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EFFECT OF FUNCTIONALIZATION OF SINGLE WALLED CARBON NANOTUBES ON ANTIWEAR PROPERTIES OF A MINERAL BASE OIL

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In this work, single walled carbon nanotubes (SWNT) were synthesized by chemical carbon vapor deposition (CCVD) method and then were carboxylic acid sidewall functionalized (SWNT_f) in order to investigate their tribological behaviors as antiwear additives for mineral base oil (SAE 20). The functional SWNT were examined by TG, UV-vis, RAMAN spectroscopy and X-Ray diffraction. Furthermore, SWNT and functional SWNT were dispersed in a mineral oil by ultrasonication and the tribological behavior of additivated mineral oil was scrutinize by high frequency reciprocating rig (HFRR) test, while the wear tests were run on a Pin on Disk CSM tribometer. The results show that by functionalization of SWNT was improved the hydrophilicity of carbon nanotubes, thereby functional SWNT being able to create more stable bonds on the metallic surface, being a more efficient antiwear additive rather than non functionalized SWNT. Moreover it was found that due to the coverage with functional groups, the stability of the suspension is high and did not precipitate even after few months.

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1. Introduction

Since their discovery in 1991 by Iijima [1], carbon nanotubes have been widely explored in different applications that reveal interesting tribological potential for numerous investigations. It was found that carbon nanotubes possess excellent mechanical properties such as high elastic modulus and high tensile strength [2, 3]. Moreover, special physical and chemical properties of the single wall carbon nanotubes, have made them very attractive for tribological applications, in few studies were found to improve wear resistance of lubricants and provided excellent extreme pressure properties, low friction and minimal deformation [4, 5].

In the last years, there is a strong tendency to replace the classic antiwear and extreme pressure additives bases on phosphorus and sulfur- sulfur and nitrogen-, chlorine- compounds with more environmentally friendly additives. In few papers was reported that addition of carbon nanotubes, with single and multiple walls, is effective in reducing wear and friction, due to their ability to slide and roll during the sliding contact. Moreover, carbon nanotubes could serve as spacer, which eliminate metal to metal contact between the asperities of the two linked surfaces [6-8].

In our previous study we have found that by dispersing small quantities of single walled carbon nanotubes in base oil, its mechanical and tribological properties can be improved tremendously [9]. Unfortunately, the major drawback of this application was the dispersibility of the nanocarbonaceous material into mineral oil. After a certain period since dispersion of carbon nanowalls into different environments (i.e. water, oils or solvents), the carbonaceous material tends to agglomerate because its high surface area and high length/diameter ratio. Therefore, in order to increase their applicability, it is essential to achieve good dispersion of carbon nanotubes.

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In few papers, it is claim that is possible to increase the dispersibility of carbon nanotubes by using ionic liquids [10, 11]. In other studies, the stability of the suspension was improved by decoration of carbon nanotubes walls with functional groups (O-H, C=O, COOH). By this procedure, carbon nanotubes functionalized with carboxyl group have negative charges and keep the solution dispersed [12].

In our paper we report preliminary results on tribological properties of SWNT in a mixture with a mineral base oil, in boundary lubrication regime. The aim of this work is to examine the effect of functionalization of SWNT walls with carboxyl group, on its tribological properties, as well as on stability of the suspension.

2. Materials and experimental methods

The experimental study was focused on synthesis, characterization and functionalization of SWNT while the second part of this study was focused on characterization of base oil and on tribological investigation of mineral base oil additivated with SWNT and functional SWNT.

2.1. Materials

SWNTs were synthesized "in house" by Catalytic Chemical Vapor Deposition (CCVD), using Co-MCM-41 as precursor. All materials used for Co-MCM-41 synthesis, as well as for synthesis and purification of SWNT were supplied by Aldrich.

The base oil used for tribological investigations was purchased from Petrotel-Lukoil Refinery Romania.

2.2. Characterization

The presence of SWNT was evidence by RAMAN spectroscopy by using a Thermo Scientific Raman Spectrometer DXR Series. The RAMAN spectrum was recorded using one excitation laser wavelengths 633 nm with a maximum laser power of 14mW.

The thermogravimetric (TG) curves were registered on a thermogravimetric analyzer (Setaram LABSYS evo), under argon atmosphere using a heating rate of 10 ^{o}C/min from room temperature to 900 ^{o}C.

