1 Molecular Dynamics Modelling and Settings

To investigate the interaction between silica nanoparticles modified with different surfactants and the mixed natural ester insulating oil, microscopic models of four types of nanoparticles combined with the natural ester were established using the Materials Studio. First, a pure silica nanoparticle model was derived from the software's crystal library, followed by hydroxylation treatment of its surface. Subsequently, four types of modifying groups were manually added to the surface of the pure silica nanoparticles. The surface-modified silica nanoparticles then underwent 10,000 steps of structural optimization and simulated annealing from 300 K to 900 K, followed by another 10,000 steps of structural optimization. Next, the Construction module was used to establish oil–nanoparticle models consisting of the modified silica nanoparticles and the mixed natural ester. A further 10,000 steps of structural optimization were performed to reduce the potential energy of the nanomodified insulating oil microscopic model.

After the construction of the binary mixed natural ester insulating oil models doped with nanoparticles, structural optimization and simulated annealing steps were carried out. The structural optimization step was set to 10,000 steps, and the simulated annealing temperature was set from 300 K to 900 K with 10 cycles to minimize the overall potential energy of the model. The model with the lowest Hamiltonian energy was selected for subsequent operations. Then, a 200 ps relaxation under the NPT ensemble was performed at a temperature of 298 K to bring the density of the doped model closer to the set value. Considering the model size and computational capacity, a 1000 ps molecular dynamics simulation was finally conducted under the NVT ensemble at temperatures of 343 K and 383 K, respectively. Temperature was controlled using the Nosé method, and pressure was controlled using the Berendsen method. The COMPASS force field was employed for the dynamics simulations. The molecular dynamics simulation process is shown in Fig. 2, and the modeling process for the binary mixed natural ester insulating oil doped with nanoparticles is shown in Fig. 1.

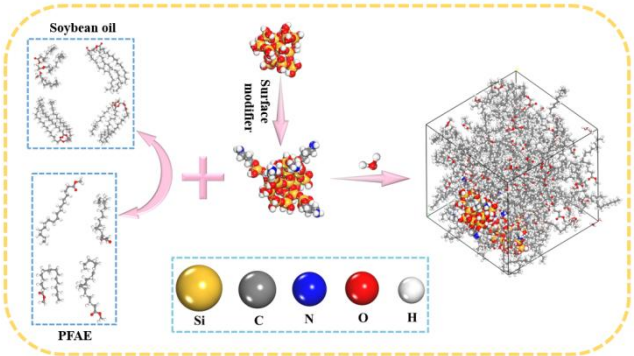

Fig. 1 Modelling of natural ester doped with nanoparticles

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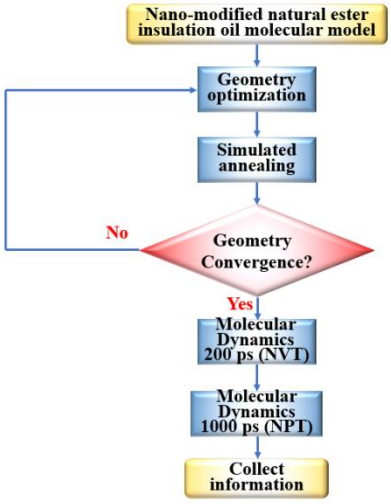

Fig. 2 Detailed molecular dynamics steps.

2.2 Nano-Modified Natural Ester Insulation Oil Preparation

Nanoparticles and natural ester insulating oil are typical inorganic solid and organic liquid materials, respectively. Therefore, the agglomeration behavior of nanoparticles is significantly influenced by the initial concentration. In this work, four types of nanoparticle-modified mixed insulation oils were prepared at four concentrations (0.02 g/L, 0.03 g/L, 0.05 g/L, 0.08 g/L), denoted as AS-O (APTES+SiO_2-Oil), PS-O (PDMS+SiO_2-Oil), DS-O (DDS+SiO_2-Oil), and PU-O (PURE+SiO_2-Oil), respectively.The specific steps for preparing the nanoparticle-modified mixed natural ester insulation oil using the two-step method are as follows: 1) The natural ester insulation oil was placed in a vacuum drying oven and dried at 90 °C for 6 hours. Subsequently, the corresponding masses of the four types of silica nanoparticles were added according to the aforementioned ratios. The mixture was stirred clockwise with a glass rod for 30 seconds, followed by magnetic stirring for 30 minutes. 2) The nanoparticle-modified mixed insulation oil was placed in a drying oven for 48 hours (90 °C/60 Pa) to remove impurities such as bubbles and moisture introduced during the preparation process. The prepared nanoparticle-modified natural ester insulation oil can be used for subsequent testing of specific parameters.

