UMYU Scientifica, Vol. 3 NO. 2, June 2024, Pp 070 – 075
https://doi.org/10.56919/usci.2432.006
ISSN: 2955 – 1145 (print); 2955 – 1153 (online)
A periodical of the Faculty of Natural and Applied Sciences, UMYU, Katsina

ORIGINAL RESEARCH ARTICLE

Effect of Silica and Alumina Nanoparticles Addition on the Dielectric and Rheological Properties of Shea Oil Methyl Ester

Aliyu Abdulraheem[1], Sadiq Umar[2], Abdelmalik Amoka Abdulghaffar[1], Habibat Abdulsalam[1], Maidawa Saidu Shuaibu[1], and Suleiman Shaibu Asuku[3]
[1]Department of Physics, Ahmadu Bello University, Zaria, Kaduna State, Nigeria.
[2]Department of Physics, Ibrahim Badamasi Babangida University, Lapai, Niger State, Nigeria.
[3]Samaru College of Agriculture, Ahmadu Bello University, Zaria, Kaduna State, Nigeria.

ABSTRACT
The increasing environmental and utility concerns of mineral-based transformer oils have impelled research into alternative insulation liquids. This study developed a green nanofluid using a two-step approach, incorporating shea methyl ester (SME) derived from shea butter oil and surface-modified Al_2O_3 and SiO_2 nanoparticles. The dynamic viscosity at 25 °C and dielectric properties of the developed nanofluid were investigated in the frequency range of 0.1–15 kHz. Adding nanoparticles into the SME noticeably increased the oil's viscosity, with SiO_2 nanoparticles having the least effect on the base liquid's viscosity. The addition of 0.6 wt% of Al_2O_3 nanoparticles increased the dielectric loss of the SME at all frequencies (0.1–15 kHz), while the addition of 0.6 wt% SiO_2 filler nanoparticles reduced the loss of the base oil at frequencies beyond 4 kHz indicative of an improved electrical property. Adding Al_2O_3 and SiO_2 to the base SME oil obtained higher relative permittivity values. This study successfully developed an SME and single nanoparticle-based nanofluid, incorporating a 0.6 wt% weight fraction of surface-modified Al_2O_3 and SiO_2 nanoparticles. The addition of these nanoparticles increased the dynamic viscosity of the base methyl ester oil, with approximately 43% and 36% increases, respectively. The nanofluid developed by incorporating SiO_2 nanoparticles showed promising dielectric performance for its application as an insulation liquid.

ARTICLE HISTORY
Received February 29, 2024.
Accepted May 12, 2024.
Published June 08, 2024.

KEYWORDS
Nanofluid, saturated oil, dielectric constant, insulation liquid, shea butter oil

INTRODUCTION

Liquid insulation technology is integral to power transformer components and pivotal in electricity transmission and distribution systems. The liquid provides both cooling and insulation, it also safeguards the transformer against arching (Pagger et al., 2023). Environmental and utility challenges linked to mineral-based insulation liquids have set off research into the viability of natural ester oils derived from plant sources. Vegetable oils, such as neem, jatropha, castor, palm kernel, yellow oleander, canola, etc., have garnered significant attention due to their non-competing usage as cooking oil, widespread availability, oilseed yield, and unique fatty acid compositions.

Shea butter is a saturated vegetable oil obtained from the shea nut. It is an industrial product widely used in cosmetic and pharmaceutical products, with a significant percentage originating from the African continent (Goumbri et al., 2022). Shea butter is readily available in Nigeria and is relatively inexpensive. Its high percentage of saturated fatty acids makes it a suitable candidate for use as an electrical insulation liquid, as the higher the saturated fatty acid content of an oil, the better its thermo-oxidative stability (Viertel et al., 2011).

Natural esters have competitive advantages over mineral-based transformer oil. They are highly biodegradable and have higher flash and fire points, better moisture absorption, and greater breakdown strength (Rao et al., 2022). However, they have inherent undesired properties such as high viscosity, high loss, and poor thermo-oxidation stability (Rao et al., 2022). Although, unlike in breathers transformers where the liquid insulation is exposed to inflowing air, natural ester oil used in hermetically sealed transformers is safe from thermally induced oxidation. The high viscosity and loss remain drawbacks.

