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Research Article

The Insulation Properties of Oil-Impregnated Insulation Paper Reinforced with Nano-TiO_2

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Oil-impregnated insulation paper has been widely used in transformers because of its low cost and desirable physical and electrical properties. However, research to improve the insulation properties of oil-impregnated insulation paper is rarely found. In this paper, nano-TiO_2 was used to stick to the surface of cellulose which was used to make insulation paper. After oil-impregnated insulation paper reinforced by nano-TiO_2 was prepared, the tensile strength, breakdown strength, and dielectric properties of the oil-impregnated insulation paper were investigated to determine whether the modified paper had a better insulation performance. The results show that there were no major changes in tensile strength, and the value of the breakdown strength was greatly improved from 51.13 kV/mm to 61.78 kV/mm. Also, the values of the relative dielectric constant, the dielectric loss, and conductivity declined. The discussion reveals that nano-TiO_2 plays a major role in the phenomenon. Because of the existence of nano-TiO_2, the contact interface of cellulose and oil was changed, and a large number of shallow traps were produced. These shallow traps changed the insulation properties of oil-impregnated insulation paper. The results show that the proposed solution offers a new method to improve the properties of oil-impregnated insulation paper.

1. Introduction

The power transformer, an important piece of power transmission equipment, is the core component of the power system [1]. Currently, most transformers are oil-immersed transformers, and their insulation is composed of the insulation oil and insulation paper. Insulation paper, which is widely used in oil-immersed transformers, is made of natural cellulose [2, 3]. Although its use began in the 1890s, natural cellulose insulation paper is still widely used in oil-immersed power transformers, although insulation materials have made significant changes and progress.

Transformer insulation should be developed concurrently with an increase in voltage level. In recent years, much research on insulation oil has been carried out to improve the insulation properties [4–6]. However, research to improve the insulation properties of oil-impregnated insulation paper has been rare.

In the traditional paper industry, various fillers are applied to improve various properties of paper. However, no filler is used in insulation paper. The reason is that the mechanical properties are reduced greatly when using the traditional micron-level filler. Nanotechnology has developed rapidly in recent years, and various nanoscale fillers are used to modify polymers [7–13]. The results of the research show that a small amount of nanofiller has a great impact on the performance of a polymer. In the papermaking industry, nanoscale fillers have also been widely used [14–17]. However, these studies were not related to the properties of insulation paper.

When TiO_2 particles are used in papermaking, it is well known that the TiO_2 particle can be attached to the cellulose surface. After the oil immersion process of insulation paper, the cellulose and TiO_2 are wrapped by oil. The unsaturated coordination titanium of the TiO_2 surface can capture electron in the oil [18]; the effect may greatly change the insulation properties in oil-impregnated insulation paper. Therefore, nano-TiO_2 was chosen to reinforce oil-impregnated insulation paper in this paper. The breakdown strength and dielectric properties of oil-impregnated insulation paper modified by nano-TiO_2 were studied for the first time. A mechanism showing that nano-TiO_2 improves the insulation properties of insulation paper was discussed.

2. Experimental

2.1. Materials. Pulp board (softwood pulp, Taizhou Xinyuan Electrical Equipment, Taizhou, China) used for making insulation paper was beaten to about 400 Canadian standard freeness (CSF) in a valley beater. Nano-TiO_2 (95ZX063, Shanghai MaiKun Chemical Company, Shanghai, China, average particle size diameter <60 nm, relative dielectric constant $\varepsilon r = 100\varepsilon_0$, and conductivity $\sigma = 1 \times 10^{11}$ S/m), anhydrous ethanol (analytical pure, ShuangShuang Chemical, Shandong, China), sodium hydroxide (analytical pure, Huludao City Chemical Reagent, Liaoning, China), and silane coupling agent (Z-6030, The United States Dow Corning Corporation, Milrand, MI, USA) were purchased for the experiment. The oil for immersing the insulation paper was conventional transformer mineral oil (numbers 25, Sichuan Chuanrun, Chengdu, China).

2.2. Surface Modification of Nano-TiO_2. Surface modification must be performed before the nano-TiO_2 can be used to reinforce the insulation paper. The surface modification process is as follows.

