Thermal stability of polyphenylsilsesquioxane-modified meta-aramid insulation paper

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Abstract: The development of new materials for use in advanced distribution transformers is required to improve their heat resistance rating, operational safety, and reliability. The combination of polymer and nanoparticles is the preferred approach to improve the thermal stability of materials. In this study, the thermal stability of laboratory-prepared meta-aramid insulation paper modified with polyphenylsilsesquioxane (PPSQ) was evaluated. The results showed that the thermal stability of the modified insulation paper was superior to that of the unmodified paper. Molecular dynamics simulations were used to analyse the internal mechanism of the performance improvement achieved by modification with PPSQ. From a microscopic perspective, the addition of PPSQ provided a relatively larger structural space for the meta-aramid fibre and increased the free volume of the entire system, which tightened the meta-aramid fibre molecular chains, increased the density of the structure of the paper, and enhanced the mutual permeability between meta-aramid fibre chains. Therefore, the stress can be better transmitted, the performance loss such as phase delamination was effectively prevented, and the bonding between the meta-aramid fibres was strengthened.

1 Introduction

As the ultra-high voltage and high capacity of power networks rise, the oil–paper insulation system inside power transformers will need to endure increasingly harsh conditions. During the long-term operation, thermal ageing of the insulation paper leads to the deterioration of its mechanical properties and thermal stability, which, in turn, leads to the decline of the performance of the transformer insulation and shortens its service life. The long service life and complicated distribution of the electric field in extra-high-voltage transformers impose strict requirements on the performance of the oil–paper insulation material [1]. Therefore, it is important to improve the thermal stability and mechanical properties of insulation paper to extend the safe service life of power transformers and ensure long-term safe operation of power networks.

With the development of nanotechnology, modification with nanomaterials has provided an opportunity to further improve the properties of polymeric materials. Such modified materials possess the advantages of inorganic nanoparticles and organic polymers. Bai et al. [2] modified the poly-m-phenylene isophthalamide (PMIA) fibre with aluminium (AlN) nanoparticles and found that the addition of nanoparticles effectively lowered the conductance of the PMIA insulation paper and inhibited the injection, migration, and accumulation of space charge. Liu and co-workers [3] modified the PMIA insulation paper with different silica (SiO2) nanoparticles. They found that the addition of nanoparticles decreased the linear average charge density and increased the densities of both deep and shallow traps inside the paper. Rodriguez-Uicab et al. [4] modified the surface of PMIA fibres with multi-walled carbon nanotubes by deposition and chemical modification. The results indicated that the presence of a fibre surface coating or mild chlorosulfonic acid treatment promotes an increase in the interaction between the fibre and the oxidised multiwall carbon nanotubes. Tang et al. [5] conducted molecular dynamics (MD) simulations and experiments to study the influence of SiO2 nanoparticles on the properties of PMIA. They proposed that a strong interfacial effect existed between nano-SiO2 and PMIA, and this effect was mainly reflected in the induction force and hydrogen bonding. Alumina (Al2O3) nanoparticle-modified cellulose insulation paper has also been prepared [6, 7]. It was found that the thermal life and electrical life of the modified insulation paper were substantially improved compared with those of the unmodified fibre insulation paper. Chi et al. [8] found that using nano-montmorillonite to modify the pressboard increased the depth of charge traps and captured carriers to increase their breakdown field strength. Abdel-Gawad and co-workers [9] functionalised the surface of SiO2 with an aminosilane coupling agent and then synthesised polyvinyl chloride (PVC)/SiO2 nanocomposites with different concentrations of nanoparticles. The chemically modified SiO2 nanoparticles enhanced both the dielectric and mechanical properties of PVC. Jindal and Singh [10] found that the addition of phenol-modified phenolic resin to cellulose paper greatly raised the mechanical bending strength, viscoelasticity, and thermal stability of the resulting composite. Du et al. [11] introduced zinc oxide (ZnO) into cellulose insulation paper by radio frequency magnetron sputtering. The results showed that the sputtering of ZnO had a significant effect on the structure of insulation paper, and led to the formation of hydrogen bond and chemical bond, as well as the increase of surface and volume conductivity. Nazir et al. [12] used AlN and SiO2 to co-fill silicone rubber to prepare a new type of silicone rubber composite material. They believed that co-filled composites have lower physical tracking and corrosion properties. In addition, the combined surface area of the co-filled particles in the composite increases, providing better scattering and reducing secondary electron collisions.

