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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 paper the tribological properties of CNTs (SWCNTs and MWCNTs) when used as lubricant additives are studied under rolling-sliding conditions in a twin-disc testing machine. The tests were performed using 5% of creepage and pressures of 0.8 GPa and 1.1 GPa. Used functionalized nanotubes were modified with carboxylic acid ultrasonically dispersed at different concentrations (0.01, 0.05%). 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).
Keywords: Carbon nanotubes; Lubricant oil and water wear; Friction coefficient.

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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 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 [1]. Nanoparticles as lubricant additives have attracted considerable attention in recent years due to their excellent mechanical and chemical properties, and anti-wear properties as well. It has been reported that the extreme-pressure properties and load carrying capacity were enhanced and friction coefficients tend to decrease with the addition of nanoparticles to oil [2-3]. 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 are used as reinforcements for metals and ceramics such as Cu [7], Ni [8] and Al_2O_3 [9], or as reinforcements in polymeric materials such as polymethyl methacrylate (PMMA) [10], ultrahigh molecular weight polyethylene (UHMWPE) [11], polyamide 6 (PA6) [12], among others.
In this paper the tribological properties of CNT's (SWCNT's [Single Walled Carbon Nanotubes] and MWCNT's [Multi Walled Carbon Nanotubes]) when used as additives for oil and water are 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. Used functionalized CNTs were prepared by chemical modification (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 for the growth 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 used were nickel for the production of MWCNT's and cobalt for SWCNT's and the gas mixture was composed of 80 cm^3/min nitrogen, 20 cm^3/min acetylene and 15 ml/min hydrogen. The processing sequence included reduction time 20 min, acetylene time 30 min and cooling time 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 Matthew W. Marshall et al, who proposed a simple procedure for functionalizing carbon nanotubes in carboxylic acid [13]. 2 mg per nanotube of a solution composed of 3:1 (V/V) HNO_3 and HCl was used and the CNT’s were subjected to ultrasonic agitation for 20 minutes in water at 20˚C using ice to control temperature. Afterwards, the CNT’s

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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 (300 rpm) and ultrasonic agitation during 1 min.

2.4 Tribological Tests

The tests to measure wear and coefficient of friction were performed by using a disc-on-disc 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 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 Medellin). The chemical composition measured by Optical Emission Spectroscopy and mechanical properties of the rail and wheel are within the ranges established by European standards EN 13674-1:2011 [14] and EN 13262:2004 [15]. The “wheel” specimens were extracted from different sections of the tread area of a commercial wheel provided by Metro de Medellin, and they were heat treated to obtain homogeneous hardness in all the contact surface within the range 245-275HB, as required in EN 13262:2004 standard.
All the laboratory tests were performed with a creepage of 5% and the contact pressure used was either 0.8 GPa or 1.1GPa. 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 10000 cycles with no interruption of the test whatsoever. Before starting each test the samples were ultrasonically cleaned in alcohol during 5 minutes, 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.

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Table 1. Description of tests

Nomenclature test	Conditions			
	Tribological pressure test 5% (GPa)	Type CNT´s	Lubricant	Concentration of CNT's (%)
E1	1.1	Ni	Oil	0.01
E2	0.8	Ni	Oil	0.01
E3	1.1	Ni	Water	0.01
E4	0.8	Ni	Water	0.01
E5	1.1	Co	Oil	0.01
E6	0.8	Co	Oil	0.01
E7	1.1	Co	Water	0.01
E8	0.8	Co	Water	0.01
E9	1.1	Ni	Oil	0.05
E10	0.8	Ni	Oil	0.05
E11	1.1	Ni	Water	0.05
E12	0.8	Ni	Water	0.05
E13	1.1	Co	Oil	0.05
E14	0.8	Co	Oil	0.05
E15	1.1	Co	Water	0.05
E16	0.8	Co	Water	0.05
E17	1.1	Ni	Oil	0.10
E18	1.1	without additive	Oil	0.00
E19	0.8	without additive	Oil	0.00
E20	1.1	without additive	Water	0.00
E21	0.8	without additive	Water	0.00
E22	1.1	without additive	Dry	0.00
E23	0.8	without additive	Dry	0.00

3 RESULTS AND DISCUSSION

3.1 CNT Synthesis

Figure 1 shows the results of structural analysis by TEM of CNT's grown with nickel as catalyst (MWCNT's). The outer diameter is about 85nm, whereas the internal diameter is circa 23nm. The analysis of Figure 1b shows that CNT's have approximately 69 layers to each side of the nanotube; they are separated from each other approximately 0.34nm (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-wall nanotube.