(1) 50 g of nano-TiO_2 was weighed and placed in a 100°C oven for 30 min.

(2) 0.5 g of silane coupling agent was weighed and put into a beaker.

(3) 100 mL of anhydrous ethanol was put into the beaker, and the pH value of the mixed solution was adjusted with sodium hydroxide.

(4) Nano-TiO_2 was added to the mixed solution. Then, the mixed solution was poured into a three-necked flask, and 400 mL of anhydrous ethanol was added.

(5) The three-necked flask was heated using the water bath method with constant stirring.

(6) After finishing the reaction, the product was placed in a beaker and put into a 100°C oven to dry for 24 h.

2.3. Preparation and Oil Immersion Process of Insulation Paper. First, the nano-TiO_2, which was modified by a silane coupling agent, was dissolved in absolute ethanol (1 : 100 wt%), and the slurry was homogenized by vigorous agitation with a magnetic stir bar for 10 min. Next, the pulp was diluted to 0.4 wt% in deionized water, and various wt% of nano-TiO_2 were added. The mixtures were stirred for 5 min at 5000 rpm in a fiber disintegration device and were used to create the insulation paper. Then, each wet insulation paper sample was dried at 105°C for 7 min under a vacuum. Insulation paper with a target basis weight of 120 g/m^2 was produced. Lastly, insulation paper was immersed in oil, using the following steps.

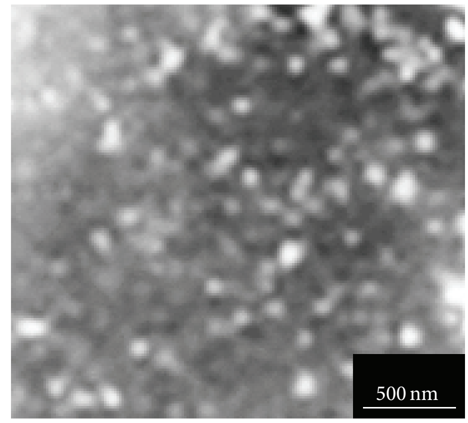

Figure 1: SEM images of insulation paper reinforced with nano-TiO_2 after oil immersion process.

(1) The insulation paper was cut into 4 and 8 cm diameter circles and placed into different glass bottles according to the sample type.

(2) All samples were put into the vacuum chamber and were dried at 90°C for 48 h. After that, the temperature of the vacuum chamber was adjusted to 40°C.

(3) Mineral oil at 40°C was infused into the glass bottles in the vacuum chamber to immerse the samples for 24 h.

As shown in Figure 1, the distribution of nano-TiO_2 in the oil-impregnated insulation paper is uniform and the average particle size of TiO_2 is less than 60 nm.

2.4. Experiment Characterization. After the insulation paper samples were prepared, they were immersed in mineral oil to measure the breakdown strength, density, polarization current, depolarization current (PDC), thermally stimulated depolarization current (TSDC), scanning electron microscopy (SEM), and frequency domain dielectric spectrum (FDS). Some other samples that were not immersed in mineral oil were used to measure tensile strength.

The breakdown strength was measured with homemade equipment according to IEC 60241-1:1998. Electrodes were made from copper. The diameters of the high-voltage (HV) electrode and ground electrode were both 25 mm. Insulation oil was used as the dielectric surrounding the equipment. The test power supply used was HV alternating current power. Its boot speed was 500 V/s, and its frequency was 50 Hz. The breakdown electric field strength of each sample was measured seven times. The diagram of the equipment used to test the breakdown strength is shown in Figure 2.

Tensile strength was measured with an electronic pull tester (AT-L-2, ANMT Instrument). The tensile speed was

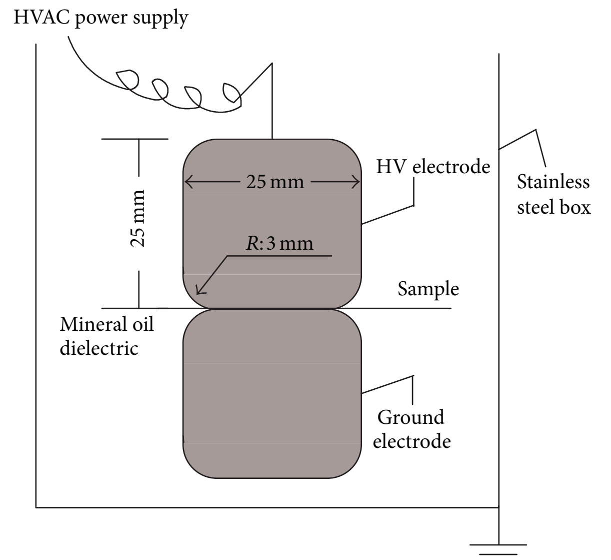

FIGURE 2: Diagram of equipment used to test the breakdown strength.