3. Results and Discussion

3.1 Simulation Results Analysis

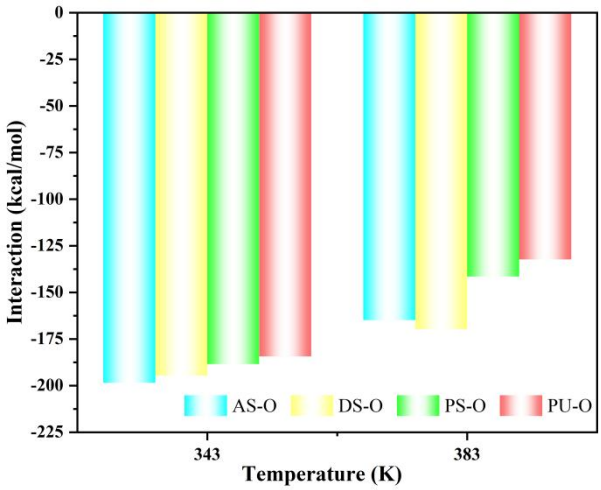

Fig. 3 The interaction between trglycerides and nanoparticles

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At the microscopic level, nanoparticles in insulating oil are enveloped by triglycerides, and the interaction between them plays a decisive role in the stable performance of the nanofluid. This interaction can be characterized by the interaction energy. In nanomodified insulating oil, the interaction energy between nanoparticles and oil molecules is of critical importance. If the particle–oil interaction energy is strong (highly negative) and greater than the particle–particle interaction energy, the nanoparticles will be uniformly dispersed in the oil. If the particle–particle attraction (van der Waals forces) dominates, the interaction energy causes the nanoparticles to agglomerate, thereby reducing the specific surface area and affecting thermal and electrical performance.

As shown in Fig. 3, the interaction energies between the surface-modified nanoparticles and the triglycerides in the natural ester are all negative, indicating the presence of adsorption between them. Meanwhile, as the temperature increases from 343 K to 383 K, the interaction energies exhibit a decreasing trend. This is attributed to the increase in molecular kinetic energy with rising temperature, which reduces the intermolecular interaction energy. Notably, the interaction energy between the pure SiO_2 nanoparticles and the triglycerides decreases most significantly, indicating the lowest high-temperature resistance of their adsorption. In contrast, the interaction energies of AS-O and DS-O decrease more slowly, suggesting that APTES and DDS can effectively mitigate the effect of temperature on adsorption performance. The enhanced lipophilicity, on one hand, delays the increase in dielectric loss caused by surface polarization of the more polar triglycerides; on the other hand, it maintains the dispersion stability of the nanoparticles, preventing agglomeration. Consequently, the specific surface area of the nanoparticles increases, and their adsorption of free electrons in the insulating oil slows down, which would otherwise lead to a reduction in the breakdown voltage of the insulating oil. Overall, the surface-modified SiO_2 nanoparticles exhibit greater interaction energy with the natural ester insulating oil, and this interaction remains more stable at high temperatures compared with that of pure SiO_2 nanoparticles. Among them, SiO_2 nanoparticles modified with APTES and DDS demonstrate superior high-temperature resistance.

Molecular Electrostatic Potential (ESP) refers to the electrostatic potential energy generated at a point in the space around a molecule by the combined effect of the positive charges of all atomic nuclei and the negative charges of all electrons in the molecule. The molecular electrostatic potential maps the internal charge distribution onto the molecular surface, serving as a crucial bridge connecting the microscopic structure of molecules with their macroscopic properties (such as solubility, binding capacity, reactivity, and dielectric properties). In fields such as insulating materials, catalysis, drug design, and nanomaterials, it serves as a key tool for elucidating intermolecular interaction mechanisms.In quantum chemical calculations, the molecular surface is typically defined as an isosurface of electron density, on which the electrostatic potential values are then calculated .