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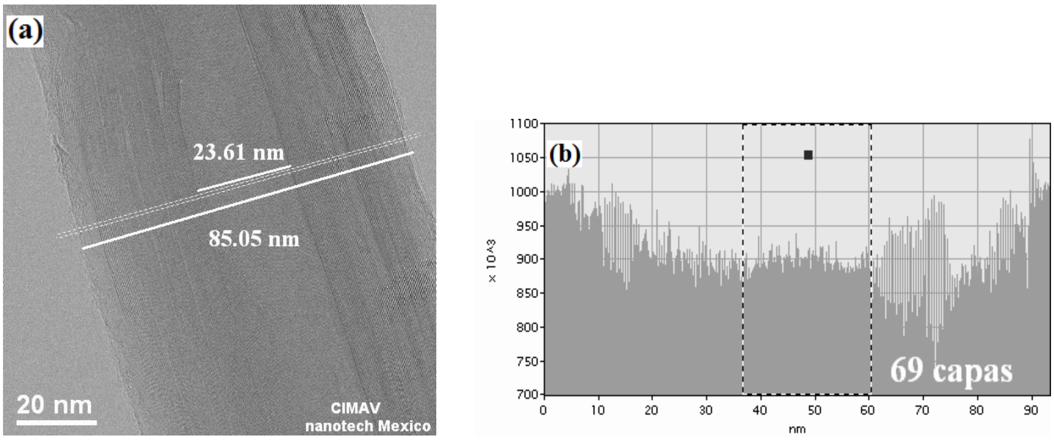

Figure 1. (a) TEM image showing an analysis of the diameter and (b) scheme profiles showing the number of layers of CNT´s grown from nickel.

Figure 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.

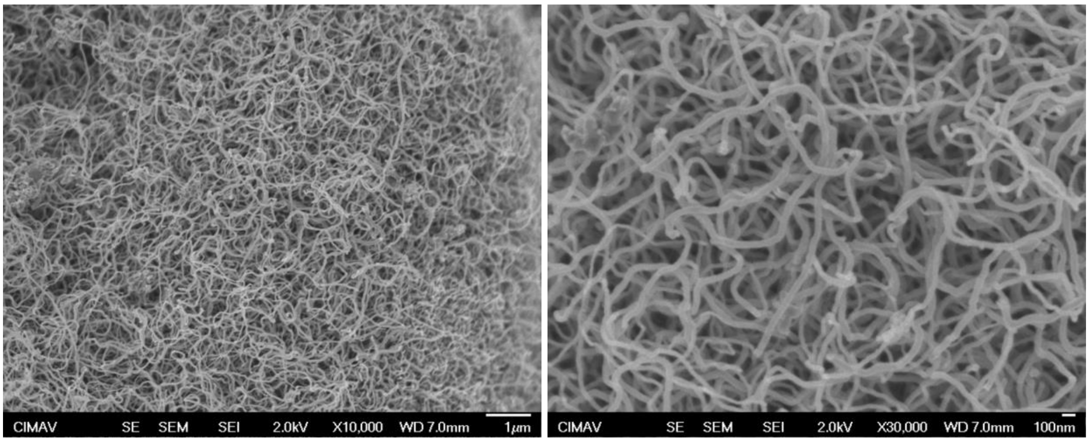

Figure 2. SEM image of grown CNT´s with Ni catalyst after being purified

Figure 3 shows the structural analysis by TEM of CNT's grown with cobalt as catalyst. It can be seen that the number of layers is small (less than 10) in comparison with the CNT's grown by applying nickel (69 layers). Figure 3a shows CNT's with only 4 layers and Figure 3b presents one with 10 layers. For 4-layer nanotube inner diameter is about 6.5nm and the outer diameter corresponds to 8nm; for the 10-layer nanotube the outer diameter is 12nm and inner diameter 5nm. It may also be noted that the nanotube is closed tip (Figure 3b). Figure 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.

