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The probe of thermophysical properties for BaTiO₃/SrTiO₃@MO hybrid nanolubricants

BaTiO₃/SrTiO₃@MO hibrit nanoyağlayıcılar için termofiziksel özelliklerin araştırılması

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The Probe of Thermophysical Properties for BaTiO₃/SrTiO₃@MO Hybrid Nanolubricants

Highlights

- ❖ Thermophysical properties of nanolubricants prepared with Barium Titanate and Strontium Titanate nanoparticles in mono and hybrid form were investigated.
- ❖ The values for density, heat capacity, thermal conductivity and viscosity of nanolubricants were calculated using the previously proven theoretical formulas.
- ❖ SEM and XRD analyzes of nanoparticles were performed. FTIR analysis for mono and hybrid nanolubricants is included.
- ❖ It was concluded that hybrid nanolubricants can perform better than mono nanolubricants.

Graphical Abstract

Thermophysical properties of nanolubricants prepared as mono and hybrid were investigated. The preparation processes of the lubricants are included.

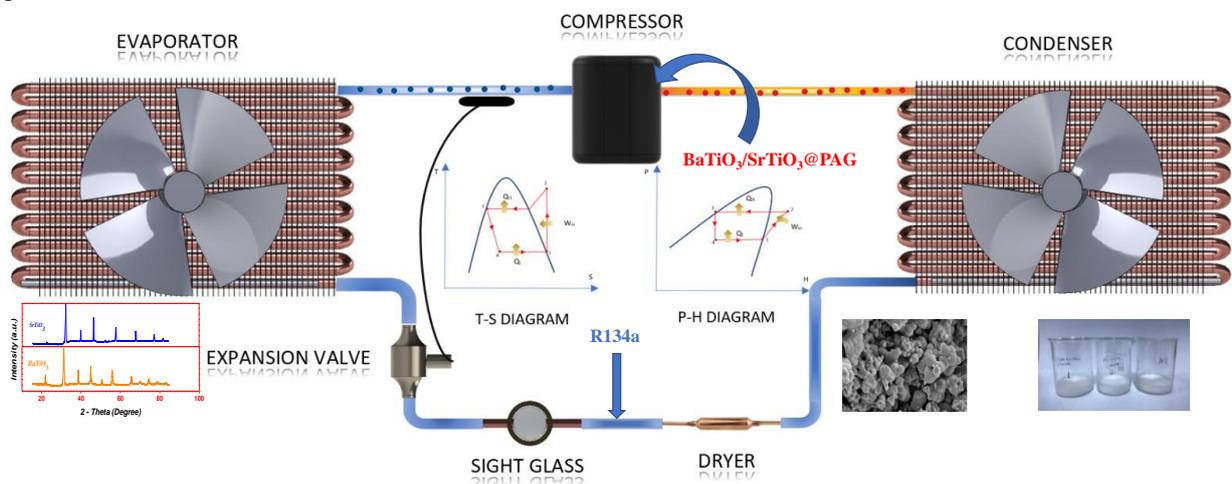


Figure. Graphical Abstract

Aim

Determination of thermophysical properties of BaTiO₃+SrTiO₃@MO nanolubricants.

Design & Methodology

Theoretical formulas were used to determine density, heat capacity, thermal conductivity and viscosity. Nanoparticle analyzes were performed.

Originality

BaTiO₃@MO, SrTiO₃@MO and BaTiO₃+SrTiO₃@MO nanolubricants were analyzed

Findings

Density, heat capacity, thermal conductivity and viscosity were calculated as 912.78 kg/m³, 1.817 kJ/(kg. K), 0.136 W/(m. K) and 1.1672 mPa.s for the hybrid nanolubricant, respectively.

Conclusion

Hybrid nanolubricants have better heat transfer performance than mono nanolubricants.

