CI&CEQ
Chemical Industry & Chemical Engineering Quarterly

Available on line at
Association of the Chemical Engineers of Serbia *AChE*
www.ache.org.rs/CICEQ

Chem. Ind. Chem. Eng. Q. 28 (1) 67–72 (2022) CI&CEQ

J. BENSAM RAJ[1]
M. MUTHURAJ[2]

[1]Department of Mechanical Engineering, Muthayammal Engineering College, Namakal, India
[2]Department of Mechanical Engineering, Vidyaa Vikas College of Engineering and Technology, Tiruchengode, Namakal, India

SCIENTIFIC PAPER

UDC 665.347.8:54:544

INFLUENCE OF GRAPHENE NANO-PLATELET DISPERSION ON THE THERMO-PHYSICAL PROPERTIES OF SUNFLOWER OIL

Article Highlights

- Usage of mineral oil resulting in serious large-scale environmental concerns
- Nanofluids are a superior heat transferring agent compared to traditional fluids
- Maximum thermal stability of about 280 °C is achieved at 1.1 wt.% of graphene nanofluid
- Dynamic viscosity diminished in an exponential shape in acquiescence with the Arrhenius equation
- Density and surface tension increase with graphene concentration

Abstract

In this article, thermal stability, viscosity, density and surface tension of graphene nano-platelet dispersed in sunflower oil are experimentally determined by varying the graphene concentration (0.1-1.1 wt.%) and temperature (40-100 °C). The SEM micrograph and the EDS spectra are used to characterize the graphene. Nanofluids are prepared by ultrasonication technique (two-step method) and the maximum thermal stability of about 280 °C is achieved at 1.1 wt.% graphene nanofluids. The dynamic viscosity diminishes in an exponential shape in acquiescence with the Arrhenius equation and the densities of samples are characteristic with linear decrement in the estimated temperature range. Density and surface tension increase with the graphene concentration, while a reverse trend is observed with temperature raise. The maximum thermal stability, viscosity, density and surface tension is obtained in the nanofluid with 1.1 wt.% concentration and the minimum is obtained in the nanofluid with 0.1 wt.% concentration.

Keywords: graphene, thermal stability, surface tension, nanofluids, sunflower oil.

Annually, about 100 million tons of bio-oils and fats are derived worldwide from plant sources and the effective utilization of bio-oils as an alternative to mineral oil-based working fluids and lubricants may lead to solving many environmental questions. The perpetual utilization and burning of mineral oils results in serious large-scale environmental concerns like global warming and environmental pollution. The exploitation of bio-oils as an effective alternative to mineral oil lubricants and fossil fuels may give a lead as how to solve many environmental questions. Also, the present industrial sectors demand rapid heat exchange equipment, rapid cooling equipment, and superior lubricating distinctiveness, which may not be achieved by the traditional working fluids. Nanofluids and nano lubricants have been discovered as unique working fluids prepared by dispersing nanoparticles into a fluid medium. Nanofluids are a proven superior heat transfer and lubricating agents in this regard due to the enhanced heat transfer capabilities and lubricating distinctiveness compared to traditional working fluids. Several parameters affect the thermo-physical property enhancements, which mainly includes the type of dispersed nanomaterials (metallic or non-metallic), weight fraction and temperature. Some of the current and significant studies associated with thermo-

---

Correspondence: J. Bensam Raj, Department of Mechanical Engineering, Muthayammal Engineering College, Namakal--637408, India.
E-mail: bensmech@yahoo.co.in
Paper received: 1 January, 2021
Paper revised: 19 April, 2021
Paper accepted: 25 May, 2021

https://doi.org/10.2298/CICEQ210101018B

-physical property enhancements of nanofluids are reported below [1-3].

