INVESTIGATION ON THE EFFECT OF TiO₂ NANOPARTICLE ADDITIVES ON THE PROPERTIES OF 10W-40 ENGINE OIL

SATHISH KUMAR. R¹, MOTHILAL THULASIRAMAN², GOKUL RAGHAVENDRA
SRINIVASAN³, VASANTHE ROYJ⁴, JOSEPH MANUEL. D⁵ & SEKAR. S. D⁶

¹Department of Mechanical Engineering, T. J. S Engineering College, Chennai, Tamil Nadu, India

^{2,5}Department of Mechanical Engineering, Velammal Institute of Technology, Chennai, Tamil Nadu, India

^{3,4}Centre for Excellence in Energy and Nano Technology (CEENT), Department of Mechanical Engineering,
S. A. Engineering College, Chennai, Tamil Nadu, India

³CO₂ Research and green technologies Centre, Vellore Institute of Technology, Vellore, Tamil Nadu, India

⁶Department of Mechanical Engineering, R. M. K. Engineering College, Chennai, Tamil Nadu, India

ABSTRACT

The aim of this study is to investigate the influence of TiO₂ nanoparticles additives on thermo-physical and tribological properties of 10w-40 engine oil for improvising the life span of the engine and enhancing the performance. Developing a nanofluid is an innovative new class of fluid which was engineered by dispersing 0.01% of TiO₂ nanoparticles in conventional 10W-40 engine oil to improve load carrying capacity, anti-wear and friction reduction properties. Conventional Sol-gel method was employed to synthesize TiO₂ Nanoparticles and was characterized using XRD, SEM and TEM. The average crystalline size was found to be 6nm and existed in anatase crystalline phase. The thermo-physical and rheological tests concluded that TiO₂ dispersed engine oil was superior in all aspects than compared to the ordinary engine oil and proved as an alternate substitute for increasing the life span of the engine.

KEYWORDS: Titanium Oxide, Anatase, (10W-40) Engine Oil, Thermal Conductivity & Pin on Disc Tribometer

Received: Jun 23, 2018; **Accepted:** Jul 14, 2018; **Published:** Sep 05, 2018; **Paper Id:** IJMPERDAUG2018122

INTRODUCTION

The increase in planet's population growth and globalization have increased the demand for energy to meet their basic amenities. In order to produce & handle this large amount of energy, the efficiency of these power producing units must be always maintained at the higher level. This can be achieved by implementing higher calorific fuels, good heat exchanging system and efficient lubrication system in addition with an energy storage system. The radiation of heat from the engine along with the better lubrication can be provided by using better engine, which simultaneously performs both functions effectively. This can be achieved by implementing nanoparticles dispersed engine oil having good thermal conductivity and lubricating properties. Various nanoparticles like Al₂O₃, SiO₂, and TiO₂ have been added with engine oil for enhancing its efficiency. TiO₂ is one such nanoparticle additive which has received attention throughout the world because of its robust nature and outstanding properties.

TiO₂ is an oxide of titanium, which occurs either naturally or synthesised by chemical techniques including green synthesis from the natural plants. It has wide ranges of applications in the field of optics as optical filters [1], antireflection coatings [2]; in the field of chemistry as catalysts [3], pigments [4] or sterilization

materials [5] because of its superior electronic and structural properties. TiO_2 is also known for its high refractive index, greater chemical stability and enhanced antimicrobial & photo catalytic activity [6]. Anatase, rutile and brookite are the three most common crystalline phases of TiO_2 . Functional properties like specific surface area, intensity of defect, phase transition temperatures and stability are influenced by its size and shape, whereas catalytic & optical properties are influenced by its crystalline phase and crystallite size.

Numerous studies have been carried on TiO_2 based nanofluids related to its thermal conductivity and lubrication properties. Yu et al., 2011 studied the role of nanoparticle additive in lubrication for TiO_2 based engine oil [7] whereas Laad et al., 2016 analysed the influence of TiO_2 in enhancing the thermal conductivity of nanoparticle dispersed engine oil [8]. The rheological properties of nanoparticles dispersed engine oil were studied to understand its behaviour in the varying temperatures inside the engine [9]. However, many studies reported the settling or agglomeration of nanoparticles with increasing time due to less steric effect. Many researchers have been trying to prevent the nanoparticles from settling or agglomeration without using any external additives as they might have a heavy impact on its properties.

In this present study, the thermo-physical and tribological properties of 10W-40 engine oil dispersed with TiO_2 nanoparticles synthesized at acidic pH have been studied and experimentally verified with ordinary 10W-40 engine oil.