Declaration of Ethical Standards

The author of this article declares that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

BaTiO₃/SrTiO₃@MO Hibrit Nanoyağlayıcılar için Termofiziksel Özelliklerin Araştırılması

Araştırma Makalesi / Research Article

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ÖZ

Son yıllarda ısıtma sistemlerinde nanoakışkanlar, soğutma ve iklimlendirme sistemlerinde de nanoyağlayıcılar çalışma sıvısı olarak kullanılmaktadır. Isı transfer özelliklerin gelişiminde, bu süspansiyonlarda metal oksitlere ve karbon bazlı bileşiklere yoğun şekilde yer verilmektedir. Birden fazla nanopartikülün hibrit olarak birleştirilmesiyle elde edilen nanoyağlayıcılar sıklıkla kullanılmaktadır. Bu bağlamda, BaTiO₃/SrTiO₃@MO hibrit nanoyağlayıcısının yoğunluk, ısı kapasitesi, termal iletkenlik ve viskozite gibi termofiziksel özellikleri hesaplanmıştır ve karşılaştırmalar yapılmıştır. Çalışmada hibrit yapı içerisinde katı parçacık olarak BaTiO₃ ve SrTiO₃ nanopartikülleri kullanılmıştır. Nanoyağlayıcı içerisindeki nanopartiküllerin termofiziksel özellikleri de incelenmiştir. Nanopartiküllerin, hibrit yapı içerisindeki karıştırma oranı 1:1 olarak katkılanmıştır. Ayrıca, 100 ml mineral yağ (MO) içerisindeki partükül kütle fraksiyonu %1.0 olarak belirlenmiştir. Tekli ve hibrit nanoyağlayıcıların termofiziksel özellikleri kıyaslandığında, soğutma sistemleri için hibrit yapıların performansının daha iyi olduğu görülmüştür.

Anahtar Kelimeler: Termofiziksel özellikler, nanoyağlayıcı, BaTiO₃, SrTiO₃.

The Probe of Thermophysical Properties for BaTiO₃/SrTiO₃@MO Hybrid Nanolubricants

ABSTRACT

In recent years, nanofluids have been used in heating systems and nanolubricants as working fluids in refrigeration and air conditioning systems. In the development of heat transfer properties, metal oxides and carbon-based compounds are mainly used in these suspensions. Often, nanolubricants are used, which are produced by combining several nanoparticles as a hybrid. In this context, the thermophysical properties of the hybrid nanolubricant BaTiO₃/SrTiO₃@MO such as density, heat capacity, thermal conductivity and viscosity were calculated and compared. In the study, BaTiO₃ and SrTiO₃ nanoparticles were used as solid particles in the hybrid structure. The thermophysical properties of the nanoparticles in the nanolubricant were also investigated. The mixing ratio of the nanoparticles in the hybrid structure was 1:1, and the particle mass fraction in 100 ml of mineral oil (MO) was also set at 1.0%. When comparing the thermophysical properties of mono and hybrid nanolubricants, it was found that the performance of the hybrid structures was better for cooling systems.

Keywords: Thermophysical properties, nanolubricant, BaTiO₃, SrTiO₃.

1. INTRODUCTION

In industrial equipment and residential heating and cooling systems, the addition of solid particles to working fluids increases thermal conductivity. These two-phase suspensions of base fluid and nanoparticles are called nanofluids. With the use of nanofluids as working fluids in the systems, an increase in energy efficiency has been observed [1,2]. Similar to nanofluids, nanolubricants are used to improve heat transfer properties in refrigeration and air conditioning systems. Nanolubricants are prepared by adding solid particles to the working fluid oils in refrigeration systems. Many studies have been conducted to improve heat transfer properties by using nanofluids [3,4]. In this study, Çiftçi found that the thermophysical properties of nanofluids have an important effect on determining their heat transfer capabilities. In this study, the author investigated the density, heat capacity, thermal conductivity and

viscosity properties of the hybrid nanofluid of AlN+ZnO/deionized water using theoretical correlations. [5]. Aljuwayhel et al. added nanodiamond particles to compressor oil with a volume fraction of 0.05-0.5%. It was reported that the thermal, tribological and stable properties improved with the use of nanolubricants as compressor oil [6]. Kamarulzaman et al. studied the thermophysical properties of nanocellulose and copper (II) oxide particles added to engine oil. It was found that the viscosity of engine oil was improved by 44.3% to 47.12% with the addition of nanoparticles. They reported that the thermal conductivity increased by 1.80566% by using nanolubricants [7]. Bakhtiyar et al. used nanofluids instead of water to improve the thermal properties in a cross-flow cooling tower. The efficiency of the cooling tower was improved by 46%, 45.3% and 43.2% when 0.1 wt% MWCNTs-COOH/H₂O, MWCNTs- OH/H₂O, and MWCNTs/H₂O nanofluids were used, respectively [8]. Aydın et al. experimentally investigated the thermophysical properties of NiFe₂O₄ nanoparticles dispersed in deionized water in a thermosiphon-type heat

