Original Article

Nano and micro structures produced from carbon rich fly ash as effective lubricant additives for 150SN base oil

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\textbf{A B S T R A C T}

Lubricant oils in cars engines are essential components for reducing friction and fuel consumption. The lubrication process can be improved by including effective additives. Carbon nanostructures have been recognized as excellent additives in lubricant oils. Amongst them carbon nanotubes (CNTs) produced from carbon rich fly ash, are found to have excellent tribological properties in the sunflower base oil. In this work, these CNTs along with other micro and nanostructures produced from carbon rich fly ash are tested as lubricant additives in the 150SN base oil. The impregnated oils with these additives are evaluated to reduce the friction between two metallic surfaces using the ball-on-disk tribometer. The obtained results showed that CNTs of fly ash have significantly reduced the frictional coefficient by around 25% at a concentration of 0.1 wt%. This result is much better than that of the other fly ash micro and nanostructures produced by sonication and ball milling techniques. It is also compared with that of a commercial multiwall CNTs and is found to be superior. The friction coefficient values are investigated as a function of load and temperature. Moreover, the rheological behavior is also studied for the pure and 0.1 wt% CNTs-impregnated oil. No significant changes are observed in the viscosity of the impregnated oil. The present CNTs of carbon rich fly ash have been proved to be effective additives for the 150SN lubricant oil, and might be useful for variety of lubricants.

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1. Introduction

Carbon nanomaterials have attracted much attention and are amongst the most studied nanostructures. One of the important materials of this family is carbon nanotubes (CNTs), which have unique mechanical and electrical properties [1]. This material has been extensively studied and evaluated for different applications. Several procedures and methods have been developed to synthesize CNTs [2–10], however, the mass production of this nanomaterial using these methods is still an issue. Due to limited success in the large-scale production and cost effectiveness of CNTs, they could not be utilized for wide range of low cost products made from polymers or rubber. Therefore, many research groups from different institutes are still working to find out a suitable, simple and low cost method using cheap precursors for CNTs synthesis. One of the suggestions to resolve this issue is to use carbon rich fly ash for producing CNTs as reported by Salah and his group [11,12]. This ash is available in huge quantities as a solid waste material and has a good amount of unburned carbon, which is more than 80% [13]. Salah and his team have successfully converted this ash into CNTs and utilized them for different applications. The transmission electron microscope (TEM) images given in Fig. 1(a and b) were obtained from Ref. [12]. They show multiwall nanotubes (image b).

Fuel consumption is an important issue for engineers and cars manufacturers. Reducing the fuel consumption and increasing the life time of the interior parts inside these machines are still a burning issue. One of the solutions is to use high efficiency lubricants. Lubricant oil is very common, which is used in a large scale mainly for reducing friction and then fuel consumption. It can act as “a coolant, cleaning the trapped particles from machinery sheds, and as a sealant that could block the surface from contaminants”. Palm oil was also suggested as lubricant [14]. Chemical additives are normally included to improve the tribological performances. But, the search is continued for advanced chemical additives to improve the tribological performances further and reduce the fuel consumption. Different nanoscale materials have been suggested as lubricant additives to enhance the tribological performances. These nanomaterials include TiO2, CuO, nanodiamonds, SiO2 and CaCO3 [15–17]. A lot of work on the evaluation of variety of nanostructure additives is still in progress. However, the main challenges in this direction could not be resolved such as the cost of these nanostructures beside their poor mechanical properties.

Carbon nanotubes were found to be excellent additives in lubricant oils. They are also found to be suitable for sliding wear behavior of other lubricant materials. The use of CNTs as lubricant additives was reported by several authors [8,18–21]. Although the needed quantities (percentage) as additives are small, the cost of CNTs is still a big challenge. The CNT agglomeration associated with their dispersion in the oil is another obstacle, which limits the use of this material at a large scale. Recently Salah et al. [22] reported the use of CNTs of carbon rich fly ash as a lubricant oil additive. They evaluated these nanotubes as lubricant additives in the sunflower base oil. Excellent tribological results were reported by using these CNTs. Other micro and nanostructures of carbon rich fly ash were also produced [23], but not yet evaluated for their applications as lubricants.

