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Effect of Modified Hybrid Nanoparticles on the Properties of Base Oil

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Abstract

Nanomaterials have an excellent potential for improving the rheological and tribological properties of lubricating oil. In this study, oleic acid was used to surface-modify nanoparticles to enhance the dispersion and stability of Nanofluid. The surface modification was conducted for inorganic nanoparticles (NPs) TiO_2 and CuO with oleic acid (OA) surfactant, where oleic acid could render the surface of TiO_2-CuO hydrophobic. Fourier transform infrared spectroscopy (FTIR), and Scanning electron microscopy (SEM) were used to characterize the surface modification of NPs. The main objective of this study was to investigate the influence of adding modified TiO_2 -CuO NPs with weight ratio 1:1 on thermal-physical properties such as kinematic viscosity, viscosity index (VI), pour point, and flash point of Iraqi base oil (40 stock) and nano-lubricating oil. The kinematic viscosity of base oil at 40 °C and 100°C increased with high concentrations of modified TiO_2 -CuO NPs. The highest value of VI of base oil 40 stock at 0.8 wt. % of modified TiO_2 -CuO NPs was 108.5. The results showed that the flashpoint value increased with the increased concentration of modified TiO_2 -CuO NPs of base oil 40, where the highest value was 220 °C. The pour point of nano lubricating oil base with 0.8 wt. % of modified TiO_2 -CuO NPs showed decreasing from -12 °C to -15 °C of base oil 40.

Keywords: Oil 40 stock, Lubricating Oil, Nanoparticles, Oleic acid, Viscosity Index, Flash Point

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1- Introduction

The word (lubricating oil) relates to various products of hundreds of specific chemicals and additives and can be either mineral or synthetically. Lubricating oil contains 80-90% of hydrocarbon petroleum distillates and 10-20% additives. Mineral oil is more commonly used than synthetic oil [1]. Improving environmental protection, durability, and fuel efficiency is a major focus in the automotive industry. New techniques are being developed, such as introducing new, less harmful materials and the controlled combustion of fuels. which manages the environmental harms caused by vehicles. The lubricant plays a crucial role in friction and wear reduction and is sometimes needed to perform other functions. It is useful as a heat-transfer medium in many applications. It eliminates heat from "hot spots" in sliding parts, thereby avoiding overheating losses such as cooling engine pistons, power-transmission systems, and metal-working operations [2]. Several different forms of lubricants are used in machinery. These lubricants are used in gasoline and diesel engines containing various forms of chemical materials known as "additives", which are used to enhance the properties of these lubricants to give the best-operating conditions instance, the efficiency of lubricating oil in engines.

In a lubricating device, where total isolation between two surfaces is achieved, the lubricant's viscosity becomes the parameter that governs the adhesion, abrasion, corrosion, and fatigue that cause various processes [3]. The base oil (natural and synthetic) typically cannot reach the required high-performance specifications without the use of advanced additives cannot reach the properties of high-performance lubricating oil without the aid of advanced additive technology [4]. The additives are the chemical component used to gain desirable base stocks that enhance existing properties. The properties that are deemed important are: viscosity, viscosity change with temperature (viscosity index), pour point, oxidation resistance, flash point, and boiling temperature [5], [6]. Organo-molybdenum compounds and organo-zinc phosphate compounds are examples of such additives. Whereas these additives are useful as modifiers of friction and wear, they may also have several drawbacks such as poor oil solubility, copper, lead to corrosion of the finished lubricant, increased sulfur, and phosphorus components level in the final lubricating oil. As a result, new types of additives can be used as replacements for traditional lubricant additives and improve the overall lubricant performance while being more environmentally friendly and compatible with pollution control devices used in automotive and diesel engines must be developed [7], [8].

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In recent years, the use of nanoparticles as lubricant additives has grown steadily. Many researchers showed that a nanoparticle-containing lubricant formulation, also known as a nano lubricant, reduced friction and wear. Nano lubricants have the potential to solve many of the problems of traditional lubricants. The main benefits of using nano lubricants are that they are insensitive to temperature and have as there are fewer tribo-chemical reactions than traditional additives [8]–[11]. Suspended NPs make nanofluids (NFs) with average sizes of less than 100 nm in standard fluids like water, oil, and ethylene glycol. When dispersed homogenously and stably in fluids, a very small amount of nanoparticles will provide important changes in the thermal properties of the base fluid [12], [13].