Correspondence: Aliyu Abdulraheem. Department of Physics, Ahmadu Bello University, Zaria, Kaduna State, Nigeria. ✉ aliyuelokene@gmail.com. Phone Number: +234 803 952 3330.
How to cite: Aliyu, A., Umar, S., Abdelmalik, A. A., Abdulsalam, H., Maidawa, S. S., & Suleiman, S. A. (2024). Effect of Silica and Alumina Nanoparticles Addition on the Dielectric and Rheological Properties of Shea Oil Methyl Ester. *UMYU Scientifica*, 3(2), 70 – 75. https://doi.org/10.56919/usci.2432.006

Incorporating a suitable volume fraction of nanoparticles into a base liquid (oil) can improve its physicochemical and dielectric properties, such as viscosity, dielectric loss, and breakdown strength (Chen et al., 2023; Das, 2023). Oparanti et al. (2021) reported reduced viscosity by adding a volume fraction of Al_2O_3 nanoparticles in a base palm kernel methyl ester (Oparanti et al., 2021b). In a separate but related study, Oparanti et al. (2021) also reported 0.6 wt% as the optimal volume ratio for Al_2O_3 nanoparticles in a base liquid for the improvement of the dielectric property of the base liquid (Oparanti et al., 2021a).

In the present study, the effect of adding 0.6 wt% volume fraction of SiO_2 and Al_2O_3 on the viscosity, relative permittivity, and loss of methyl ester of shea oil is studied. The dielectric properties of shea oil and its derivatives were investigated over a frequency range of 0.1 kHz to 15 kHz at a temperature of 25 °C. Shea oil is the base oil due to its relatively low cost, availability, and high percentage of saturated fatty acid content. The work provides insights into the loss reduction effects of some nanoparticles and the rheological effect of adding nanoparticles to a base liquid.

MATERIALS AND METHOD

Materials

Crude shea butter was purchased from local sellers in Zaria, mineral-based transformer oil was purchased from…oiloleic acid (99.8% Kermel, China), citric acid crystal (99%, Kermel China), sodium hydroxide pellet (98.9%, CDH, New Delhi, India), potassium hydroxide pellets (85%, Molychem, India), sodium sulfate anhydrous (99%, JHD Guangdong, China), fuller´s earth (BDH, England), ethanol absolute (99.7%, JHD Guangdong, China), LCR bridge (HM8118, Rohde & Schwarz), magnetic hot plate stirrer (IKA C-MAG HS 10), digital weighing balance (A&D GF-2000, Japan), vacuum drying oven (Jim-Bomb Ltd, Taiwan) and RVDV-I digital viscometer all available at the materials science laboratory, Ahmadu Bello University, Zaria. Aluminum oxide (Al_2O_3) NPs and silicon oxide (SiO_2) NPs purchased from Skyspring Materials Inc.Houston, USA.

Table 1. Some material properties of the nanoparticles used

Nanoparticle(s)	Properties	Description
Silicon Oxide (SiO_2)	Particle size	10-20 nm
	Form	powder
	Purity (%)	99.5
	Material type	Semi-conducting
Aluminium Oxide (Al_2O_3)	Av. particle Size	<100 nm
	Form	powder
	Purity (%)	99.8
	Material type	Insulating

Sample Preparation

Table 2. Description of samples

Identifier	Description	Filler Particle Conc.
MO	Mineral Oil	-
CSBO	Crude Shea Butter Oil Sample	-
PSO	Purified Shea Oil Sample	-
SME	Shea Methyl Ester Sample	-
SENF+A	Shea Ester-based Nanofluid with Al_2O_3 as filler particle	0.6 wt%
SENF+S	Shea Ester-based Nanofluid with SiO_2 as filler particle	0.6 wt%

Purification of the Crude Shea Oil

Shea butter was melted by heating at about 50 °C for 30 min. 500 ml of the melted Crude Shea Butter Oil (CSBO) was heated in a round bottom flask placed in a thermostatically controlled water bath at 60 °C. Then, 3.75 ml of citric acid aqueous solution was added and mixed thoroughly with a hot plate magnetic stirrer and a magnet stirrer bar at the rotational speed of 500 rpm for 15 minutes. Then, 10 ml of 8% NaOH solution was added and stirred for 20 minutes while maintaining the reaction at 60 °C. To reduce moisture content, the mixture of oil and chemicals was allowed to dry in a vacuum oven at 70 °C for 60 minutes. Afterward, 5 g of silica gel was added and stirred, followed by adding 5 g fuller´s earth at 85 °C and stirring for 30 minutes. The mixture was then filtered using Whatman filter paper No. 1 in an oven to expedite the filtration.

