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Influence of morphology of anti-wear nano additives on Tribological behavior of Chemically Modified Rapeseed Oil

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Abstract. This study compared the improvement of tribological characteristics of chemically modified rapeseed oil with two different anti-wear nano additives such as titania (TiO2) and alumina wire (Al2O3) as potential bio-degradable automotive lubricant. The tribological investigations were performed using a pin-on-disc tribometer. The commercial TiO2 nano particle of anatase and rutile phase, commercial Al2O3 nano wire of α and γ phase have been characterized by X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and Selected Area Electron Diffraction (SAED) pattern. The chemically modified rapeseed oil with fibrous nano alumina wire showed higher friction coefficient than one with spherical titania nano particles. The SEM images of the worn pin surfaces tested using spherical titania based nano lubricant is found smoother compared to that of nano alumina wire-based lubricant.

1. Introduction
In recent years, deliberate and accidental lubricant losses to the environment by means including evaporation, leakages and spills have led to major concerns regarding pollution and environmental health. Further, the depletion of the world’s crude oil reserve, increasing crude oil prices, and issues related to conservation have brought about renewed interest in the use of bio-based materials as reported by Horner [1]. The present emphasis is on the use of vegetable oils for non-edible purposes. Attention has been focused by Aluyor et al. [2] and Metzger [3] on technologies that incorporate vegetable oil as biofuels and industrial lubricants due to the fact that they are renewable and bio-degradable. Vegetable oil-based lubricants and derivatives have excellent lubricity when compared to mineral oils, for which they are being investigated as a base stock for automotive lubricants. However, their widespread use in formulating lubricants is restricted owing to insufficient thermal and oxidative stability, poor low temperature fluidity and hydrolytic instability. The genetic and chemical modification of vegetable oils can overcome these limitations. Although plenty of information is available on synthesis of polymeric
materials from rapeseed oil, there are few literatures on the synthesis of automotive lubricants from rapeseed oil. Unquestionably, the chemical modifications like epoxidation, hydroxylation and esterification greatly improves thermo-oxidative stability and cold flow behaviour of rapeseed oil. Xuedong Wu et al. described the application of epoxidized rapeseed oil as a potential biodegradable lubricant [4]. Hwang and Erhan produced chemically modified soybean oil with improved low-temperature and oxidation stability by a ring-opening reaction of epoxidized fatty acid esters with alcohols followed by esterification process. They showed that the epoxidation treatment has no adverse effect on the biodegradability of the base stock. However, the anti-wear behavior of chemically modified vegetable oil is still inferior [5].

Nano technology is a revolutionary concept introduced in the 21st century that has the potential to improve the characteristics of materials in many fields. In recent years, nano-sized materials have emerged as a new additive alternative because nano materials possess many special properties, such as the quantum size effect, the small size effect, and surface and interface effects; the application of nano particles in tribology has received considerable attention. A variety of mechanisms have been proposed to explain the lubrication enhancement of the nano particle suspended lubricating oil (i.e., nano-oil), including the ball bearing effect by Wu et al; mending effect by Liu et al; and polishing effect by Tao et al [6-8].

Titanium dioxide or titania (TiO₂) is obtained from a variety of ores. The bulk material of TiO₂ is widely nominated for three main phases of rutile, anatase and brookite. Among them, the TiO₂ exists mostly as rutile and anatase phases which both of them have the tetragonal structures as reported by Kim, et al. [9]. Perry and Wu et al. have reported alumina is a hard, highly resistant towards bases and acids, allows very high temperature applications and has excellent wear resistance characteristics [10, 11]. Xian Chen et al. demonstrated that nano-TiO₂ is an effective heterogeneous catalyst for the ring-opening of epoxide with aromatic amines to afford β-amino alcohols in good to excellent yields at room temperature under solvent-free conditions [12]. Hu and Dong have reported less than 1% of TiO₂ and 0.05% of DDP-Pbs by Chen et al., nano particles is sufficient to improve tribological properties of vegetable oil [13, 14]. Yujin Hwang et al. investigated the carbon-based nano particles dispersed in mineral oil to systematically examine the effect of the size and shape of nano particles on the properties of frictional behavior [15]. Wu et al. demonstrated nano particles such as CuO, TiO₂ and nano diamond used as additives in API-SF engine oil and mineral oil exhibit good friction reduction and anti-wear behavior [16]. Recently Manu Varghese Thottackkad et al. studied the use of copper oxide (CuO) nano particles as anti-wear additives in coconut oil as possible automotive lubricants[17].