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pipe. They reported that the boiling temperature of the base fluid for all concentrations decreased with the addition of NiFe_2O_4 nanoparticles. Moreover, it was found that the high mass fraction of nanoparticles and the low magnetic flux density effectively increased the heat transfer [9]. Tuncer et al. compared the thermal performance and thermal properties of a single TiO_2 /water nanofluid and a hybrid CuO-TiO_2 /water nanofluid. They reported that the use of hybrid nanofluids outperformed single nanofluids [10]. In another study, Aytac prepared nanofluids with CuO and ZnO nanoparticles and investigated their thermophysical properties. When nanofluids were used, it was highlighted that the efficiency increased and the thermal resistance of the heat pipe decreased at all Reynolds numbers [11].

In this study, the thermophysical properties of the hybrid nanolubricant $\text{BaTiO}_3/\text{SrTiO}_3$ @MO such as density, heat capacity, thermal conductivity and viscosity were investigated. Theoretical calculations were performed separately for the single and hybrid nanolubricant, and the thermal performance was evaluated. In the preparation of the hybrid nanolubricant, BaTiO_3 and SrTiO_3 nanoparticles were mixed in a ratio of 1:1, and the nanoparticles were used at a mass fraction of 1.0%. To prevent agglomeration in the suspension, an SDBS surfactant was used at a volume fraction of 0.5%. The physical properties of the nanoparticles added to the nanolubricant were studied and compared using special methods. According to the obtained results, interpretations were made for the use of these prepared nanolubricants as compressor oil for the cooling system.

2. MATERIAL and METHOD

2.1. Preparation of Nanolubricants and Analysis of Nanoparticles

BaTiO_3 and SrTiO_3 nanoparticles are commercially available (*Nanografi*). BaTiO_3 nanoparticles have a cubic structure, as can be seen in Figure 1. It can also be seen that the particles are about 50 nm in size. It has been reported that BaTiO_3 nanoparticles are 99.9% trace metals. The density of BaTiO_3 nanoparticles was reported to be 6080 kg/m^3 . Moreover, the heat capacity for BaTiO_3 nanoparticles is 101.87 J/K.mol [12] and the thermal conductivity is 3.672 W/m.K [13].

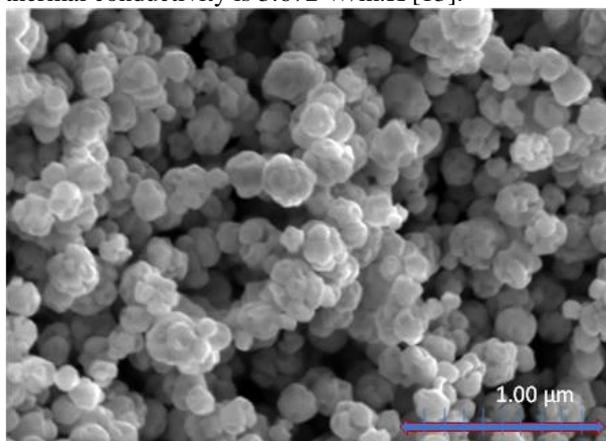


Figure 1. SEM image of BaTiO_3 nanoparticles

As shown in Figure 2, the particle size of SrTiO_3 nanoparticles is reported to be $<100 \text{ nm}$. It has been reported that SrTiO_3 nanoparticles are 99% trace metal-based. The density of SrTiO_3 particles is about 4810 kg/m^3 . Moreover, the heat capacity for SrTiO_3 nanoparticles is 99.292 J/K.mol [14] and the thermal conductivity is 12 W/mK [15].

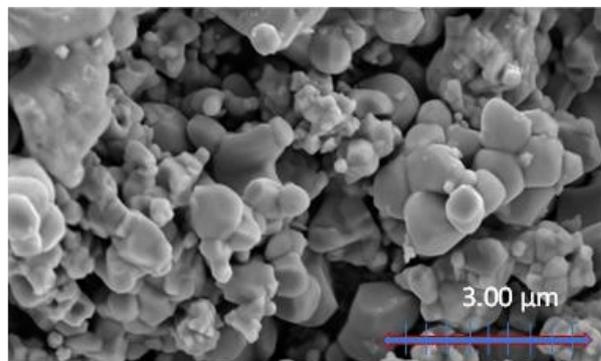


Figure 2. SEM image of SrTiO_3 nanoparticles

The XRD patterns of BaTiO_3 and SrTiO_3 nanoparticles are shown in Figure 3. By examining the XRD analyzes, it is found that the particles are compatible with the literature [16].

