Research Article

Influence of Monodisperse Fe$_3$O$_4$ Nanoparticle Size on Electrical Properties of Vegetable Oil-Based Nanofluids

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Insulating oil modified by nanoparticles (often called nanofluids) has recently drawn considerable attention, especially concerning the improvement of electrical breakdown and thermal conductivity of the nanofluids. In this paper, three sized monodisperse Fe$_3$O$_4$ nanoparticles were prepared and subsequently dispersed into insulating vegetable oil to achieve nanofluids. The dispersion stability of nanoparticles in nanofluids was examined by natural sedimentation and zeta potential measurement. The electrical breakdown strength, space charge distribution, and several dielectric characteristics, for example, permittivity, dielectric loss, and volume resistivity of these nanofluids, were comparatively investigated. Experimental results show that the monodisperse Fe$_3$O$_4$ nanoparticles not only enhance the dielectric strength but also uniform the electric field of the nanofluids. The depth of electrical potential well of insulating vegetable oils and nanofluids were analyzed to clarify the influence of nanoparticles on electron trapping and on insulation improvement of the vegetable oil.

1. Introduction

Recent research works have shown that conductive and semiconductive nanoparticles can be dispersed in mineral and vegetable insulating oils to enhance dielectric strength or thermal conductivity of the insulating oils. Magnetic Fe$_3$O$_4$ nanoparticles have been proved of increasing the AC breakdown voltage of insulating oils for the case that the nanoparticles were well dispersed in oil [1–5]. It is also documented that both mineral and vegetable insulating oils are possible to show enhanced AC breakdown voltages and partial-discharge-inception voltages after the oils are modified by semiconductive TiO$_2$ nanoparticles [6, 7]. The electrical properties and dispersion stability of three nanofluids that are prepared by dispersing Fe$_3$O$_4$, TiO$_2$, and Al$_2$O$_3$ nanoparticles, respectively, in transformer oils have been discussed at a certain level [8]. The main process of charge transport in nanofluids is considered as the trapping and detrapping of electrons in shallow traps which has been argued in [7, 9].

It is already clarified that the dielectric performance of nanofluids is critically determined by nanoparticles’ size [10, 11]. However, comparative and systematic studies on the influence of nanoparticle size on the breakdown and the dielectric properties of vegetable oil-based nanofluids are still an open issue, which is becoming more important for applying such nanofluids in large power transformers. Moreover, nanoparticles often tend to agglomerate in oil because of nanoparticle’s high surface-energy. It is technically difficult to prepare sufficiently good nanoparticles (single-crystalline, well-shaped, and narrow size-distribution) for analyzing the relationship between nanoparticle size and nanofluids’ dielectric responses. Recently, several models are proposed to explain the improving breakdown characteristics of nanofluids [9, 12]. However, these mechanisms are always hard to explain influence of nanoparticle size on breakdown voltages and dielectric properties of nanofluids.

Our work aims to explore how the size of monodisperse nanoparticles generates various dielectric performances of nanofluids. The insulating vegetable oil-based nanofluids were prepared by adding three sized monodisperse Fe$_3$O$_4$ nanoparticles. Their basic physical and chemical properties are first presented briefly. The dispersion stability of nanofluids was determined by comparison of zeta potential...
measurement. Next, the different dielectric properties of nanofluids are presented and discussed. The space charge distribution and electrical potential well depth were analyzed for the explanation of different breakdown voltages between the nanofluids and insulating vegetable oils.

2. Experimental

2.1. Materials. All reagents used in the experiment were of analytical grade without further purification.

2.2. Preparation of Nanofluids. The insulating vegetable oil-based nanofluids are obtained via three main procedures: preparation of the iron oleate precursor, preparation of the monodisperse Fe$_3$O$_4$ nanoparticle, and synthesis of the nanofluids.

2.2.1. Iron Oleate Precursor. 6.48 g of iron (III) chloride hexahydrate was dissolved in the mixture of 48 mL ethanol and 84 mL N-hexane. The obtained solution was slowly added by 21.9 g sodium-oleate-vigorous with magnetic string at 60 °C for 12 h. The precipitated iron oleate was washed twice with methanol and was redissolved in hexane afterwards. The solution was additionally washed three times with warm (∼60 °C) deionized water in a separatory funnel and subsequently dried in vacuum at 80 °C for 24 h.