The viscosity and thermal stability are the significant characteristics of any working fluids while sizing and selecting pipelines and pumps. Temperature significantly influences the kinematic viscosity which diminishes with temperature raise [4]. The dynamic viscosity of any nanofluid decreases with the reduction of nanoparticle size [5]. The random Brownian action of dispersed nanoparticles in a two-phase solution enhances the rate of energy exchange which increases with decrease in nanoparticle size [6]. Guntreddi *et al.* (2021) reported that the graphite nano-oil arrested adhesion of interacting surfaces and diminished the coefficient of friction by 82% due to the dispersion of nano-graphite [7]. Peng *et al.* (2021) formulated and studied the mechanism of action of eco-friendly Al_2O_3-soybean oil nanofluid and revealed that the nanofluid has the best surface integrity due to the bearing effect [8]. The experimental report of Goodarzi *et al.* (2021) concludes that the presence of graphene in nano-suspension induces superior fouling resistance [9]. The experimental report of Timofeeva *et al.* (2004) exhibits that the nanofluids consisting cylindrical nanoparticles produce superior thermal conductivity and dynamic viscosity at different working conditions [10]. Cui *et al.* (2016) reported the impact of parameters like nanomaterial shape, size, and type of nanomaterials on the liquid-solid interfaces [11]. The effect of graphene concentration in water (base fluid) was investigated by Hajjar *et al.* (2014) [12]. Ghozatloo *et al.* (2014) reported 33.9% in thermal conductivity enhancement in a shell and tube heat exchanger when the traditional heat transfer fluid is replaced by graphene nanofluids [13]. The typical physical properties of sunflower oil such as density, flash point, thermal conductivity, kinematic viscosity and cetane number are very low compared to the industrial heat transfer and lubricating agents. Homogeneous dispersion of graphene into sunflower oil is a promising approach to improve their thermo-physical properties. In this study, thermal stability, viscosity, density and surface tension of sunflower oil, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.1 wt.% of graphene-sunflower oil nanofluids are experimentally investigated and the contribution of graphene nano-platelet dispersion in the property enhancements is also reported.

MATERIALS AND METHODS

The sunflower plant (*Helianthus*) has nearly 70 species that acclimatize to all climatic conditions and grow on all continents (around 20 million ha). The typical physical properties of sunflower oil such as density, flash point, thermal conductivity, kinematic viscosity and cetane number at room temperature are 920 kg/m^3, 250 °C, 0.168 W/mK, 34 mm^2/s and 37, respectively [14]. The fatty acid contents like linoleic acid, oleic acid, palmitic acid and stearic acid are 45.35, 49, 4.02 and 1.49%, respectively. The graphene (Plasma Chem GmbH, Germany) was dispersed into sunflower oil for preparing the graphene-sunflower oil nanofluid which has superior specific surface area and tap density (average particle size and thickness are <2 microns and 1-4 nm, respectively). All weight fractions of the nanofluids were formulated by ultrasonication technique (40 kHz ultrasonic agitator). The prepared nanofluids are stable for 168 h (evaluated by sedimentation technique) which can be further improved by adding suitable stabilizing agents. However, the surfactant is not added to insure the limpidness of the graphene-sunflower oil nanofluids.

The thermal analysis of sunflower oil and graphene nanofluids are analyzed in a thermogravimetric analyzer (TGA 851 Thermo Balance, Mettler & Toledo) with a heating rate of 10 °C/min without any antioxidants until 500 °C. About 50 mg of sunflower oil was kept in an alumina crucible and the thermal analysis was carried out in helium atmosphere (25 ml/ /min). The dynamic viscosity of sunflower oil and graphene nanofluids were studied in a LV-DVIII viscometer (Brookfield, USA) by varying the graphene concentration (0.1-1.1 wt.%) and temperature (40-100 °C) without using any stabilizing agents. Further, the density and surface tension of sunflower oil and graphene nanofluids were determined by the Archimedean method [15] and pendant drop method (Krüss goniometer, Hamburg, Germany) [16], respectively.

RESULTS AND DISCUSSION

The SEM micrograph and the EDS spectra of graphene are presented in Figure 1. The SEM micrograph shows that dry graphene is completely apparent, wrinkled and completely agglomerated due to high surface energy (BET: 800 m^2/g). The agglomerations approximately have 5-10 stacks with 3-5 nm height with average particle size of <2 μm. The EDS spectrum of graphene confirms their existence (purity >91%) with the impurities O (<7%), N (<2%) and <1% of metals (Al, Fe, K, Si, Ti, Zn).