10 mm/min. The length of the samples was 100 mm, and the width was 15 mm. The tensile strength of each sample was measured 10 times.

Dielectric properties under different frequencies (10^{-2} to 10^7 Hz) at room temperature were measured by broadband dielectric spectroscopy equipment (Novocontrol concept 80, GmbH, Germany). The oil on the surface of the oil-impregnated insulation paper was cleared before the samples were measured. The measuring electrodes were two copper plates with 4 cm diameters. The density of the oil-impregnated insulation paper was measured by the Archimedes method.

The polarization and depolarization current analyses were carried out with a PDC-Analyser-1MOD (ALFF Engineering, Switzerland), and the measurement time was set to 5000 s.

Trapping parameters of electrons in the dielectric is determined by using the thermally stimulated depolarization current technique. The experiment was carried out using Novocontrol TSDC equipment. Considering the temperature tolerance of the insulation oil, the test temperature range was set from −30°C to 130°C.

3. Results and Discussion

The nano-TiO_2 contents in the insulation paper were 0, 1, 2, 3, and 4%, and they were designated as P0, P1, P2, P3, and P4, respectively.

Relations between tensile strength and different nano-TiO_2 contents in the insulation paper are shown in Figure 3. The tensile strength of insulation paper slightly decreases with increasing nano-TiO_2 content in the insulation paper. The tensile strengths of P0, P1, P2, P3, and P4 are 8.58 kN/m, 8.56 kN/m, 8.52 kN/m, 8.55 kN/m, and 8.32 kN/m, respectively.

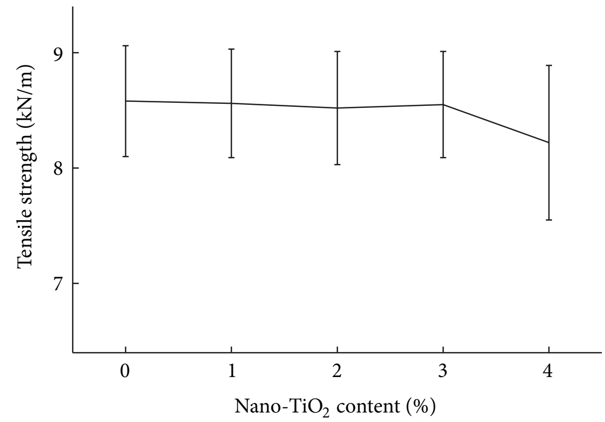

FIGURE 3: Effect of nano-TiO_2 content on the tensile strength of insulation paper.

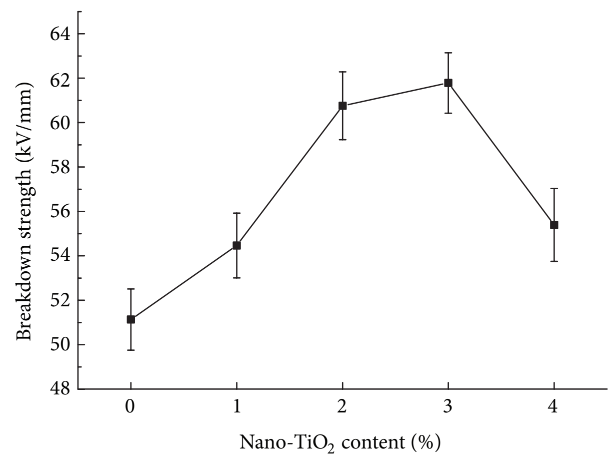

FIGURE 4: Effect of nano-TiO_2 content on the breakdown strength of oil-impregnated insulation paper reinforced with nano-TiO_2.

