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Thermal properties of nanoliquids prepared on the basis of natural ester modified by nanoparticles TiO₂ and C₆₀

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In this paper the results of the researches concerning thermal properties of insulting nanoliquids received on the basis of natural ester, titan dioxide TiO_2 and fullerene C_{60} were presented. Thermal conductivity, viscosity, density and specific heat are these thermal properties. The range of the temperature was changing from 25°C to 80°C. These properties are crucial from the viewpoint of heat transfer coefficient by insulating liquid used in insulating system of power equipment; thus, they influence on temperature distribution inside the equipment. The possibility of receiving steady nanoliquids was also analyzed. The impact of natural ester modification by nanoparticles and surfactant on thermal properties of received nanoliquids was proved.

KEYWORDS: natural esters, thermal conductivity, viscosity, density, specific heat, high voltage power transformers, heat transfer coefficient, nanoliquids

1. Introduction

Application of alternative insulation liquid for mineral oil such as natural esters in electrical equipment is not a new idea. The beginnings of the use of natural esters as insulation in electrical equipment back to the late nineteenth century, when during exhibition in Frankfurt transmission systems with a rated voltage of 20 kV were demonstrated. Then it was also confirmed the necessity of the use of transformers as part of ensuring the transmission of electricity at a voltage AC [1]. With the development of the electricity and petroleum industry natural esters were gradually superseded by mineral oils.

The use of mineral oil is justified by its satisfactory and very well recognized insulating properties. However, in situations where fire safety and environmental protection are the determining factors, the use of power transformers filled with natural esters is entirely appropriate, which is associated with their high flash point and rapid biodegradability.

The dynamic development of energy networks all over the world based on technologies based on renewable and environmentally friendly sources resulted in a tendency to use natural esters in place of previously commonly used mineral oil.

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Since the beginning of the XXI century, there is an increase interest in natural esters as insulating liquid, mainly in the context of distribution transformers (Fig. 1.1). There is also a trend involving the use of natural esters in large power transformers. Currently power transformers, in which natural ester were used as insulating liquid, are already present in operation.



Fig. 1.1. The number of distribution transformers in the world filled with natural esters in individual years [2]

In several research centers around the world some actions connected with the modification of the natural esters and other insulating liquids are carried [3-12]. This modification is aimed at improving their insulating and thermal properties.

The improvement of the thermal properties of the natural esters may be obtained by adding to them a suitable nanoparticles. As a result of doping esters of nanoparticles stable insulating nanoliquids can be achieved as appropriate solutions or colloids. In appropriate solutions nanoparticles are dissolved in a base liquid, and in the colloids they are dispersed and suspended throughout the volume.

This paper presents the research results of the impact of natural ester modification of nanoparticles (TiO₂ and C₆₀) on its thermal properties such as thermal conductivity, viscosity, specific heat and density. These properties determine the heat transfer in electric power equipment.

2. Preparation of nanoliquids

This section describes a method of preparing insulating nanoliquids based on natural ester and nanoparticles titanium oxide TiO_2 and fullerene C_{60} .

In view of the fact that nanoparticles belong to soluble or insoluble compounds in the insulating liquids, preparation of a stable insulating nanoliquids requires use of various techniques for dissolution, or in case of insoluble nanoparticles, appropriate means allowing the formation of a stable colloids. Example of nanoparticles, that are soluble in the natural ester, is fullerene C_{60} .

Depending on the concentration of fullerene in the ester, the time of its dissolution is from two to several weeks. To the nanoparticles, that are not soluble in natural ester, belongs titanium oxide TiO₂. In order to uniformly disperse it in the base liquid it is necessary to use dispersant (surface active agent).