MATERIALS AND METHODOLOGY

Synthesis of TiO_2 Nanoparticles

Sol-gel method was predominantly used for preparation of TiO_2 nanoparticles keeping titanium tetraisopropoxide $\text{Ti} [\text{OCH} (\text{CH}_3)_2]_4$ as precursor. The nanoparticles were synthesised by dissolving titanium tetraisopropoxide with acetic acid and distilled water for a volumetric ratio of TTIP: H_2O : CH_3COOH as 1:1:2. The pH of the overall mixture was maintained slightly above mild acidic at 4.

The process was initiated by adding 10 ml of titanium tetraisopropoxide in 20ml glacial acetic acid solution under continuous stirring until the white slurry mixture was formed. 10 ml of demineralised water was into a slurry added to the mixture gradually until the slurry mixture turned solution. This solution was stirred further for another 40 minutes under slow speed constant stirring at room temperature until it turned into a white gel. This gel was calcinated inside the furnace at 250°C for 4 hours to eliminate any solvent content and also enhances the crystal stability.

Estimation of Volume Fraction for TiO_2 Nanoparticles

Based on law of mixture formula, the amount of TiO_2 nanoparticles required for preparing 100ml TiO_2 dispersed engine oil was calculated using the following relation in Equation 1:

$$\text{Volume fraction \%} = \frac{\frac{W_{\text{TiO}_2}}{\rho_{\text{TiO}_2}}}{\frac{W_{\text{TiO}_2}}{\rho_{\text{TiO}_2}} + \frac{W_{\text{bf}}}{\rho_{\text{bf}}}} \quad (1)$$

Based on the calculation, the volume fraction required for producing nanofluid was found to be 0.01% and the amount of TiO_2 required for preparing the nanofluid was 0.077 g.

Preparation of TiO_2 based Nanofluid

The TiO_2 dispersed engine oil was prepared by keeping 10W-40 engine oil as a base fluid without the addition of any surfactants or acids. The surfactant was not added in order to avoid any alteration in the thermo physical properties of

nanofluid whereas acids were not used in order to avoid corrosion on the surfaces during practical applications.

Based on the volume fraction, 0.077g of TiO₂ nanoparticles was mixed with 350ml of 10W-40 engine oil. The mixture was homogeneously mixed using magnetic stirring for 2 hours and was further mixed using ultrasonic sonicator for another 3 hours to improvise the stability of nanoparticles in the engine oil to avoid any agglomeration before being subjected to studies related to thermal conductivity and viscosity. In addition to nanoparticles, Polyvinylpyrrolidone (PVP) was added as a stabilizing agent without any addition of surfactant.

Pin on Disc Tribometer

The friction force and friction co-efficient was measured in DucomTR-20 Pin on Disc Tribometer and wear tester under 10N & 30N at 1200rpm for 60 minutes. It consists of a driving spindle and a lever arm device to hold the pin. The tribometer was loaded with a friction force measuring system to determine the coefficient of friction. The technical specification of DucomTR-20 Pin on Disc Tribometer is listed in the Table 1. Figure 1 shows the experimental setup of DucomTR-20 Pin on Disc Tribometer.

Table 1: Technical Specifications of DucomTR-20 PIN ON DISC TRIBOMETER

Type: DucomTR-20 PIN ON DISC TRIBOMETER	
PIN Specification	
Material	Aluminium (Al 35)
Length	32mm
Diameter	10mm
DISC Specification	
Material	(EN 31)
Hardness	(59-60) HRC
Diameter	160 mm
Thickness	10mm

Figure 1: Pin on Disc Tribometer

RESULTS AND DISCUSSIONS

Characterization of TiO₂ Nanoparticles

SEM Images

The effect of pH on the size and morphology of nanoparticles was evaluated by studying the synthesised TiO₂ nanoparticles at pH level 4. Based on the SEM image, it was confirmed that the nanoparticles existed in anatase crystalline phase. TiO₂ nanoparticles prepared using strong acidic solvent resulted in smaller size than compared to other solvents was mainly because of high acidic solvent [10]. It also showed that there was a poor agglomeration in nanoparticles because of

optimal acidic pH and low ionic strength. Since synthesis was carried out in pH level 4, the positive charge encapsulation reduced the chances of agglomeration. The size of individual nanoparticles was drastically improved along with dispersivity and homogeneity as the pH level increased towards strong acidic. Figure 2 depicts the SEM image of Synthesized TiO₂ nanoparticles.