All weight fractions of the nanofluids were formulated by ultrasonication technique. The dispersion stability of the graphene-sunflower oil nanofluids is estimated through sedimentation technique and it is exhibited in Figure 2; it was stable for about 168 h.

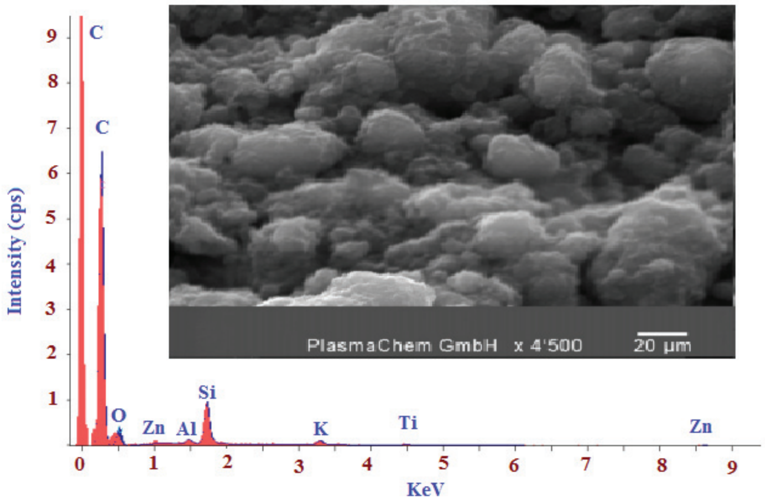

Figure 1. SEM micrograph and the EDS spectra of graphene.

The thermal analysis measures the thermodynamic distinctiveness like enthalpy, oil stability, phase change and decomposition temperatures as a function of temperature or time [17,18]. The thermograms of refined sunflower oil and 0.1, 0.5 and 0.9 wt.% of graphene nanofluids are presented in Figure 3.

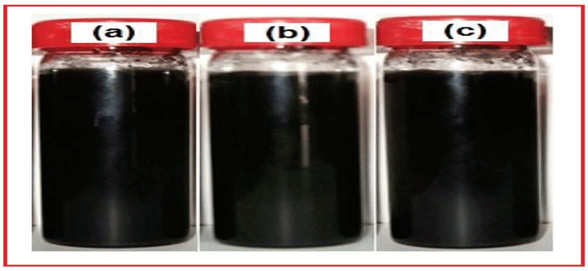

Figure 2. Dispersion stability of graphene nanofluids: a) 0.5 wt.% of nanofluids, b) 0.9 wt.% of nanofluids and c) 1.1 wt.% of nanofluids.

Figure 3 depicts that the thermal decomposition of sunflower oil and graphene nanofluids occurs in a well-defined similar pattern with less than 1% scum residual at around 500 °C which also confirms that the decomposition occurs at a distinct stage. The sunflower oil decomposes only after 250 °C due to the presence of citric acid in the sunflower oil as an artificial antioxidant. However, the decomposition temperature of the 1.1 wt.% of graphene nanofluids is enhanced to 280 °C (16.67%) due to the dispersion of graphene. Further, temperature significantly influences the viscosity of oil samples which generally exponentially diminishes with temperature raise. Generally, oil molecules are strongly bonded by cohesive forces (intermolecular forces) which decreases as the temperature of the oil increases in compliance with the Arrhenius correlation. The relationship between the temperature, activation energy and viscosity are expressed in the Arrhenius equation, Eq. (1), where η, η_o, E_A, R and T are the dynamic viscosity, reference dynamic viscosity, activation energy, gas constant and absolute temperature, respectively [19]. The change in viscosity of sunflower oil and graphene nanofluids are related to their change in molecular structure due to the shift of fluid molecules into the vacancies:

$$\eta = \eta_0 e^{\frac{E_A}{RT}} \qquad (1)$$

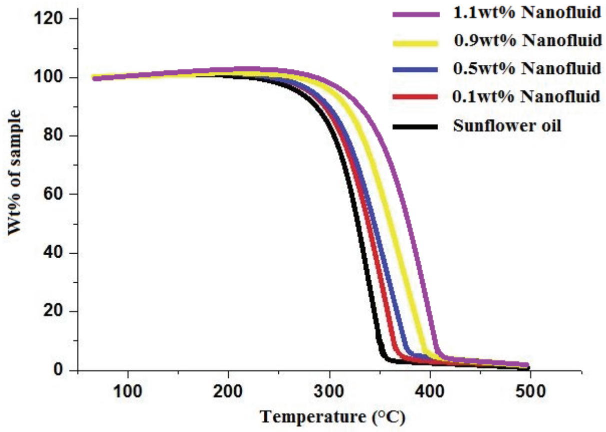

Figure 3. Thermograms of sunflower oil and graphene nanofluids.

Figure 4 depicts the dynamic viscosity of the oil and graphene nanofluids are determined by the LV--DVIII viscometer by varying the graphene concentration (0.1-1.1) wt.% and temperature (40-100) °C. In any preliminary experimental investigation, it is necessary to validate the accuracy of the measuring instrument. The accuracy of the Brookfield viscometer was determined by measuring the dynamic viscosity of pure sunflower oil at a temperature range of 40-100 °C and comparing with the reference [20] which had good concordance. Considering the sunflower oil's viscosity, it is impalpable that the dynamic viscosity of sunflower oil and graphene nanofluids confirms the diminishing trends with temperature raise. With the addition of graphene content from 0.1 to 1.1 wt.%, the viscosity of graphene-sunflower oil nanofluid improves from 28.52 to 40.1 mm^2/s at the measured 40 °C and it rises from 21.02 to 32.1, 15.1 to 26.8, 12 to 23.5, 9.8 to 21.2, 7.81 to 19.2 and 6.1 to 18.4 mm^2/s during successive 40-100 °C, respectively. Furthermore, it shows that the dynamic viscosity of graphene nanofluids is higher than that of the base fluid, which would have been caused by the dispersed graphene. The raise in the graphene nanofluid temperature reduces the ability of sunflower oil and graphene nanofluids to oppose an external force which significantly reduces the molecular bonding strength. The cohesive molecular interactions arise with the temperature raise which influence the Brownian motion of graphene. The velocity of Brownian motion decreases with increasing the graphene weight fraction in the graphene nanofluids and indicates Newtonian behavior. Thus, the maximum viscosity is obtained in the nanofluid with 1.1 wt.% concentrations and the minimum viscosity is obtained in the nanofluid with 0.1 wt.% concentration. The experimental viscosity data of the graphene nanofluids are further compared with the viscosity equations of Smoluchowski, Bull, Jefferey, Vand, Williams, Roscoe, Maron, Gbadeyan and Colak [21-29]. However, these equations predict the viscosity of the graphene nanofluids with more than 25% deviation.

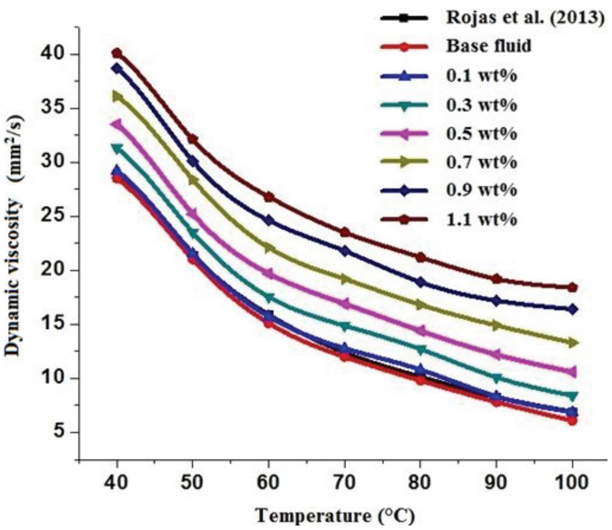

Figure 4. Dynamic viscosity of sunflower oil and graphene nanofluids.

