Study of the lubricating properties of hybrid liquid paraffin with TiO$_2$ and CuO as nano-additives for engine oil application

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Abstract. Mineral based paraffin oil (L14480) lubricant finds it difficult to give optimum characteristics for modern engine application. In this work, possibility of hybrid paraffin oil which consists of paraffin oil (PO) and sesame oil (SESO) in equal proportions to be used for engine oil application is investigated. Properties of hybrid paraffin oil and SAE 20W40 were estimated and compared. Estimation of thermal characteristics of hybrid paraffin oil shows it have comparable properties with SAE 20W40. Low viscosity characteristics of hybrid paraffin oil can be improved by addition of EVA particles. Addition of TiO$_2$ and CuO nanoparticles shows enough improvement in tribological properties of hybrid paraffin oil. Poor oxidative stability of hybrid paraffin oil can be improved by addition of butylated hydroxytoluene (BHT).

1. Introduction

Nanotechnology is remarked as the most wide ranging technology of the 21st century. It can be preowned in many areas and lead engineering into a new generation. There have been many research on the tribological properties of lubricants with distinct nanoparticles combination. In literature it has been reported that blending of nanoparticles in lubricants exhibit good reduction in wear and friction. The friction-reduction and anti-wear behaviours were relying on the attribute of nanoparticles, like shape, size, and concentration [1–6]. The dimensions of nanoparticles are usually in the limit of 2–120 nm. Use of copper oxide nanoparticles to improve tribological and anti-wear properties are reported [8-9]. TiO$_2$ nanoparticles displayed satisfactory dispersion capacity and attractive anti-wear behaviour in liquid paraffin [10]. In the present work, properties of hybrid paraffin oil which is a blended mixture of paraffin oil (PO) and sesame oil (SESO) were evaluated and it is compared with the evaluated properties of SAE 20W40. Nanoparticles of copper oxide (CuO) and Titanium di-oxide (TiO$_2$) are added to the hybrid paraffin oil to improve the tribological properties. Properties of these mixtures were evaluated and compared with SAE 20W40. Similar additions of EVA particles and butylated hydroxytoluene are carried out to improve rheological properties and oxidative stability. EVA particles polymers were selected for improving rheological properties considering their remarkable physical and chemical properties coupled with less cost, excellent process ability and recyclability.
2. Materials and Methods

2.1 Preparation of modified paraffin oil
The hybrid paraffin oil (PO) is prepared with sesame oil (SESO) in 50/50 weight fractions. The mixing was done using a magnetic stirrer at a speed of 500 rpm at room temperature for 5-6 hours, formulating uniformly diffuse samples. For improving the rheological properties, EVA particles were combined in percentage weight proportions ranging from 2% to 5%. EVA particles were heated with hybrid paraffin oil in a magnetic stirrer at 500 rpm at 70°C for 4-5 hours. The blend was kept overnight and the homogeneity was confirmed. Improvement of tribological properties of hybrid paraffin oil was made by adding nanoparticles of copper oxide (CuO) and Titanium di-oxide (TiO$_2$). The average size (40nm) and structure of the TiO$_2$ and CuO nanoparticle were characterized by adopting field emission scanning electron microscope (FESEM). The nanolubricants samples are subjected to the magnetic stirrer for 5 hour and then a water bath sonication was used to dissolve the nanolubricants properly in the base oil for 6 hours. The BHT particles were added in the percentage weight proportion of 1%, 1.25%, 1.5% and 2.25% to improve the oxidative stability. BHT particles were heated with hybrid paraffin oil in a magnetic stirrer at 400 rpm at 80°C for 6-7 hours.

![Figure 1. Experimental Setup of Four Ball Tester.](image)

2.2 Evaluation of thermal properties
Thermal properties of hybrid paraffin oil were evaluated by using flash point, fire point, pour point and cloud point. A Cleveland open cup setup was adopted for the determination of Fire and Flash point according to ASTM D92. The pour point was calculated to an exactness of ±3°C as per ASTM D97-96.

2.3 Evaluation of rheological properties
Dynamic viscosities were estimated for a temperature range of 25°C to 100°C. A Modular Compact Rheometer (MCR 102, Anton Paar Austria) having parallel plate tool geometry was used.

