# Preparation and Testing of Biodegradable Nanofluids

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*Abstract*—Inseparable part of the high voltage transformers is electro insulating liquid. As known, for one hundred years are used mainly mineral oil based insulating fluids since having good electrical and physical properties and being relatively cheap. Over the years other liquids has been considered/used as replacement to mineral oils such as polyfluorobiphenyls (PFB), poly-chlorobiphenyls (PCB), silicones, synthetic esters, gas to liquid (GTL), etc. This paper and research is dealing with testing of modern biodegradable and sustainable oil Envitrafol and its improvements by nanoparticles. As known natural ester-based electro insulating fluids are polar substances with relatively high viscosity and corresponding properties. This paper is focusing on the study of the impact of the modification of natural ester-based fluid by nanoparticles on breakdown voltage (BDV).

*Keywords*—electro insulating oil, break down voltage, nanoparticles, natural ester, nanofluid.

## I. INTRODUCTION

Mineral oil used to act as both an insulating and cooling medium in electrical insulation systems (EIS), just as it still does today. Its use made it possible to increase the power output and voltage of transformers, which are still used today. Since then, mineral oil has undergone some development. Petroleum-based paraffinic oil was used at first; however had some problems with its properties, which were largely based on where the source material was extracted. The biggest problem has been the high freezing point of paraffinic, which is between -45 and -60 °C. These and other shortcomings were solved by the use of naphthenic-based oil, which has been widely used since its first use and is still in use today [1]. This mineral oil is nowadays easily available, cheap and has excellent electrical insulating properties. However, the availability of the source material - oil - may become problematic in the near future. Another problem is the often discussed issue of environmental protection [2]. The overall problem of the waste oil need to be solved.

In the last several years has been published a lot of information [3]–[5] about the properties of "new ester oils"

(NEO). The dielectric properties have been discussed (eg. dissipation factor, resistivity breakdown voltage, etc.) as a function of temperature, a voltage level, or frequency. Also, the properties of NEO in the system with cellulose paper have been studied. It has been proved, that natural ester in combination with cellulose-based solid part can fulfill some of the requirements of transformer paper-oil insulating system. The problems remain with the facts of lower oxidation stability, higher viscosity, chemically bounded water, and different properties in high electric fields, compared to regular mineral-based oils. The paper [4] is showing the properties of the paper oils system in the terms of thermal aging and ongoing chemical reactions.

A relatively new area of research is so-called nano-based insulating fluids. Generally, nanofluid is a fluid containing nanometer-sized particles, usually in the form of colloidal suspensions of nanoparticles in a base fluid [6]. The nanoparticles used in dielectric nanofluids are typically oxides (TiO<sub>2</sub>, SiO<sub>2</sub>, CuO, ZnO, MgO and Al<sub>2</sub>O<sub>3</sub>) [7], [8]. However, the main problem with these fluids is the poor long-term stability of the nanofluid. At first, homogeneously dispersed nanoparticles are a prerequisite for stable nanofluid. It can be stated that nanoparticles will remain dispersed if the Van der Waals forces (attractive forces) are compensated by repulsive forces (forces acting against attractive forces) such as electrostatic steric or electro-steric forces. These forces are important for stability because they form a barrier that the particle must surpass to interact and create agglomerates with other particles. If the energy of this barrier is greater than the kinetic energy of the particle, the solution remains stable and homogeneously dispersed. In practice, to improve the stability of the nanoparticle, surfactants [9] are used, i.e. surface treatments that reduce the surface tension in the liquid acting at the interface between the particles and the liquid. This interface determines the forces (mainly steric) acting on the formation of bonds between the particles. When using a surface treatment, it is necessary to select the proper type based on the application (not all surfactants interact suitability with the liquid) and then the proper amount, because a too large amount of surfactant leads to "bubble creation" around the particle that easily captures the surrounding parts, which again leads to the formation of agglomerates.

This research was supported by Technology Agency of the Czech Republic under the project TK02020017 - "Development of a distribution transformer with an environmentally friendly electro-insulating liquid", by the Student Grant Agency of the University of West Bohemia, grant No. SGS-2021–003 - "Materials, technologies and diagnostics in electrical engineering" and by Visegrad Fund 52210674.