Development of Shea Oil Methyl Ester

The methyl ester sample of the oil was produced from the purified oil sample. In a 500 ml round-bottom flask, 300 g of the purified Shea oil was heated to approximately 60 °C. Sodium methoxide was prepared by adding 3.6 g of NaOH to 65.7 g of methanol in a beaker. The prepared sodium methoxide was poured into the heated oil while stirring at 750 rpm for 60 minutes. Subsequently, the resulting mixture was collected and poured into a separation funnel mounted on a clamp stand, allowing it to separate into two layers in an oven due to the saturated nature of the oil. The bottom layer containing glycerol was removed from the separating funnel, leaving the top layer containing the methyl ester in the funnel. The ester was water-washed using warm distilled water four times to eliminate excess sodium hydroxide and glycerol. The obtained sample (ester) was then dried in a vacuum oven at 80 °C to remove excess water molecules and methanol for 2 hours.

Surface Coating of Nanoparticles

The nanoparticles underwent functionalization to establish a more effective bonding interface with the base oil and prevent particle settling. Initially, 50 ml of methanol was combined with 5 g of nanoparticles (Al_2O_3 or SiO_2) at 60 °C while stirring at 600 rpm for 15 minutes, ensuring proper dispersion. Subsequently, 0.25 ml of oleic acid was introduced into the methanol-nanoparticle mixture and stirred thoroughly for 2 hours. Following the functionalization process, the nanoparticles were separated by filtration using Whatman filter paper No. 1 to isolate methanol and oleic acid. The resulting filtrate, constituting the treated nanoparticles, was then dried in an oven at 65 °C to remove excess methanol.

Development of the Nanofluid(s)

The nanofluid was prepared by heating 100 g of the base shea methyl ester oil to a temperature of 60 °C. 0.6 g (6 wt%) of the functionalized nanoparticles (Al_2O_3 or SiO_2) was added while stirring at 500 rpm for 30 minutes. The resulting mixture was then degassed in a vacuum-drying oven.

Measurement of Dynamic Viscosity

Viscosity as a property measuring the ease with which layers of a liquid slide over one another, is crucial for understanding the performance of transformer oil. It significantly influences the cooling efficiency of the oil, with lower viscosity promoting easier flow. Additionally, the viscosity of insulating oil plays a vital role in the dynamics of charge flow within the liquid.

To assess the dynamic viscosity of the oil samples, an RVDV-I digital viscometer was employed. The oil sample was carefully placed in the viscometer's holder using a syringe to prevent bubble formation. Afterward, an appropriate spindle was selected, and three measurements were taken, with the average value estimated for accurate characterization. The measurement was made at a temperature of 30 °C.

Measurement of Dielectric Loss and Relative Permittivity

The dielectric loss represents the energy dissipation within a dielectric liquid when subjected to a varying electric field. The experimental setup for evaluating dielectric loss and the dielectric constant (relative permittivity) is depicted in Figure 1. The measurements were conducted using the LCR Bridge.

Figure 1. Experimental setup for the measurement of dielectric loss and relative permittivity

Dielectric loss readings were directly obtained from the LCR bridge, while the dielectric constant was derived through calculations using measured values of capacitance recorded at various frequencies within the range of 100 Hz to 15 kHz. The calculations incorporated the dimensions of the dielectric test cell utilized for the measurement. Under a varying electrical field, the relative permittivity is a complex physical quantity characterized by real and imaginary parts. The real permittivity represents the relative permittivity of the sample measured in the setup depicted in Figure 1 and is defined using the following equation.

$$\varepsilon' = \frac{C}{C_0} \qquad (1)$$

Where C is the measured capacitance of the dielectric liquid in farad (F), and C_o is the measured capacitance with air as dielectric, and it is estimated from the geometry of the dielectric test cell using the equation;

$$C_0 = \varepsilon_0 \frac{\pi r^2}{d} \qquad (2)$$

Where d is the separation between the electrodes, r is the radius of the electrodes, and ε_0 is the permittivity of the vacuum.