The functionalization of SWNT can be confirmed by UV-Vis spectroscopy. UV-Visible spectra were recorded on a JASCO 540 V spectrophotometer, using 1:1000000 (v/v) dilution ratio in dimethylformamide (DMF). All spectra were recorded in ultraviolet domain (UV=200-900 nm).

The XRD measurements before and after functionalization were conducted using a Bruker D8 instrument (λ=0.154 nm, 40 kV and 40 mA) with CuKα X-Ray, at a scanning rate of 2 ^{o}/min and were explored in 2-theta range of 10-70°. The current was 40 mA and the voltage used was 40 kV.

Tribological tests: The wear rate resulting after friction of mineral base oil and mineral base oil additivated with SWNT and SWNT_f was investigated on Pin on Disk tribometer. The Pin on Disk test consists in friction of a 100Cr6 steel ball against a 41MoCr4-2 steel disk in the presence of 10 ± 0.2 ml lubricant at, 4 N load and 0.15 m/s sliding speed. Steel ball with 6 mm diameter, roughness of Ra=0.060 µm and hardness of RC 60-62 were used. The disks with 30 mm diameter used for all experiments had roughness of Ra=0.020µm and a hardness of RC 25-27. The relative humidity was 30%, while the ambient temperature was between 20-24°C.

High Frequency Reciprocating Rig (HFRR) test is used to establish the lubricating ability of the lubricant. HFRR test consist in friction of an AISI-E 52100/535A99 steel ball (with a roughness of Ra=0.050 μm and a hardness of RC 58-66) against an AISI-E 52100/535A99 disk (with 10 mm diameter and a roughness of Ra=0.020 μm and a hardness of RC 76-79) in the presence of 2 ± 0.2 ml lubricant at a frequency of 50 ± 1 Hz, 1000 um stroke, 1000 ± 1 g load and 60 ± 2°C, (according to ASTM D-6079). The relative humidity was kept between 40 and 60%, while the ambient temperature was between 24 and 26°C. HFRR investigations were used to determinate the friction coefficient and the wear scar diameter scar imprinted on the steel ball. High dimension of the wear scar diameter means poor lubricating properties of lubricant.

2.3. Synthesis of SWNT by CCVD method

SWNTs were synthesized by CO disproportionation by using Co-MCM-41 (with 3 wt. % Co loading) as catalyst, following a method described elsewhere [9]. Prior utilization, SWNT were purified by hydrothermal treatment, in order to remove the silica source of the catalyst, amorphous carbon and metal particles. Detailed description of the SWNT synthesis and purification methods can be found in our previous studies [9, 13].

2.4. Functionalization of SWNT

SWNT were functionalized according to a method described elsewhere [14-16]. The method used to obtain functional SWNT consists in oxidizing of SWNT. Anchoring of carboxylic group to the carbon nanotubes walls was realized by oxidizing of ≈ 100 mg of SWNT with a mixture of H_2SO_4 and HNO_3 (3:1 vol) by treating the mixture in a ultrasonic bath for 30 min and refluxing at 80 ^oC for 60 minutes. Then, the mixture was vacuum filtered by using a PTFE membrane and washed with distillated water until the pH of filtrate was neutral. By this procedure were created carboxylic defects in their structure, as represented in figure 1. Finally, the filter cake was dried in air at 110 ^oC for 24 h, resulting SWNT-COOH.