Nanomaterials (NMs) are typically scattered in liquids at low concentrations to produce NFs. Higher concentrations of nanoparticles in liquid can cause sedimentation because of their poor stability in fluids. NMs are typically scattered in liquids at low concentrations to create nanofluids. Higher concentrations of NPs in the fluid can produce sedimentation because of their low stability in fluids. Metal oxides like CuO, TiO2, Al2O3, ZnO, MgO, and SiC are highly thermal conductivity nanoparticles.[14], [15]. In comparison to mono nanofluids, hybrid NFs are expected to replace basic nanofluids for various reasons, such as a larger absorption range, lower extinction, high thermal conductivity, and low frictional losses[16]. The potential for more progress in thermal conductivity and thermophysical properties of hybrid nanofluids compared to traditional nanofluids is one of several reasons why researchers were led to the use and analysis of these types of nanofluids [17]. Several study results have shown that lubricating oil formulations containing nanoparticles, also known as nano-lubricants, decrease friction and wear. Nano lubricants have always had the potential to solve many of the issues associated with traditional lubricants [9], [10].

In the current study, surface modification of inorganic nanoparticles work as an additive in organic liquid using an oleic acid surfactant to enhance the stability of nano-lubricating oil and Improve the rheology and tribology properties of two types of Iraqi base oil (40 stock) by using modified hybrid TiO_2-CuO NPs

2- Experimental Work

2.1. Materials

In this work, Nano copper oxide CuO and Nano Titanium (IV) oxide TiO_2 were purchased from (Sky Spring Nanomaterials, Inc. Houston, USA) and (Hongwu International Group Ltd., Guangdong, China), respectively. Oleic acid surfactant was purchased from (Alpha Chemika, India). The base oil (40-stock) was collected from (Al-Dura Refinery, Middle refineries Company, Baghdad, Iraq). The NPs properties are presented in Table **1**, and the base oil (40-stock) specifications are shown in Table **2**.

Table 1. Specifications of TiO_2 and CuO NPs

Specification	TiO	CuO
Average diameter(nm)	71.14	73.09
Colour	White	black
Purity (%)	>99.9	99
surface area (m^2/g)	119.9	50
Pore volume (cm^3/g)	0.237	0.1606

Table 2. Properties of base oil 60 stocks

Specification	Oil (40 stock)
Kinematic viscosity @ 40 C (cSt)	61.163
Kinematic viscosity @ 100 C (cSt)	8.2209
Viscosity index	102.6
Density @15 (g/cm^3)	0.8617
Flash Point (C)	226
Pour point (C)	-6

2.2. Experimental Procedures

a. Preparation of surface modification of NPs

Preparation of surface modification of NPs was completed by adding (1gm) oleic acid to 100ml of ethanol solvent. Two grams of NPs were added to the solution after homogenizing the solution with mixing using a magnetic stirrer. The solution was heated to 75 °C for two hours. After the reaction was over, the oven was used for 4 hours less than 80 °C to ensure all the ethanol was vaporized. Then, it was washed with methanol to remove unreacted oleic acid. The sample was dried at 80 °C for 6 hours to produce modified NPs OA/TiO_2 and OA/CuO.

b. Preparation of Nano-lubricating oil

Modified NPs were added to two base oil (40 stocks), for preparing Nano lubricating oil. The modified TiO_2 and CuO NPs were added directly as hybrid additives with a weight ratio of 1:1 to both base oil at different concentrations of (0.2, 0.5, 0.8, and 1% wt.).

Stable nano-lubricant is an essential need in this study.

According to this, different methods were used, like a magnetic stirrer, ultrasonic probe, and surface modification. Nano-lubricating oil was prepared by dispersing surface-modified nanoparticles into the base oil. The required amount of NPs was weighed carefully using an accurate electronic balance. A magnetic stirrer was used to mix the NPs with base oil for 2 hours.