2.2.2. Fe$_3$O$_4$ Nanoparticles. 2.1 g iron oleate precursor and 0.64 mL oleic acid were mixed in 10 mL octadecene followed by transferring into a three-neck-round-bottom flask and drying at 120 °C for 30 min under nitrogen protection to remove water and oxygen. Then, the resulting mixture was heated to 320 °C with 12 h, 24 h, and 48 h, respectively, to realize Fe$_3$O$_4$ nanoparticles with varied sizes. After cooling down to room temperature, the nanoparticles were subsequently centrifuged and washed several times with ethanol and cyclohexane before drying in air at 70 °C.

2.2.3. Preparation of Nanofluids. The three Fe$_3$O$_4$ nanoparticles obtained by different reaction time were dispersed in the insulating vegetable oil through ultrasonic treatment. They were tagged by samples A, B, and C, respectively. The FR3 natural ester was used as received [13]. Before electrical characterization, three nanofluids and the FR3 were dried at 85 °C under 50 Pa for 72 h. Some physical and chemical parameters of the FR3 and nanofluids are listed in Table 1.

2.3. Nanoparticle Characterization. The X-ray diffraction (XRD) pattern was obtained by using a powder X-ray diffraction meter equipped with a rotating anode and a Cu-Kα radiation source. The scan step was 0.02°. Figure 1 shows the XRD results of typical Fe$_3$O$_4$ nanoparticle according to [5] and different samples were obtained by high temperature decomposition method. It can be seen from the figure that the XRD patterns of Fe$_3$O$_4$ nanoparticle near 2θ have a very wide amorphous peak; this is because the nanoparticles surface

![Figure 1: XRD patterns of pure Fe$_3$O$_4$ and Fe$_3$O$_4$ nanoparticle at different reaction time: (A) 12 hours, (B) 24 hours, and (C) 48 hours.](image)

Table 1: Basic physical and chemical properties of the FR3 and the insulating vegetable oil-based nanofluids.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>FR3</th>
<th>Nanofluids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Light yellow</td>
<td>Dark yellow</td>
</tr>
<tr>
<td>Density (kg·m$^{-3}$, 20°C)</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>Kinematic viscosity (mm$^2$·s$^{-1}$, 40°C)</td>
<td>43.0</td>
<td>44.0</td>
</tr>
<tr>
<td>Pour point (°C)</td>
<td>−18</td>
<td>−18</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>325</td>
<td>325</td>
</tr>
<tr>
<td>Acid value (mg·KOH·g$^{-1}$)</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Interfacial tension (mN/m)</td>
<td>30</td>
<td>30</td>
</tr>
</tbody>
</table>


was coated with a large number of oleic acid. As the reaction time of sample A is not sufficient and the size is too small, there was no peak corresponding with Fe$_3$O$_4$ observed. The sharp peaks of samples B and C reveal that the nanoparticles have high crystallinity. According to JCPDS card number 65-3107, the $2\theta$ values of 30.1°, 35.5°, 43.1°, 56.9°, and 62.6° are signatures of (220), (311), (400), (511), and (440) crystal face for Fe$_3$O$_4$, respectively. Therefore, these XRD patterns may be indicative of the spinel structure of the Fe$_3$O$_4$ nanoparticles.

The morphologies of the three sized nanoparticles were observed by transmission electron microscopy (TEM), as shown in Figure 2. It is seen that the nearly spherical Fe$_3$O$_4$ nanoparticles prepared by high temperature decomposition (at 320°C) have achieved monodispersion. Each nanoparticle consists of two differentiated contrast regions. The darker central-core is the Fe$_3$O$_4$ crystal, which is surrounded by a lower-density shell, that is, the oleic acid. The covalent bonding between oleic acid and Fe$_3$O$_4$ prevents agglomeration of Fe$_3$O$_4$ nanoparticles but also improves the compatibility between nanoparticles and vegetable insulating oil [14].

The average size of the Fe$_3$O$_4$ crystal in Figure 2(a) is estimated as $\sim$6.6 nm. Here the size represents the diameter of Fe$_3$O$_4$ crystal without the shell. With longer reaction time, that is, from 12 to 48 h, the thickness of oleic acid shell grows slightly from $\sim$2 to $\sim$3 nm. Therefore sized Fe$_3$O$_4$ nanoparticles are obtained with varying diameter from $\sim$8.6 (Figure 2(a)) to $\sim$24.4 nm (Figure 2(c)) via $\sim$15.2 nm (Figure 2(b)). The zoomed TEM image (inset in Figure 2(c)) better indicates the border between oleic acid shell and Fe$_3$O$_4$ crystal.