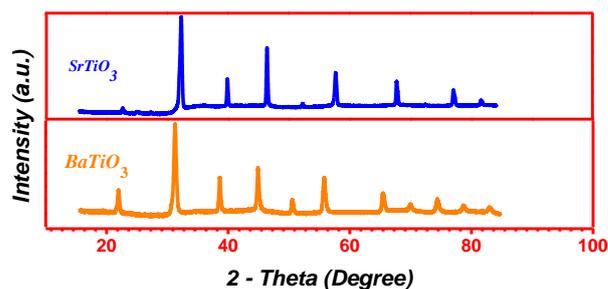


Figure 3. XRD analysis of BaTiO_3 and SrTiO_3 nanoparticles

The production of nanolubricants takes place in two steps. After the solid-liquid suspension is prepared, it is first mixed in an ultrasonic water bath for 6 hours. In the second stage, it is kept in a magnetic stirrer for 6 hours to obtain a homogeneous and hydrophobic mixture. After adding the compressor to the system as a structure, it is important that there is no precipitation. Even if a surfactant is used to prevent the problem of agglomeration of the particles and overcome the surface tension, it is necessary to use these two methods. The prepared nanolubricants are used as compressor oil. It has been shown that the performance of cooling systems increases with the use of nanolubricants in different mass fractions in the compressor [17,18]. Mineral oils are preferred as compressor oil. A nanolubricant is prepared by adding solid particles in mineral oil. The thermophysical properties of mineral oil are listed in Table 1 [19].

Table 1. Thermophysical properties for mineral oil

Properties	25 °C
Thermal Conductivity (W/m.K)	0.133
Kinematic Viscosity (mm ² /s)	17.08
Heat Capacity (J/kg.K)	1902
Density (g/l)	867
Heat Transfer Factor (W/m ² .K)	93.56

The schematic diagram of a simple cooling system in which nanolubricants can be used is shown in Figure 4.

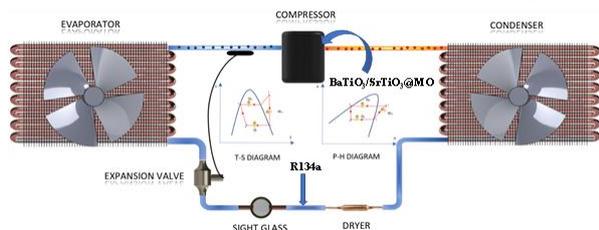


Figure 4. Schematic diagram of a cooling system

2.2. Determination of Thermophysical Properties of Nanolubricants

Various formulas are used to determine the thermophysical properties of BaTiO₃ and SrTiO₃ nanoparticles used to prepare nanolubricants. The density, heat capacity, thermal conductivity and viscosity of these nanoparticles are studied as thermophysical properties [5]. The density of the single and hybrid nanolubricants prepared were calculated using the following formula [20].

$$\rho_{NL} = (1 - \phi)\rho_{bf} + \phi\rho_{NP} \tag{1}$$

Eq. 2 and Eq. 3 are obtained when Eq. 1 is adapted for a nanolubricant formed by adding BaTiO₃ and SrTiO₃ nanoparticles to MO.

$$\rho_{BaTiO_3 NL} = (1 - \phi)\rho_{MO} + \phi\rho_{BaTiO_3} \tag{2}$$

$$\rho_{SrTiO_3 NL} = (1 - \phi)\rho_{MO} + \phi\rho_{SrTiO_3} \tag{3}$$

The calculations are performed using the formula in Eq. 4 for the hybrid nanofluid obtained by mixing BaTiO₃ and SrTiO₃ nanoparticles in a 1:1 ratio [21].