In this work, the authors have used CNTs produced from carbon rich fly ash along with other micro and nanostructures of this material as lubricant additives in the most common Saudi Aramco base oil. The code of this oil is 15OSN, which is quite popular base oil used for car engines. The fly ash CNTs synthesized by the chemical vapor deposition method along with the other fly ash micro and nanostructures produced by sonication and ball milling techniques, were dispersed in the 15OSN base oil. The friction coefficient values were measured and investigated in more details. The obtained results were also compared with a commercial multiwall CNTs. It is concluded that the CNTs produced from fly ash might be useful for variety of lubricants.

2. Experimental procedure

2.1. Materials

Carbon rich fly ash was collected from the Jeddah power plant, Saudi Arabia. The other carbon nanomaterial used for comparison in this study is multiwall CNTs. It was obtained from Nanostructured & Amorphous Materials Inc. (http://www.nanoarmor.com/) and used without further treatment or functionalization. The used base oil in this work is 15OSN. It was obtained from Petromen Company, Jeddah, Saudi Arabia (the raw materials of Petromen is supplied by Saudi Aramco, Saudi Arabia).

2.2. Synthesis of fly ash micro and nanostructures

Three different types of structures were produced from carbon rich fly ash and were evaluated as lubricant additives. These are (i) carbon nanotubes, (ii) micro/sub micrometer sized sonicated fly ash and ball milled nano/micrometer sized particles of fly ash. The first one was synthesized by the chemical vapor deposition method described earlier by Salah et al. [11,12], while the second and third structures were produced by the method described elsewhere [23]. Slight modification was included on the samples produced by the high energy ball milling system. No suspension or particles separation was performed in this work as it was adopted in the earlier work [23]. The ball milled carbon rich fly ash powder for 15 h was completely used without removing any part. The samples formation was confirmed by scanning electron microscope (using the JSM-7500 F model of JEOJ, Japan) and Raman spectroscopy (DXR-Thermo scientific, USA) with 532 nm laser as an excitation source. Commercial multiwall CNTs obtained from Nanostructured & Amorphous Materials Inc. were also used as standard material for comparison.

2.3. Friction coefficient measurements

The friction coefficient values were measured at room temperature using a Tribometer model, TRB-S-DE-0000 CSM Instruments, Switzerland. The procedures used for these measurements are similar to those reported earlier [22]. The ball-on-disk test was used with the desired applied load and
Fig. 1 – TEM images of CNTs of carbon rich fly ash: (a) at low magnification and (b) at high magnification (High resolution). These images were obtained from Ref. [12].

| Table 1 – Properties of SN-150 Aramco base oil. |
|-------------------------------|------------|---|-----------------|
| #                             | Parameters | ASTM | UNIT | 150 SN |
| 1 Color (max)                 |            | D-1500 | – | 1.5 |
| 2 Density @ 15 °C             |            | D-1298 | kg/m³ | TBR |
| 3 Appearance                  | Visual     | – | C & B | |
| 4 Kinematic Viscosity at 40 °C|            | D-445 | cSt | 28–31 |
| 5 Viscosity Index (min)       |            | D-2270 | – | 101 |
| 6 Flash Point COC (min)       |            | D-92 | °C | 200 |
| 7 Pour point (max)            |            | D-97 | °C | –12 |
| 8 Neutralization # (max)      |            | D-974 | mg KOH/g | 0.05 |
| 9 Copper Corrosion (max)      |            | D-130 | 100 °C/3 h | 1A |
| 10 Sulfur Content (max.)      |            | D-2622 | % | 1.0 |
| 11 Ash Content (max.)         |            | D-482 | Wt% | 0.01 |

Fig. 2 shows SEM images of carbon rich fly ash (a), ball milled carbon rich fly ash for 15 h (b), sonicated carbon rich fly ash for 4 h (c) and CNTs of carbon rich fly ash (d). The fly ash particles have almost spherical shapes with sizes in the range of 20–100 μm. They are similar to those reported earlier [12,23]. The ball milled fly ash have a mixture of micro, submicro and nano sized particles (Fig. 2b). It is well known that high energy ball milling technique can significantly reduce the grounded materials into the nanoscale [24]. The sonicated fly ashes are of micro, submicro particles and fragments (Fig. 2c). They have a high porosity at their surfaces. This result is in accordance with that reported earlier [23]. The CNTs of fly ash observed here are similar to those reported earlier [11,12]. They have a uniform structure with lengths in the micrometer range and diameters around 20–40 nm.