In this paper, attention is paid to the modification of natural ester (based on rapeseed) by selected simple metal oxides  $(SiO_2, TiO_2)$  and also on the effect of surface treatment by silane coupling agent ((3-aminopropyl) triethoxysilane). The results show a change in the observed dielectric parameters.

## II. MATERIALS

### A. Raw Materials

Envitrafol, a fully biodegradable rapeseed-based electrical insulating oil was used as the base fluid [10]. The doped nanoparticles were selected as SiO<sub>2</sub> in hydrophilic modification, SiO<sub>2</sub> in hydrophilic and lipophilic modification by (3-aminopropyl) triethoxysilane coupling agent and TiO<sub>2</sub> without any sruface treatment or modification. Non treated particles of SiO<sub>2</sub> and TiO<sub>2</sub> have a purity of 99+ %, and the rest ist composed of inorganic impurities. The purity of silica with surface treatment (SiO<sub>2</sub> SF) is approx. 98 % and the rest are coupling agent and impurities. All types of nanoparticles used were around 20 nm in diameter. The morphology of used particles with the important parameters are shown in Figure 1.



Fig. 1. Morphology of investigated particles [11].

#### B. Sample Preparation

The nanoparticles were first dried at 60 °C for 48 h to eliminate moisture, as SiO<sub>2</sub> nanoparticles are hydrophilic and tend to bind water molecules. Mixing undried nanoparticles into the oil would also result in the addition of moisture, which would degrade the dielectric properties of the sample. Envitrafol (440 ml) was placed in a vacuum chamber and exposed to vacuum for 60 minutes. Meanwhile, nanoparticles corresponding to a concentration of 0.25 % were weighed and subsequently dispersed into the oil. The nanoparticle infused oil was stirred on a magnetic stirrer at 520 rotation per minute for 60 minutes, then subjected to ultrasonic mixing (50 % power), again for an hour. As a final step, the nanofluid was placed in a vacuum chamber for 60 minutes to eliminate inhomogeneities created during mixing. The preparation diagram can be seen in Figure 2.

### **III. METHODS AND RESULTS**

The breakdown voltage of Envitrafol and Envitrafol with nanoparticles was measured on a high voltage source (High Volt, Germany) and the dissipation factor and permittivity in relation temperature were measured on a vector bridge



Fig. 2. Process of nanofluid preparation.

2830/2831 (Tettex Instruments, Switzerland). Dynamic viscosity was measured via vibration viscometer SV-10 (A&D Company, Japan) for reference value, set at 40°C. The nanofluid values were compared with values of Envitrafol in the delivered state without treatment.

#### A. Breakdown Voltage Measurement

After preparing the nanofluid, 400 ml was used to measure the breakdown voltage (according to IEC 60156, semispherical electrodes, 2,5 mm), with a rise of 1.5 kV/s. Breakdown voltage was measured 6 times, with 3 minutes selected for oil mixing and recovery. The average value was calculated for each sample. The highest value of breakdown voltage was achieved by the Envitrafol with SiO<sub>2</sub> nanoparticles without surface treatment, voltage reaching the value of 66 kV. Non modified Envitrafol reached a value of 42 kV.



Fig. 3. Breakdown voltage of individual tested samples

## B. Dissipation Factor Measurement

For the measurement of the dissipation factor: 40 ml of nanofluid was used using temperature controlled Tettex electrode system cell to and measuring procedure according to IEC 60247, using a Tettex 2830/2831 analyzer. Applied voltage was 500 V. Measurements were performed as temperature incremental form ambient to 90 °C. As expected, the dissipation factor increased in relation to temperature. The largest observable change was in the surface-treated SiO<sub>2</sub> sample, where the loss factor was not significantly different from pure Envitrafol at 27 to 50 °C, but reached the lowest values (0.004) at 90 °C.



Fig. 4. Dissipation factor of individual tested samples

#### C. Relative permittivity Measurement

The temperature dependence of relative permittivity was measured. Relative permittivity decreased as a function of temperature. The sample with  $SiO_2$  without surface treatment had the lowest values.