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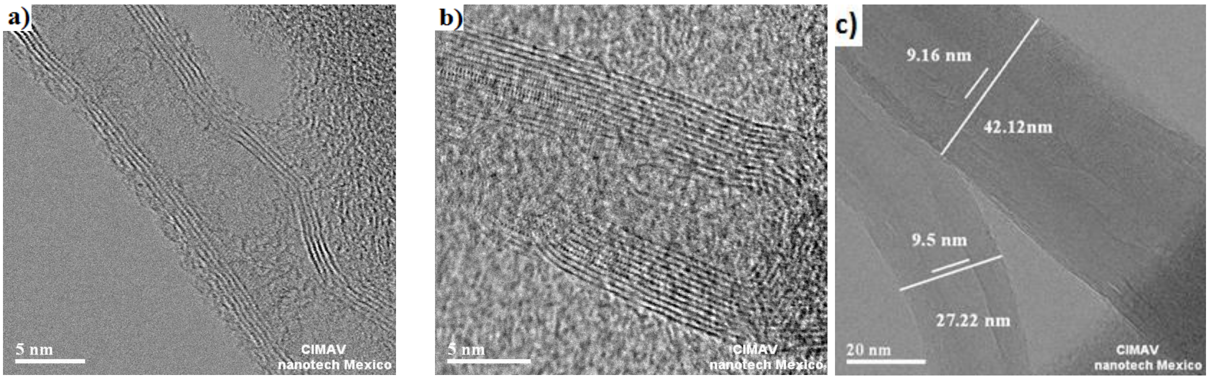

Figure 3. TEM images in which the number of layers of nanotubes grown from Co catalyst as shown, (a) nanotube with 4 layers, (b) nanotube with 10 layers. c) TEM image showing 2 nanotubes with different sizes.

3.2 Tribological Tests

The tests performed show that higher 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 (1.1GPa, MWCNT's, Water, creepage 5%) and E20 (1.1GPa, no CNT's, Water), while the lower mass loss was observed after E10 test (0.8GPa, MWCNT's, Oil 5% creepage) as shown in Table 2.

Table 2. Summary of results of COF and mass loss after disc-on-disc tests.

Test	Condition: **pressure (GPa)**, **Type CNT´s (SWCNT´s, MWCNT´s)**, **Lubricant (O: Oil, W: Water, D: Dry)**, **CNT's concentration (%)**	Coefficient of friction		Mass loss (g)		
		value	deviation	Rail	Wheel	Total
E1	1.1, MW, O, 0.01	0,063	0,003	0,236	0,162	0,397
E2	0.8, MW, O, 0.01	0,069	0,002	0,093	0,128	0,221
E3	1.1, MW, W, 0.01	0,197	0,004	0,470	0,107	0,577
E4	0.8, MW, W, 0.01	0,182	0,005	0,072	0,188	0,260
E5	1.1, SW, O, 0.01	0,066	0,002	0,264	0,165	0,429
E6	**0.8, SW, O, 0.01**	**0,070**	**0,001**	**0,073**	**0,124**	**0,197**
E7	1.1, SW, W, 0.01	0,148	0,005	0,416	0,165	0,581
E8	0.8, SW, W, 0.01	0,182	0,003	0,189	0,141	0,330
E9	1.1, MW, O, 0.05	0,066	0,005	0,283	0,156	0,439
E10	**0.8, MW, O, 0.05**	**0,076**	**0,002**	**0,074**	**0,081**	**0,155**
E11	**1.1, MW, W, 0.05**	**0,194**	**0,002**	**0,696**	**0,141**	**0,837**
E12	0.8, MW, W, 0.05	0,199	0,010	0,170	0,122	0,292
E13	1.1, SW, O, 0.05	0,067	0,003	0,284	0,128	0,412
E14	0.8, SW, O, 0.05	0,076	0,002	0,082	0,125	0,208
E15	1.1, SW, W, 0.05	0,105	0,016	0,366	0,126	0,492
E16	0.8, SW, W, 0.05	0,108	0,008	0,109	0,159	0,268
E17	1.1, MW, O, 0.10	0,074	0,003	0,296	0,119	0,416
E18	1.1, O	0,070	0,003	0,318	0,207	0,525
E19	0.8, O	0,082	0,002	0,256	0,054	0,309
E20	**1.1, W**	**0,129**	**0,006**	**0,688**	**0,183**	**0,872**
E21	0.8, W	0,206	0,008	0,239	0,162	0,401
E22	1.1, D	0,491	0,009	0,087	0,327	0,414
E23	0.8, D	0,593	0,007	0,068	0,123	0,191

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3.2.1 Coefficient of friction

Figure 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 (5000 cycles total). In the tests where nanotube-free water was used the COF stabilized only after 5000 cycles (9000 cycles total), and in tests run with nanotube-free oil the time needed for stabilization was even longer.