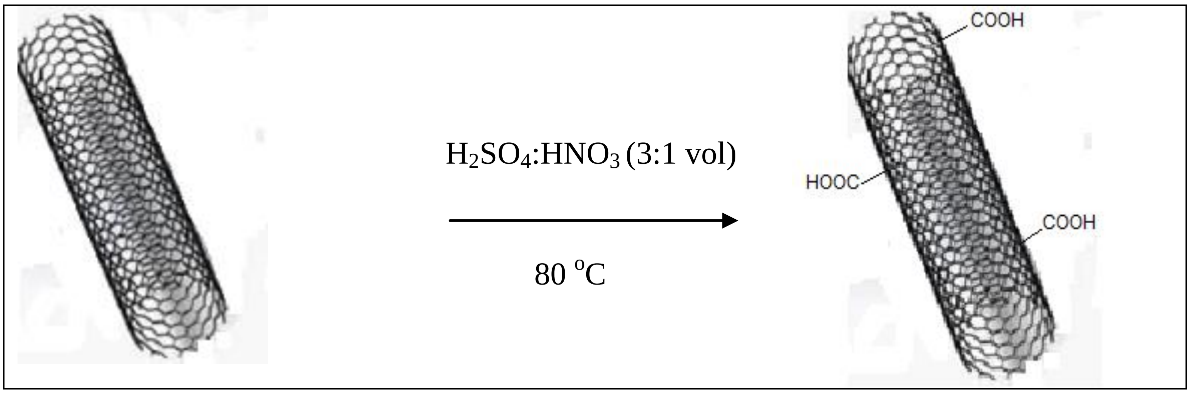


Fig.1.Functionalization procedure of SWNT

2.5. Base oil

In order to formulate a lubricant for metalworking fluids or gearboxes we selected as mineral base oil SAE 20. The physical characteristics of base oil are described in table 1.

Table 1. Physical-chemical properties of mineral base oil (SAE 20)

Properties	SAE 20	Methods
Density (20°C, kg/m^3)	882	ASTM D-1298
Kinematic viscosity (40°C, cSt)	31.86	ASTM D-445
Kinematic viscosity (100°C, cSt)	5.85	ASTM D-445
Visosity index	129	ASTM D-2270
Flash point (°C)	>210	ASTM D-92
Pour point, (°C)	-14	ASTM D-97
Copper corrosion (at 100°C)	1a	ASTM D-130
Acid value (mgKOH/g)	0.12	ASTM D-974

3. Results and Discussion

3.1. SWNT and functionalized SWNT characterization

The synthesized SWNT, before and after functionalization, were characterized by multiple excitation wavelength Raman. The Raman spectra collected at 633 nm laser energy for the Co-MCM-41 sample containing 3 wt.% Co after SWNT growth are given in figure 2.

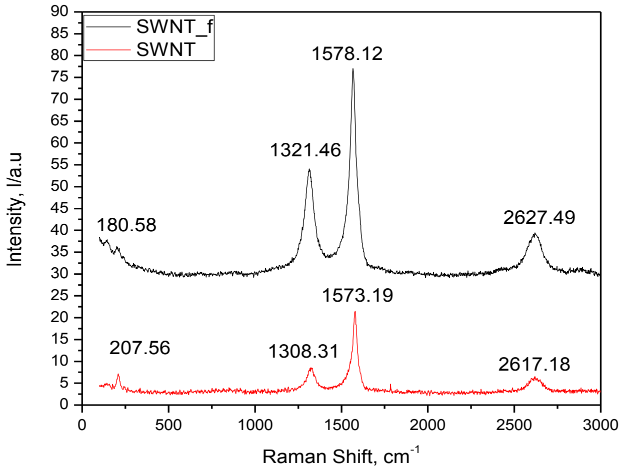


Fig.2. Raman shift recorded after SWNT growth (at 633 nm wavelength)

Raman spectrum of SWNT shows three features: The Radial Breathing Mode (RBM) below 300 cm^{-1} characteristic for SWNT, the Disorder-induced band (D-band) around 1300 cm^{-1} assigned to defective and disordered carbon species and the Graphite-like band (G-band) around 1550-1600 cm^{-1} which is characteristic for ordered carbon species such as carbon nanotubes and graphite. The presence of the characteristic features for the RBM around 160-220 cm^{-1} and the peak centered at 1590 cm^{-1} indicate the presence of SWNT. Another significant peak is that around 1300-1350 cm^{-1} (D-band) corresponding to the disorder mode introduced the sp3-hybridized carbon in the hexagonal framework of the nanotubes walls. In table 2 are presented Raman data for G and D peaks of SWNT and functionalized SWNT.