PMIA, which is better known as meta-aramid fibre, is an organic synthetic fibre with high strength, high modulus, good thermal resistance, and low density [13]. Due to its unique properties of heat resistance, insulation ability, flame retardancy, and radiation resistance, PMIA has been widely used as the main insulation material in transformers, cables, motors, generators, and other equipment [14–17]. The preparation of organic–inorganic nano-compounds of PPSQ has become a research hotspot in recent years. The organic–inorganic hybridisation and cage structure of PPSQ led to unparalleled performance after composite formation with polymers and wide application potential [18, 19]. In view of this, here PPSQ is used to modify the PMIA insulation paper. The effect of PPSQ on the thermal stability of PMIA insulation paper...
and the associated mechanism are studied by MD simulations and experimentally verified.

2 Experiment and analysis

The modified and unmodified insulation paper was subjected to an accelerated thermal ageing test at 130°C and differential scanning calorimetry (DSC) simultaneously. Firstly, the mechanical properties of the modified insulation paper and the viscosity of the insulation oil with different degrees of thermal ageing were compared. In addition, the thermal stability test for the insulation paper by DSC was described. The effect of PPSQ on the thermal stability of PMIA was evaluated.

2.1 Preparation and thermal ageing

In this experiment, the conventional paper sheet forming method was used. Chopped fibres and fibrids used to prepare an insulation paper handsheet were provided by Yantai Spandex Co. Ltd. First, a fibre disintegrator was used to evenly disperse the chopped fibres and fibrids in water. Then, the uniformly dispersed fibre suspension was filtered and moulded under vacuum, and then pressed and dried to obtain the base paper for the insulation paper handsheet. The moulding process was conducted using a sheet former. Finally, a high-temperature calendar was used to heat the base paper to achieve densification and internal bonding. The insulation paper handsheet was denoted as C₀ [2, 3, 20].

PPSQ came from Sinopharm Chemical Reagent Co. Ltd. An appropriate amount of PPSQ (14 wt%) was added to deionised water and ultrasonically dispersed using an ultrasonic cleaner. Aramid fibres were chopped evenly in the fibre disintegrator and then dispersed in water. The PPSQ aqueous dispersion was poured into the chopped fibre slurry and stirred. An appropriate amount of aramid fibril was mixed into the slurry. After filtration, papermaking, drying, and hot pressing, a PPSQ-modified insulation paper handsheet was obtained, which was labelled as C₁.

The two kinds of insulation paper handsheets were immersed in Xinjiang Karamay 25th insulation oil with an oil:paper ratio of 20:1 for 48 h [7, 21] and then placed in a vacuum ageing chamber. The accelerated thermal ageing test was carried out in the ageing box at 130°C. Sampling was performed after 0, 5, 12, 23, and 31 days.

2.2 Mechanical properties

The mechanical properties of insulation paper are closely related to the length and thickness of the fibres in it. Generally, as thermal ageing progresses, the degree of polymerisation of insulation paper decreases. This is macroscopically represented by a decrease in mechanical strength. In this paper, the tensile strength of the two kinds of insulation papers after ageing for different times was used to characterise the mechanical properties of the insulation paper during ageing and thus indirectly determines the degree of ageing of the insulation paper. The data were measured by an AT-L-1 tensile testing machine (Jinan Animeite Instrument Co. Ltd.) according to the ISO 1924-2 standard.

Fig. 1 showed that the tensile strengths of the C₀ and C₁ insulation papers decreased to some extent as the degree of ageing increased. The tensile strength of C₀ decreased relatively faster than that of C₁, especially after 5 d. This was because C₁ showed high density, lower porosity, and better thermal ageing resistance than the case for C₀, which indicated that adding PPSQ effectively improved the anti-ageing ability of aramid insulation paper.

