Original Article

Tribological properties of carbon nanotubes as lubricant additive in oil and water for a wheel-rail system

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ABSTRACT

Since their discovery in 1991 carbon nanotubes (CNTs) have attracted much interest due to their remarkable mechanical, thermal, electrical, chemical and optical properties. In connection with their mechanical properties, CNTs have been studied in various forms for tribological applications including their use as lubricant additives for oil and water. In this work, the tribological properties of functionalized nanotubes (single and multi-walled) modified with carboxylic acid when used as lubricant additives at different concentrations (0.01, 0.05%) were studied under rolling-sliding conditions in a twin-disk testing machine. The tests were performed using 5% of creapage and pressures of 0.8 GPa and 1.1 GPa. The results indicated that the presence of carbon nanotubes leads to a decrease in both friction coefficient and wear rate for both systems studied (oil and water).

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1. Introduction

Friction and wear reduction is critical in modern transport industry due to its impact on the energy consumption and maintenance costs. High quality lubrication is of great significance for operation under harsh working conditions such as high temperatures and extreme pressures. Under these severe conditions, additives are typically used to improve the tribological properties of lubricants. Traditional additives such as sulfides, chlorides, and phosphates are adopted to prevent materials from suffering severe wear and seizure \cite{1}. Nanoparticles have emerged as potential lubricant additives in recent years due to the wide variety of effects that can be obtained in...

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terms of rheological, chemical and anti-wear properties of the lubricants. It has been reported, for example, that the extreme-pressure properties and load carrying capacity are enhanced and friction coefficients tend to decrease with the addition of nanoparticles to oil [2,3]. Following this trend, since their discovery in 1991 carbon nanotubes (CNT’s) have attracted much interest due to their remarkable mechanical, thermal, electrical, chemical and optical properties [4].

In connection with their mechanical properties, CNT’s have been studied in various forms for tribological applications including their use as lubricant additives for oil [5] and water [6]. Also, CNT’s have been used as reinforcements for metals and ceramics such as Cu [7], Ni [4] and Al₂O₃ [8], or as reinforcements in polymeric materials such as poly-methyl methacrylate (PMMA) [9], ultrahigh molecular weight polyethylene (UHMWPE) [10], polyamide 6 (PA6) [11], among others.

In this work the tribological properties of Single Walled Carbon Nanotubes (SWCNT’s) and Multi Walled Nanotubes (MWCNT’s) when used as additives for oil and water were studied under rolling-sliding conditions. All tests were performed with 5% creepage and contact pressures of 0.8 and 1.1 GPa during 14,000 cycles. The functionalized CNT’s were prepared by chemical modification in carboxylic acid to improve the dispersive state of CNT’s in oil and water.

2. Materials and methods

2.1. CNT’s synthesis

CNT’s were synthesized by chemical vapor deposition. A quartz tube was used to grow of CNT’s and a furnace equipped with a high precision temperature controller allowed to achieve the desired reaction temperature (700 °C), which is automated and controlled by a computer. Acetylene was used as carbon source. The catalysts were nickel for the production of MWCNT’s and cobalt for SWCNT’s and the gas mixture was composed of 80 cc/min nitrogen, 20 cc/min acetylene and 15 cc/min hydrogen. The processing sequence included reduction time of 20 min, acetylene time of 30 min and cooling time of 60 min.

2.2. Functionalization and purification of CNT’s

Once synthesized the CNT’s were removed from the substrate to be purified by an acid treatment. The method is based on the research done by Marshall et al., who proposed a simple procedure for functionalizing carbon nanotubes in carboxylic acid [12]. 2 mg per nanotube of a solution composed of 3:1 (V/V) HNO₃ and HCl was used and the CNT’s were subjected to ultrasonic agitation for 20 min in water at 20 °C using ice to control the temperature. Afterwards, the CNT’s were washed in deionized water to remove the excess of acid until a pH of about 5 was reached and finally dried in oven at 60 °C.

2.3. Dispersion of CNT’s in oil and water

Oil-based and water-based solutions were prepared with concentrations of 0.01% and 0.05% of MWCNTs and SWCNTs, with mechanical stirring for 30 min and ultrasonic agitation during 1 min.