Table 2. Raman data for G and D peaks of SWNT and SWNT_f

Sample	**I_G**	**X_G (cm^{-1})**	**I_D**	**X_D (cm^{-1})**	**I_G/I_D**
SWNT	21.46	1573.19	7.98	1308.31	2.69
SWNT_f	77.59	1578.12	53.64	1321.46	1.45

The low intensity of the D band centered at 1308cm^{-1} for SWNT and 1321 cm^{-1}, for functional SWNT coupled with a supra unitary purity index (I_G/I_D) for the SWNT evidence good selectivity for SWNT synthesized and could give significant information about functionalization of SWNT. As it was expected, after oxidation process, the I_G/I_D ratio decreases from 2.69 calculated for SWNT to 1.45 for functional SWNT and the RBM is suppressed and shifted to 180 cm^{-1} by the anchoring of the carboxyl group. Raman spectra reveal a significant increasing of the D band intensity of the functional SWNT showing the presence of the scattering defects on the sidewalls of the nanotubes, attributed to functionalization process. Moreover, the maximum of G band was shifted at higher frequency for SWNT_f with about 5 cm^{-1}. A change of sp^2-hybridized carbons into sp^3-hybridized carbons revealed by Raman, is an indicator of an efficient anchoring of covalently bound to the SWNT framework.

By UV-Vis spectroscopy we determine the quantitative measurement of functionalization of SWNT. The UV-Vis spectra are presented in figure 3.

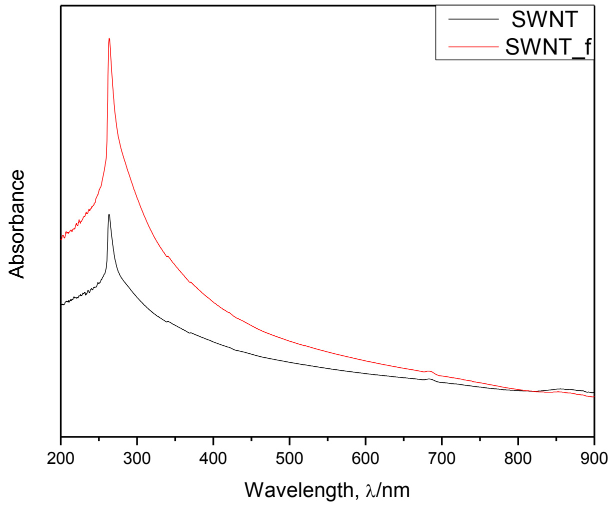


Fig.3. UV-vis spectra for SWNT and SWNT_f

UV-Vis spectra for both samples show a characteristic peak at 262 nm, which can be related to $\pi - \pi^*$ transitions due to π electrons of the double bond in the SWNT. It is also evident a complete loss of the van Hoff singularities, related to covalent modification of SWNT due to functionalization. By functionalization of SWNT, we bring into their structure sp^3-hybridized carbon atoms that disrupted the π-network of the sp^2-hybridized nanotubes, which confirmed successful modification of SWNT [17].

Fig. 4 shows the XRD profiles of the single walled carbon nanotubes before and after functionalization.

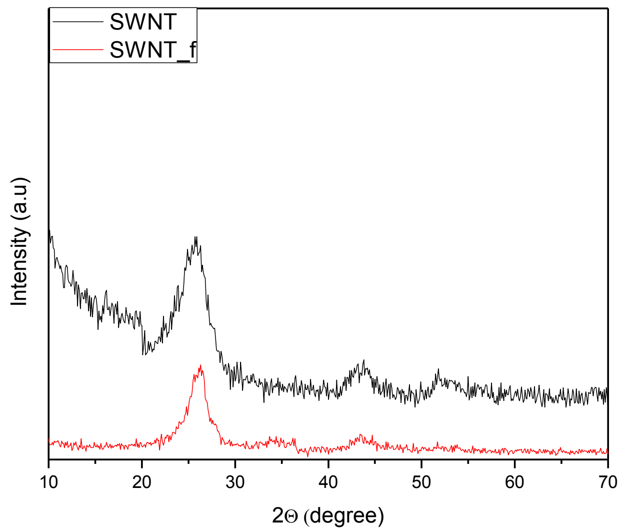


Fig.4. XRD profile for SWNT before and after functionalization

From XRD profile can be found that both samples have similar structure to that of the graphite crystal, with the main peak at 2θ value of 25.7^o for SWNT and 26.6^o for functional SWNT, which indicates that during the functionalization process the bulk structure of nanotubes does not change.

Thermal gravimetric analysis (TG) was used to estimate the degree of functionalization. TG images are presented in figure 5. TG curves indicate that the percentage weight loss of SWNT during the process is about 1 wt. % and could be caused by degassing while for functional SWNT is about 5 wt. % and this could be correlated to the decomposition of the functional groups.