Then an ultrasonic probe-type VCX 750 (Sonics and Materials Inc., USA fitted out with a 13 mm diameter Ti-6Al-4V alloy tip) was used at the operating conditions shown in Table **3** to obtain high dispersion and prevent agglomeration of NPs.

Sonication was carried out for each pulsed irradiation, alternating 5 s of t/ON and 5 s of t/OFF. A water bath jacket was used to avoid overheating of the sample during ultrasonic dispersion.

Fig. **1** shows the photo of nano-lubricating oil by the ultrasonic probe. The general steps of the experimental work are represented in Fig. **2**.

Table 3. Ultrasonic probe specifications

The condition	Value
Power	60 %, 750W
Time	1 hr.
Temperature	40 °C
Frequency	20 kHz
Sample quantity	100 ml

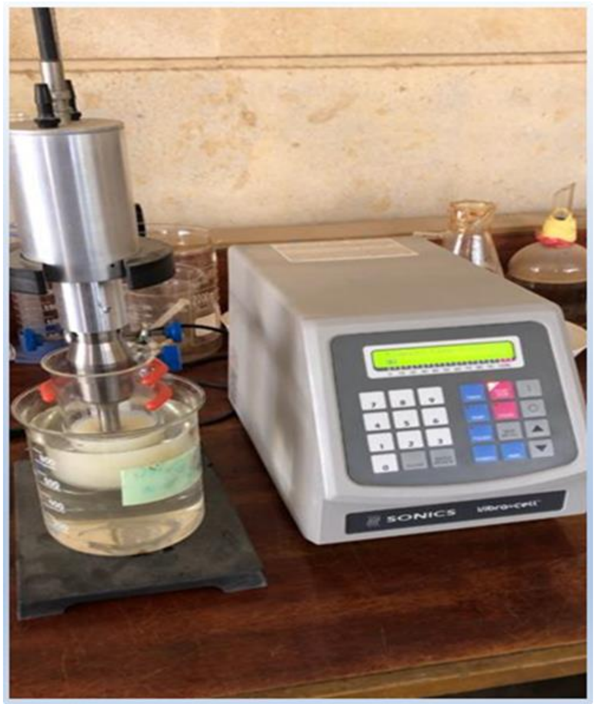


Fig. 1. Dispersion of NPs into lubricating oil by an ultrasonic probe

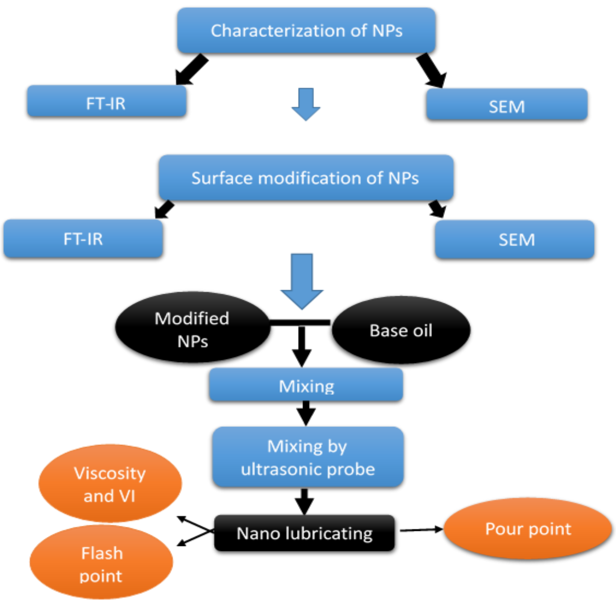


Fig. 2. Flow diagram of the experimental work

3- Results and Discussion

3.1. FT-IR Characterization of Modified Tio_2 and Cuo Nanoparticles.

The FT-IR characterized oleic acid (OA) and NPs in the range of 4000-500 cm $^{-1}$. Fig. **3** shows the FT-IR of oleic acid. The peak at 1707cm -1 represents C=O stretching, and peaks around 2920 -2850 cm $^{-1}$ are attributed to the long alkyl chain[18]–[21].