2.4. Tribological tests

The tests to measure wear and coefficient of friction were performed by using a twin-disk machine (MDDv2) installed in the laboratory of tribology and surfaces of the National University of Colombia at Medellin. The MDDv2 is used to simulate the wheel-rail contact under conditions similar to those present in railway systems. This device consists of two discs that rotate in parallel axes, which are put in contact under controlled relative speed, contact pressure and percentage of local slippage (creepage). All the “rail” specimens were extracted from sections of R260 and R370CrHT rails manufactured by Voestalpine Schienen GMBH-Austria and supplied by the Company of Massive Transport of the Valle de Aburrá (Metro de Medellín). The chemical composition measured by Optical Emission Spectroscopy and mechanical properties of the rail and wheel are within the ranges established by European standards EN13674-1:2011 [13] and EN13262:2004 [14]. The ‘wheel’ specimens were extracted from different sections of the tread area of a commercial wheel provided by Metro de Medellín, and they were heat treated to obtain homogeneous hardness in all the contact surface within the range 245-275HB, as required in EN13262:2004 standard.

All the laboratory tests were performed with a creepage of 5% and the contact pressure used was either 0.8 GPa or 1.1 GPa. In order to have significant evidence of fatigue all the specimens were subjected to a pre-cracking period corresponding to 4000 cycles in dry condition, after which the lubricant was added to the contact interface for 10,000 cycles with no interruption of the test whatsoever. Before starting each test the samples were ultrasonically cleaned in alcohol during 5 min, then dried at room temperature and weighed in a scale with resolving power of 0.0001 g.

The detailed testing conditions for all the experiments are shown in Table 1.

2.5. Viscosity tests

The rheological characterization of the lubricating oils was carried out with the aid of a conventional Brookfield LVDV-II+ Pro viscometer with temperature bath, a bi-directional RS-232 PC Interface and the software Rheocalc®. The equipment has variable speed capability of 0.01-200 rpm a testing temperature range from 0 °C to 100 °C and a maximum shear rate of 57 s⁻¹ at 195 rpm.

Controlled Rate Ramp tests were performed by using a SC4-16 LV spindle in such a way that the rotational speed of the spindle increased the RPM every 30 s and the viscosity changes were recorded to determine the Newtonian or non-Newtonian behavior of the lubricants studied. The effect of temperature on viscosity was also measured by carrying out tests in the range between 0 °C and 100 °C with a fixed speed of 30 rpm. Finally, the lubricants were tested at a specific shear rate for 600 s in order to observe any changes in viscosity over time.
Table 1 – Description of tribological tests.

<table>
<thead>
<tr>
<th>Nomenclature test</th>
<th>Maximum contact pressure (GPa)</th>
<th>Type of CNT’s</th>
<th>Lubricant</th>
<th>Concentration of CNT’s (%)</th>
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<tr>
<td>E1</td>
<td>1.1</td>
<td>MWCNT’s</td>
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<td>MWCNT’s</td>
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<td>0.01</td>
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<tr>
<td>E3</td>
<td>1.1</td>
<td>MWCNT’s</td>
<td>Water</td>
<td>0.01</td>
</tr>
<tr>
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<td>0.8</td>
<td>MWCNT’s</td>
<td>Water</td>
<td>0.01</td>
</tr>
<tr>
<td>E5</td>
<td>1.1</td>
<td>SWCNT’s</td>
<td>Oil</td>
<td>0.01</td>
</tr>
<tr>
<td>E6</td>
<td>0.8</td>
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<td>0.01</td>
</tr>
<tr>
<td>E7</td>
<td>1.1</td>
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<tr>
<td>E8</td>
<td>0.8</td>
<td>SWCNT’s</td>
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</tr>
<tr>
<td>E11</td>
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<td>MWCNT’s</td>
<td>Water</td>
<td>0.05</td>
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<tr>
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<td>Water</td>
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<tr>
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<td>None</td>
<td>Dry</td>
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</table>

3. Results and discussion

3.1. CNT’s synthesis

Fig. 1 shows the results of structural analysis by TEM of multi walled CNT’s grown with nickel as catalyst (MWCNT’s). The outer diameter is about 85 nm and the internal diameter is circa 23 nm. The analysis of Fig. 1b shows that CNT’s have approximately 69 layers to each side of the nanotube; they are separated from each other approximately 0.34 nm (corresponding to the separation between graphene sheets in the graphite distance). Therefore, there is a Van der Waals-type force between the concentric tubes according to the definition of a multi walled carbon nanotube.