From Figure 4, the breakdown strength of oil-impregnated insulation paper significantly increases and then decreases with increasing nano-TiO_2 content. When the nano-TiO_2 content reached 3%, the breakdown strength reached its maximum value of 61.78 kV/mm, while the breakdown strength of P0 was 51.13 kV/mm. The breakdown strength of P3 increased by 20.83% compared to that of P0.

When the nano-TiO_2 content reached 4%, breakdown strength began to decrease. Therefore, the maximum content was set at 3% in the following experiments.

The variation of the relative permittivity of oil-impregnated insulation paper reinforced with different nano-TiO_2 contents at different frequencies is shown in Figure 5. The trend for the four kinds of samples is similar. The changes in relative permittivity range from 10^{-2} Hz to 10^7 Hz. The relative permittivity of oil-impregnated insulation paper reinforced with nano-TiO_2 is lower than that of oil-impregnated insulation paper that is not reinforced with nano-TiO_2 within the test frequency range. Furthermore, at 50 Hz, the relative permittivity decreases with increasing nano-TiO_2 content, and the relative permittivity of P3 has a minimum value

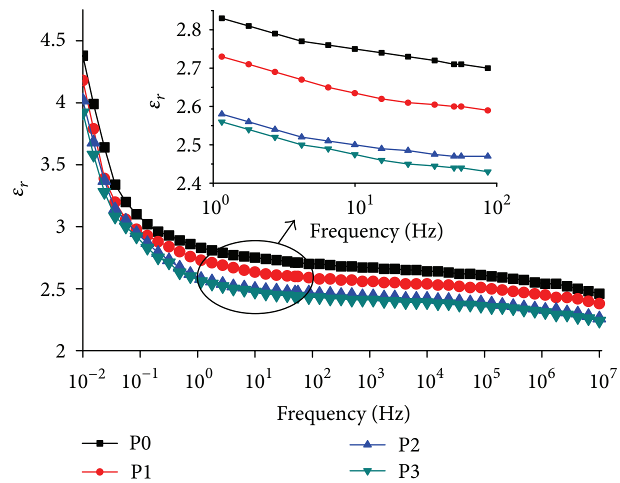

Figure 5: Variation of relative permittivity of oil-impregnated insulation paper reinforced with different nano-TiO_2 contents at different frequencies.

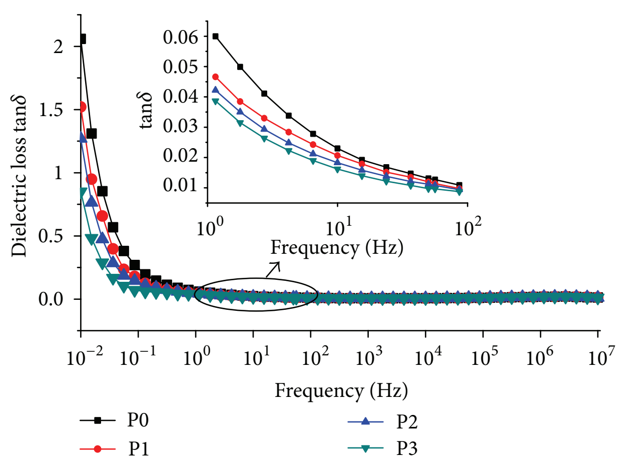

Figure 6: Variation of the dielectric loss of oil-impregnated insulation paper reinforced with different nano-TiO_2 contents at different frequencies.

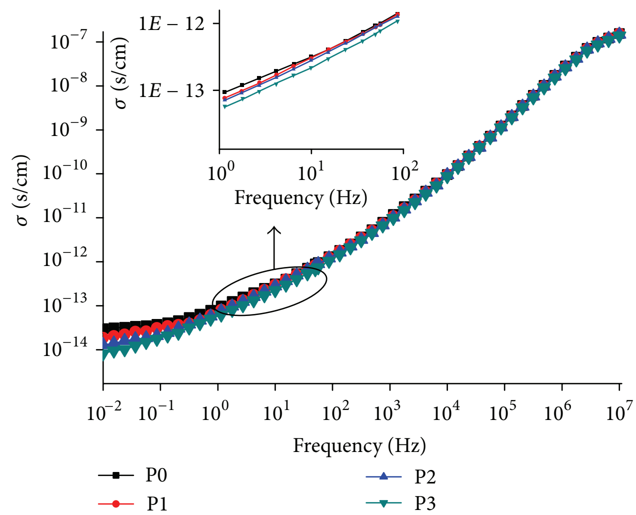

Figure 7: Variation of the conductivity of oil-impregnated insulation paper reinforced with different nano-TiO_2 contents at different frequencies.