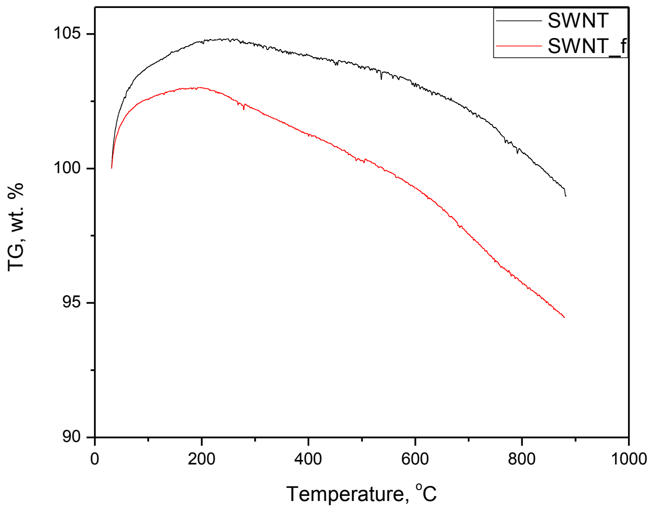
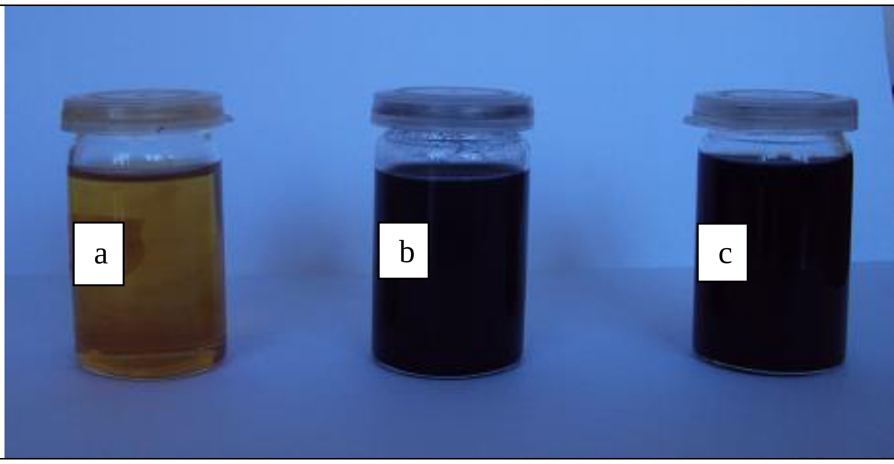


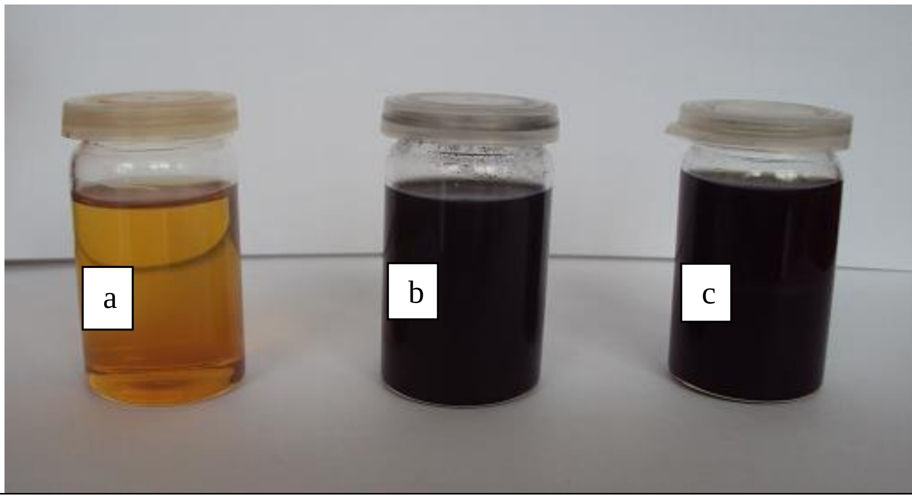
Fig.5. Thermogravimetric analysis in argon of SWNT and SWNT_f