The real, ε' and imaginary, ε'' Permittivity is related to the loss of tangent through the equation

$$\varepsilon'' = \varepsilon' \tan\delta \qquad (3)$$

RESULTS AND DISCUSSION

Rheological Characterization

Viscosity

The dynamic viscosity of the oils provides information on the flow characteristics of the oil samples.

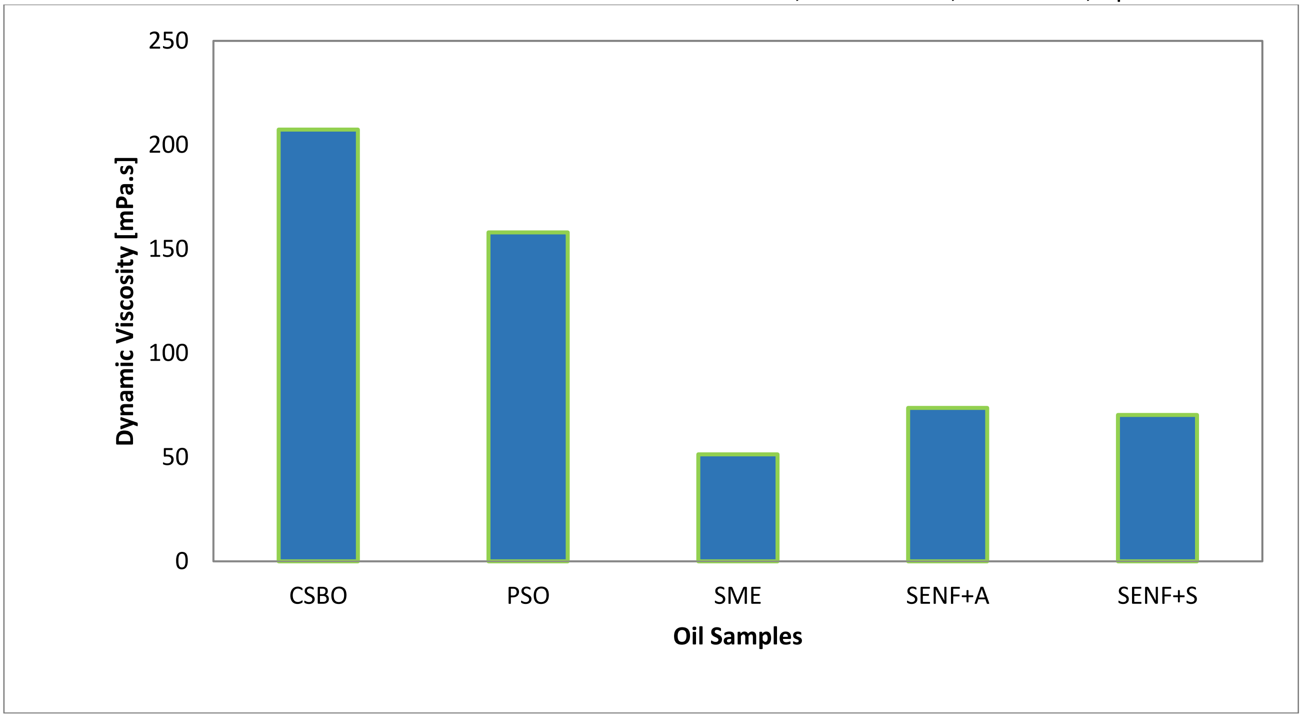

Figure 2. Measured dynamic viscosity of the oil samples at 30 °C

The crude shea oil sample exhibited viscosity values higher than those of the purified oil sample, with a discernible difference of approximately 0.0494 Pa.s. The oil purification process led to a notable reduction in viscosity, amounting to about 23.8%. The oil purification process involves degumming, which effectively eliminates impurities such as phosphatides (gums) from the oil, followed by a bleaching process, which is employed to remove color bodies like chlorophyll and carotene, pro-oxidant metals, traces of soap, and phosphatides (Sonawane & Waghmode, 2023). These impurities are materials that are likely to increase the viscosity of the liquid. Hence, the removal of such impurities resulted in lower viscosity values.

The removal of impurities from the shea oil during transesterification further reduced its viscosity, as evidenced by a significant decrease in Figure 2. A substantial 67.5% viscosity reduction was observed compared to the purified sample. Transesterification involves eliminating the shea oil's high molecular weight glycerol content, contributing to the viscosity reduction.