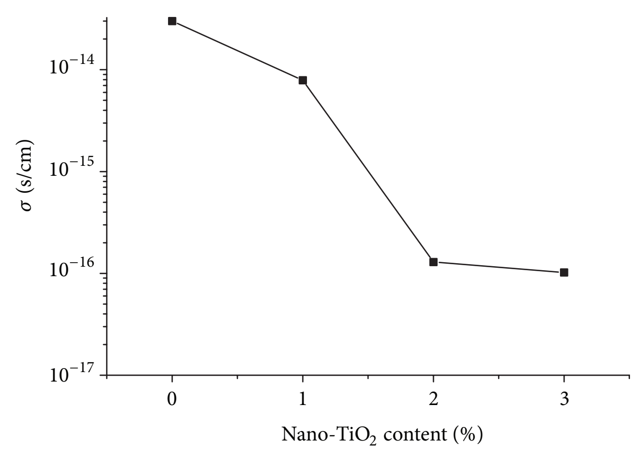

Figure 8: Volume conductivity of oil-impregnated insulation paper reinforced with different nano-TiO_2 contents (measured under DC).

of 2.41. The electric field strength distribution of each part of the composite insulation has an inverse correlation with relative permittivity. The relative permittivity of insulation paper is higher than that of insulation oil, and the breakdown strength of insulation oil is lower than that of insulation paper. Therefore, the decrease in relative permittivity is crucial to the improvement of the insulation property of the oil-paper insulation system.

Figure 6 shows the variation of the dielectric loss of oil-impregnated insulation paper reinforced with different nano-TiO_2 contents at different frequencies, and the trends for the four kinds of samples are similar. The dielectric loss of the four kinds of oil-impregnated insulation paper decreases with increasing frequency. When the nano-TiO_2 content increases, the dielectric loss of oil-impregnated insulation paper decreases. There is little difference from 10 Hz to 10^7 Hz. However, there is a visible difference in the dielectric loss of oil-impregnated insulation paper from 10^{-2} Hz to 10 Hz.

The variation of the conductivity of oil-impregnated insulation paper reinforced with different nano-TiO_2 contents at different frequencies is shown in Figure 7. In the test frequency, the four kinds of oil-impregnated insulation paper had similar variation trends, and the conductivity increased with increasing frequency. The conductivity decreased with increasing nano-TiO_2 content. From 10^{-2} Hz to 10 Hz, the conductivity of the four kinds of oil-impregnated insulation paper is significantly different. However, the conductivities of the four kinds of oil-impregnated insulation paper are very similar from 10 Hz to 10^7 Hz. As can be seen in Figure 8, the volume conductivity of oil-impregnated insulation paper is reduced with increasing nano-TiO_2 content under a DC electric field.