Fig. 2 shows SEM images of grown CNT’s with Ni catalyst after being purified. The high productivity obtained by applying nickel as catalyst can be qualitatively appreciated.

Fig. 3 shows the structural analysis by TEM of CNT’s grown with cobalt as catalyst. It can be seen that the number of

Fig. 1 – (a) TEM BF image showing an analysis of the diameter and (b) scheme profiles showing the number of layers of CNT’s grown from nickel.
layers is small (less than 10) in comparison with the CNT’s grown with nickel (69 layers). Fig. 3a shows CNT’s with only 4 layers and Fig. 3b presents one with 10 layers. For a 4-layer nanotube the inner diameter is about 6.5 nm and the outer diameter corresponds to 8 nm; for the 10-layer nanotube the outer diameter is 12 nm and inner diameter is 5 nm. It may also be noted that the nanotube is closed tip (Fig. 3b). Fig. 3c shows the analysis of two nanotubes grown under the same conditions as shown above. The outer diameters are between 27.22 and 42.12 nm and the inner diameters ranges from 9.16 to 9.5 nm.

3.2. Tribological tests

The results of the tests performed show that higher values of coefficient of friction (COF), ranging from 0.105 to 0.199, are obtained for water with CNT’s. In the case of oil with CNT’s the values of COF were between 0.063 and 0.076. The greater mass loss was measured after tests E11 (1.1 GPa, MWCNT’s, water) and E20 (1.1 GPa, no CNT’s, water), while the lowest mass loss was observed after E10 test (0.8 GPa, MWCNT’s, oil) as shown in Table 2.

Fig. 4 shows the variation of COF with the number of cycles during the tribological tests. Generally speaking, the effects of adding nanotubes to water or oil are opposite, since COF tends to reduce in tests with oil-CNT’s mixtures while it increases in tests with water-CNT’s mixtures.

Also, it can be seen that in the tests where CNT’s were added to the lubricant the time required to stabilize the COF after the lubricant is applied is shorter, usually below 1000 cycles (in tests with 5000 cycles total). In the tests where nanotube-free water was used the COF stabilized only after 5000 cycles (in tests with 9000 cycles total), and in tests run with nanotube-free oil the time needed for stabilization was even longer.

Fig. 5 shows the average COF measured in the stable zone after applying the lubricants to the contact interface (see Fig. 4). Fig. 5a shows the results for the condition of 1.1 GPa and 5% creepage for both oil and water, and Fig. 5b shows the results for the condition of 0.8 GPa and 5% creepage for both oil and water.

Comparing the tribological performance of the samples in all the tests where nanotubes were added to the lubricant it was found that the lowest values of COF are obtained when MWCNT’s at low concentration (0.01%) are added to oil, while the highest COF values arise when SWCNT’s with a concentration of 0.05% are added to water.

3.2.1. Wear resistance

Fig. 6a shows the results of mass loss measurements of the samples after the twin-disk tests with a contact stress of 1.1 GPa. The highest wear resistance of the samples was found in the condition where 0.01% SWCNT’s were added to the lubricant oil, while the worst condition occurred when 0.05% of MWCNT’s was added to water.
In the case of contact pressure of 0.8 GPa (Fig. 6b) the lowest mass loss was observed in the condition where 0.05% MWCNT’s were added to the oil, while the highest mass loss occurred when 0.01% of SWCNT’s was added to water.

### Surface damage

Fig. 7 shows representative images of the worn surfaces after different testing conditions. Some of the surfaces have a distinctive dark color due to the attachment of CNT’s, especially in samples from the tests E1, E9, E10, E11 and E16. All surfaces present signs of damage related to detachment of small particles, most likely due to rolling contact fatigue (RCF). In some cases, ratcheting marks are also visible with the naked eye. The analysis of the mass loss results indicated that the surfaces with substantial adhesion of CNT’s had less surface damage, and the best tribological performance was obtained when the interfacial media was composed of oil with SWCNT’s. The addition of MNCNT’s to oil was also beneficial, but its effect was clearer in the tests with lower contact pressure (0.8 GPa).