Many researchers have tried to improve the tribological characteristics of mineral and synthetic lubricants to minimize the friction and wear. However, the studies devoted to tribological improvement of vegetable oil-based lubricants with nano additives are limited. In the present investigation, the base lubricant used was chemically modified rapeseed oil, and spherical titania nano particle of particle of size ~20nm and alumina nano wire of size ~10nm were used to formulate the nano lubricants focusing on the influence of nano additives on tribological behavior of chemically modified rapeseed oil.

2. Materials & Methods

2.1. Synthesis of Nano based bio lubricant

In the present investigation, bio lubricant was formulated through chemical modification process such as epoxidation, hydroxylation and esterification process. The detailed procedure for the chemical modification of rapeseed oil was tracked from study by Arumugam et al. [18]. The commercially available Degussa spherical TiO₂ nano particle of size ~20nm and fibrous Al₂O₃ nano wire of size ~10nm supplied by M/s Sigma-Aldrich Ltd., Bangalore, was used to improve anti-wear characteristics of chemically modified rapeseed oil. One of the major hurdles in introducing the nano additive into oil is agglomeration, inhibiting ideal homogeneity and dispersion. An ultrasonic sonicator–OSCAR®-PR-1000, with 750W maximum power output and 20kHz operating frequency has been used to ensure
homogeneous mixing and dispersion of the nano additives into chemically modified vegetable oil without agglomeration.

The size and distribution of the nano particles was verified using XRD, SEM and TEM. These nano additives were added to the chemically modified rapeseed oil by 0.05% (mass basis) to prepare the required sample and 1% of glycol was used as dispersant. Two different nano lubricants have been prepared. 1. Chemically modified rapeseed oil with 0.05% spherical TiO$_2$ nano particles. 2. Chemically modified rapeseed oil with 0.05% fibrous Al$_2$O$_3$ nano wire. Each lubricant sample comprised of 90% chemically modified rapeseed oil and 10% of nano additives (0.05% TiO$_2$ or Al$_2$O$_3$ + 9.95% glycol). The mixture was then agitated using ultrasonic sonicator at room temperature to ensure uniform dispersion and good suspension stability [16]. Table 1 shows the properties of chemically modified rapeseed oil with and without nano additives.

| Properties                          | Chemically modified rapeseed oil | TiO$_2$ based nano lubricant | Al$_2$O$_3$ based nano lubricant |
|-------------------------------------|----------------------------------|------------------------------|----------------------------------|
| Biodegradability (OECD 301F), %     | >95                              | >85                          | >85                              |
| Viscosity index (ASTM D-2270)       | 160                              | 155                          | 148                              |
| Flash point (ASTM D93), °C          | 240                              | 236                          | 225                              |
| Pour point (ASTM D97), °C           | <-15                             | <-15                         | <-15                             |
| Viscosity @40°C (ASTM D445), cSt    | 140.20                           | 137.2                        | 133.8                            |
| Viscosity @100°C (ASTM D445), cSt   | 16.52                            | 15.6                         | 14.5                             |

2.2 Tribological Investigation
The friction coefficient is an important parameter in evaluating the characteristics of nano lubricants. To establish tribological characteristics of nano-lubricant, a pin-on-disc (TR-201C) tribometer was used. A pin was made out of piston ring material and the disc was made out of cylinder liner material with hardness of 65 HRC as per the standard dimensions specified by the manufacturer of pin-on-disc tribometer. The detailed descriptions of experimental preparation, conditions have been reported in our earlier study [19]. All the tests were performed in accordance with ASTM G99 standard at different sliding velocities, i.e., 1-4 m/sec. The initial lubricant temperature was maintained at 35°C and load applied at the pin and disc interface was 100N.