The densities of sunflower oil and graphene nanofluids are determined by the Archimedean method in which a stainless-steel ball is immersed into the oil sample through a wire. The oil sample is kept inside a beaker and heated and the density of samples estimated from 40-100 °C. The wire and steel ball are also heated. The density measurements were recorded in triplicate. Finally, the density of sunflower oil and graphene nanofluids are determined with Eq. (2) where σ, m_v, m_f, v_1 and v_2 are the surface tension, mass of stainless steel, mass of oil sample, volume of stainless steel and volume of oil sample, respectively [15]:

$$Density(\rho) = \frac{\sigma + m_v - m_f}{V_1 - V_2} \qquad (2)$$

Both viscosity and density of sunflower oil and graphene nanofluids are affected by temperature change which becomes less viscous when the temperature is increased. Considering the sunflower oil's density, the dependencies of sunflower oil and graphene nanofluids density on temperature and graphene concentration are presented in Figure 5. The density of sunflower oil is in the range of 967.1-868.3 kg/m^3 and decreases linearly with the temperature raise (40-100 °C) and arises depending on the graphene concentration (0.1-1.1 wt.%). However, it proves that the density of graphene nanofluids is higher than that of the base fluid, which would be caused by the dispersed graphene. With the homogeneous addition of graphene content from 0.1 to 1.1 wt.%, the apparent density of the graphene-sunflower oil nanofluid improves from 967.1 to 972.5 kg/mm^3 at 40 °C whereas it rises from 954.6 to 958.5, 940.3 to 945.6, 927.5 to 933.2, 907.2 to 915, 890 to 896.3 and 868.3 to 875.5 kg/mm^3 during the next 50-100 °C, respectively. The bonds in sunflower oil and graphene nanofluids break and tend to expand as the temperature increases while they break more slowly as temperature decreases. It is the reason for the change in density of nanofluids with temperature. The highest densities are acquired at lower working temperatures and highest graphene concentration (1.1 wt.%). Further, the surface tensions of the sunflower oil and 0.1, 0.5 and 0.9 wt.% of graphene nanofluids are estimated through the pendant drop method in which a steel needle (22 gauge) is kept inside the environmental chamber. The temperature of the measuring system and the needle are integrated by a temperature control system (Succasunna, USA) through a thermocouple (Stamford, USA). During each experiment, acetone was used to clean the parts to avoid contamination. The surface tension is calculated by Eötvös correlation (Eq. (3)) which mainly depends on molar mass of the oil sample (M_{oil}), density of the oil sample (ρ_{oil}) and temperature (T). K_E and T_C are the Eötvös constant (5.4 dyne cm/mol$^{2/3}$ K) and critical temperature, respectively [14]:

$$\sigma \frac{M_{\text{oil}}^{\frac{2}{3}}}{\rho_{\text{oil}}} = K_{\text{E}}(T_{\text{C}} - T)\ (3)$$

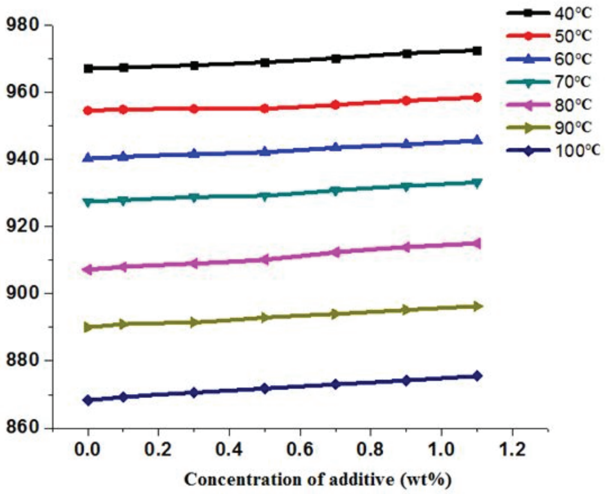

Figure 5. Density of sunflower oil and graphene nanofluids.