3.2. Stability of the suspension

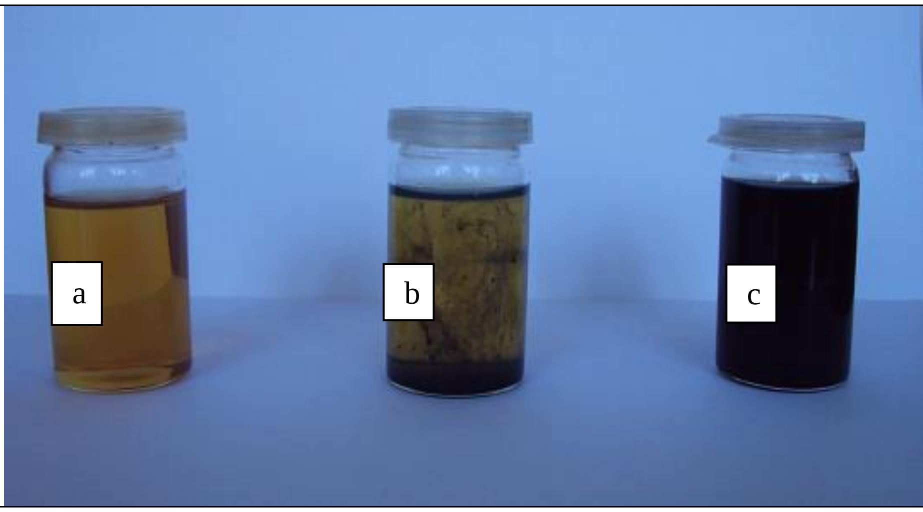
Prior utilization in tribological investigation, 1 wt.% SWNT and 1 wt.% functional SWNT samples were dispersed by ultrasonication in mineral base oil and was examined the stability of the suspension, in time (after 24 and 336 hours). The images of these suspensions are presented in figure 6.



Initial (after ultrasonication)



After 24 h



After 336 h

Fig.6. Stability of the suspension in time for (a) SAE 20, (b) SAE 20 + 1wt% SWNT, (c) SAE 20 + 1wt% SWNT_f

From these images it is obvious that by functionalization of single walled carbon nanotubes it is possible to increase the solubility of the carbon nanotubes, those being easily dispersed in mineral oil and the suspension remains stable in time, for about 336 hours.

3.3. Friction and wear behavior of base oil additivated with SWNT and functional SWNT

Figure 7 shows the evolution of the friction coefficient for the non additivated oil and for the oil additivated with 1 wt%. SWNT or 1wt% functionalized SWNT during 1 hour HFRR test, for 10 N loading and 180 000 cycles.

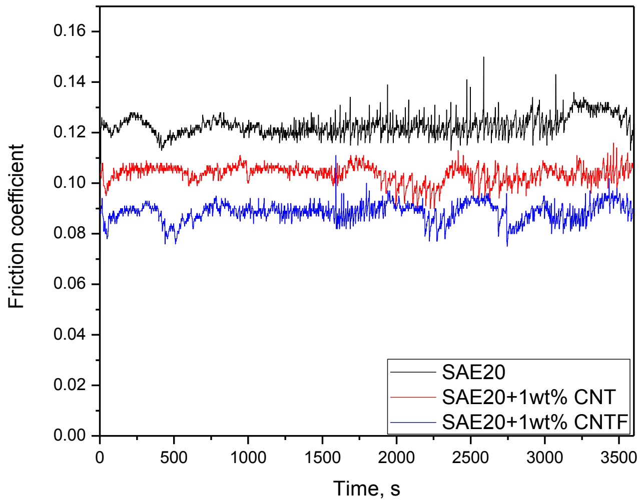


Fig.7. Effect of SWNT functionalization on friction coefficient during the HFRR tests

For all three samples, in these severe operating conditions, is produced a stable friction coefficient, throughout during the 180 000 cycles. Addition of carbon nanoparticles is favorable because reveal superior friction reduction abilities, utilization of SWNT and SWNT_f produce a decreasing of the friction coefficient with about 17% and 32% respectively, when compared to friction coefficient recorded for non additivated oil.

However, HFRR investigation gave also information about wear scar diameter imprinted on the steel ball during tests and the average lubricant film thickness. These two parameters provide useful information about the quality of the lubricant; lubricants with superior lubrications properties are able to maintain the film thickness even in severe operation condition. The values of these parameters for all three samples are depicted in table 3.