The adapted version of the formula for the nanoparticles to be used in the preparation of the nanolubricant is given in Eq. 5.

$$\rho_{hNL} = (1 - \phi_{np1} - \phi_{np2})\rho_{bf} + \phi_1\rho_{np1} + \phi_2\rho_{np2} \tag{4}$$

$$\rho_{BaTiO_3+SrTiO_3 NL} = (1 - \phi_{BaTiO_3} - \phi_{SrTiO_3})\rho_{MO} + \phi_{BaTiO_3}\rho_{BaTiO_3} + \phi_{SrTiO_3}\rho_{SrTiO_3} \tag{5}$$

When determining thermophysical properties, one of the most important parameters is heat capacity. The heat capacity is calculated as in Eq. 6 [22]. The adapted formulas for the nanoparticles analyzed in this study were given in Eq. 7 and Eq. 8.

$$c_{p,NL} = (1 - \phi)c_{p,bf} + \phi c_{p,np} \tag{6}$$

$$c_{p,BaTiO_3 NL} = (1 - \phi)c_{p,MO} + \phi c_{p,BaTiO_3} \tag{7}$$

$$c_{p,SrTiO_3 NL} = (1 - \phi)c_{p,MO} + \phi c_{p,SrTiO_3 NL} \tag{8}$$

Eq. 9 and Eq. 10 is given for the calculation of the heat capacity of the hybrid nanolubricant used [21].

$$\rho_{hNL} c_{p,hNL} = (\phi_{np1}\rho_{np1}c_{p,np1}) + (\phi_{np2}\rho_{np2}c_{p,np2}) + [(1 - \phi_{np1} - \phi_{np2})\rho_{MO}c_{p,MO}] \tag{9}$$

$$\rho_{BaTiO_3+SrTiO_3 NL} c_{p,BaTiO_3+SrTiO_3 NL} = (\phi_{BaTiO_3}\rho_{BaTiO_3}c_{p,BaTiO_3}) + (\phi_{SrTiO_3}\rho_{SrTiO_3}c_{p,SrTiO_3}) + [(1 - \phi_{BaTiO_3} - \phi_{SrTiO_3})\rho_{MO}c_{p,MO}] \tag{10}$$

The Maxwell model is used to calculate the thermal conductivity of nanolubricants. The formula is given in Eq. 11 [23].

$$\frac{k_{NL}}{k_{MO}} = \frac{k_{np} + 2k_{MO} + 2\phi(k_{np} - k_{MO})}{k_{np} + 2k_{MO} - \phi(k_{np} - k_{MO})} \tag{11}$$

$$\frac{k_{BaTiO_3 NL}}{k_{MO}} = \frac{k_{BaTiO_3} + 2k_{MO} + 2\phi(k_{BaTiO_3} - k_{MO})}{k_{BaTiO_3} + 2k_{MO} - \phi(k_{BaTiO_3} - k_{MO})} \tag{12}$$

$$\frac{k_{SrTiO_3 NL}}{k_{MO}} = \frac{k_{SrTiO_3} + 2k_{MO} + 2\phi(k_{SrTiO_3} - k_{MO})}{k_{SrTiO_3} + 2k_{MO} - \phi(k_{SrTiO_3} - k_{MO})} \tag{13}$$

The revised Maxwell equation for hybrid nanolubricants is given in Eq. 14 [23].

$$k_{hNL} = k_{MO} \left[\frac{\frac{\phi_{np1}k_{np1} + \phi_{np2}k_{np2}}{\phi} + 2k_{MO} + 2(\phi_{np1}k_{np1} + \phi_{np2}k_{np2}) - 2\phi k_{MO}}{\frac{\phi_{np1}k_{np1} + \phi_{np2}k_{np2}}{\phi} + 2k_{MO} - (\phi_{np1}k_{np1} + \phi_{np2}k_{np2}) + \phi k_{MO}} \right] \quad (14)$$

The revised Maxwell equation is arranged as in Eq. 15 for BaTiO₃+SrTiO₃/MO hybrid nanolubricant.

$$k_{hNL} = k_{MO} \left[\frac{\frac{\phi_{np1}k_{np1} + \phi_{np2}k_{np2}}{\phi} + 2k_{MO} + 2(\phi_{np1}k_{np1} + \phi_{np2}k_{np2}) - 2\phi k_{MO}}{\frac{\phi_{np1}k_{np1} + \phi_{np2}k_{np2}}{\phi} + 2k_{MO} - (\phi_{np1}k_{np1} + \phi_{np2}k_{np2}) + \phi k_{MO}} \right] \quad (15)$$

The viscosity of the oil changes with the addition of nanoparticles to the lubricant. The viscosity is calculated using the following Eq. 16 [21]. Eq. 17 and Eq. 18 are valid for hybrid nanolubricants.