Fig. 5. Relative permittivity of individual tested samples.

## D. Dynamic Viscosity Measurement

A reference value for 40 °C was measured for pure Envitrafol and Envitrafol with  $TiO_2$  nanoparticles. The dynamic viscosity for pure Envitrafol was 31.29 mPas at 40 °C. For Envitrafol with  $TiO_2$ , the dynamic viscosity was not significantly higher with a value of 31.45 mPas.

In Tab. 1, results are compared with similarly oriented studies [12], [13] which contain properties of such fluids, including dynamic or kinematic viscosity. If the density is known, relation between dynamic and kinematic viscosity is defined according to ISO 3104:2020.

 TABLE I

 KINEMATIC VISCOSITY OF SIMILAR LIQUIDS AT 40 °C [12], [13]

Parameter	Envitrafol	Envitrafol	Envirotemp	Natural
	pure	+ TiO <sub>2</sub>	FR3	Ester
Viscosity	34.68	34.84	33	36

Acquired values have been used only as reference for occasional calculation of kinematic viscosity and comparison with other studies. Obtained results report only slight difference as density has been determined as 907.45 kg/m<sup>3</sup> for pure Envitrafol and 908.66 kg/m<sup>3</sup> for the one which was modified by TiO<sub>2</sub>. Density reported for nature ester in [13] is very similar (908 kg/m<sup>3</sup>).

## IV. DISCUSSION AND CONCLUSION

As seen from the results the modification of the natural ester based fluid by the nanoparticles is possible. Some properties, also based on previous results, could be improved.

For the use such as nanofluid in the real application the stability of the nanofluid must be studied and improved. Since in the transformer the fluid is stirred and mixed by the pump of the cooling system, it can be expected that the sedimentation of the nanoparticles can be relatively low. A "filtration" effect solid part of the transformer insulating system need to be tested.

Based on this and previous experiments further improving of the dielectric properties of biodegradable nanofluids is achievable. What need to be further studied is detail nanoscale dielectric phenomena explanation. Both, increase of the local electric field in close to nanoparticle as well as high breakdown voltage of obtained when measured in nanometric scale [14] . Also, behavior of the biodegradable nanofluid in high inhomogeneous field (positive and negative) should be studied regarding results presented in [3] .

The high permittivity of natural esters fluids owing the problems with application of very high voltages. This problem is also proposed to being solved by the application of the nanoparticles a "compensation" of the higher space charge in natural esters. This space charge is higher than in the mineral based oils because of polar nature of the natural esters. The actual phenomena acting in the nanometric scale need to be further studied. The increased breakdown voltage in well dispersed nanofluid can be explained similarly to electrical treeing in polymers. When estimating local electric field in the scale of the mixed nanoparticles, we can estimate as much as 30 times higher local electrical field ( $E_L$ ) in the particle itself then in surrounding homogeneous field in the liquid. On the other hand breakdown voltages of nanoparticles measured in sub-micro scale is as high as 300 kV/mm [15]. Also the particles mixed in the base liquid creates a barrier to the ions and electrons moving in the outer electrical field, these charge sticks to the surface of the nanoparticles and therefore create a local space charge acting against applied outer electric filed and therefore reducing electric field in the way of the developing breakdown. This phenomena is possibly responsible for increasing of the breakdown voltage of the nanofluid compared to pure oil.

The open question for use of the nanofluids in electrical machinery is the issue of sedimentation and filtering" the particles. This issues need to be further studied.