Raman spectra of the above mentioned carbon nanomaterials samples, i.e., CNTs of fly ash, fly ash powder, ball milled fly ash and sonicated fly ash, are shown in Fig. 3, curves a, b, c and d, respectively. These samples have the G and D bands of graphitic materials. They are located at their regular positions at around 1575 and 1340 cm⁻¹, respectively [25–27]. The only difference in this case is the intensity of these peaks. The intensity of G and D bands is high in case of CNTs (curve a) followed by that of fly ash (curve b). The intensity ratio of G to D band of the produced CNTs is around 1.4, which is identical to that reported earlier [12]. These results indicate that there is a considerable amount of carbons in graphitic form in the used fly ash. The sonicated fly ash sample (d) has showed smaller amounts of graphitic materials compared to the other presented samples. The ball milled sample has also lost some of its graphitic structure. This might be due to the destruction occurred in the graphitic contents in this fly ash as a result of ball milling and sonication for long time. These results are a confirmation to those reported earlier [23]. The used commercial MWCNTs for comparison in this work were also characterized. Fig. 4 shows Raman spectrum of this material. The figure in the inset shows the SEM image of this

2.4. Rheological analysis

The rheological measurements reported in this study for pure and 0.1 wt% CNTs impregnated 150SN base oil were performed using an AR-G2 Rheometer (TA Instruments). These measurements were recorded in the temperature range 25–100 °C with a ramp rate of 5 °C/min. A stainless steel cone of 60 mm parallel plate (Peltier plate steel) was used in these measurements in steady or oscillatory shear. The gap was fixed at 1000 μm with a loading gap of 45 mm.

3. Results and discussion
The G and D bands in the Raman spectrum are clearly shown in their regular positions [25-27]. The intensity of D band is high indicating a presence of high amount of defects. The SEM image of these nanotubes clearly shows long MWCNTs with average diameters around 40 nm. These MWCNTs have perfect structure and seems to be ideal for comparison propose.

The friction coefficient measurement results using the above mentioned materials as additives in the 150SN base oil are presented in Fig. 5. The concentration of these additives is 0.1 wt.%. The friction coefficient values were recorded at a fixed load, which is 4 N. The mean value for the pure oil is 0.159. This value has been observed to decrease on the impregnated base oils with the above mentioned additives. It drastically dropped from 0.159 to 0.120 by adding CNTs of fly ash. The other carbon rich fly ash showed significant decrease in the friction coefficient values, but lower than that of CNTs-fly ash. The later has showed improved lubrication result even better than that of the commercial MWCNTs, which could decrease the friction coefficient up to 0.140. These results suggest that the CNTs of fly ash can be considered as an ideal lubricant additive and might be used for a broad range of lubricants. The reason for superiority of CNTs of fly ash was explained earlier [22], which may be attributed to “the existence of active
radical sites on the side wall of CNTs. These radicals might help the CNTs adhere to the metal surface, thus reducing friction”.

The tribology results by using the CNTs of fly ash were found to be better than that of the other structures, i.e., ball milled and sonicated fly ash. These results were obtained at a typical additive concentration; therefore, it is quite important to optimize the concentration of these additives for best reduction of friction. Table 2 shows the magnitude of the friction coefficient as a function of concentrations of fly ash-CNTs impregnated in the 150SN base oil. The load was fixed at 5 N. The start, minimum, maximum and mean friction coefficient values are listed in this table. The obtained result showed that the optimum value for a minimum friction was found at a CNTs concentration of 0.1 wt%. The lower and higher concentrations were found to slightly reduce the friction coefficient values.

The mean values for the friction coefficient were also plotted as a function of CNTs concentrations and presented in Fig. 6. The presented curve in this figure shows a drastic drop in values of the friction coefficient below 0.1 wt%. Beyond this value this curve starts to increase gradually. The pure and impregnated base oil samples are also shown in the inset of Fig. 6. They showed a homogeneous dispersion of the CNTs within the 150SN base oil. It is quite interesting to get the optimum value for less friction at a very tiny concentration of CNTs, i.e., 0.1 wt%. It is possible that these nanotubes at higher concentrations could form large clusters [18,28]. These clusters may be formed and agglomerate within the oil as a result of their overlapping over each other. There might be some attractive forces also existing between the surfaces of these CNTs [22]. These cluster expected to have less stability between the two sliding surfaces during the motion as compared with individual nanotubes, thereby, showing higher values of friction coefficient. Small consternations of fly ash CNTs (<0.1 wt%) will not be enough to protect the surface. In other words, there will not be sufficient material to cover the surfaces completely and reduce the friction between them (i.e., some gaps on the surfaces will be there). These observations are similar to those reported by other workers [18,28].