Modifying insulating liquid with the use of nanoparticles alone can lead to sedimentation (solid slurry sedimentation). The occurrence of sedimentation is undesirable in the electrical equipment because it can lead to the formation of large groups of nanoparticles and their deposition on the elements of the insulation system causing a significant deterioration of its properties and consequently equipment failure. In order to counteract surfactants known as dispersants are used. Dispersants allow the formation of stable suspensions and also enhance the effectiveness of fragmentation of larger particles in a base liquid, whereby can produce colloids. An additional advantage is that they prevent the binding of nanoparticles dispersed in a liquid in the particles units of large size.

Depending on the used nanoparticles and base liquid, preparing stable colloidal solutions may require the use of different surfactants. It is also the use of an appropriate concentration of dispersant in the base liquid. Too high concentration of surfactant dramatically lowers the surface tension of the insulating liquid worsening at the same time their properties. Surface tension is a measure of the hydrophilic components in the insulating liquid. Too high concentration of hydrophilic components in the insulating liquid may cause deterioration of their dielectric properties [13].

As mentioned above, the base liquid used for the preparation nanoliquids was natural ester. The modification of the natural ester was conducted using fullerene C_{60} and nanoparticles of titanium oxide TiO₂ (average particle size of 21 nm).

In order to dissolve the nanoparticles in the base liquid, modified liquid was subjected to sonication. In the case of fullerene C_{60} , it is allowed to obtain a proper solution. An attempt to obtain a proper solution by dissolving the TiO₂ nanoparticles in natural ester resulted in the onset of sedimentation. Therefore, an attempt was made to prepare a colloidal solution. To the base liquid was added surfactant - SPAN 20 ($C_{18}H_{34}O_6$). Then, in order to achieve the effect of its uniformly dispersion in the liquid, the resultant liquid was subjected to the sonication process.

After dispersion of the surfactant in the base liquid the nanoparticles of titanium oxide TiO_2 are added to it. The resulting nanoliquid was sonicated again. In order to ensure a constant temperature of nanoliquid, sonication process was conducted in a water bath. The duration of sonication process was 7 hours. After this time a stable colloid was obtained.

Before starting studies, prepared samples of nanoliquids allowed to leave for several hours to remove the air bubbles created in the results of ultrasound.

As a result of the activities described above following insulating liquids were prepared for testing:

- natural ester,
- natural ester + C60 concentration of the fullerene in the ester of $0.1g \cdot l^{-1}$,
- natural ester + SPAN concentration of SPAN in the ester of 5gl,
 - natural ester + SPAN + TiO₂ concentration of SPAN and TiO₂ in the ester of respectively 5 g·1⁻¹ and 0.816 g·1⁻¹.

3. Measurment results

For testing thermal conductivity coefficient of insulating liquids, the measuring system described in articles was used [14-16]. Viscosity measurements of insulating liquids were carried out using the measurement system described in the article [17]. The measurement was performed in accordance with standard [18]. In turn, the density measurement was made in accordance with the standards [19,20]. The specific heat of analyzed insulating liquids was measured using a differential scanning calorimeter Mettler Toledo DSC1 (Fig. 3.1).



Fig. 3.1. Differential scanning calorimeter Mettler Toledo DSC1 [21]

The measurement of specific heat using Mettler Toledo DSC1 was to determine the heat flux supplied to the sample of the tested liquid, which during heating is placed in an open aluminum pan. Before measurements temperature program, setting out the course of the measuring procedure, was defined. In order to correctly determine the specific heat of the tested sample liquids at 25°C and 80°C, measurement of the heat flux supplied to the samples had to be started from a temperature of 5°C and end at a temperature of 105°C. In the first stage of measurement, a liquid sample was cooled to 5°C and held at this temperature for 5 minutes. Then, the sample of the tested liquid was heated at a rate of 5°C per minute to 105°C. In the last stage of measurement, sample was maintained at a constant temperature of 105°C for 5 minutes.