Figure 2: SEM Images of Synthesized TiO₂ Nanoparticles

TEM Images

The TEM image provided a better visualization of synthesized nanoparticles and predicted the size particles to be in a range of 5-8nm and was completely in accordance with other studies [11]. This was in accordance with the calculated value of TiO₂ using Scherer's equation [12]. The increase in pH level to 4 improvised the particle size in Nano scale and also helped in maintaining the size throughout uniformly. The TEM images were in good accordance with the obtained X-ray diffraction patterns. Figure 3 depicts the TEM image of Synthesized TiO₂ nanoparticles.

Figure 3: TEM Images of Synthesized TiO₂ Nanoparticles

Crystal Structure

TiO₂ Nanoparticles synthesized using sol gel technique are largely amorphous in nature, in order to transit it from amorphous to anatase phase, it is annealed at temperature higher than 300°C. Based on the XRD spectrum, three distinctive peaks were obtained at 27.5°, 36.1°, and 54.4° respectively, corresponding to the reflection planes of crystal (110), (101) and (211) respectively [13]. The obtained peaks were in excellent accordance with the reference peaks corresponding to anatase obtained from Joint Committee Powder Diffraction Standards (JCPDS 21-1272) [14]. The average crystalline size of the synthesized nanoparticles was calculated by using Scherrer's formula by considering the full width & half maximum (FWHM) value.

$$D = \frac{K\lambda}{(\beta \cos \theta)} \quad (2)$$

Where D is the crystal size, λ is the wavelength of the X-ray radiation ($\lambda=0.15406$ nm), k is usually taken as 0.9 and β is the full width at half-maximum height. Figure 4 depicts the XRD spectra of Synthesized TiO_2 nanoparticles.

Figure 4: XRD Spectra of Synthesized TiO_2 Nanoparticles

Based on the Scherrer's formula, average crystalline size of synthesized TiO_2 nanoparticles was found to be 6nm.

Based on the characterization, various physical properties of the synthesized TiO_2 nanoparticles were analysed and determined. Table 2 consolidates the physical properties of synthesized TiO_2 nanoparticles.

Table 2: Physical Properties of Synthesized TiO_2 Nanoparticles

Sample	pH Range	Crystalline Phase	Angle(2θ) (degree)	Crystalline size (nm)	Average Crystalline size (nm)
TiO_2 Nanoparticles	4	Anatase	27.5°,36.1°,54.4°	6,4.3,7.71	6

Stabilization of Nanofluid

The stability of nanofluid was determined using sedimentation and centrifugation method. It was found that the synthesised nanoparticles were stable for more than one month when left undisturbed. In addition to that, the nanofluid remained unsettled for more than 10 hours after centrifuging at 30,000rpm during centrifugation test. This excellent stability was because of the PVP which retraded the agglomeration of nanoparticles by introducing the steric stabilization [15].

Thermo-Physical Properties of TiO_2 Dispersed Engine Oil

The important properties like density, flash & fire point, thermal conductivity and kinematic viscosity were determined for the TiO_2 dispersed engine oil by using standard ASTM methods and were compared with an ordinary engine oil in order to examine the influence of nanoparticles in the engine oil. The overall time taken for the analysis of properties were less than the time required for the first sedimentation of nanoparticles, however no sedimentation was noticed throughout the study. Also, the prepared nanofluids were assumed to be isentropic, Newtonian in behaviour and their thermo-physical properties were presumed as uniform and constant with time throughout the sample. The obtained results were compared with the values predicted using theoretical equations.

Density of TiO_2 Dispersed Engine Oil

The density of TiO_2 dispersed engine oil was measured using hydrometer and was compared with the value obtained using the density correlation stated as equation 3. Based on equation 3, the density of the TiO_2 dispersed engine oil was found to be 770 Kg/m^3 . The error between the experimental result and theoretical results were very close hence the

correlation was used throughout the study for determination of nanofluid density.

$$\rho_{nf} = \phi \rho_p + (1 - \phi) \rho_{bf} \quad (3)$$

Where,

ρ_{nf} – density of TiO₂ dispersed engine oil, Kg/m³

ρ_{bf} – density of base oil, Kg/m³

ρ_p – density of TiO₂ nanoparticles, Kg/m³

The density of any nanofluid can be determined for any volume fraction by substituting the density of base oil and the density of nanoparticles in the Equation 3.