3. Results and discussion
3.1. Morphological and structural characterization
The phase composition of the titania nano particle and alumina nano wire were determined using X-ray diffraction (Rigaku 6000, Japan) using Cu- Kα radiation at 50kV and 20mA. The peak positions and relatively intensities of the powder pattern were identified by comparison with powder diffraction file (PDF) data. The calculation on the size of nano particle/wire was based on Scherrer’s equation:

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$

Where D is the size of the particles, λ the wavelength of the X-ray and β is the width of the base of diffraction line at half its maximum intensity. The XRD pattern of nano-TiO$_2$ in anatase and rutile phases are as shown in Fig. 1 (a). The XRD pattern exhibited strong diffraction peaks at 25°, 48° indicating nano TiO$_2$ in the anatase phase, on the other hand 27°, 36° and 55° indicating nano TiO$_2$ in the rutile phase. All peaks were in good agreement with the standard spectrum of JCPDS no.:88-1175. These results suggested that the nano TiO$_2$ is composed of amorphous structure. The amorphous revealed a broad pattern with low intensity; the effect of amorphous materials on the broadening of the XRD pattern of nano sized TiO$_2$ is found. Fig. 1(b) shows the XRD pattern of fibrous alumina nano wire. It can be seen from the Fig. 1 (b) that both α-phase and γ-phase Al$_2$O$_3$ were found in lubricant sample. The XRD
pattern exhibited strong diffraction peaks at 38°, 44° indicating γ-phase alumina, while the other peaks indicating alumina at α-phase. Fig. 2 and 3 shows the Scanning Electron Microscope (SEM) image of spherical TiO₂ and fibrous Al₂O₃ nano wire. From the SEM image, the distributions of both the nano particles present in bio-lubricant (chemically modified rapeseed oil) are found more uniform.

Figure 1. (a) XRD pattern of TiO₂ nano particles (b)XRD pattern of nano Al₂O₃ wire.

Figure 2. SEM image of nano TiO₂.

Figure 3. (a) & (b) - SEM images of nano Al₂O₃ wire.
JEOL JSM-1200 EX-Transmission Electron Microscope (TEM) was employed to examine the particle size and morphology of nano lubricants. TEM bright field images of TiO$_2$ nano particles in anatase and rutile phases are shown in Fig. 4. In general, the TiO$_2$ nano particles in rutile phase consist of both spherical and rod shapes but the anatase phase is of spherical morphology. From the TEM image, it is clearly observed that the TiO$_2$ particles present in chemically modified rapeseed oil is in anatase phase. Similarly, Fig. 5 (a) shows the bright field TEM image of alumina nano wire presents in chemically modified rapeseed oil. Fig. 5 (b) shows the bright field TEM image of single alumina nano wire and corresponding inner view shows the selected area electron diffraction (SAED) pattern. It reveals that the alumina nano wires are uniform and neat, with the wire diameter of about ~10nm. Also, by recording the SAED pattern of nano wires, it is evident that each individual α-Al$_2$O$_3$ nano wire is a single crystal.

Figure 4. TEM image of spherical TiO$_2$ nano particles.

Figure 5. TEM image of nano wire a) general view b) view of one wire with SAED pattern (inner view).

3.2. Tribological characterization
Fig. 6 shows the tribological test results as a function of sliding velocity. It is observed that the friction coefficient of chemically modified rapeseed oil and nano particle included lubricants decreased gradually with an increase in sliding velocity. At higher sliding velocity, the friction coefficient was significantly decreased by 32% and 11% respectively for spherical titania based nano lubricant and fibrous alumina wire based nano lubricant compared to that of chemically modified rapeseed oil without nano additives. These results indicate that the presence of spherical titania nano particles in chemically modified oil resulted in less metal contact as compared to that of fibrous nano alumina wire. This is mainly attributed to the higher aspect ratio of fibrous nano alumina wire, resulting in more contact between the frictional surfaces. This result is also in good agreement with addition of spherical copper oxide (CuO) nano particles with coconut oil-based lubricant [17].
Figure 6. Variation of co-efficient of friction.

Fig. 7 shows the average temperature of the pin surface as a function of sliding velocity. The temperature is increased upto 120°C when using chemically modified rapeseed oil as bio-lubricant, whereas the average temperature of pin surface of the titania and alumina based nano lubricants were lower than that of bio-lubricant. In the case of nano based bio-lubricant, the lower friction between the disc-pin contact surfaces decreased the lubricant temperature, and also the presence of nano particles decreases the surface contact.

Figure 7. Variation of lubricant temperature.