Fig. 7 shows a plot of the friction coefficient values against time and distance for fly ash CNTs impregnated base oil at a typical concentration (0.1 wt%). The plot in the inset is the corresponding extended values for this curve. The steady state is observed in this curve on the whole range, which is 10 m. But a uniform oscillation/fluctuation can be seen in this curve between the minimum and maximum values of the friction coefficient. This fluctuation is related to the surface roughness, which has been observed by other groups [29]. The presence of nanostructures can smoothen the surface and minimizes its roughness. In other words, these nanostructures will fill the gaps and holes in the surface, which results in less fluctuation in value of the recorded friction coefficient. The extended values for this curve shown in the inset of Fig. 7 have a uniform repeating pattern, which might be a good indication for a formation of uniform protection layer with no
clusters. The presence of clusters within the formed layer on the surface might show non-uniform and bigger fluctuation.

The mean values of the friction coefficient for pure and CNTs impregnated 150SN base oils (at 0.1 wt%) were recorded as a function of load. The obtained results were plotted and presented in Fig. 8. It can be observed that, by increasing the load from 1 to 10 N, the friction coefficient value was, respectively, increased from around 0.08 to 0.25 for pure oil and from 0.047 to 0.22 approximately for CNTs impregnated base oil. It is clear that the CNTs impregnated oil shows improved tribological performance at different loads compared to that of pure oil. The increase in values of the friction coefficient as a function of load is well documented in the literature [30] and may be attributed to the nanostructures deformations, which enhance the rolling effect. Higher loads result in greater contacts between the two sliding surfaces. The major increases on values of the friction coefficient is expected to be induced mainly from the non-covered sites on the surface. The formed protection layers might not be covering the entire surface and some sites will remain unprotected. This will increase the friction particularly at higher loads. Nevertheless, addition of small amount of CNTs into the base oil is still providing a significant reduction in values of the friction coefficient under different loads.

In Fig. 9 the mean values of the friction coefficient were plotted as a function of temperature for pure and fly ash CNTs impregnated 150SN base oil. The obtained results were recorded at a concentration of 0.1 wt% and 5 N load. The friction coefficient values were increased with increasing the temperature. They were increased from 0.158 to 0.192 by increasing the temperature from 25 to 100 °C for the pure base oil, and from 0.129 to 0.172 for the CNTs impregnated base oil. The increase in values of the friction coefficient may be due to the decrease in lubricant viscosity over this temperature range. Similar observations were also reported and attributed to the decrease in lubricant viscosities [31]. This decrease in the viscosities may be due to the thermal decomposition of the lubricant oils molecules. In this case, the CNTs may have less stability within the oil and also may be less bonded with the molecules of the lubricant oil and finally have lower ability on making protective layers on the surface.

Fig. 10 shows high resolution optical microscopy images of the used disk in this work before (a) and after (b) the measurement. This figure also shows SEM image (c) of the formed layer of CNTs on the disk under 4 N load and Raman spectrum (d) of these nanotubes after the measurement. The formed layer of CNTs produced from carbon rich fly ash on this disk could act as an effective protection layer, which results on reducing the friction. These nanotubes can be easily aligned under the applied load and form this layer. It is well established that carbon nanostructures included in lubricants can form strong protective layers between sliding surfaces [32]. The formed layer in the present case contains CNTs with shorter lengths.

Fig. 7 – Plot of the friction coefficient values versus time and distance for CNTs impregnated 150SN base oil (at a concentration of 0.1 wt%). The plot in the inset is the corresponding extended values for this curve.

Fig. 8 – Plot of the mean values of the friction coefficient as a function of load for pure and CNTs of fly ash impregnated 150SN base oil at a concentration of 0.1 wt%.