The FT-IR spectrum of TiO_2 Fig. **4** and Fig. **5** shows two curves. In curve (a) of Figure (4), peaks around 450 and 750cm ¯1 in the range of 400–800 cm¯1 are contributed to anatase titania for pure TiO_2. The vibration absorption of the Ti-O-Ti links in TiO_2 nanoparticles is attributed to a large absorption band between 450 and 800 cm $^{-1}$ (Praveen et al., 2014). The observed peak at 3415 and 1633 cm^{-1} refer to hydroxyl group –OH and water Ti-OH [22].

In both curves (b) of Fig. **4** and Fig. **5**, the adsorption peaks of 2924.09 and 2852.72 cm^{-1} are attributed to OA's long alkyl groups and the absorption bands around 1710.8 attributed to carbonyl group C=O from oleic acid [23].

The absorption band around 542 cm^{-1} as shown in curve (a) of Fig. **5**, refers to the Cu–O functional group's vibrations, and the peak at 3448.7 and 3452 cm^{-1} relate to the –OH group[24], [25]. In curves (b) of Fig. **4**, and Fig. **5**, the peaks around 2854 and 2924 cm–1 are attributed to CH_2 and CH_3 groups formed on the surface of NPs.

The carbonyl group at the peak of around 1710 cm^{-1} in oleic acid form is decreased sharply in these curves. The presence of carboxylate (-COO-) at peaks of around 1428-1550 cm-1 indicates the reaction of oleic acid and bonded on the surface of NPs. And also the −OH groups on the surface of TiO_2, and CuO NPs decreased in modified TiO_2 and CuO nanoparticles. Meanwhile, OA groups of carboxyl (COOH) reacted with hydroxyl (OH) groups to produce carboxylate in modified NPs [20], [26]–[28].

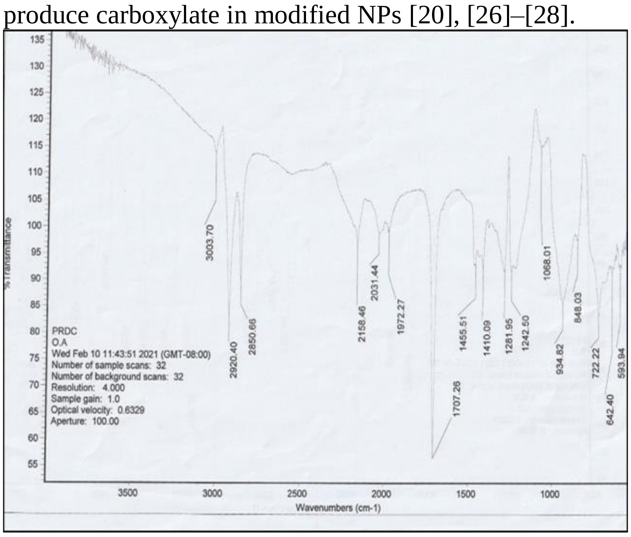


Fig. 3. FTIR spectrum of pure oleic acid

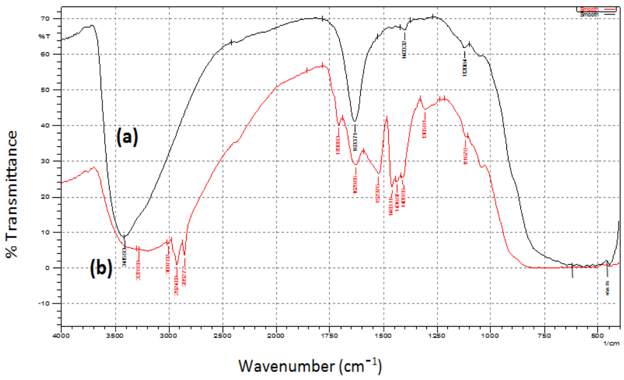


Fig. 4. FTIR spectrum of TiO_2 (a) and OA/ TiO_2 (b)