2.4 Evaluation of tribological properties
Standard four ball tester equipment (figure 1) was used to evaluate tribological properties of samples. Chrome alloy steel balls with a diameter of 12.7 mm and a hardness of HRC 61-64 were used for the test. Washing of balls and attachment was carried out using acetone in an ultra-sonication bath for 40
min and then in n-hexane. Wear test was performed with a load of 40 kg at 1200 rpm for a duration of 60 min according to ASTM D 4172-94. Lubricant was maintained at a temperature of 75°C.

2.5 Analysis of oxidative properties
Hot Oil Oxidation Tests (HOOT) were conducted on samples by keeping it in a dark oven at 100°C for 140 hours in a box container. Before and after the tests, viscosities of samples were estimated 40°C.

3. Results and Discussion

3.1 Result of thermal analysis
Estimated flash point, fire point, cloud point, and pour point are given in Table 1. Flash and fire point of hybrid paraffin oil are greater than SAE 20W40 indicates that hybrid paraffin oil is thermally more stable. Cloud point and pour points are also comparable with SAE 20W40.

| S. NO | SAMPLE             | THERMAL PROPERTIES (°C) |
|-------|--------------------|-------------------------|
|       |                    | FLASH POINT | FIRE POINT | CLOUD POINT | POUR POINT |
| 1.    | Hybrid paraffin oil| 226         | 239        | -10         | -17        |
| 2.    | SAE 20W40          | 204         | 209        | -15         | -20        |

3.2 Result of rheology modifiers
Table 2 shows the viscosities of sample at 40°C and 100°C. The viscosity of hybrid paraffin oil is low compared to SAE 20W40. Table 3 shows the variation of viscosities of hybrid paraffin oil with different weight proportions of EVA particles. It can be seen that addition of 2-3% EVA particles improves the viscosity of hybrid paraffin oil which is comparable with SAE 20W40. Intermolecular forces among the molecules and difference in molecular weight of the polymers are believed to be the reason for this.

| S. No | SAMPLE             | VISCOSITY at 40°C (mPa-s) | VISCOSITY at 100°C (mPa-s) |
|-------|--------------------|---------------------------|----------------------------|
| 1.    | Hybrid paraffin oil| 39.42                     | 8                          |
| 2.    | SAE 20W40          | 117.86                    | 14.18                      |
Figure 2. Comparison of various percentages of EVA particles in hybrid paraffin oil and SAE 20W40.

Table 3. Effect of addition of EVA particle on viscosity of hybrid paraffin oil.

| TEMPERATURE (°C) | SAE 20W40 | VISCOSITY (mPa-s) |
|------------------|-----------|-------------------|
|                  | Hybrid Paraffin oil + EVA | 2% EVA | 3% EVA | 4% EVA | 5% EVA |
| 40               | 117.86    | 85                | 125    | 152    | 260    |
| 60               | 49.37     | 41                | 60     | 72     | 121    |
| 80               | 24.78     | 23                | 32     | 39     | 62     |
| 100              | 14.18     | 14.66             | 20     | 23.71  | 38     |

3.3 Additives to improve tribological properties

Table 4 shows the wear scar diameter and friction coefficient of hybrid paraffin oil SAE 20W40. It can be noted that wear scar diameter of hybrid paraffin oil is 50% higher than SAE 20W40. Table 5 shows the wear scar diameter with addition of nano particles to hybrid paraffin oil. The following points can be noted: (i) Addition of nano-particles decrease the wear scar diameter, and (ii) Addition of 0.15% TiO$_2$ decrease the wear diameter by about 22%. This can be due to spherical shape of TiO$_2$ nanoparticles operating as a rolling medium within the contacting surfaces, which eliminates the metal to metal contact between the asperities of the two mating surfaces.
Table 4. Comparison of Wear Scar Diameter of hybrid paraffin oil and SAE 20W40.

| S. No | SAMPLE       | COEFFICIENT OF FRICTION | WEAR SCAR DIAMETER (mm) |
|-------|--------------|-------------------------|-------------------------|
| 1.    | Hybrid paraffin oil | 0.0779                  | 0.6577                  |
| 2.    | SAE20W40     | 0.0823                  | 0.4381                  |

Table 5. Effect of nanoparticles additives on wear scar diameter of hybrid paraffin oil.

| S. No | Samples                     | Wear Scar Diameter (mm) | % Reduction in WSD |
|-------|------------------------------|-------------------------|---------------------|
| 1.    | Hybrid paraffin oil         | 0.6577                  |                     |
| 2.    | Hybrid paraffin oil + 0.5% CuO | 0.5939                  | 9.7004%             |
| 3.    | Hybrid paraffin oil + 1% TiO₂ | 0.5203                  | 20.890%             |
| 4.    | Hybrid paraffin oil + 0.15% TiO₂ | 0.5130                  | 22.009%             |
| 5.    | SAE 20W40                   | 0.4381                  |                     |