Table 3. Wear scar diameter and lubricant film thickness according to HFRR tests

Sample	**WS 1.4, μm**	**Film thickness, %**
SAE 20	299.5	56
SAE 20 + 1wt% SWNT	292.0	51
SAE 20 + 1wt% SWNT_f	275.0	48

There are not significant differences between the wear scar diameters of the samples with or without nanotubes, thus for the wear rate investigations we are not expecting major modification as result of additivation. Instead, special attention should be given to the lubricant thickness. The average value of the lubricant thickness is low, most certainly because of the severe experimental condition, but is still above the minimum permissible, as long as it remains constant throughout the tests.

In table 4 are presented the results obtained after investigations on microtribometer.

Table 4. Wear rate on ball and disk according to microtribometer tests

Sample	Max. Hertzian Pressure [GPa]	Wear rate on ball [mm^3/N/m]	Wear rate on disk [mm^3/N/m]
SAE 20	1.038	6.210E-009	3.030E-006
SAE 20 + 1wt% SWNT		6.010E-009	3.001E-006
SAE 20 + 1wt% SWNT_f		5.880E-009	2.862E-006

The highest wear rates were obtained for non additivated mineral oil while the lowest was observed for mineral oil additivated with functional SWNT. Both carbonaceous materials reduce friction and wear and could be effective antiwear additives for mineral base oils.

4. Conclusions

Single walled carbon nanotubes were tested as potential antiwear additive for a mineral base oil. In order to improve the dispersibility of carbon nanotubes and the stability of the suspension, the walls of single walled carbon nanotubes were decorated with carboxylic groups. It was found that dispersion of SWNT in mineral base oil is beneficial because decreases the friction coefficient and wear rate when compared to the results observed for non additivated base oil. We successfully improved the stability of suspension by functionalization of SWNT.

SWNT_f, are contributing to the reduction of the friction, being potential antiwear additives for lubricating oils.

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References

[1] S. Iijima, Nature **354**, 56 (1991)
[2] J.P. Salvetat, J.M. Bonard, N.H. Thomson, A.J. Kulik, L. Forró, W. Benoit, Appl Phys A **69,** 255 (1999)
[3] E. Dervishi E, Z.Y. Li, Y. Xu, V. Saini, A.R. Biris, D. Lupu, et al., Particul Sci Technol **27**, 107 (2009)
[4] J.R. Vail, D.L. Burris, W.G. Sawyer, Wear **267**, 619 (2009)
[5] M. Valcarcel, S. Cardenas, B.M. Simonet, Trends in Analytical Chemistry, **21** (3) 187 (2002)
[6] D.L. Cursaru, I. Ramadan, C. Tanasescu, R. Rîpeanu, Digest Journal of Nanomaterials and Biostructures **8** (2), 805 (2013)
[7] L. Joly-Pottuz, F. Dassenoy, B. Vacher, J.M. Martin, T. Mieno, Tribology International **37**, 1013 (2004)
[8] Y.Y. Wu, W.C. Tsui, T.C. Liu, Wear **262**, 819 (20107)
[9] D.L. Cursaru, C. Andronescu, C. Pîrvu, R. Rîpeanu, Wear **290-291**, 133 (2012)
[10] B. Yu, Z. Liu, F. Zhou, W. Liu, Y. Liang, Material Letters **62**, 2967 (2008)
[11] H.B. Kim, J.S. Choi, S.T. Lim, H.J. Choi, H.S. Kim, Synthetic Metals **154**, 189 (2005)
[12] C.Y. Chen, M.J. Fu, C.Y. Tsai, F.H. Lin, K.Y. Chen, Journal of Magnetism and Magnetic Materials **367**, 47 (2014)

[13] D.L. Cursaru, D. Enescu, D. Ciuparu, Revista de Chimie **62** (8), 792 (2011)
[14] C.M. Damian, S.A. Garea, E. Vasile, H. Iovu, Composites Part B **43**, 3507 (2012)
[15] X.H. Men, Z.Z. Zhang, H.J. Song, K. Wang, W. Jiang, Composites Science and Technology **68**, 1042 (2008)
[16] J. Chen, Q. Chen, Q. Ma, Journal of Colloid and Interface Science **370**, 32 (2012)
[17] N.A. Mirza, J.Y. Xie, Y.H. Ma, W.T. Yang, New Carbon Materials **25** (2), 134 (2010)