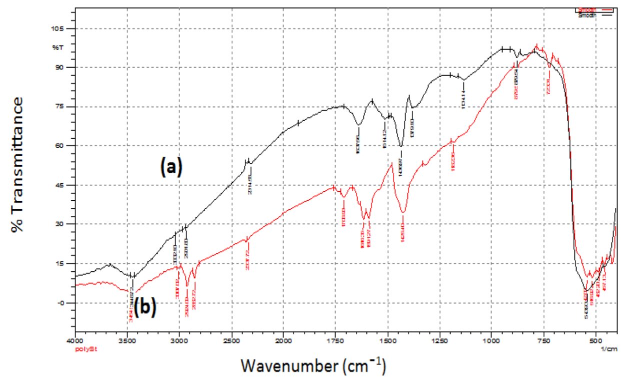


Fig. 5. FTIR spectrum of CuO (a) and OA/ CuO (b)

3.2. Scanning electron microscopy (SEM) of Oleic acid / NPs

Scanning electron microscopy (SEM) is used to characterize the morphology of nanoparticles before and after modification. In Fig. **6** (a) and (b), the images illustrate the morphology of unmodified TiO_2, CuO, and Al_2O_3 NPs, and they were fairly spherical. According to the images in Fig. **6** (b) and (c), it can be seen that the dispersibility of modified NPs was improved, and the pattern of modified NPs appear a little hazy in the pictures, which indicates to coated of OA on the surface of NPs[27], [29], [30].

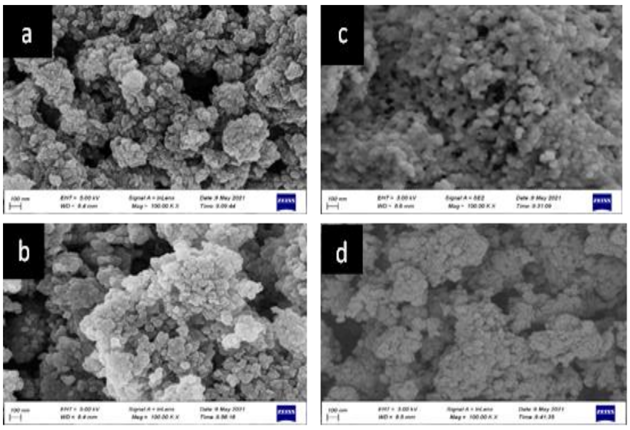


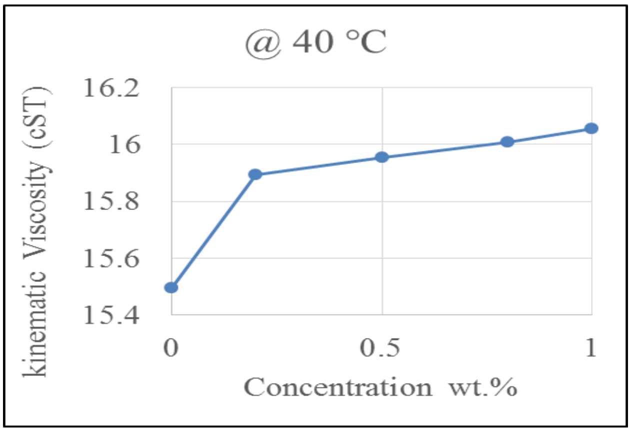
Fig. 6. FE-SEM of unmodified NPs (a) TiO_2, and (b) CuO, and modified NPs (d) OA/ TiO_2, and (d) OA/ CuO