Figure 6 represents the temperature and graphene concentration dependencies of surface tensions of sunflower oil and graphene nanofluid samples. The surface tension of sunflower oil at 40 °C is 7.38 dyne/cm which diminishes to 4.12 dyne/cm at 100 °C. With the homogeneous addition of graphene content from 0.1 to 1.1 wt.%, the measured surface tension of the graphene-sunflower oil nanofluid improves from 7.38 to 10.3 dyne/cm at 40 °C whereas it raises from 6.59 to 9.5, 6.01 to 8.9, 5.56 to 8.6, 5.03 to 8.2, 4.6 to 7.8 and 4.12 to 7.5 dyne/cm during the next 50-100 °C, respectively. The surface tension is the ability of sunflower oil surfaces to contract into the least surface area due to the shearing of cohesive forces between the oil molecules. It also refers to the ability of sunflower oil's and graphene nanofluids' surfaces to oppose an external force. The cohesive molecular interactions arise with the temperature raise which significantly alters the surface tension of sunflower oil and graphene nanofluids. The surface tensions of sunflower oil and 0.1-0.3 wt.% of graphene nanofluids are very close to each other during the estimated temperatures which is in the range of 7.53-4.25 dyne/cm between 40-100 °C. Further, a significant rise in the surface tension is observed due to the homogeneously dispersed graphene with the base fluid, whereas it diminishes with temperature raise and the slopes are very similar in which density plays an imperative role. Density influences oil absorption rate with the temperature raise. The dynamic reduction of interfacial tension between the molecules of sunflower oil and graphene nanofluids are the reason for the decrement of surface tension.

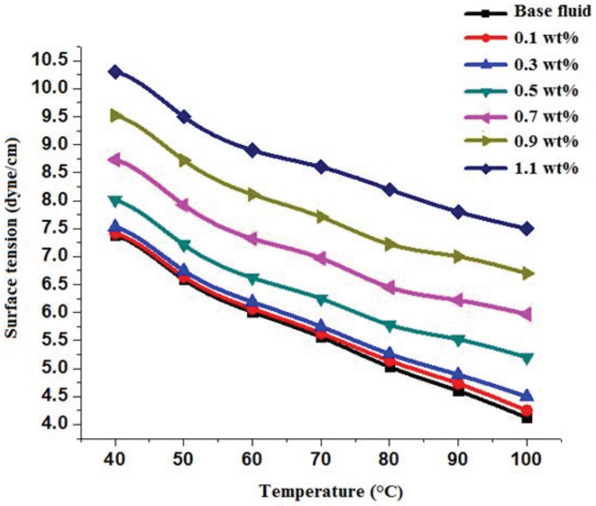

Figure 6. Surface tension of sunflower oil and graphene nanofluids.

CONCLUSION

This article deals with the influence of graphene nano-platelet dispersion on the thermal stability, viscosity, density and surface tension of sunflower oil. The following conclusions are made based on the experimental results obtained:

– The dynamic reduction of interfacial tension between the molecules of sunflower oil and graphene nanofluids are the reason for the decrement of surface tension.

– Viscosity of graphene nanofluids indicates Newtonian behavior.

Density and surface tension increase with graphene concentration, while a reverse trend is observed with temperature raise.

The maximum thermal stability (up to 280 °C), viscosity (40.7%) and surface tension (39.4%) enhancements are obtained in the nanofluid with 1.1 wt.% of graphene concentration.

REFERENCES

[1] N. Arora, M. Gupta, Renewable Sustainable Energy Rev. 134 (2020) 110242

[2] M. S. Alnarabiji, M. M. Husein, Fuel 267 (2020) 117262

[3] R. Maheswaran, J. Sunil, J. Mol. Liq. 223 (2017) 643-651

[4] O.O. Fasina, Z. Colley, Int. J. Food Prop. 11 (2008) 738--746

[5] H. Zhang, S. Qinga, Y. Zhaia, X. Zhanga, A. Zhang, Powder Technol. 377 (2021) 748-759

[6] R. Haris, R. Sivakumar, Int. J. Mech. Sci. 190 (2021) 106033

[7] B. Guntreddi, A. Ghosh, Tribol. Int.153 (2021) 106596

[8] R. Peng, X. He, J. Tong, X. Tang, Y. Wu, J. Clean Prod. 278 (2021) 123498

[9] M. Goodarzi, I. Tlili, H. Moria, E.M. Cardoso, T.A. Alkanhal, A.E. Anqi, M.R. Safaeighi, Powder Technol. 377 (2021) 10-19