**Fig. 8** shows the aspect of worn surfaces observed in the SEM. Fig. 8a corresponds to a dry condition in which ratcheting can be identified; Fig. 8b–d shows surfaces tested with lubricants composed of either water or oil and nanotubes in areas where adherence of CNT’s was previously observed. It can be seen that the surfaces are smoother due to the deposition of solids provided by the lubricant although several ratcheting marks are still present due to the pre-cracking stage during the first 4000 cycles of the tests.

Several hypotheses have been raised to explain the positive effect that the addition of carbon nanotubes has on lubricants properties. First, as the elastic modulus of CNTs is very high,
**Fig. 5** – (a) Average friction coefficient at 1.1 GPa and (b) average friction coefficient at 0.8 GPa.

**Fig. 6** – (a) Total mass loss at 1.1 GPa and (b) total mass loss at 0.8 GPa.

**Fig. 7** – Aspect of the worn surfaces after disk-on-disk tests. ML, mass loss; SW, SWCNT’s; MW, MWCNT’s; O, oil; W, water; C, concentration of CNT’s.
the ability of the lubricant to avoid metallic contact between surfaces is improved, which leads to reduction of adhesive wear and friction coefficient. Also, if contact pressures are too high, it has been reported that CNTs can deform and adopt a lamellar shape, i.e. they act as a solid lubricant that forms a transfer layer onto the surfaces of the tribological pair [15,16]. While such a transfer layer was observed at the surface of the samples analyzed in this work, its detailed characterization falls beyond the scope of this particular study and will be addressed by the authors in future works. The role of the transfer film is to reduce the shear strength at the interface while maintaining the stiffness of the contact surfaces. In this study, the particular functionalization of the CNTs added to the lubricant may also have played an additional function as to improve adhesion between the lamellar solids and the metallic surfaces.

3.3. Viscometric tests

3.3.1. Effect of shear rate

Fig. 9 shows the viscosity as a function of shear rate for lubricant oils at 25 °C. It can be seen that the viscosity increases with the shear rate from the beginning of the tests up to the point where a shear rate of 30 s⁻¹ is reached. After that, all the samples tested showed a stable behavior. Generally speaking, the lubricants containing MWCNT’s showed slightly lower viscosity values at the end of the tests. The shear thickening observed for shear rates below 30 s⁻¹ is commonly

![Fig. 8 – SEM images of the tested surfaces.](image)

![Fig. 9 – Viscosity vs shear rate, 25 °C.](image)

![Fig. 10 – Viscosity–temperature curves.](image)
associated to rearrangements in the distribution of the CNT’s in the fluid [17].

3.3.2. **Effect of temperature**

Fig. 10 shows the variation of viscosity with temperature for all the lubricants studied. No significant effect of the addition of CNT’s is observed on the temperature behavior of the lubricant oil.

3.3.3. **Effect of time**

Fig. 11 shows the results of the tests performed for 600 s at 25 °C and constant shear rate, in which it can be observed that the viscosity was independent of time for all the samples analyzed.

4. **Conclusions**

In this study the tribological properties of CNT’s used as lubricant additives were investigated with the aid of a twin-disk testing machine. The friction coefficients and mass losses measured in the tests were consistently lower when the nanotubes were added to either oil or water, and friction coefficients as low as 0.063 were obtained.

The best tribological response of the pair evaluated (rail steel in contact with wheel steel) was obtained when MWCNT’s at a concentration of 0.01% was added to oil. When the lubricant used was water the friction coefficients were also low, but the tribological performance was better for a higher concentration of SWCNT’s (0.05%).

The viscometric results indicate that the concentrations of carbon nanotubes used led to changes in the response of the lubricants with the shear rate, especially for low speed tests. On the other hand, no effects of the addition of nanotubes on the response of the lubricants with temperature were observed.

The reduced coefficient of friction and high wear resistance may be related to the formation of an amorphous carbon film transferred from the CNT’s. The dark-colored aspect of the surfaces supports this hypothesis but more studies on the chemistry of the worn surfaces are needed to disclose the actual mechanisms of enhancing the tribological properties of the tribo-system.

**Conflicts of interest**

The authors declare no conflicts of interest.

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**REFERENCES**