### 3. Results and Discussion

#### 3.1. Dispersion Stability of Nanofluids

Natural sedimentation is an indicator of the dispersion stability for nanoparticles in nanofluids. Three sized Fe$_3$O$_4$ nanoparticles were dispersed in the vegetable oil, to realize nanofluids that are recognized as 1, 2, and 3 to examine their storage-time dependent dispersion stability. As shown in Figure 3, nanofluids show no visible agglomeration for the nanoparticles in oil after 6 months standing in ambient condition.

The zeta potential measurement is another method to evaluate stability of the nanofluids. As the stabilization theory [15] describes, the electrostatic repulsion among nanoparticles should increase prominently for the case that the zeta potential stands at a high level which signifies good suspension stability [16]. Table 2 lists several key zeta potential values that indexed the suspension stability of nanofluids.
The zeta potential for all the three nanofluids 1, 2, and 3 display values above 30 mV, that is, 74.0, 60.7, and 47.4 mV, respectively. It has been well accepted that a zeta potential which is greater than 30 mV should mark a sufficiently good dispersion stability [15]. As a general rule, the smaller nanoparticles in nanofluids, the higher the zeta potential and certainly the more stable the nanofluids.

3.2. Breakdown Voltage of Nanofluids. The absolute moisture content of all nanofluids was controlled at a value below 200 mg/kg. The AC breakdown voltages of each nanofluid were characterized in accordance with IEC 60156 [17]. All the measurements were made on 9 nanofluids samples. The FR3 oil was also included in measurements for comparison.

The lightning-impulse breakdown voltages for nanofluids were obtained by means of a configuration consisting of a container and an electrode in Figure 4. The high-voltage electrode and the grounding electrode were a steel needle and a 13 mm diameter steel sphere, respectively. The gap between the needle tip and the sphere was 15 mm. These dimensions comply with IEC 60897 [18] for liquid dielectrics.

1.2/50 μs standard lightning-impulse voltages are employed to determine the lightning-impulse breakdown voltages.

Figure 5 lists the AC breakdown voltages of the three nanofluids and the FR3 oil, in which the oil was marked as 0 ppm nanoparticles added. It is seen that the breakdown strength of each nanofluids increases to a top value and slightly decreases afterwards with higher nanoparticle content. For example, the breakdown strength enhances by 23% from 55.1kV for FR3 to 67.8kV for nanofluids C that was added with 200 ppm nanoparticles. On the other hand, the breakdown strength tends to increase for nanofluids with larger size nanoparticles added.

The lightning-impulse breakdown voltages of the three nanofluids and FR3 oil for both polarities are summarized in Table 2: Zeta potential and associated suspension stability.
Figures 6 and 7. For negative lightning-impulse the nanofluids provide insignificant effects, but for the AC profile or for the positive lightning-impulse the attained improvement is significant. Here the positive lightning-impulse leads to strongly increased breakdown voltages. The nanofluid C, which contains 300 ppm nanoparticles, exhibits the highest breakdown voltage of 69.7 kV for positive lightning-impulse. This is a significantly higher voltage which is enhanced by 64% compared to that of FR3 oil. However the nanofluids show only slightly improved (7%) breakdown behavior for the case of negative lightning-impulse application. The increases of the positive lightning breakdown voltages are greater than that of the negative lightning-impulse breakdown voltages. For positive lightning-impulse, nanoparticles in nanofluids will weaken the field strength and extremely increase positive breakdown voltages. However, the effect is inconspicuous for negative lightning-impulse [4]. Our results point out an opposite tendency with the breakdown behavior that has been observed in mineral oil-based nanofluids [1, 8]. This should be attributed to the much different molecular conformation of insulating vegetable oil, which certainly generates different streamer development.

From the results in Figures 5–7, one can note that the measured breakdown voltage of nanofluids follows a sequence \( A < B < C \) with nearly no influence from polarity or nanoparticle content. This encourages us to conclude that the breakdown strength of nanofluids is mainly determined by the size of nanoparticles.

3.3. Dielectric Properties of Nanofluids. The frequency dependences of permittivity between \( 10^{-2} \) and \( 10^{6} \) Hz for FR3 oil and the three nanofluids are summarized in Figure 8. There is no big difference over the frequency range among samples. As well known, the relative permittivity of \( \text{Fe}_3\text{O}_4 \) nanoparticles is ca. 80 [12], which is much greater than that of FR3 oil. Therefore nanoparticles may contribute more to the permittivity of nanofluids than FR3 oil. Furthermore, at 50 Hz, the relative permittivity decreases with increasing nanoparticle size and the relative permittivity of sample A has a maximum value of 3.06.