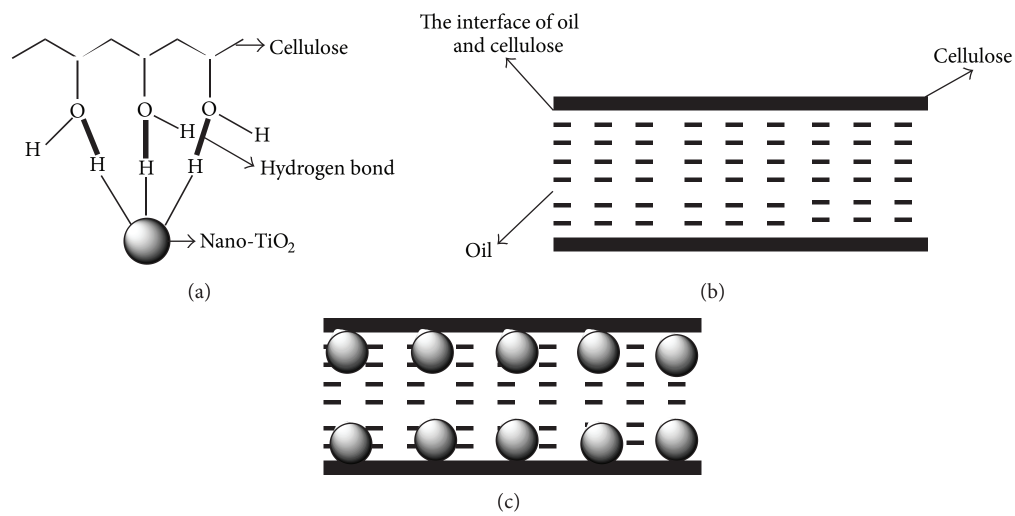

Figure 9: Structure of gap. (a) Interaction between cellulose and nano-TiO_2; (b) oil gap; (c) oil gap reinforced by nano-TiO_2.

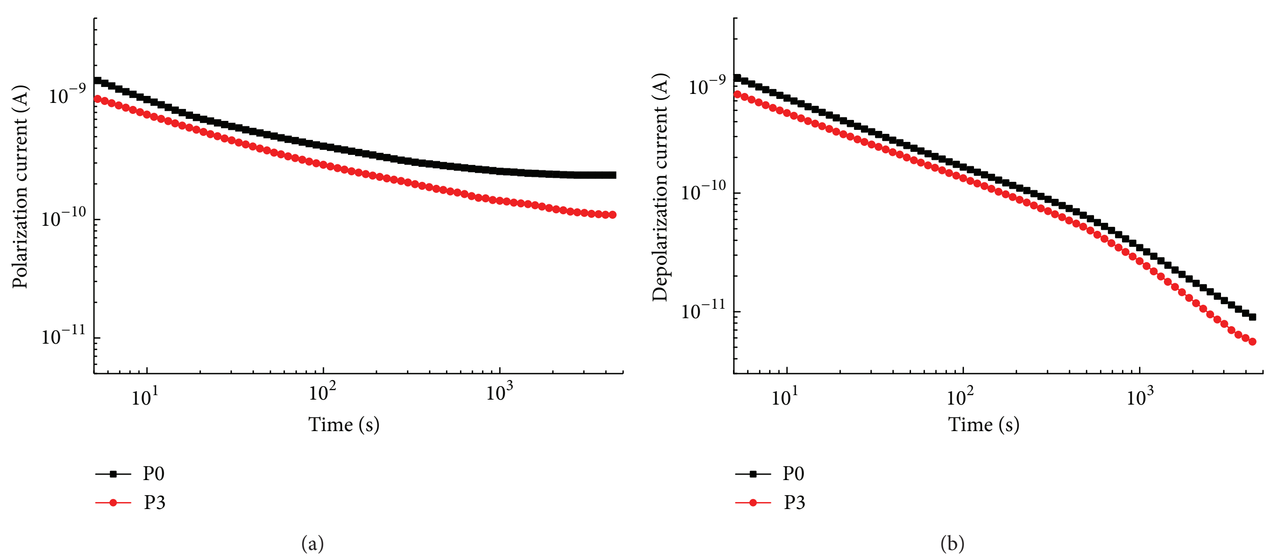

Figure 10: The polarization current and depolarizing current of oil-impregnated insulation paper.

Insulation paper is composed of cellulose, which is linked by hydrogen bonds. There are a large number of gaps in the interior of insulation paper; when the insulation paper is immersed in insulation oil, those gaps are filled with the insulation oil. Under an electric field, the breakdown first occurs in the weakest part. Because the electric field strength distribution of each part of composite insulation has an inverse correlation with relative permittivity, the relative permittivity of cellulose is higher than that of insulation oil and the breakdown strength of insulation oil is lower than that of cellulose. Therefore, those gaps that are filled with insulation oil in the interior of the oil-impregnated insulation paper are broken down first.