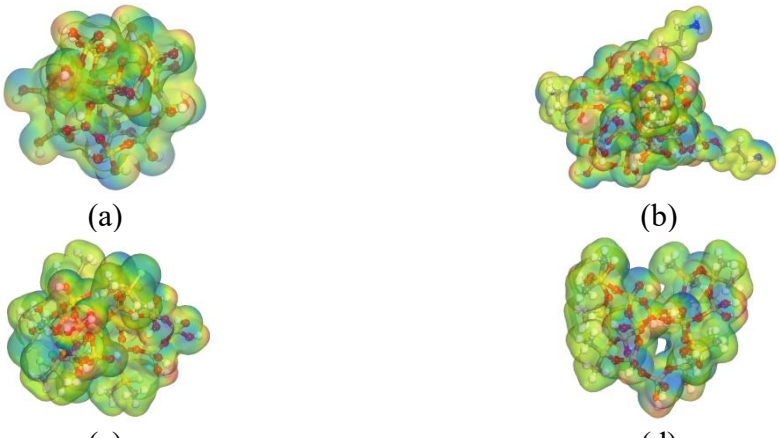

Fig. 4 The ESP distribution of modified SiO_2 NPs: (a) PURE-SiO_2; (b) APTES-SiO_2; (c) DDS-SiO_2; (d) PDMS-SiO_2.

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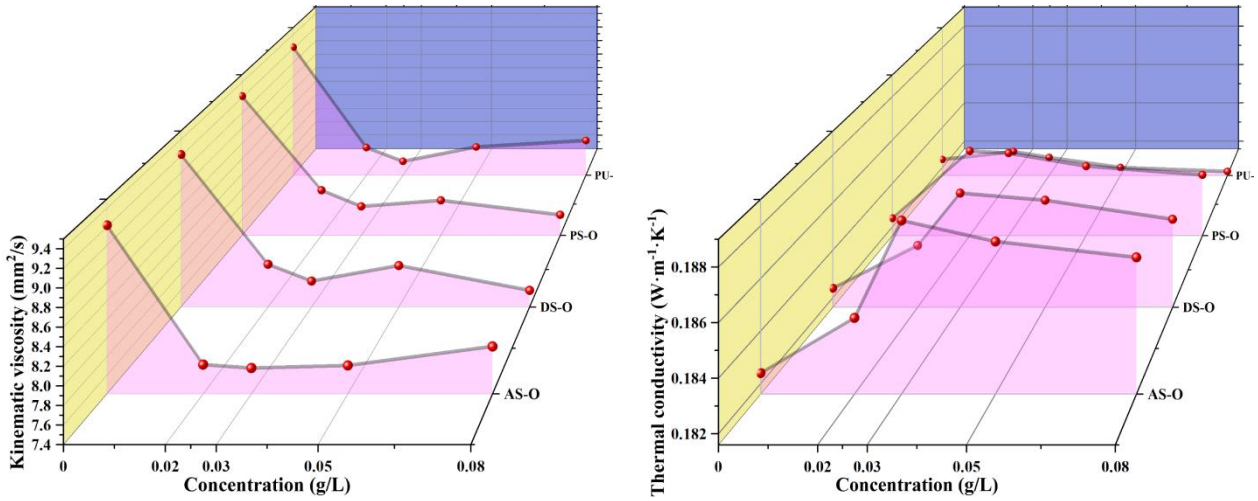
In Fig. 4, red regions indicate a positive surface electrostatic potential, while blue regions indicate a negative surface electrostatic potential; deeper colors correspond to larger absolute values of the electrostatic potential. As can be seen from the figure, the surface of pure SiO_2 contains only a small number of hydroxyl groups (–OH), with red regions distributed more broadly but appearing mostly in light red, indicating a relatively weak positive electrostatic potential. In contrast, APTES-SiO_2 contains more amino groups (–NH_2), and DDS-SiO_2 contains a large number of methyl groups (–CH_3). These groups exhibit a relatively high positive electrostatic potential, creating more electron traps on the surfaces of APTES-SiO_2 and DDS-SiO_2, which have a certain adsorption effect on free electrons in the oil–paper insulation system. As a result, free electrons are captured and then released by the modified SiO_2 nanoparticles during their movement, a process that reduces the mobility of free electrons in the oil–paper system. Meanwhile, the surface of PDMS-SiO_2 contains silicon–chlorine bonds. Due to the strong electronegativity of chlorine atoms, these bonds exert a strong attraction on nearby electrons, thereby slowing down the movement of free electrons in the oil–paper insulation system, inhibiting the generation and development of electron avalanches, and indirectly enhancing the breakdown voltage of the nanomodified insulating oil.