It is obvious that the permittivity values of nanofluids varied with the size of nanoparticles. Considerable results have confirmed that smaller sized nanoparticles usually possess higher permittivity than that of larger ones. The reason can be found from an internal-stress model which has been introduced by Buessem et al. [19]; that is, the permittivity of...
a nanoparticle is determined by the relatively strong internal stress which is the result of free-energy balance.

The dielectric loss of nanofluids and FR3 oil shows a decrease with increasing frequency as the results shown in Figure 9. However the nanofluids’ loss decreases for larger sized Fe$_3$O$_4$ nanoparticles. The three nanofluids and the FR3 oil behave almost identical between 1 and $10^6$ Hz. They present obvious difference at the range of $10^{-2}$–$1$ Hz.

The loss of a fluid is composed of two contributions, that is, conductance loss and polarization loss. Vegetable insulating oil (e.g., FR3 oil in this work) is a weak polar liquid dielectric, which implies that the conductance loss dominates at low frequency [20]. The crystal defects within nanoparticles, which are unavoidable and usually are brought during chemical preparation, emerge more for larger sized nanoparticles. The high conductivity of these nanoparticles certainly leads to much increased dielectric loss.

Figure 10 gives the frequency dependence of the volume resistivity for FR3 oil and the three nanofluids. There is no visible difference among nanofluids and FR3 oil at a frequency above 0.1 Hz. When frequency downs below 0.1 Hz, the curves start to diverge, with a changeless tendency that the volume resistivity of nanofluids is always higher than that of FR3 oil.

Nanoparticles dispersed in nanofluids are polarized when the nanofluids are subjected to an externally applied electric field [12]. These nanoparticles provide traps free electrons, thereby decreasing the concentration of highly mobile electrons in the nanofluids and increasing the concentration of low-mobility negatively charged nanoparticles. As a result, the volume resistivity of the nanofluids is larger than that of the vegetable insulating oil. Increasing the frequency decreases both the duration of each half cycle of the electrical field and the probability of electron capture by the nanoparticles. These phenomena explain the smaller difference in volume resistivity between the FR3 oil and the nanofluids at frequencies greater than approximately 0.1 Hz.

3.4. Space Charge Distribution of Nanofluids. In order to investigate the influence of sizes of monodisperse Fe$_3$O$_4$ nanoparticle on charge carriers transport characteristics of the vegetable oil and vegetable oil-based nanofluids, the pulse electroacoustic (PEA) tests were carried out to investigate the space charge density of all samples, stressed 15 kV/mm for varying time (0.5, 1, 5, 10, and 30 min). As shown in Figure 11, the charge density in vegetable oil is increasing with time and the maximum charge density was about 34.2 C/m$^3$. However, the charge density in nanofluids was first increased and then decreased with time, less than half of that in vegetable oil. The

![Figure 8: Variation of the relative permittivity of vegetable oil modified by Fe$_3$O$_4$ nanoparticles with different sizes at different frequencies.](image8)

![Figure 9: Variation of the dielectric loss of vegetable oil modified by Fe$_3$O$_4$ nanoparticles with different sizes at different frequencies.](image9)

![Figure 10: Variation of the volume resistivity of vegetable oil modified by Fe$_3$O$_4$ nanoparticles with different sizes at different frequencies.](image10)
maximum charge density of the three nanofluids was about 16.6, 12.5, and 7.5 C/m$^3$, respectively.

The similar results also can be found in [7, 21, 22]. Interaction between nanoparticles and vegetable oil molecule will significantly improve the charge mobility of nanofluids. And the rapid charge mobility may inhibit space charge accumulation, resulting in uniform electric field of nanofluids.

3.5. Possible Mechanism. To understand why the breakdown voltage of nanomodified insulating vegetable oil is higher than that of pure vegetable oil, a dipole model of nanoparticles in [23] is proposed. The charge relaxation time constant of nanoparticles has a major bearing on the extent to which the electrodynamics processes in the liquid are modified. If the nanoparticles’ charge relaxation time constant is short, then the timescales of interest for streamer growth and their presence in the oil will significantly modify the electrodynamics.