However, the subsequent addition of 0.6 wt% of filler nanoparticles led to the development of a shea methyl-based nanofluid with increased viscosity. As depicted in Figure 1, there was an increase of 0.0223 Pa.s and 0.0189 Pa.s with adding Al_2O_3 and SiO_2, respectively, representing approximately 43% and 36% increases, respectively. The introduction of particles resulted in higher viscosity for the base SME oil. Madavan et al. 2018 reported increased viscosity with the addition of 0.05-0.5 wt% of Al_2O_3 nanoparticles in vegetable oil (Madavan et al., 2018), while Shill et al. (2019) observed up to a 12% increase with the addition of 0.06 wt% silica nanoparticles in a base liquid (Shill et al., 2019). Notably, the addition of Al_2O_3 induced a more significant increase in viscosity compared to SiO_2 nanoparticles, possibly attributed to enhanced drag forces between layers of the base liquid

Dielectric Characterization

Frequency Dependence of Relative Permittivity

The dielectric dispersion is the decrease in permittivity with respect to the frequency of an applied electric field. As seen in Figure 3, the dielectric constant decreases only slightly with increased frequency.

The variations in the relative permittivity of the oil samples exhibited similar patterns, showing a slight decrease with an increase in frequency within the considered range. The observed decline with increasing frequency can be attributed to molecules' in-phase and out-phase components in the oil and nanoparticles. This behavior results from their inertia, preventing displacement in tandem with the varying electric field, ultimately leading to a reduction in the net polarization of the nanofluid and a consequent decrease in dielectric constant values.

Adding both types of nanoparticles resulted in an increased relative permittivity, as illustrated in Figure 3, with Al_2O_3 nanoparticles inducing a greater increase than SiO_2 nanoparticles. The crude oil sample exhibited higher permittivity values than the purified samples, which can be attributed to impurities. Also, the relative permittivity of the base methyl ester fell within the range of 2.86–2.91 in the frequency range of 0.1–15 kHz. The SENF+A and SENF+S samples had dielectric constants values ranging from 3.42–3.25 and 3.34–3.21, respectively, within the frequency range considered. Notably, these values surpassed those of mineral oil, measured to be 2.01–1.85 in the considered frequency range.

Dielectric Loss

The energy loss in the sample medium under varying frequencies of an electrical signal is depicted in Figure 4. The crude oil sample demonstrated higher loss than all samples within the considered frequency range, while the purified oil sample exhibited the least loss. Upon the addition of Al_2O_3 nanoparticles, an increased loss was observed compared to the base SME across all considered frequencies (see Figure 4). In contrast, the addition of SiO_2 had a marginal effect on loss, causing a slight increase in the frequency range of 100 Hz to 4 kHz and a slight reduction in loss at frequencies beyond 4 kHz. This loss reduction could be attributed to fewer mobile electrons trapped by the base liquid nanoparticles (Amalanathan et al., 2023). In electrical systems, a dielectric liquid with low loss is preferred, as energy dissipation contributes to system heating and may lead to thermal-induced degradation of the insulation system in power facilities.