3.2 Heat Disspation Analysis



(a) (b)

Fig. 5 (a) Comparison chart of kinematic viscosity of four insulation oil samples; (b): Comparison of thermal conductivity of four insulation oil samples

Fig. 5 presents a comparison of the thermal conductivity of insulating oils doped with four types of modified nanoparticles at room temperature. As can be seen from the figure, the incorporation of nanoparticles increases the thermal conductivity of the mixed insulating oil. The thermal conductivity of the pure insulating oil is 18.236 $W \cdot m^{-1} \cdot K^{-1}$. After doping, the thermal conductivity increases significantly; however, as the nanoparticle concentration increases, the thermal conductivity exhibits a decreasing trend. The figure also shows that the enhancement effect of nanoparticles on the thermal conductivity of the mixed insulating oil is only pronounced at relatively low concentrations, with the peak thermal conductivity occurring at approximately 0.02 g/L or 0.03 g/L. Moreover, the enhancement of thermal conductivity by the three types of modified SiO_2 nanoparticles is significantly greater than that by pure nanoparticles. As typical solid materials, nanoparticles are widely favored in materials research for their excellent thermal conductivity. Since the thermal conductivity of nanoparticles is higher than that of natural ester insulating oil, dispersing nanoparticles into the natural ester insulating oil can improve the thermal conduction network of the oil. The dispersed nanoparticles partially fill the gaps between triglycerides, thereby enhancing the overall thermal conductivity of the nanofluid.

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Based on the combined test results of kinematic viscosity and thermal conductivity for the four oil samples, it can be observed that compared with the pure natural ester insulating oil, both properties show a certain degree of improvement. The kinematic viscosity of the insulating oil decreases significantly after nanoparticle addition but does not respond strongly to changes in nanoparticle concentration. Meanwhile, nanoparticles also improve thermal conductivity to some extent. However, among the four oil samples, only the oil doped with pure SiO_2 nanoparticles exhibits a thermal conductivity lower than that of the base oil as the nanoparticle concentration increases. For the other oils doped with modified nanoparticles, the thermal conductivity initially increases and then decreases with increasing nanoparticle concentration. This is attributed to the better dispersibility of surface-modified nanoparticles in the oil, which results in more solid–liquid exchange sites and a larger contact area, facilitating heat exchange between the oil and nanoparticles. However, as the nanoparticle concentration increases, the imbalance between attractive and repulsive forces among nanoparticles leads to some degree of agglomeration, destabilizing the solid–liquid heat transfer network and causing a slight decrease in thermal conductivity. Nevertheless, the overall thermal conductivity remains superior to that of the insulating oil doped with pure nanoparticles.

4. Conclusion

A two-step method was employed to prepare four types of nanomodified mixed natural ester insulating oils at different concentrations, and their physicochemical properties were tested to determine the relative optimal concentration for enhancing heat dissipation performance. Molecular simulation methods were further used to reveal, at the microscopic level, the mechanisms by which surface-modified SiO_2 nanoparticles improve the dielectric properties of the insulating liquid. It was found that the modifying groups can enhance the thermal conductivity of the insulating oil to varying degrees while improving dielectric properties by inhibiting the generation and propagation of streamers within the liquid insulating material. However, when the nanoparticle concentration is too high, this enhancement effect becomes less pronounced, which is attributed to nanoparticle agglomeration reducing the efficiency of improvement. How to suppress the agglomeration of nanoparticles in natural ester insulating oil remains to be further investigated.

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