The spherical nanoparticles (diameter $2a$, relative dielectric constant $\epsilon_2$) were dispersed in the insulating oils (relative dielectric constant $\epsilon_1$) as shown in Figure 12, and an external electric field $E_0$ was applied to the vegetable oil-based nanofluids consisting of $\epsilon_1$ and $\epsilon_2$ dielectrics. According to the calculation, the relaxation time constant of the nanoparticle $Fe_3O_4$ used in the test is less than the propagation time of the streamer [4]. Electric charges will be induced by the electric field $E_0$ at the interface between the $\epsilon_1$ and $\epsilon_2$ dielectrics:

$$\delta_p = \epsilon_0 E_0 \left(1 - \frac{3\epsilon_1}{2\epsilon_1 + \epsilon_2}\right) \cos \varphi_p \sin \theta_p.$$  

(1)
Figure 12: Diagram depicting the dipole surface charge density, \( \sigma_p(\theta_p, \varphi_p) \), and the electrical potential, \( V(r, \varphi) \), in spherical coordinates.

As the direction of \( E_0 \) was set in the direction of the \( x \)-axis, angle \( \varphi = 0 \), the positive dipole surface charge, \( +\sigma_p(\theta_p, \varphi_p) \), was induced within the angle range \( -\pi/2 < \varphi_p < +\pi/2 \), and the negative dipole surface charge, \( -\sigma_p(\theta_p, \varphi_p) \), was induced within the angle range \( \pi/2 < \varphi_p < 3\pi/2 \). The electrical potential distribution, \( V(r, \varphi) \), induced by the dipole surface charge density, \( \sigma_p(\theta_p, \varphi_p) \), expressed as (1), is given by (2). Equation (2) is normalized by the potential difference \( aE_0 \):

\[
V(r, \varphi) = \frac{aE_0}{4\pi} \left( 1 - \frac{3\varepsilon_1}{2\varepsilon_1 + \varepsilon_2} \right) \int_{-\pi}^{+\pi} \int_{0}^{+\pi} \sin^2 \theta_p d\theta_p d\varphi_p \cos \varphi_p \cos(\varphi - \varphi_p) \sqrt{1 + (r/a)^2 - 2(r/a) \sin \theta_p \cos(\varphi - \varphi_p)}.
\]

Figure 13 showed the electrical potential well distribution, \( V(r) \), at \( \varphi = 0 \) which was obtained from (2). The size of nanoparticle was \( a = 10 \), 20 and 30 nm, respectively, and the external electric field is \( E_0 = 200 \) kV/mm. Furthermore, the relative dielectric constant of the \( \text{Fe}_3\text{O}_4 \) nanoparticle was \( \varepsilon_1 = 80 \) and vegetable insulating oil was \( \varepsilon_2 = 3.2 \).

In Figure 13, it can be seen that the maximum electrical potential well occurred at the surface of the nanoparticle. The maximum electrical well of nanoparticle grows linearly with increasing the nanoparticle size. When the nanoparticle size was 10 nm, 20 nm, and 30 nm, the maximum electrical potential well depth was 5.86, 11.73, and 17.59 eV, respectively. The electrical potential well depth was much higher than that of insulating oil (about 0.45 eV) [23]. The increased electrical potential well depth in nanofluids could inhibit the free charge spread and enhance the capability of breakdown performance of nanofluids.

4. Conclusion

(1) The nanofluids were developed by dispersing \( \text{Fe}_3\text{O}_4 \) nanoparticles with different sizes in insulating vegetable oil to enhance its breakdown strength. For negative lightning-impulse the nanofluids provide insignificant effects, but for the AC profile or for the positive lightning-impulse the attained improvement is significant. Meanwhile, the increasing nanoparticle size will improve the breakdown performance of nanofluids.

(2) With increasing the nanoparticle size, the volume resistivities of the nanofluids are almost equal and their dissipation factors increase at frequencies below 0.1 Hz. The relative permittivities of the nanofluids are greater than that of the FR3 oil between \( 10^{-2} \) and \( 10^7 \) Hz, probably because of the much higher relative permittivity of the \( \text{Fe}_3\text{O}_4 \) nanoparticles.

(3) The addition of monodisperse \( \text{Fe}_3\text{O}_4 \) nanoparticle into vegetable insulating oil will increase the electrical potential well depth and nanoparticle size could significantly influence the electrical potential well depth. The increased electrical potential well depth could enhance the capability of breakdown performance of nanofluids.

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 our paper.

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