Fig. 9 – Plot of the mean values of the friction coefficient as a function of temperature for pure and CNTs of fly ash impregnated 150SN base oil. The result was obtained at load = 5 N, concentration = 0.1 wt%, d = 10 m, R = 2 mm and linear speed = 0.65 cm/s.
With the formation of such layer under the applied load some distraction in the CNTs can be noticed. Not only the length of these nanotubes becomes shorter, but the graphitic content in these nanotubes were also affected. The D band in Raman spectrum (Fig. 10d) becomes more prominent as compared with that of the original D band of this sample (Fig. 3a). In other words, the D/G intensity ratio has been increased in the formed CNTs layer after the measurement. However, the CNTs of fly ash still have a major graphitic structure. They were not completely deformed or formed new transfer layers. It is reported that MWCNTs can form a transfer layer made of amorphous carbon [33]. But it is not the case in the present material. These are remarkable results that the CNTs of fly ash have a unique structure, which may require further investigation about its mechanical properties. This will be conducted in near future and will be reported in a separate report.

The track formation and wear loss on the used disk were also studied. The friction coefficient was measured at room temperature. The applied load was fixed at 10 N for a 10 m sliding distance. This measurement was performed for pure as well as fly ash-CNTs impregnated 150SN base oil. Dimensions of the formed tracks on the worn surfaces were measured by a surface profiler. The formed wear track on the disk with pure oil has average depth and width, which is equal to 780 nm and 190 μm, respectively. On the other hand, the worn surface of the used disk in the presence of fly ash-CNTs within the base oil has almost shallow track with average depth and width of 170 nm and 340 μm, respectively. It is clear that, there is a significant reduction in the wear volume by using CNTs as additive in the 150SN base oil. The specific wear rate values were calculated in both cases using the equation:

\[
\text{The specific wear rate} = \frac{\text{Wear volume (m}^3\text{)}}{\text{Normal load (N) \times Sliding distance (m)}} \quad (1)
\]

![Fig. 10 – High resolution optical images of the (a) used disk before the measurement, (b) used disk after the measurement (c) SEM image of the formed layer of CNTs on the disk under 10N load (d) Raman spectrum of the CNTs present on the formed layer.](image1)

![Fig. 11 – Viscosity as a function of temperature for pure and 0.1 wt% CNTs of fly ash impregnated 150SN base oil.](image2)

The obtained results for the specific wear rate values for both the cases (i.e., with pure and fly ash-CNTs impregnated base oil) were found to be \(14.82 \times 10^{-12}\) and \(0.58 \times 10^{-12} \text{ m}^3/\text{Nm}\), respectively. This reduction in the wear loss from \(14.82 \times 10^{-12}\) to \(0.58 \times 10^{-12} \text{ m}^3/\text{Nm}\) by adding CNTs of fly ash can be attributed to the presence of protective thin layers made from these nanotubes.

Rheological behavior is another important factor, which needs to be investigated in the 150SN base oil impregnated with CNTs of fly ash. A typical concentration of CNTs i.e., 0.1 wt.% was included in the base oil. Then they were investigated with the help of the temperature dependence of viscosity. Fig. 11 shows the obtained viscosity values at a certain range of temperature for pure and CNTs-impregnated 150SN base oil. In case of pure oil, the viscosity value has been
observed to decrease from 0.02 to around 0.005 Pa.s by increasing the temperature of the oil from 25 to 100 °C. The CNTs impregnated base oil showed similar behavior, but with slight decrease by around 6% in the viscosity values. These results showed that the viscosity of the CNTs-impregnated base oil did not show any significant change in comparison with that of the pure oil. This may be due to the use of small concentration of CNTs. Perhaps this concentration is not enough to produce a change in the viscosity of the lubricant. Similar results were also reported on the literature about the low effect of CNTs on viscosity of the lubricant oil with different temperatures [33]. From the application point of view, the obtained results showed that CNTs of fly ash can be recommended as a good additive in the 150SN lubricant oil, which is used for different engines. Moreover, the low cost of CNTs obtained from a waste material beside their well-dispersion within the base oil are other remarkable findings.

4. Conclusions

CNTs of carbon rich fly ash were tested as lubricant additives for 150SN base oil of Saudi Aramco Company. Superior tribological performance was observed at a very tiny concentration of CNTs of fly ash. The obtained result on reducing the friction between two metallic surfaces was found to be superior to that of the commercial MWCNTs. The value of the friction coefficient was reduced by around 25% at a concentration of 0.1 wt%. The friction coefficient values were also investigated as a function of load and temperature. The values were found to increase by increasing these factors. The rheological behavior was also studied and showed that the viscosity of the 0.1 wt% CNTs-impregnated base oil slightly changed compared to that of the pure oil.

Conflicts of interest

The authors declare no conflicts of interest.

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