Measurement of the specific heat by using a differential scanning calorimeter Mettler Toledo DSC1 took place in the presence of an inert gas (nitrogen) flowing at a rate of 150 ml per minute through the apparatus chamber DSC. The weights of tested insulating liquids samples were about 25 mg. Initially, in order to obtain the baseline, measurements for open, empty vessels of aluminum were performed in accordance with the above-described temperature program. Then, in one of the vessels tested liquid sample is placed and treated it according to a predetermined measurement procedure. On the basis of obtained curves showing the relationship of heat flow delivered to the tested sample liquid (designated by cutting the curve of dH/dt of the test sample liquids of the baseline) from the temperature using the Mettler STARe Evaluation program, determined the specific heat of tested liquid sample according to the relationship:

$$c_p = \frac{dH}{dt} \frac{dt}{dT_c} \frac{l}{m_c} \tag{1}$$

where: dH/dt - heat flux, dT_s/dt - the heating rate of ample, m_s - weight of sample.

Table 3.1 presents the results of the thermal conductivity λ viscosity v, density ρ and the specific heat c_p of natural ester and nanoliquids formed on its basis, depending on the temperature. Studies of all listed thermal properties were carried out for four temperatures: 25°C, 40°C, 60°C and 80°C.

Table 3.1. The test results of thermal properties of natural ester and nanoliquids formed on its base; λ – thermal conductivity, v – viscosity, ρ – density, c_p – specific heat

1.p.	Liquid	Properties	Temperature			
			25°C	40°C	60°C	80°C
1	Natural ester	$\lambda [W \cdot m^{-1} \cdot K^{-1}]$	0.182	0.180	0.178	0.175
		$v [\mathrm{mm}^2 \cdot \mathrm{s}^{-1}]$	56.29	32.66	18.30	11.50
		$\rho \left[\mathbf{g} \cdot \mathbf{l}^{-1} \right]$	916	906	893	881
		$c_p \left[J \cdot kg^{-1} \cdot K^{-1} \right]$	2028	2082	2166	2259
2	Natural ester +C ₆₀	$\lambda [W \cdot m^{-1} \cdot K^{-1}]$	0.182	0.180	0.178	0.176
		$v [\mathrm{mm}^2 \cdot \mathrm{s}^{-1}]$	56.38	32.67	18.32	11.52
		$\rho \left[\mathbf{g} \cdot \mathbf{l}^{-1} \right]$	917	907	894	880
		$c_p \left[J \cdot kg^{-1} \cdot K^{-1} \right]$	2040	2108	2210	2320
3	Natural ester +SPAN	$\lambda [W \cdot m^{-1} \cdot K^{-1}]$	0.182	0.180	0.179	0.175
		$v [\mathrm{mm}^2 \cdot \mathrm{s}^{-1}]$	56.45	32.70	18.34	11.53
		$\rho \left[\mathbf{g} \cdot \mathbf{l}^{-1} \right]$	918	908	895	882
		$c_p \left[J \cdot kg^{-1} \cdot K^{-1} \right]$	1983	2036	2118	2209
4	Natural	$\lambda [W \cdot m^{-1} \cdot K^{-1}]$	0.185	0.183	0.180	0.178
	ester	$v [\mathrm{mm}^2 \cdot \mathrm{s}^{-1}]$	56.53	32.77	18.38	11.56
	+SPAN	$\rho \left[g \cdot l^{-1} \right]$	919	909	894	882
	+TiO ₂	$c_p \left[J \cdot kg^{-1} \cdot K^{-1} \right]$	1962	2011	2088	2174

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Performed studies showed the impact of the nanoparticles and the surfactant on the thermal properties of tested insulating liquids.