Morphology of frictional surfaces lubricated by raw and nano lubricant were investigated by SEM and it is displayed in Fig. 8. Since the hardness of the pin surface is lower than the disc surface, only the morphology of pin was taken into account for the SEM analysis. Fig. 8(a) shows the SEM morphology of specimen corresponds to chemically modified rapeseed oil without nano additive. From the Fig. 8(b) it is clear that wear scar obtained is comparatively smoother while using spherical TiO₂ nano particles with chemically modified lubricant than with fibrous Al₂O₃ nano wire as shown in Fig. 8(c). This may be attributed to the fact that the spherical TiO₂ particles in lubricant at nano level develop a third body rolling effect between the sliding surfaces causes a lower wear, whereas the fibrous nano particles causes higher agglomeration, and agglomerated fibrous nano particles may not play the effect of roll or ball bearings and thus wear was somewhat higher than the spherical shaped nano particles.
Figure 8. SEM image of the pin wear surface a) Chemically modified rapeseed oil b) titania based nano lubricant c) alumina based nano lubricant.

4. Conclusions

- The addition of spherical titania nano particles to the chemically modified rapeseed oil enhanced the lubrication characteristics as compared to fibrous nano alumina wire. This is mainly attributed to spherical titania nano particles possess zero-dimensional structure have fewer contact points than one-dimensional structured fibrous alumina nano wire.

- SEM images of the worn surfaces tested with spherical titania based nano lubricant is found smoother as compared to that of fibrous alumina nano wire based nano lubricant.

- The flash point of lubricant does not get changed with the addition of nano particles, due to the non-flammable characteristics of titania/alumina particles. Further, the addition of nano particles to the chemically modified rapeseed oil does not affect its oxidation stability and cold flow behavior.

- To sum up, the spherical shaped nano TiO$_2$ is found best suited as anti-wear nano additive to chemically modified rapeseed oil to improve its anti-wear and friction reduction behavior.

5. References

[1]. Horner, J. Syn. Lubr., 2002, 18, 327-347.
[2]. Aluyor, E. O., Obahiaagbon, K. O., and Ori-jesu, M. Sci. Res. Essay 2009; 4: 543-548.
[3]. Metzger, J. O. European Journal of Lipid Science and Technology 2009; 111: 865-876.
[4]. Xuedong Wu., Xingang Zhang., Shengrong Yang., Haigang Chen and Dapu Wang. Chemical Society 2000; 77: 561-563.
[5]. Hwang, H., and Erhan, S. Z. Journal of American Oil Chemical Society 2001; 78: 1179-1184.
[6]. Wu, Y. Y., Tsui, W. C., and Liu, T. C. Wear 2007; 262: 819-825.
[7]. Liu, G., Li, X., Qin, B., Xing, Y., Guo, Y., and Fan, R. Tribology Letter 2004; 17(4): 961-966.
[8]. Tao, X., Jiuzheng, Z., and Kang, X. Journal of Physics D Applied Physics 1996; 29: 2932-2937.
[9]. Kim, T. K., Lee, M. N., Lee, S. H., Park, Y. C., Jung, C. K., and Boo, J. H. Thin Solid Films 2005; 475: 71-177.
[10]. Perry, R. H. Chemical Engineers Handbook, 6th ed., McGraw-Hill, New York, 1984; 23.
[11]. Wu, Y. Q., Zhang, Y., Huang, X., and Guo, J. Ceramics International 2001; 27: 265-268.
[12]. Xi'an Chen., Huayue Wu., Shun Wang., and Shaoming Huang. An International Journal for Rapid Communication of Synthetic Organic Chemistry 2011.
[13]. Hu, Z. S., and Dong, J. X. Wear 1998; 216: 92-96.
[14]. Chen, S., and Liu, W. Material Research Bulletin 2001; 36: 137-143.
[15]. Yujin Hwang., Changgun Lee., Youngmin Choi., Seongir Cheong., Doohyun Kim., Kwangho Lee., Jaekeun Lee., and Hyung Kim. Journal of Mechanical Science and Technology 2011; 25: 2853-2857.
[16]. Wu, Y. Y., Tsui, W. C., and Liu, T. C. Wear 2007; 262: 819-825.
[17]. Manu Varghese Thottackkad., Rajendrakumar Krishnan Perikinalil., and Prabhakaran Nair Kumarapillai. International Journal of Precision Engineering and Manufacturing 2012; 13: 111-116.
[18]. Arumugam, S., Sriram, G., and Santhanam, V. IEEE-International Conference on Advances in Engineering, Science and Management, 2012; 25-30.
[19]. Arumugam, S., and Sriram, G. Tribology Transaction 2012; 55: 438-445.