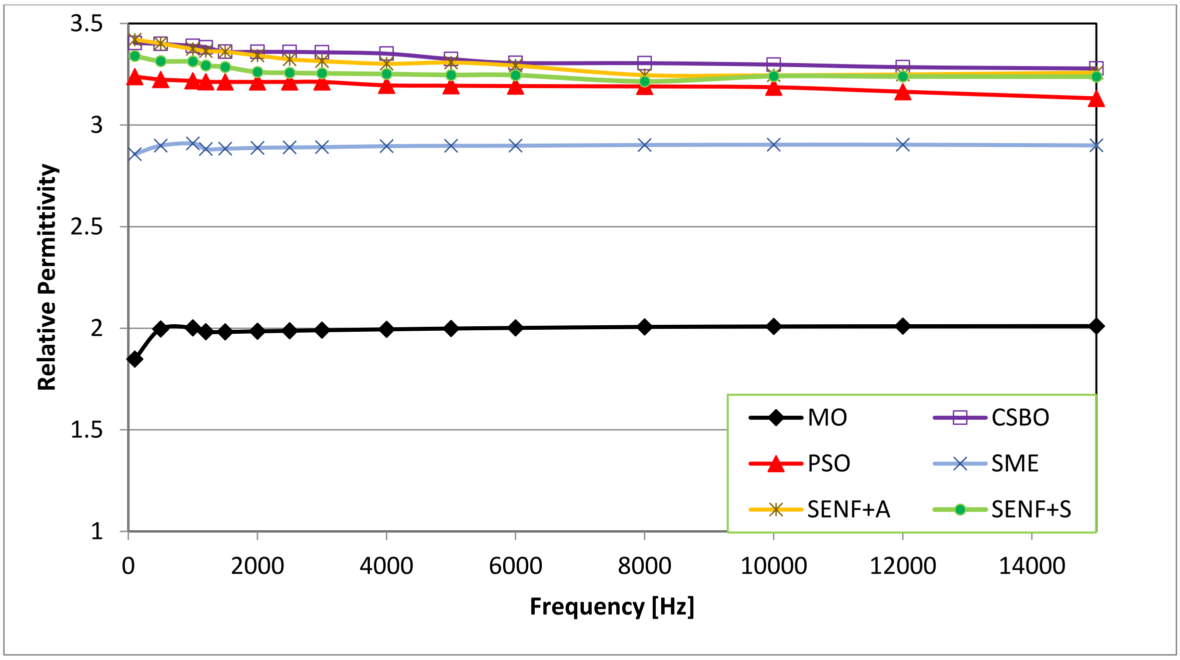

Figure 3. The frequency dependence of dielectric constant in the range of 100 Hz to 15 kHz 25 °C