$$\mu_{NL} = \mu_{MO}(1 + 2.5\phi) \quad (16)$$

$$\frac{\mu_{hNL}}{\mu_{MO}} = 1 + 13.5\phi + 904.4\phi^2 \quad (17)$$

$$\frac{\mu_{BaTiO_3+SrTiO_3 hNL}}{\mu_{MO}} = 1 + 13.5\phi + 904.4\phi^2 \quad (18)$$

3. RESULTS and DISCUSSION

By adding BaTiO₃ and SrTiO₃ nanoparticles to the working fluid MO, nanolubricants in different mass fractions are obtained. It is important to calculate the thermophysical properties of these nanolubricants to determine the advantages of their use as compressor oil. Density, heat capacity, thermal conductivity and viscosity parameters of mono and hybrid nanolubricants were calculated using the formulas given in the previous section. The density parameters of BaTiO₃/MO and SrTiO₃/MO as single nanolubricants and BaTiO₃+SrTiO₃/MO as hybrid nanolubricants were calculated as follows.

$$\rho_{BaTiO_3 NL} = (1 - 0.01) \times 867 + 0.01 \times 6080 = 919.13 \text{ kg/m}^3$$

$$\rho_{SrTiO_3 NL} = (1 - 0.01) \times 867 + 0.01 \times 4810 = 906.43 \text{ kg/m}^3$$

$$\begin{aligned} \rho_{BaTiO_3+SrTiO_3 hNL} &= (1 - 0.005 - 0.005) \times 867 \\ &+ 0.005 \times 6080 + 0.005 \times 4810 \\ &= 912.78 \frac{\text{kg}}{\text{m}^3} \end{aligned}$$

The heat capacity parameters of BaTiO₃/MO and SrTiO₃/MO single nanolubricant and BaTiO₃+SrTiO₃/MO hybrid nanolubricant were calculated as follows.

$$\begin{aligned} c_{p,BaTiO_3 NL} &= (1 - 0.01) \times 1902 + 0.01 \times 436.84 \\ &= 1.887 \frac{\text{kJ}}{\text{kg.K}} \end{aligned}$$

$$\begin{aligned} c_{p,SrTiO_3 NL} &= (1 - 0.01) \times 1902 + 0.01 \times 541.14 \\ &= 1.888 \frac{\text{kJ}}{\text{kg.K}} \end{aligned}$$

$$\begin{aligned} 912.78 \times c_{p,BaTiO_3+SrTiO_3 hNL} &= (0.005 \times 6080 \\ &\times 0.436) + (0.005 \times 4810 \times 0.541) \\ &+ [(1 - 0.005 - 0.005) \times 867 \\ &\times 1.902] \end{aligned}$$

$$c_{p,BaTiO_3+SrTiO_3 hNL} = 1.817 \frac{\text{kJ}}{\text{kg.K}}$$

The thermal conductivity parameters of BaTiO₃/MO and SrTiO₃/MO single nanolubricant and BaTiO₃+SrTiO₃/MO hybrid nanolubricant were calculated as follows.

$$\begin{aligned} \frac{k_{BaTiO_3 NL}}{0.133} &= \frac{3.672 + 2 \times 0.133 + 2 \times 0.01 \times (3.672 - 0.133)}{3.672 + 2 \times 0.133 - 0.01 \times (3.672 - 0.133)} \end{aligned}$$

$$k_{BaTiO_3 NL} = 0.1366 \frac{\text{W}}{\text{m.K}}$$

$$\begin{aligned} \frac{k_{SrTiO_3 NL}}{0.133} &= \frac{12 + 2 \times 0.133 + 2 \times 0.01 \times (12 - 0.133)}{12 + 2 \times 0.133 - 0.01 \times (12 - 0.133)} \end{aligned}$$

$$k_{SrTiO_3 NL} = 0.1368 \frac{\text{W}}{\text{m.K}}$$

$$0.133 \left[\frac{0.005 \times 3.672 + 0.005 \times 12}{0.01} + 2 \times 0.133 + 2(0.005 \times 3.672 + 0.005 \times 12) - 2 \times 0.01 \times 0.133 \right]$$

$$k_{BaTiO_3+SrTiO_3 hNL} = 0.136 \frac{W}{m.K}$$

The viscosity parameters of BaTiO₃/MO and SrTiO₃/MO single nanolubricant and BaTiO₃+SrTiO₃/MO hybrid nanolubricant were calculated as follows.