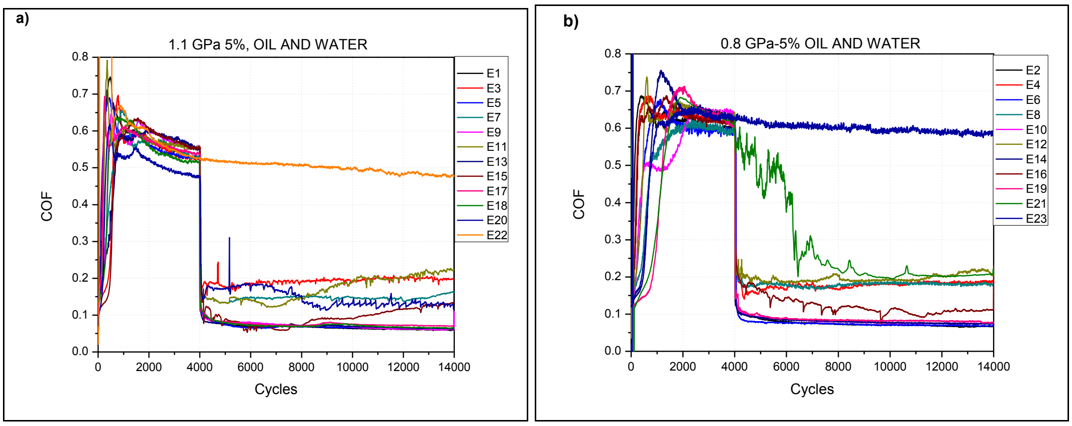

Figure 4. (a) Friction coefficients at 1.1GPa, (b) Friction coefficients at 0.8GPa

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

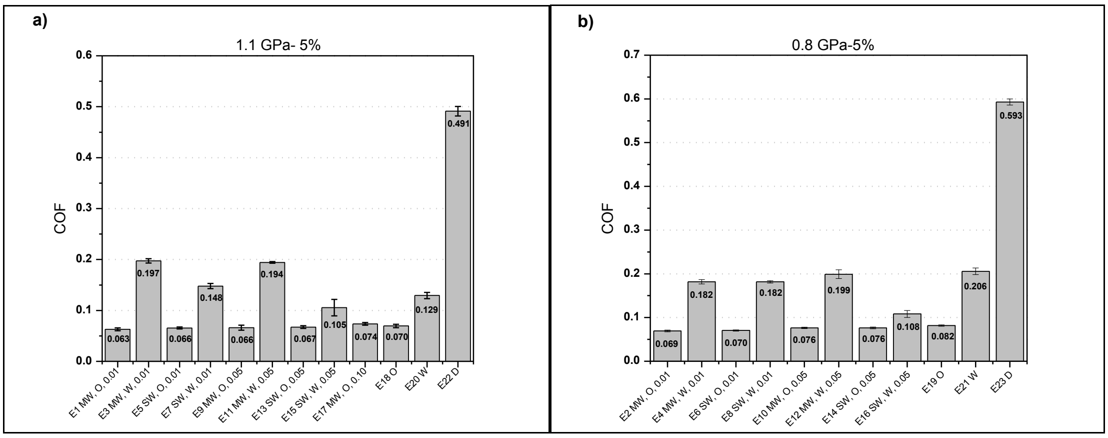

Figure 5. (a) Average friction coefficient at 1.1GPa, (b) Average friction coefficient at 0.8GPa.

3.2.2 Wear

Figure 6a shows the results of mass loss of the samples after the disc-on-disc tests with a contact stress of 1.1GPa. The best wear resistance of the samples was found

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in the condition where 0.01% SWCNT's were added to the lubricant oil, while the highest mass loss occurred when 0.05% of MWCNT's was added to water.
In the case of contact pressure of 0.8GPa (Figure 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.