3.4 Additives to improve the oxidative properties

Table 6 shows the change in viscosity of hybrid paraffin oil and SAE 20W40 after the HOOT (Hot Oil Oxidation Test). Viscosity of hybrid paraffin oil changes by 69.44 mPa-s which is relatively high compared to change in viscosity of SAE 20W40. Table 7 shows the improvement of viscosity of hybrid paraffin oil with blending of antioxidants Butylated hydroxytoluene (BHT). It can be seen that 1% of BHT blending reduce the change in viscosity of about 14 mPa-s. But higher % addition increases the change in viscosity.

Table 6. Comparison of oxidative stability of hybrid paraffin oil and SAE20W40.

| SAMPLE             | CHANGE IN VISCOSITY (mPa-s) |
|--------------------|------------------------------|
| Hybrid paraffin oil| 69.44                        |
| SAE 20W40          | 2.26                         |
4. Conclusions
Properties of hybrid paraffin oil which consists of equal proportions of paraffin oil and sesame oil were estimated to be used as lubricant oil. Properties are compared with the commercially available SAE 20W40. The following conclusions can be made, (i) Thermal properties of hybrid paraffin oil are comparable with SAE 20W40, (ii) Hybrid paraffin oil have lower viscosity compared with SAE 20W40. Addition of EVA particles can improve the rheological properties, (iii) Tribological tests shows higher wear scar diameter for hybrid paraffin oil. Addition of TiO$_2$ can improve the tribological properties, (iv) Oxidative stability of hybrid paraffin oil can be improved by adding butylated hydroxytoluene.

References
[1] F. Chinas-Castillo and H.A. Spikes, (2003), Mechanism of action of colloidal solid dispersions, Trans, ASME 125, 552–557.
[2] J. Zhou, J. Yang, Z. Zhang, W. Liu and Q. Xue, (1999), Study on the structure and tribological properties of surface-modified Cu nanoparticles, Mater. Res. Bull. 34 (9), 1361–1367.
[3] L. Rapoport, Y. Feldman, M. Homyonfer, H. Cohen, J. Sloan and J.L. Hutchison, (1999), Inorganic fullerene-like material as additives to lubricants: structure–function relationship, Wear 225–229, 975–982.
[4] S. Chen, W. Liu and L. Yu, (1998), Preparation of DDP-coated PbS nanoparticles and investigation of the antwear ability of the prepared nanoparticles as additive in liquid paraffin, Wear 218, 153–158.
[5] Q. Xue, W. Liu and Z. Zhang, (1997), Friction and wear properties of a surface modified TiO$_2$ nanoparticle as an additive in liquid paraffin, Wear 213, 29–32.
[6] W. Liu and S. Chen, (2000), An investigation of the tribological behavior of surface modified ZnS nanoparticles in liquid paraffin, Wear 238, 120–124.
[7] Wu Y, Tsuia W and Liub T (2007) Experimental analysis of tribological properties of lubricating oils with nanoparticle additives. Wear 262, 819–825.
[8] Thottackkad MV, Perikinalil RK and Kumarapillai PN (2012), Experimental evaluation on the tribological properties of coconut oil by the addition of CuO nanoparticles. Int J Precis Eng Manuf 13, 111–116
[9] Qunji, Liu and Zhijun Zhang (1997): ‘Friction and wear properties of a surface-modified TiO$_2$ nanoparticle as an additive in liquid paraffin’.
[10] Z.S. Hu and J.X. Dong, (1998), Wear 216, 92–96

Table 7. Effect of oxidative additives on hybrid paraffin oil.

| SAMPLE                     | CHANGE IN VISCOSITY (mPa-s) |
|----------------------------|------------------------------|
| Hybrid paraffin oil+1% BHT | 14.641                       |
| Hybrid paraffin oil        | 28.199                       |
| +1.25%BHT                  |                              |
| Hybrid paraffin oil +1.5%  | 18.798                       |
| BHT                       |                              |
| Hybrid paraffin oil        | 24.759                       |
| +2.25%BHT                  |                              |
| SAE 20W40                  | 2.26                         |

Table 7. Effect of oxidative additives on hybrid paraffin oil.