3.3. Effect of Addition Modified Tio_2-Cuo Nps on the Kinematic Viscosity and Viscosity Index of Nano-Lubricating Oil

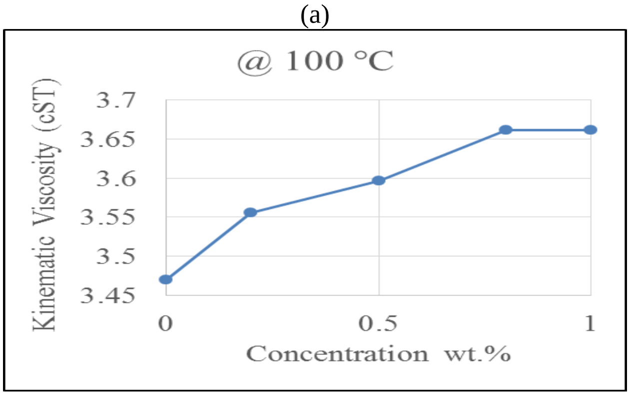
Viscosity is one of the essential properties of any lubricant, which is one of the most significant considerations when selecting oil for equipment. Fig. **7** (a) and (b) demonstrate the influence of modified TiO_2 and CuO NPs on the kinematic viscosity of base oil 40 stock at temperatures 40 °C and 100 °C, respectively. The viscosity increased slightly on increasing modified NPs concentration at both temperatures.

At high concentrations, the presence of larger, spherical particles within oil layers, which prevents movement, might explain increased viscosity [31]. The highest increase of viscosity was 2.9 %, 3.31 %, and 3.7 %, related to TiO_2 and CuO NPs concentration 0.5 wt. %, 0.8 wt.%, and 1 wt.% at 40 °C, respectively.

Increasing the viscosity of light base oil 40 stock after adding nanomaterials Figure (8) shows the viscosity index changes with adding modified TiO_2- CuO NPs. The viscosity index increased by 4.5%, 8.4%, 9.92%, and 7.7% relative to the different NPs concentrations at 0.2 wt.%, 0.5 wt.%, 0.8 wt.%, and 1 wt.%, respectively. The maximum increase was observed at 8 wt. % concentration. The higher viscosity index indicates a more stable kinematic viscosity with variable temperatures, thus giving more resistance to oil film thinning [32].



(a)



(b)

Fig. 7. Effect of TiO_2- CuO on the Kinematic viscosity of base oil 40 stock at (a) 40 °C, and at (b) 100°C

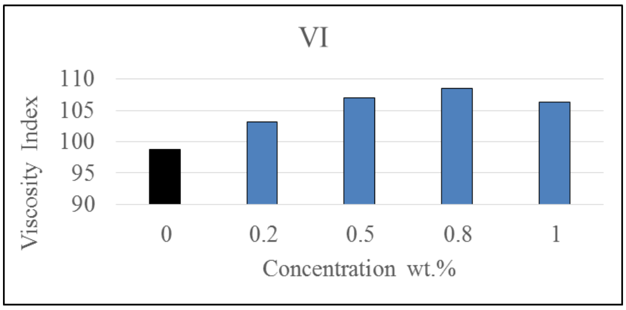


Fig. 8. Effect of TiO_2- CuO NPs on the viscosity index of base oil 40 stock

3.4. Flashpoint and Pour Point of Nano-Lubricating Oil

The flashpoint (F.P) can be defined as the less temperature that a flammable mixture in the air can be formed. In an instant, the oil follows the ignition line and then suddenly switches off. Fig. **9** and Fig. **10** demonstrate the effect of modified TiO_2 – CuO NPs on the flashpoint and pour point property of base oil 40 stock, respectively. It can be seen that the flashpoint increased with adding the NPs to base oil 40 stock attributed to the high thermal conductivity of nanoparticles, and it can be said that it allows the oil to resist ignition better [33].

The rate of improvement in F.P is 14 °C at 0.2 wt% concentration of NPs and the greater improvement was 32℃ at 1 wt.% concentration. while the pour point of base oil improved by 3 °C at 0.2 wt.%, 0.5 wt%, and 0.8 wt.% compared with base oil. The higher improvement was at 1wt % by 6 °C.