Flash Point of TiO₂ Dispersed Engine Oil

The flash points of plain and TiO₂ dispersed engine oil were determined using ASTM D93-16a method. The flash point of plain engine oil was found to be 230°C whereas flash point of TiO₂ dispersed engine oil was found to be 300°C. The flash point for TiO₂ dispersed engine oil was found to be slightly greater than that of plain engine oil and increased with the increase in concentration of nanoparticles in the base fluid. This was because of the absorption of heat by the nanoparticles itself before dissipating the heat to its surrounding base oil to get vapourised and then ignited. This enhanced feature provides delay in ignition on exposure to direct heat, thereby making it suitable for high temperature applications with easy handling and ensured safety. Figure 5 illustrates the comparison of Flash point between Engine oil (with and without TiO₂ additives).

Figure 5: Flash Point between Engine oil (with and without TiO₂ Additives)

Kinematic Viscosity of TiO₂ Dispersed Engine Oil

Kinematic viscosity is a measure of fluid's resistance to flow and shear under the forces of gravity or through any surfaces and is directly proportional to the size of molecular structures. The homogeneity of uniform and consistently sized molecules can be achieved in the synthetic oil manufacturing process than compared to mineral oil. Upon aging, the viscosity of mineral oil changes because of degradation of its molecular structure leading to smaller molecular size. In addition to the molecular structure, the viscosity is based upon the volume fraction of nanoparticles and the surfactants used. The viscosity of the TiO₂ dispersed engine oil was determined using redwood viscometer following ASTM D88 standards under steady state condition with temperature range between 30°C and 90°C. The kinematic viscosity of engine oil with and without TiO₂ nanoparticles additives were found to be 1.677 and 1.317 cSt respectively. Based upon the

results from redwood viscometer, it can be concluded TiO₂ dispersed engine oil had higher viscosity than compared to plain engine oil throughout the experiment. This was due to the colloidal consistency of engine oil because of TiO₂ dispersion, where the TiO₂ nanoparticles were encapsulated by engine oil. However, the reduction in viscosity rate was found to be much higher in engine oil with nanoparticles because of the high conductivity of nanoparticles on exposure to heat. The variation in the kinematic viscosity between two engine oils (with and without TiO₂ additives) reduced drastically from 45 % to 30% when the temperature was increased 30°C to 90°C. Figure 6 illustrates the comparison of Kinematic Viscosity between Engine oil (with and without TiO₂ additives).

Figure 6: Kinematic Viscosity between Engine Oil (with and without TiO₂ Additives)

Thermal Conductivity of TiO₂ Dispersed Engine Oil

Engine oil serves both as lubrication oil for reducing wear and cooling oil for radiating heat from the engine to the environment. Thermal conductivity and specific heat are of two important parameters, considered for coolant oil design and are functions of temperature. Oil with larger thermal conductivity and specific heat value transfers large amount of heat with lower temperature rise, thereby increasing its conductivity efficiency to a greater extent. The transient short hot-wire technique was employed to determine the thermal conductivity of engine oil with and without TiO₂ additives by varying temperatures between 60°C to 120°C. The thermal conductivity of engine oil with and without TiO₂ nanoparticles additives were found to be 0.242 W/mK and 0.122 W/mk respectively. The thermal conductivity of TiO₂ dispersed engine oil was found to be nearly twice than that of ordinary engine oil. This was because of the high conductivity rate of smaller grain sized nanoparticles suspended in the engine oil. The rate of thermal conductivity is influenced by the concentration of nanoparticles added and thermo-physical properties of plain engine oil. Figure 7 illustrates the comparison of thermal conductivity between Engine oil (with and without TiO₂ additives).

Figure 7: Thermal Conductivity between Engine Oil (with and without TiO₂ Additives)

Tribological Behaviour of TiO₂ Dispersed Engine Oil

The tribological properties of lubricating oil were enhanced due to the addition of TiO₂ nanoparticles. The coefficient of friction was reduced by 10% for nanofluid with 0.01% nanoparticle concentration than compared to engine oil with no additives for a load of 30N. This effect could be due to the rolling of the sphere like nanoparticles between the rubbing surfaces, thus reducing friction. With an increase in the concentration of nanoparticles, the co-efficient of the friction increases, but not more than the coefficient friction of oil without TiO₂nanoparticles, this effect can be observed due to the agglomeration of TiO₂nanoparticles dispersed in the engine oil. The reduction in the wear and enhancement of tribological properties was because of the dispersion of TiO₂ nanoparticles on the surface which reduced the shearing resistance and the nanoparticles acted as nanobearings[8]. The Weight loss of the pin at 10N for the plain engine oil and TiO₂ dispersed engine oil were found to be 0.082gms and 0.078gms respectively, whereas weight loss of the pin at 30N for the plain engine oil and tio2 dispersed engine oil were found to be 0.054gms and 0.023gms respectively. Figure 8 illustrates the coefficient of friction for both plain engine oil and TiO₂ dispersed engine oil at 10N and 30N load conditions.