2.3 Viscosity

The insulation oil in a transformer plays the dual role of insulation and circulating the dissipated heat. The kinematic viscosity of the oil is an important indicator to characterise its heat dissipation performance [21]. For a running transformer, a change in the oil will seriously affect the heat dissipation performance of the coil, which will adversely influence the thermal ageing of the oil–paper insulation system.

The viscosity of the oil was measured by a viscometer during the ageing test. The results, as shown in Fig. 2, revealed that during the early stage of ageing, the viscosities of C₀ and C₁ were similar. As the ageing time increased, the viscosity of C₀ continued to rise at a fast rate, which indicated that a higher amount of ageing byproducts were produced from the paper insulation system during thermal ageing and were accumulated in the oil. This increased the viscosity of the oil, thereby decreased. This increased the viscosity of the oil, which decreased its ability to dissipate heat. By comparison, the viscosity of C₁ increased more slowly than that of C₀. The gap between the viscosities of C₀ and C₁ increased with the ageing time, which indicated that C₁ helped to suppress the thermal ageing of the oil–paper insulation system.

2.4 Thermal stability

To study the thermal stability of the unmodified and PPSQ-modified aramid insulation paper, DSC was performed with a Q2000 differential scanning calorimeter (American TA Company). DSC can directly measure the effect of heat on a sample by measuring its glass transition temperature (T_g) and decomposition temperature (T_d). The DSC results for the two kinds of aramid insulation papers, as shown in Figs. 3 and 4, indicate the relationship between the compensation power difference between the samples and temperature.

As shown in Figs. 3 and 4, an endothermic peak below 150°C was generated by the evaporation of the adsorbed water in the fibres and the intensity of this peak for C₀ was higher than that for C₁. Between 150 and 350°C, the DSC curve increased slowly and smoothly. The two kinds of insulation papers exhibited an exothermic peak and turning point, which indicated T_d of the samples, where oxidation and cross-linking reactions may occur. Above 400°C, the endothermic peak associated with the melting of
the crystalline portion appeared; the intensity of this peak for \( C_1 \) was stronger than that for \( C_0 \). Finally, oxidative degradation occurred and the samples decomposed, were gasified, and absorbed heat until the endothermic peak appeared. Above 500°C, the heat flow started to increase. During the cooling process, no cold crystallisation was observed.

Fig. 3 revealed that \( T_g \) of \( C_0 \) was 283.4°C, which is in good agreement with that reported in the literature [22, 23]. \( T_g \) of \( C_1 \) was 304.3°C (Fig. 4), which was 20.9°C higher than that of \( C_0 \). Above 370°C, a cold-crystallisation exothermic peak appeared, the intensity of which was greater for \( C_1 \) than for \( C_0 \), which indicated that the cold crystallisation ability of \( C_1 \) was higher than that of \( C_0 \). Above 460°C, both types of insulation paper were oxidised and degraded. The degree of degradation of \( C_1 \) was greater than that of \( C_0 \) at the same temperature. In addition, the \( T_g \) of \( C_1 \) was 4.7°C higher than that of \( C_0 \). This illustrated that the molecular chain displacement ability of the amorphous region was enhanced by the addition of PPSQ, which increased the molecular weight of the insulation paper, thereby raising its thermal stability.

3 Molecular dynamics simulations

The thermal ageing test and DSC results of the PPSQ-modified and unmodified PMIA insulation paper showed that modification of the insulation paper with PPSQ improved its thermal stability. The MD simulation method was used to construct models of PPSQ-modified and PMIA insulation paper. The intrinsic mechanism of the influence of PPSQ on the thermal stability of aramid insulation paper was analysed from the perspective of microscopic parameters such as radius of gyration, free volume, cohesive energy, solubility parameters, and \( T_g \).