It is well known that electron is accelerated in the insulation oil more easily than in the cellulose. These electrons may develop into fast electrons, which possibly leads to the oil-impregnated insulation paper breakdown. When nano-TiO_2 is added to the insulation paper, it enters the interior of insulation paper and is present on the surface of cellulose. All the contact interfaces of cellulose and oil have the nano-TiO_2. As shown in Figure 9, one side of nano-TiO_2 is firmly attached to the cellulose surface and the other side is immersed in insulation oil. According to the literature [18], a large number of traps are likely generated because of nano-TiO_2; these traps form a protective tape. When the fast electrons enter the protective tape, the fast electrons can be converted to slower electrons by repeated trapping and detrapping in the protective tape.

We measured the polarization current, depolarizing current, and trap characteristics of oil-impregnated insulation paper by the PDC and TSDC methods in order to understand the effect of TiO_2 nanoparticles. Figure 10 shows the changes

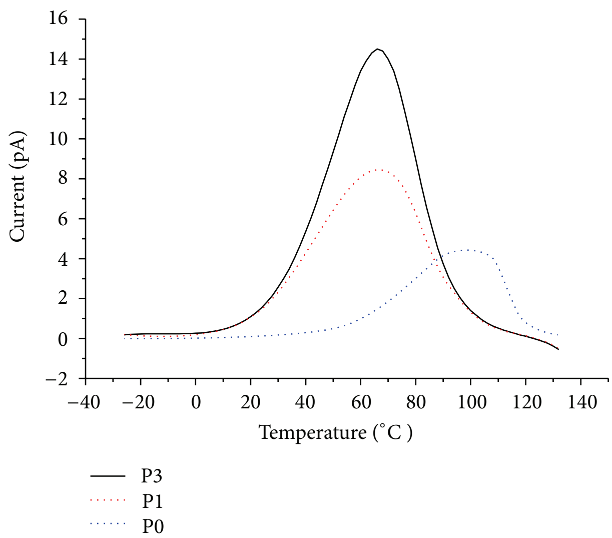

Figure 11: The results of thermally stimulated depolarization current measurement.

in the polarization current and depolarizing current with time. The polarization current and depolarizing current of oil-impregnated insulation paper reinforced with nano-TiO_2 both decrease. It is well known that the depolarization current from 1 s to more than 1000 s is mainly caused by interfacial polarization [19]. And the value of depolarization current is determined by the permittivity and conductivity of oil and cellulose on both sides of the interface. Now that the value is changed, it can be proposed that the permittivity and conductivity of oil and cellulose on both sides of the interface are changed because of nano-TiO_2. The changes may be the reason why the permittivity and conductivity of oil-impregnated insulation paper reinforced with nano-TiO_2 are changed.

As shown in Figure 11, the results of thermally stimulated depolarization current of oil-impregnated insulation paper reinforced with nano-TiO_2 and oil-impregnated insulation paper are greatly different. The peak value of TSDC curve for P3 is 3.25 times that of P0. Since the peak value of TSDC curve is related to maximum trap density in a dielectric, P3 and P1 is assumed to have a higher trap density than the P0. The integration of TSDC over temperature gives the total number of trap charge released from the trap center. It is found that the total number of charge trapped in P3 and P1 are 6.10 nC and 4.21 nC, respectively. But the total number of charge trapped in P0 is 1.96 nC. The peak position of P3 and P1 is the same; it can be proposed that the increased traps are generated because of nano-TiO_2. These results demonstrate that the presence of TiO_2 nanoparticles in the oil-impregnated insulation paper dramatically increases the electron trap density.

4. Conclusions

(1) The breakdown strength of oil-impregnated insulation paper is first increased and then decreased, with increasing nano-TiO_2 content. P3 has the maximum breakdown strength of 61.78 kV/mm. The value increased by 20.83% compared to P0.

(2) The relative permittivity, dielectric loss, and conductivity decreased with increasing nano-TiO_2 content.

(3) The most likely reason that nano-TiO_2 can affect the insulation properties of oil-impregnated insulation paper is because the addition of nano-TiO_2 can increase the total number of trap.

Conflict of Interests

The authors declare that they have no financial or personal relationship with any people or any organization that may inappropriately influence their work and there is no professional or commercial interest of any kind in all of the commercial entities mentioned in their paper.

Authors' Contribution

Ruijin Liao and Cheng Lv contributed equally to this study.

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