Figure 8: Friction Coefficient between Engine oil (with TiO₂ and without Additives)

CONCLUSIONS

The investigation on the effect of TiO₂ nanoparticle additives on the properties of 10W-40 engine oil was successfully carried out and the results were compared between plain engine oil with TiO₂ dispersed engine oil. The kinematic viscosity and thermal conductivity were found to be higher for TiO₂ dispersed engine oil than compared to plain engine oil. The flash point of TiO₂ dispersed engine oil was found to be greater than that of plain engine oil and this was because of the influence of nanoparticles dispersed in the engine oil. Apart from the thermo-physical properties, the TiO₂ dispersed engine oil performed better lubrication than plain engine oil, thereby making this synthesized oil an efficient alternate for engine applications.

REFERENCES

1. Hinczewski, D. S., Hinczewski, M., Tepehan, F. Z., & Tepehan, G. G. (2005). Optical filters from SiO₂ and TiO₂ multi-layers using sol-gel spin coating method. *Solar Energy Materials and Solar Cells*, 87 (1-4), 181-196.
2. San Vicente, G., Morales, A., & Gutierrez, M. T. (2001). Preparation and characterization of sol-gel TiO₂ antireflective coatings for silicon. *Thin solid films*, 391 (1), 133-137.

3. Maira, A. J., Yeung, K. L., Lee, C. Y., Yue, P. L., & Chan, C. K. (2000). Size effects in gas-phase photo-oxidation of trichloroethylene using nanometer-sized TiO₂ catalysts. *Journal of Catalysis*, 192 (1), 185-196.
4. Sahu, K. K., Alex, T. C., Mishra, D., & Agrawal, A. (2006). An overview on the production of pigment grade titania from titania-rich slag. *Waste management & research*, 24(1), 74-79.
5. Matsunaga, T., Tomoda, R., Nakajima, T., Nakamura, N., & Komine, T. (1988). Continuous-sterilization system that uses photoconductor powders. *Applied and environmental microbiology*, 54(6), 1330-1333.
6. Garzella, C., Comini, E., Tempesti, E., Frigeri, C., & Sberveglieri, G. (2000). TiO₂ thin films by a novel sol-gel processing for gas sensor applications. *Sensors and Actuators B: Chemical*, 68(1-3), 189-196.
7. Wu, Y. Y., & Kao, M. J. (2011). Using TiO₂ nanofluid additive for engine lubrication oil. *Industrial Lubrication and Tribology*, 63(6), 440-445.
8. Laad, M., & Jatti, V. K. S. (2016). Titanium oxide nanoparticles as additives in engine oil. *Journal of King Saud University-Engineering Sciences*.
9. Murshed, S. M. S., Santos, F. J. V., & de Castro, C. N. (2013). Rheology of nanofluids containing TiO₂ and SiO₂ nanoparticles. In *Proc. 8th World Conference on Experimental Heat Transfer, Fluid Mechanics, and Thermodynamics*.
10. Krishna, V. M. Heat Transfer Enhancement By Using CuO-Water Nanofluid In A Concentric Tube Heat Exchanger-An Experimental Study.
11. Tsega, M., & Dejene, F. B. (2017). Influence of acidic pH on the formulation of TiO₂ nanocrystalline powders with enhanced photoluminescence property. *Heliyon*, 3(2), e00246.
12. Reyes-Coronado, D., Rodríguez-Gattorno, G., Espinosa-Pesqueira, M. E., Cab, C., de Coss, R. D., & Oskam, G. (2008). Phase-pure TiO₂ nanoparticles: anatase, brookite and rutile. *Nanotechnology*, 19(14), 145605.
13. Viana, M. M., Soares, V. F., & Mohallem, N. D. S. (2010). Synthesis and characterization of TiO₂ nanoparticles. *Ceramics International*, 36(7), 2047-2053.
14. Dai, S., Wu, Y., Sakai, T., Du, Z., Sakai, H., & Abe, M. (2010). Preparation of highly crystalline TiO₂ nanostructures by acid-assisted hydrothermal treatment of hexagonal-structured nanocrystalline titania/cetyltrimethylammonium bromide nanoskeleton. *Nanoscale research letters*, 5(11), 1829.
15. File, P. D. (1967). Joint committee on powder diffraction standards. *ASTM*, Philadelphia, Pa, 9-185.
16. Napper, D. H., & Netschey, A. (1971). Studies of the steric stabilization of colloidal particles. *Journal of Colloid and Interface Science*, 37(3), 528-535.