3.1 Model establishment

The whole simulation process was conducted using the Materials Studio software. The initial model was constructed in the amorphous cell module. The degree of meta-aramid polymerisation was 10 [24, 25] and the initial density of both models was 1.25 g/cm³. The selection of the simulated temperature and force field, model optimisation, energy balance evaluation, the number, pressure, temperature/number, volume, temperature/number, volume, energy ensemble process, and other related operational steps and parameter settings have been described previously [5, 20, 24–32]. A schematic diagram of the constructed models is shown in Fig. 5.

3.2 Analysis of parameter calculation results

The radius of gyration, free volume, cohesive energy density (CED), and solubility parameters of the model were selected to analyse the effect of the addition of PPSQ nanoparticles on the heat resistance of meta-aramid fibre in the temperature range of 70–150°C. In addition, \( T_g \) in the temperature range of 30–550°C was calculated using the simulated volume–temperature curve. The thermal stability of the modified meta-aramid fibre was also analysed.

3.2.1 Radius of gyration: A polymer is a long-chain macromolecule consisting of polymerised small molecules. A single bond in a molecule can rotate within this structure, which results in polymers possessing many different conformations. Thermal motion causes the molecular conformation of polymers to change constantly and their molecular size will also change. The mean-square radius of gyration can be used to characterise the molecular size. The size of the mean-square radius of gyration can reflect the flexibility of the polymer chains, as described in (1) [33]:

\[
R_g^2 = \frac{\sum_{i=1}^{N} m_i \hat{s}_i^2}{\sum_{i=1}^{N} m_i} = \frac{\sum_{i=1}^{N} \hat{s}_i^2}{N} \tag{1}
\]

Fig. 6 shows that as the temperature increases, the mean-square radius of gyration also increased, which indicated that the polymer
activity was enhanced in both models with elevating temperature. Compared with that of the unmodified model, the mean-square radius of gyration of the composite model was larger, which indicated that the addition of PPSQ nanoparticles increased the motion of the PMIA molecules, which resulted in the higher activity of the composite model polymer than that of the unmodified model polymer. This was because the structure of PPSQ provided a larger motion space for the PMIA chains [34]. In addition, the Si–O–Si bonds in PPSQ have low viscous activation energy [35], which increased the fluidity between the molecular chain and nanoparticles, while the organic groups attached to the silicon atoms increased the reactivity PPSQ and the compatibility of the inorganic and organic components [34].

3.2.2 Free volume: The concept of the free volume was first reported by Hirschfelder et al. [36], and this concept was gradually improved upon in on-going research. The volume inside a material can be divided into the occupied volume and free volume. The free volume characteristics of a polymer, especially its nanoscale free volume characteristics, are considered to have an important influence on the macroscopic properties of the material. The free volume theory can be used to study the diffusion and transport properties of polymers.

Figs. 7a–e show the free volumes of the unmodified model and Figs. 7f–j illustrate the free volumes of the composite model. The distribution area of the free volume in both models increased with temperature, which is consistent with the variation of the fractional free volume shown in Table 1.

In the unmodified model, the free volume distribution was relatively random, and the distribution of free volume became more dispersed as the temperature increased. This was because the molecular chain motion increased with rising temperature owing to the enhanced thermal field. The distance between the molecules increased and the molecular chains were more dispersed as the temperature increased. In the composite model, the distribution of the free volume was also relatively dispersed at the initial temperature of 70°C. However, as the temperature increased, the distribution of the free volume gradually approached that of PPSQ and the distribution of the free volume gradually began to concentrate. This was because the addition of PPSQ filled some gaps between the PMIA chains, so the PMIA chains were closer
molecule will result in a greater force between molecules and larger CED and vice versa. CED can also be used as a rough indicator to determine the thermal and mechanical properties of materials. A greater CED will result in a higher $T_g$ and modulus of elasticity [39].