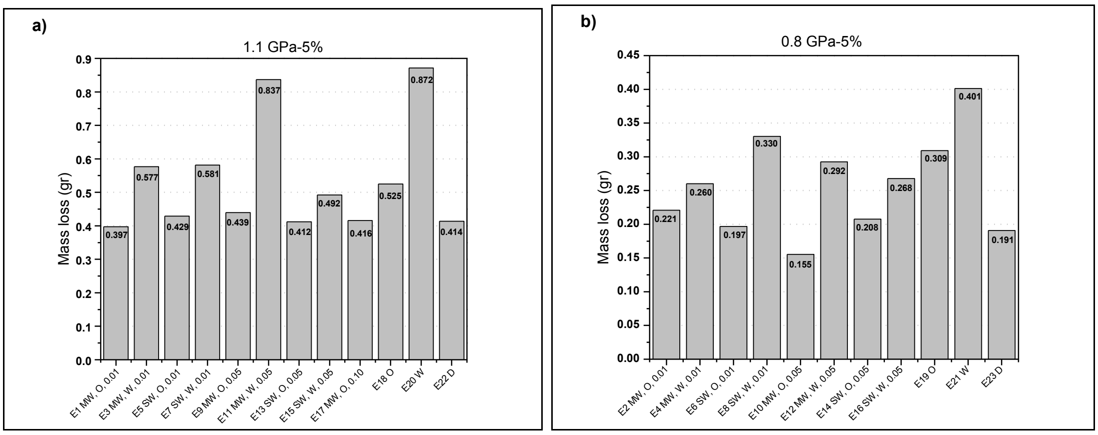


Figure 6. (a) Total mass loss at 1.1GPa (b) Total mass loss at 0.8GPa

3.2.3 Surface damage

Figure 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) and in some cases ratchetting 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 more clear in the tests with lower contact pressure (0.8GPa).

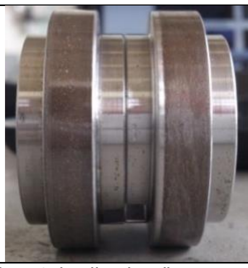
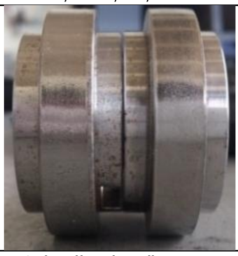
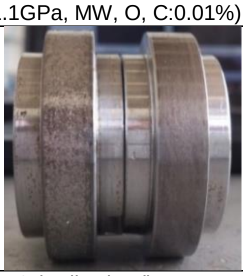
			
a) E12 (Rail-Wheel) COF: 0,199. ML: 0,292g (0.8GPa, MW, W, C:0.05%)	**b)** E1 (Rail-Wheel) COF: 0.063, ML: 0.397g (1.1GPa, MW, O, C:0.01%)	**c)** E10 (Rail-Wheel) COF: 0.076, ML: 0.155g (0.8GPa, MW, O, C:0.05%)	**d)** E11 (Rail-Wheel) COF: 0,194, ML: 0.837g (1.1GPa, MW, W, C: 0.05%)
			
e) E3 (Rail-Wheel) COF: 0.197, ML: 0.577 (1.1GPa, MW, W, C: 0.01%)	**f)** E9 (Rail-Wheel) COF: 0.066, ML: 0.439g (1.1GPa, MW, O, C:0.05%)	**g)** E16 (Rail-Wheel) COF: 0.108, ML: 0.268g (0.8GPa, SW, W, C: 0.05%)	**h)** E7 (Riel-Wheel) COF: 0.148, ML: 0.581g (1.1GPa, SW, W, C: 0.01%)

Figure 3. Aspect of the worn surfaces after disc-on-disc tests. ML: mass loss, SW:SWCNT's, MW:MWCNT's, O:Oil, W: Water, C: concentration of CNT's.

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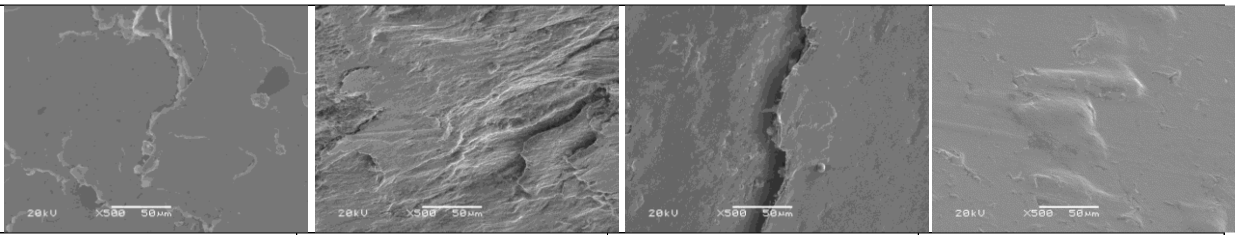
Figure 8 shows the aspect of worn surfaces observed in the SEM. Figure 8a corresponds to a dry condition in which ratchetting can be identified; Figures 8b to show surfaces tested with lubricants composed of either water or oil and nanotubes in areas where adherence of CNT's was previously observed.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



a) E23	b) E16	c) E11	d) E1

Figure 4. SEM images of the tested surfaces.

4 CONCLUSIONS

In this study the tribological properties of CNT's used as lubricating additives were investigated with the aid of a disc-on-disc 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 values as low as 0.063 for COF 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 COF were also low, but the tribological performance was better for higher concentration of SWCNT's (0.05%).
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 tribosystem.

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