#### REFERENCES

- P. Totzauer, Aspects of using biodegradable electroinsulating fluids. Doctoral Dissertation, Supervisor: P. Trnka, 2019, Pilsen, Czech Republic.
- [2] P. Totzauer, P. Trnka, Different Ways to Improve Natural Ester Oils, *Transportation Research Proceedia*, vol. 40, 2019, pp. 102-106, doi: 10.1016/j.trpro.2019.07.017.
- [3] P. Trnka, J. Hornak, P. Prosr, O. Michal and F. Wang, "Various Aging Processes in a Paper-Natural Ester Insulation System in the Presence of Copper and Moisture," in IEEE Access, vol. 8, pp. 61989-61998, 2020, doi: 10.1109/ACCESS.2020.2983907.
- [4] K. Wang et al., "Breakdown and streamer behavior in homogeneous synthetic trimethylolpropane triesters insulation oil," in IEEE Transactions on Dielectrics and Electrical Insulation, vol. 27, no. 5, pp. 1501-1507, Oct. 2020, doi: 10.1109/TDEI.2020.008546
- [5] Mentlik, et. al. Development of a Biodegradable Electro-Insulating Liquid and Its Subsequent Modification by Nanoparticles. Energies 2018, 11, 508. https://doi.org/10.3390/en11030508

- [6] V. Kugarajah, A. K. Ojha, H. Hadem, N. Dasgupta, B. N. Mishra, S. Ranjan, Chapter 2 - Nanoparticles and nanofluids: Characteristics and behavior aspects, In *Micro and Nano Technologies, Food, Medical, and Environmental Applications of Nanomaterials*, K. Pal, A. Sarkar, P. Sarkar, N. Bandara, V. Jegatheesan (Eds.), Elsevier, 2022, Pages 41-71, ISBN 9780128228586, doi: 10.1016/B978-0-12-822858-6.00002-9.
- [7] K.S. Suganthi, K.S. Rajan, Metal oxide nanofluids: Review of formulation, thermo-physical properties, mechanisms, and heat transfer performance, Renewable and Sustainable Energy Reviews, Volume 76, 2017, Pages 226-255, ISSN 1364-0321, https://doi.org/10.1016/j.rser.2017.03.043.
- [8] S. N. Suhaimi, A. R. A. Rahman, M. F. Md. Din, M. Z. Hassan, M. T. Ishak, M. T. bin Jusoh, "A Review on Oil-Based Nanofluid as Next-Generation Insulation for Transformer Application", *Journal* of Nanomaterials, vol. 2020, Article ID 2061343, 17 pages, 2020. https://doi.org/10.1155/2020/2061343
- [9] P. Totzauer, J. Kudelcik, J. Hornak, O. Michal, P. Trnka and V. Mentlik, "Analysis of Particle Size Distribution and Other Parameters of Nanoparticles in Natural Ester Oil," 2019 *IEEE 20th International Conference on Dielectric Liquids* (ICDL), 2019, pp. 1-4, doi: 10.1109/ICDL.2019.8796658.
- [10] O. Michal, V. Mentlik, P. Trnka, J. Hornak, and P. Totzauer, Dielectric properties of biodegradable vegetable oil based nanofluid", in 2018 19th International Scientific Conference on Electric Power Engineering, EPE 2018 - Proceedings, June 2018, s. 1–4, doi: 10.1109/EPE.2018.8396036.
- [11] Nanostructured & Amorphous Materials Inc. Products: Nanoscale elements, oxides, carbides & nitrides, accesed from: https://www.nanoamor.com/products.
- [12] G. Frimpong, J. Hajek, and K. Kulasek.Eco-friendly ester liquid transformer designs. URL: https://search.abb.com/library/Download . aspx ?DocumentID=9AKK107046A6496.
- [13] G. Dombek, Z. Nadolny, A. Marcinkowska. "Thermal properties of natural ester and low viscosity natural ester in the aspect of the reliable operation of the transformer cooling system". In: *Ekspo- latacja i Niezawodnosc - Maintenance and Reliability* 21, 2019, pp. 384–391. doi: 10.17531/ein.2019.3.4.
- [14] Neusel C., Schneider A. Size-dependence of the dielectric breakdown strength from nano- to millimeter scale, Journal of the Mechanics and Physics of Solids, Vol. 63, February 2014, Pp. 201–213, doi: 10.1016/j.jmps.2013.09.009
- [15] Wang, Z.; Zhou, Y.; Lu, W.; Peng, N.; Chen, W. The Impact of TiO2 Nanoparticle Concentration Levels on Impulse Breakdown Performance of Mineral Oil-Based Nanofluids. *Nanomaterials* 2019, 9, 627. https://doi.org/10.3390/nano9040627