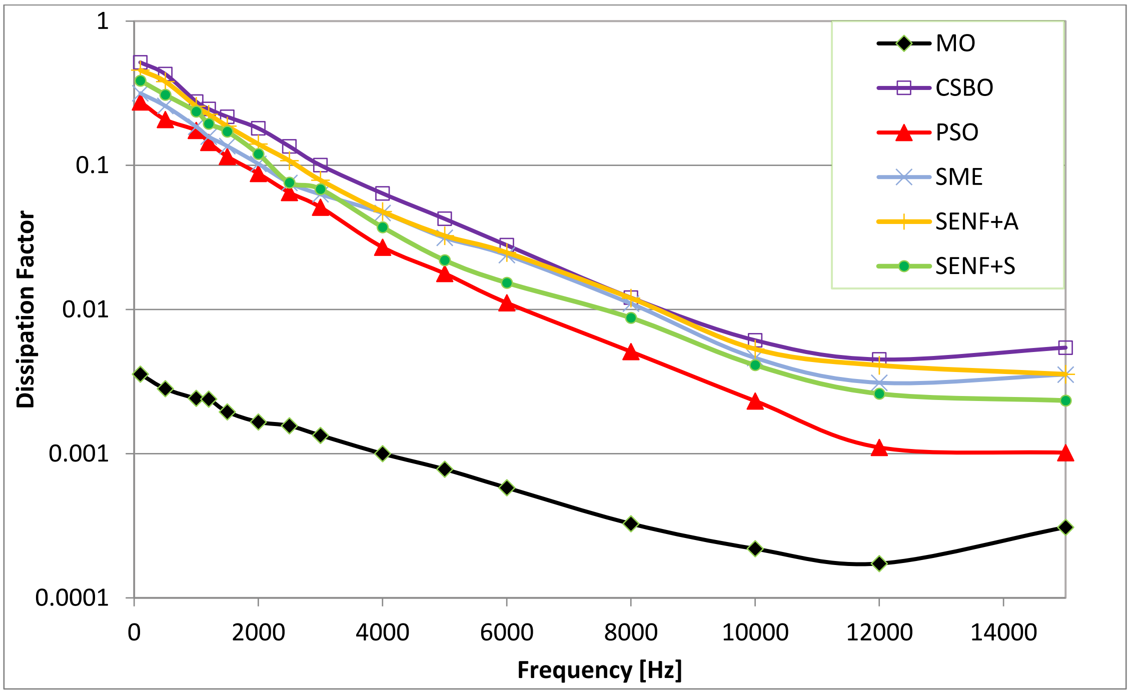

Figure 4. Dielectric loss characteristics of the oil samples at 25 °C

CONCLUSION

This study successfully developed an SME and single nanoparticle-based nanofluid, incorporating a 0.6 wt% weight fraction of surface-modified Al_2O_3 and SiO_2 nanoparticles. The addition of these nanoparticles increased the dynamic viscosity of the base methyl ester oil, with approximately 43% and 36% increases, respectively. Introducing Al_2O_3 nanoparticles increased dielectric loss within the considered frequency range (100 Hz to 15 kHz). However, a distinct loss reduction was observed with the addition of SiO_2 at frequencies beyond 4 kHz, coupled with an increase at frequencies below 4 kHz. Also, the incorporation of 0.6 wt% of both nanoparticles enhanced relative permittivity across the frequency range of 100 Hz to 15 kHz. While these findings provide valuable insights into the nanofluid's electrical properties, a comprehensive investigation covering aspects such as dielectric breakdown strength, stability of the nanoparticles in the base SME, and compatibility of the nanofluid with transformer paper insulation is essential to fully assess the feasibility of the developed nanofluid, derived from Al_2O_3 and SiO_2 nanoparticles and SME, as an insulation oil. Such a comprehensive study would provide a more rounded understanding of the nanofluid performance and applicability in transformer systems.

ACKNOWLEDGMENT

The Authors thank the Management of the Materials Science Laboratories, Department of Physics, Ahmadu Bello University, for providing the laboratory space and the major tools for this research.

REFERENCES

Amalanathan, A. J., Sarathi, R., & Zdanowski, M. (2023). A Critical Overview of the Impact of Nanoparticles in Ester Fluid for Power Transformers. *Energies*, *16*(9), 3662. **[Crossref]**

Chen, B., Yang, J., Li, H., Su, Z., Chen, R., & Tang, C. (2023). Electrical properties enhancement of natural ester insulating oil by interfacial interaction between KH550-TiO2 and oil molecules. *Surfaces and Interfaces*, *42*, 103441. **[Crossref]**

Das, A. K. (2023). Investigation of electrical breakdown and heat transfer properties of coconut oil-based nanofluids. *Industrial Crops and Products*, *197*, 116545. **[Crossref]**

Goumbri, B. W. F., Da Silva, T. L. T., Marini, R. D., Semdé, R., Somé, T. I., & Danthine, S. (2022). African Shea Butter Properties Related to Common Extraction Technologies: A Review. *Food and Bioprocess Technology*, *15*(2), 231–248. **[Crossref]**

Madavan, R., Senthil Kumar, S., & Willuice Iruthyarajan, M. (2018). A comparative investigation on effects of nanoparticles on characteristics of natural esters-based nanofluids. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *556*, 30–36. **[Crossref]**

Oparanti, S. O., Khaleed, A. A., & Abdelmalik, A. A. (2021a). AC breakdown analysis of synthesized nanofluids for oil-filled transformer insulation. *The International Journal of Advanced Manufacturing Technology*, *117*(5–6), 1395–1403. **[Crossref]**

Oparanti, S. O., Khaleed, A. A., & Abdelmalik, A. A. (2021b). Nanofluid from Palm Kernel Oil for High Voltage Insulation. *Materials Chemistry and Physics*, *259*, 123961.

Pagger, E. P., Pattanadech, N., Uhlig, F., & Muhr, M. (2023). Properties of New Insulating Liquids and Main Differences. In *Biological Insulating Liquids* (pp. 65–140). Springer, Cham.

Rao, U. M., Fofana, I., Rozga, P., Beroual, A., Malde, J., Martin, R., Wang, F., Casserly, E., Pompili, M., & Calcara, L. (2022). Next Generation Insulating Liquids. *2022 IEEE 21st International Conference on Dielectric Liquids (ICDL)*, 1–4. **[Crossref]**

Shill, D. C., Kumar Das, A., & Chatterjee, S. (2019). Measuring Electro-Thermo-Physical Properties of Mineral and Synthetic Ester Based Dielectric Fluid Dispersed with Silica Nanoparticles. *2019 IEEE 4th International Conference on Condition Assessment Techniques in Electrical Systems (CATCON)*, 1–4. **[Crossref]**

Sonawane, A., & Waghmode, S. (2023). A Review on Vegetable Oil Refining: Process, Advances and Value Addition to Refining by-Products. In *Environmental Sciences* (Vol. 0). IntechOpen. https://doi.org/10.5772/intechopen.108752

Viertel, J., Ohlsson, K., & Singha, S. (2011). Thermal aging and degradation of thin films of natural ester dielectric liquids. *2011 IEEE International Conference on Dielectric Liquids*, 1–4. **[Crossref]**