$$\mu_{BaTiO_3 NL} = \mu_{SrTiO_3 NL} = 0.9525 \times (1 + 2.5 \times 0.01)$$

$$= 0.9763 \text{ mPa.s}$$

$$\frac{\mu_{BaTiO_3+SrTiO_3 hNL}}{0.9525} = 1 + 13.5 \times 0.01 + 904.4 \times 0.01^2$$

$$\mu_{BaTiO_3+SrTiO_3 hNL} = 1.1672 \text{ mPa.s}$$

Examining the results, it was found that the density value for mono and hybrid nanofluids did not change significantly. We can say that the formation of a hybrid nanofluid has little effect on the thermophysical properties of the density. Additionally, with the addition of solid nanoparticles to the working oil, the heat capacity decreases and thus the thermal performance increases. The heat capacity decreased more for hybrid nanolubricants than for simple nanolubricants. In this case, it can be said that hybrid nanolubricants made a significant contribution to the improvement of thermal performance. As a result of the calculations, it was found that the value of thermal conductivity for nanolubricants also changed slightly. No significant change was found in the viscosity parameter.

To obtain structural and functional data on the suspension using the FTIR analysis method, nanofluids were prepared in the form of BaTiO₃ and SrTiO₃ nanoparticles. In the preparation of the nanofluids, 1.0% by mass of the particles, 0.5% by volume of surfactant were used.



Figure 5. Mono and hybrid nanofluids prepared from different mass fractions

The FTIR analysis confirming the presence of SDBS on the surface of the nanoparticles was shown in Figure 6. As can be seen from the curves in the figure, strong characteristic of SDBS bands are seen on mono and hybrid nanofluids. It is also clear from this analysis that the SDBS surfactant material has a homogeneous distribution in the solid warm suspension. Two measurements were made for each suspension and are shown in Figure 6.

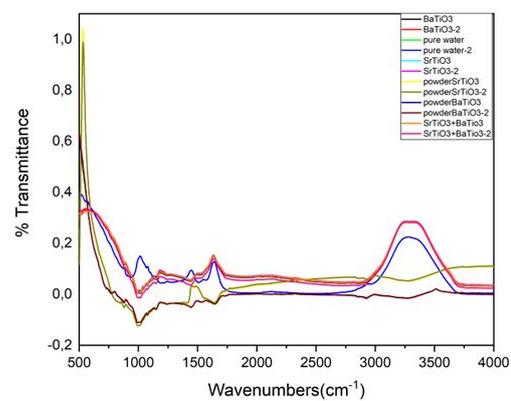


Figure 6. FTIR analysis for mono and single nanofluids

4. CONCLUSION

In this study, the change in thermophysical performance due to the addition of solid BaTiO₃ and SrTiO₃ nanoparticles in compressor oil was investigated MO. Mono and hybrid nanolubricants (1:1) containing BaTiO₃ and SrTiO₃ nanoparticles at a mass fraction of 1.0% were prepared. The advantages of the hybrid nanolubricants were attempted to prove by calculations with the appropriate mass fraction based on the theoretically obtained formulas. In this context, density, heat capacity, thermal conductivity, viscosity and wetting capability of BaTiO₃/MO, SrTiO₃/MO and BaTiO₃+SrTiO₃/MO hybrid nanolubricant suspensions were investigated. A series of experiments were conducted to investigate the effect of surfactant SDBS on surface tension. As a result of the theoretical calculations, analyzes and experiments, it can be said that the preparation of nanolubricants with hybrid nanoparticles contributes positively to the thermophysical properties. The results obtained in this study are important to get an idea for the use of hybrid nanolubricants in cooling systems.

ABBREVIATIONS LIST

MO	Mineral Oil
BaTiO ₃	Barium Titanate
SrTiO ₃	Strontium Titanate
AlN	Aluminium Nitride
ZnO	Zinc Oxide
TiO ₂	Titanium Dioxide
MWCNT	Multi-Walled Carbon Nanotube
NiFe ₂ O ₄	Nickel Ferrite
CuO	Copper Oxide
SDBS	Sodium Dodecyl Benzene Sulfonate
XRD	X-ray Diffraction
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectrofotometre
hNL	Hybrid Nanolubricant
NL	Nanolubricant
np	Nanoparticle
bf	Base Fluid

DECLARATION OF ETHICAL STANDARDS

The author of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission

AUTHORS' CONTRIBUTIONS

Mustafa AKKAYA: Performed the experiments and analyse the results. Writing process and control of the article.

CONFLICT OF INTEREST

There is no conflict of interest in this study.

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