[10] E.V. Timofeeva, J.L. Routbort, D. Singh, J. Appl. Phys. 106 (2009) 014304

[11] W. Cui, Int. Commun. Heat Mass Transfer 71 (2016) 75--85

[12] Z. Hajjar, A.M. Rashidi, A. Ghozatloo Int. Commun. Heat Mass Tran. 57 (2014) 128-131

[13] A. Ghozatloo, A. Rashidi, M.S. Niassar, Exp. Therm. Fluid Sci. 53 (2014) 136-141

[14] D. Karefyllakis, A.J. Goot, V. Nikiforidis, Curr. Opin. Food Sci. 29 (2019) 35-41

[15] N.S. Shreya, V.R. Martinez, Meghan. O.M, E.F. Brian, Int. J. Food Prop. 20 (2017) S1965-S1981

[16] R. Geibler, S. Bozorgzard, T. Streibel, E. Kaisersberger, T. Denner, R. Zimmermann, J. Therm. Anal. Calorim. 96 (2009) 813-820

[17] M.J.B Souza, A.O.S Silva, J.M.F.B. Aquino, V.J. Fernandes, A.S. Araujo, J. Therm. Anal. Calorim. 2 (2004) 693-698

[18] L.O. Figura, A.A. Teixeira, Food Physics, Physical properties-measurement and applications, Springer-Verlag Berlin, 2007

[19] E.E.G. Rojas, J.S.R. Coimbra, J.T. Romero, Int. J. Food Prop. 16(2013) 1620-1629

[20] S.R. Palit, Nature 177 (1956)1180-1180

[21] M.V. Smoluchowski, Kolloidzschr, 80 (1916) 190-195

[22] H. Bull, Trans. Faraday Soc. 80 (1940) 80-84

[23] G.B. Jeffery, Phys. Eng. Sci. 102 (1922) 161-179

[24] V. Vand, J. Phys. Chem. 19 (1948) 277-299, 1948

[25] P.S. Williams, J. Appl. Chem. 3 (1953) 120-128

[26] R. Roscoe, J. Appl. Phys. 267 (1952) 3-6

[27] S. Maron, S. Fok, J. Colloid Sci. 85 (1953) 540-542

[28] J.A. Gbadeyan, E.O. Titiloye, A.T. Adeosun, Heliyon 6 (2020) e03076

[29] A.B. Colak, Powder Technol. 381 (2021) 338-351.

J. BENSAM RAJ[1]
M. MUTHURAJ[2]

[1]**Department of Mechanical Engineering, Muthayammal Engineering College, Namakal, India**
[2]**Department of Mechanical Engineering, Vidyaa Vikas College of Engineering and Technology, Tiruchengode, Namakal, India**

NAUČNI RAD

UTICAJ DISPERZIJE GRAFENSKIH NANOPLOČICA NA TERMO-FIZIČKA SVOJSTVA SUNCOKRETOVOG ULJA

U ovom radu, eksperimentalno su određeni termička stabilnost, viskozitet, gustina i površinski napon suncokretovog ulja sa dispergovanim grafenskim nano-pločicama u opsegu koncentracije grafena od 0,1 do 1,1% i opsegu temperature od 40 do 100 °C. SEM mikrografija i EDS spektri su korišćeni za karakterizaciju grafena. Nanofluidi se pripremaju tehnikom ultrazvučne obrade (metoda u dva koraka) i maksimalna termička stabilnost od oko 280 °C se postiže pri 1,1% grafena. Dinamički viskozitet se smanjuje eksponencijalno u skladu sa Arenijusovom jednačinom, a gustina uzoraka se linearno smanjuje u korišćenom temperaturnom opsegu. Gustina i površinski napon rastu sa koncentracijom grafena, dok se sa porastom temperature primećuje obrnuti trend. Maksimalna termička stabilnost, viskozitet, gustina i površinski napon se dobijaju u nanofluidu sa koncentracijom od 1,1% grafena, a minimum u nanofluidu sa koncentracijom od 0,1%.

Ključne reči: grafen, termička stabilnost, površinski napon, nanofluidi, suncokretovo ulje.