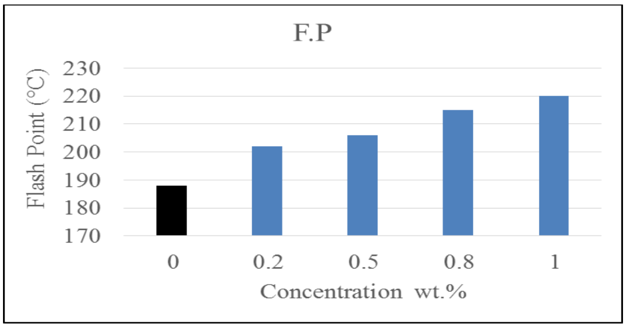


Fig. 9. Effect of nano additive modified TiO_2-CuO wt. % on flash point of base oil 40 stocks

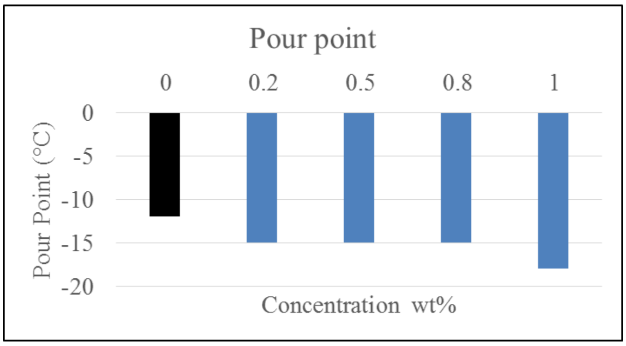


Fig. 10. Effect of nano additive modified TiO_2-CuO wt. % on pour point of base oil 40 stocks

4- Conclusions

- Using oleic acid surfactant in surface modification of TiO_2, and CuO NPs improved the stability of lubricating oil
- The kinematic viscosity of modified TiO_2-CuO / base oil 40 stock at 40°C and 100 °C increased slightly with the addition of modified nanoparticles.
- The viscosity index increased by 4.5% for 40 stock base oil when 0.2% of modified TiO_2- CuO nano-lubricating oil was used. And the highest increase in VI was 9.92 % at 0.8 wt.% of modified TiO_2-CuO.
- Adding TiO_2 - CuO NPs to base oil 40 at varying concentrations improved nano-lubricant oil's flash point compared to parent oil. The highest flash point value was 220 °C

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تأثير الجسيمات النانوية الهجينة المعدلة على خصائص الزيت الأساسي

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الخلاصة

لتحسين الخصائص الانسيابية والترايبولوجية لزيت التزييت في هذه الدراسة ، تم استخدام حامض الأوليك لتعديل سطح الجسيمات النانوية لتعزيز تشتت واستقرار الموائع النانوية. تم إجراء تعديل السطح للجسيمات النانوية غير العضوية TiO_2 (NPs) ، و CuO مع خافض التوتر السطحي بحامض الأوليك OA، حيث يمكن أن يجعل حامض الأوليك سطح TiO_2–CuO كارهًا للماء. تم استخدام مطيافية فورييه لتحويل الأشعة تحت الحمراء FTIR، والمسح المجهري الإلكتروني SEMلوصف تعديل سطح .NPs كان الهدف الرئيسي من هذه الدراسة هو التحقق من تأثير إضافة TiO_2–CuO NPs المعدلة مع نسبة وزن 1:1 على الخواص الحرارية الفيزيائية مثل اللزوجة الكاينماتيكية و معامل اللزوجة اللزوجة VI ونقطة الانسكاب ونقطة الوميض من الزيت الأساسي العراقي (40 زيت الاساس) وزيت التزييت النانو. تم الحصول على أن اللزوجة الحركية للزيت الأساسي عند 40 درجة مئوية و 100 درجة مئوية تزداد بتركيزات عالية من TiO_2–CuO NPs المعدلة. أعلى قيمة لـ VI الزيت الأساسي 40 عند 0.8 وزن. كانت ٪ من TiO_2–CuO NPs المعدلة 108.5. أظهرت النتائج أن قيمة نقطة الوميض تزداد مع زيادة تركيز TiO_2–CuO NPs المعدلة من الزيت الأساسي 40 ، حيث كانت أعلى قيمة 220 درجة مئوية. نقطة صب زيت التزييت النانوي عند 0.8 % بالوزن. أظهرت النسبة المئوية من TiO_2–CuO NPs المعدلة تناقصًا من −12 درجة مئوية إلى −15 درجة مئوية من الزيت الأساسي 40

الكلمات الدالة: الزيت الاساس 40، زيت التزييت النانوي، الجسيمات النانوية، معامل اللزوجة، نقطة الوميض