The solubility parameter ($S_p$) is defined as the square root of the CED of a material. The purpose of introducing this concept was to characterise the strength of the interaction between simple liquid molecules. To date, $S_p$ has been widely used in the field of polymer research as an important parameter for determining the compatibility between materials. Fig. 8 shows that the $S_p$ of the two models decreased with increasing temperature and the difference between the models increased with temperature. The change of $S_p$ simulated using the unmodified model was consistent with reported experimental findings [40]. Meanwhile, the $S_p$ of the composite model was slightly higher than that of the unmodified model. The addition of siloxane increased the interpenetration of PPSQ and PMIA to achieve mixing at the supramolecular level. This enhanced the interfacial bonding force, which facilitated stress transmission and prevented performance loss through factors such as phase delamination. These results further confirmed the compatibility between the two types of fibres.

Fig. 8 also reveals that CED decreased with increasing temperature. According to the physical meaning of the CED, for the same model, an increase in temperature causes the combined effects of various attractive and repulsive forces in the model to decrease. However, the CED of the composite model was higher than that of the unmodified model, which indicated that PPSQ filled the original voids in PMIA and acted like a binder. A higher volume fraction resulted in smaller pore size and larger CED. The increase of CED indicated that the aramid paper structure became denser, the fibre molecular chain spacing shortened, and the hydrogen bonding on the phthalamine group strengthened, which made the bonds between PMIA stronger. It has been proposed that CED not only can be used to evaluate the compatibility of two polymers, but also has an obvious effect on many properties of the polymeric materials, such as mechanical, thermodynamic, light, electrical, and magnetic properties. $T_g$ is usually determined from specific volume–temperature curves [43]. Therefore, $T_g$ was extracted from volume–temperature curves in this paper. The temperature range was 30–550°C and data were measured every 40°C. The plotted $T_g$ curves of the unmodified and composite models are shown in Figs. 9 and 10, respectively.

Fig. 9 reveals that as the temperature was increased, the specific volume of the model increased and the specific volume near $T_g$ exhibited a jump. $T_g$ of the unmodified model was 279°C, which is somewhat different from that reported in the literature [9, 44–46] and in Section 2.4 of 280–300°C. The main reason for this discrepancy was that the materials used in the literature consist of blended aramid fibre and pulp. The different preparation and papermaking processes made $T_g$ of the real samples differ from those of the models constructed in this paper.

As presented in Fig. 10, the composite model exhibited a $T_g$ of 330°C, which was 51°C higher than that of the unmodified model. This indicated that the addition of PPSQ increased the $T_g$ of the composite. $T_g$ is closely related to the mechanical properties and thermal stability of a material. Our results indicate that PPSQ can improve the thermal stability of PMIA insulation paper.

### 4. Conclusions

The properties of PPSQ-modified PMIA insulation paper were studied, which yielded the following conclusions:
(i) The tensile strength of PPSQ-modified PMIA insulation paper was higher than that of the unmodified insulation paper. The elongation at break and viscosity of the insulation oil were lower than that of the unmodified insulation paper, which decreased the loss of mechanical strength during the ageing process of the PMIA insulation paper. DSC analysis revealed that the modified insulation paper exhibited a $T_g$ of 204.3°C and the $T_d$ of 472.3°C. Compared with those of unmodified insulation paper, PPSQ modification caused $T_g$ to increase by 20.5°C and the $T_d$ to increase by 4.7°C. That is the thermal stability of meta-aramid insulation paper was enhanced by modification with PPSQ.

(ii) Microscopic mechanistic analysis based on MD simulations showed that the spatial structure of PPSQ provided a large space for localisation, which allowed the meta-aramid fibre chain to become more compact than in the case of the unmodified fibres. Thus, the space for the meta-aramid fibre chains decreased and the paper became denser following PPSQ modification, which increased the interpenetration between the aramid fibre chains, shortened the fibre molecular chain spacing, enhanced the interfacial bonding force, and optimised the hydrogen bonding on the phthalalime group. As a result, the stress transmission was facilitated, performance loss through paths such as phase delamination was effectively prevented, the bonding between the macromolecules of the aramid paper fibre was strengthened, and the thermal stability of the meta-aramid fibre was improved through modification with PPSQ. The agreement between our MD simulation findings and experimental results confirmed that the addition of PPSQ can improve the thermal stability of PMIA insulation paper.

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6 References

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