The thermal conductivity of a natural ester doped with fullerene C_{60} , and natural ester modified by surfactant (SPAN 20) has not changed compared to the thermal conductivity of the natural ester (Fig. 3.2). The small increase in thermal conductivity, at the border of the measurement uncertainty, is noticeable in the case of colloid formed by modifying natural ester by surfactant (SPAN 20) and nanoparticles TiO₂. At temperatures of 25°C, 40°C and 80°C, the thermal conductivity of analyzed nanoliquid is 0.003 W·m⁻¹·K⁻¹ times greater than the heat conductivity of the natural ester. In turn, at temperature of 60°C the thermal conductivity of natural ester modified by surfactant and nanoparticles of TiO₂ is 0.002 W·m⁻¹·K⁻¹ times greater than the conductivity of natural ester.

As in the case of natural ester, thermal conductivity of all resulting nanoliquids decreases with increasing temperature.



Fig. 3.2. Thermal conductivity coefficient of natural ester and nanoliquids formed of its basis, as a function of temperature

Analyzing data contained in Table 3.1 and in Figure 3.3 it can be noted that modifying the natural ester by surfactant and nanoparticles C_{60} and TiO_2 results in minimal, almost imperceptible increase in viscosity resulting nanoliquids. The lowest viscosity among all evaluated nanoliquids has a natural ester doped fullerene C_{60} . Doping natural ester by fullerene C_{60} causes a slight increase in viscosity compared to the base liquid. In the case of modification of the natural ester by nanoparticles TiO_2 , in order to obtain the colloid, it adding surfactant to it was necessary. Modification of the natural ester by surfactant caused an

increase in viscosity from 0.03 mm²·s⁻¹ at temperature of 80°C to 0.16 mm²·s⁻¹ at temperature of 25°C, with respect to the base liquid. However, in the case of natural ester modified by surfactant and nanoparticles TiO₂ were observed increase in viscosity from 0.06 mm²·s⁻¹ at temperature of 80°C to 0.25 mm²·s⁻¹ at temperature of 25°C, relative to the base liquid. Viscosity of all tested nanoliquids decreases with increasing temperature.



Fig. 3.3. Viscosity of natural ester and nanoliquids formed of its basis, as a function of temperature

Modification of natural ester by fullerene C_{60} increases the specific heat of the resulting nanoliquids in relation to the base liquid (Fig. 3.4). At 25°C the specific heat of analyzed nanoliquids is 12 J·kg⁻¹·K⁻¹ greater than the specific heat of natural ester. At temperature of 80°C the specific heat of natural ester doped with fullerene C_{60} is 61 J·kg⁻¹·K⁻¹ greater than the specific heat of natural ester. In contrast, modification by surfactant causes a reduction in the specific heat of 45 J·kg⁻¹·K⁻¹ at temperature of 25°C and 50 J·kg⁻¹·K⁻¹ at temperature of 80°C. In turn, nanoliquid created as a result of modifying natural ester by surfactant and nanoparticles TiO₂ is characterized by specific heat lower at 64 J·kg⁻¹·K⁻¹ (25°C) and 85 J·kg⁻¹·K⁻¹ (at 80°C) relative to the base liquid. This may be due to the strong hygroscopicity of nanoparticles TiO₂. With temperature growth, the specific heat of all analyzed insulating liquids increases.

There was no effect of natural ester modification by surfactant and nanoparticles C_{60} and TiO_2 on density of both tested nanoliquids. The density is affected by temperature only. With increasing temperature, the density of all the tested insulating liquids decreases (Fig. 3.5).



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Fig. 3.4. Specific heat of natural ester and nanoliquids formed of its basis, as a function of temperature



Fig. 3.5. Density of natural ester and nanoliquids formed of its basis, as a function of temperature

4. Summary

Assessed the performed studies it can be concluded that modifying the natural ester of nanoparticles TiO_2 and C_{60} affects its thermal properties, which is important from the point of view of heat transfer in electric power equipment. The studies showed improvement in thermal conductivity of nanoliquids formed by modifying natural ester by surfactant and nanoparticles TiO_2 , and the increase of the specific heat of natural ester doped with fullerene C_{60} with respect to the base liquid. The increase in thermal conductivity and specific heat is desired to improve the efficiency of the cooling power.

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