STUDY OF THE TRIBOLOGICAL BEHAVIOR OF DIFFERENT CARBONACEOUS NANOMATERIALS SUCH AS ANTIWEAR ADDITIVES FOR AN ENVIRONMENTALLY FRIENDLY LUBRICANT

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The tribological behavior of different carbonaceous nanomaterials such as single wall carbon nanotubes (SWNTs), functionalized single wall carbon nanotubes (SWNTf), multiwall carbon nanotubes (MWNTs) and fullerene were investigated with a Pin on Disk friction and wear tester. The wear surfaces of the steel disk lubricated with the environmentally friendly lubricant (sunflower oil was selected for our investigations) additivated with different concentrations of carbonaceous nanomaterials were analyzed by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and atomic force microscopy (AFM) in order to understand the action mechanism on atomic scale. It has been found that by addition of carbonaceous nanomaterials the antiwear ability of the sunflower oil was improved and it was noticed the remarkable antiwear features of the functionalized single wall carbon nanotubes and fullerene.

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Keywords: Antiwear additives, carbonaceous nanomaterials, AFM, XPS, wear testing

1. Introduction

Worldwide mineral and synthetic oils are dominating the lubricants market but from environmental point of view become more obvious the necessity to formulate biodegradable lubricants based on natural oils, respectively vegetable oils.

Generally, lubricating oils or functional fluids are omnipresent due to their widespread use and consequently they pollute environment but in small or widely-spread amount and only rarely in large quantities [1]. However, biodegradable lubricants are required to replace conventional hydraulic fluids or metal working oils and are essential for few applications such as two stroke engine for small boats, chain for chainsaw and all other devices that demand total-loss lubrication.

Biodegradable lubricants must meet general features such as lubricants formulated from mineral or synthetic oils and more than that, an environmentally friendly lubricant must have high biodegradability, specific water solubility, low toxicity, low emissions in use and superior compatibility with conventional lubricants and materials.

Usually, biolubricants are formulated based on vegetable oils from harvestable raw materials, for example rapeseed or sunflower oil, from semi-saturated transesterified ester oils with natural fatty acids, from fully saturated synthetic esters based on chemical modified vegetable oil or even from renewable raw materials and specific additives [1]. Unfortunately, beside having excellent biodegradability or being environmentally compatible lubricants, vegetable oils have few deficiencies that must be counterbalanced by the beneficial actions of additives.

Utilization of the same additives, successfully used for many years to improve the properties of the mineral or the synthetic oils seems to be an outdated idea at least from two points of view; only few consecrate additives can boost the existing properties of vegetable oils and

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secondly, fewer additives can be suitable in order to preserve the ecological attribute of the future lubricant.

Most vegetable oils used for formulation of biolubricants, display a high degree of polarity that results in superior lubricity rather than mineral oils in boundary conditions.

There are only few antiwear additives suitable for lubricants based on vegetable oils, which can prevent the welding of the moving parts and reduce the wear of the metallic components being in the direct contact. Sulfurized fatty materials or active sulfur carriers have provided antiwear (AW) effect.

Because of high price level or because of high reactivity with non-ferrous metals, active sulfur carriers cannot be used in the machining of non-ferrous metals and utilization of these compounds as AW additives has been restricted, and the actual tendency is to develop more environmentally friendly additives [1, 2].

Utilization of nanostructured carbon materials such as antiwear additives for biolubricants is a new idea, although solid additives such as graphite and molybdenum disulfide have been successfully used for additivation of lubricating oils based on mineral oils because of its excellent emergency running properties when the oil supply is breaking down [1-5].

Different carbon allotropes such as diamond, graphite and fullerene, together with the newest member of the fullerene structural family respectively, single wall carbon nanotubes have been investigated for their tribological properties. These carbonaceous materials are suitable for many applications due to their special physical and chemical properties, because of low friction coefficients, low wear and because present self-lubricating properties [6-9]. In few studies, single walled carbon nanotubes were found to improve wear resistance of lubricants, to provide low friction and minimal deformation [2, 10-12].

In this paper are presented the preliminary results on the friction behavior of different carbonaceous materials as potential antiwear additives for biolubricant oils based on sunflower oil.

A Pin on Disk tribometer was used to evaluate the tribological properties of the nanostructured materials. The analytical analyses were also performed by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and atomic force microscopy (AFM) in order to understand the action mechanism on atomic scale.

A physical and chemical characterization of vegetable oil was essential in order to provide scientific rigor and to enable reliable conclusions.

2. Materials and experimental methods

The experimental study was focused on synthesis and characterization of SWNTs while the other carbonaceous nanomaterials were provided by Iolitec. The second part of this study was focused on the tribology characteristic tests for vegetable oil additivated with different concentration of carbon nanomaterials.

2.1 Materials

2.1.1 Vegetable oil

Sunflower oil is conventional oil, commonly used for the synthesis of biolubricants therefore, sunflower oil with the physical-chemical characteristics presented in table 1, was selected as base oil for our study.

Table 1: Physical-chemical characteristics of sunflower oil.

Properties	Sunflower oil	Methods
Density (kg/m^3)	917	ASTM D-1298
Kinematic viscosity (40°C, cSt)	30.8	ASTM D-445
Kinematic viscosity (100°C, cSt)	7.6	ASTM D-445
Visosity index	231	ASTM D-2270
Flash point (°C)	>210	ASTM D-92
Pour point, (°C)	-14	ASTM D-97
Copper corrosion (at 100°C)	negative	ASTM D-130
Acid value (mgKOH/g)	0.12	ASTM D-974

2.1.2. Single wall carbon nanotubes synthesis and purification

SWNTs were synthesized by chemical carbon vapor deposition (CCVD) method by using Co-MCM-41 as catalyst.

Prior to the utilization of SWNTs as additive for vegetable oil, after the synthesis step of SWNTs it was essential to purify them by hydrothermal treatment, in order to remove the silica, amorphous carbon and metal particles. Detailed description of the CCVD synthesis and purification methods can be found in our previous studies [2, 13, 14].

2.1.3. Single wall carbon nanotubes characterization

Prior to the tribological measurements, SWNTs were investigated by RAMAN spectroscopy (figure 1) and TEM (figure 2).

Raman spectra of the SWNTs sample were recorded by using a Jasco LASER Raman Spectrophotometer NRS-3100 Series. All spectra were recorded at 785 nm (1.58 eV) excitation wavelength.

The SWNTs present Radial Breathing Mode (RBM) (at about 300 cm^{-1}), the Disorder-induced band (D-band) around 1300 cm^{-1} and the Graphite-like band (G-band) around 1550-1600 cm^{-1}.

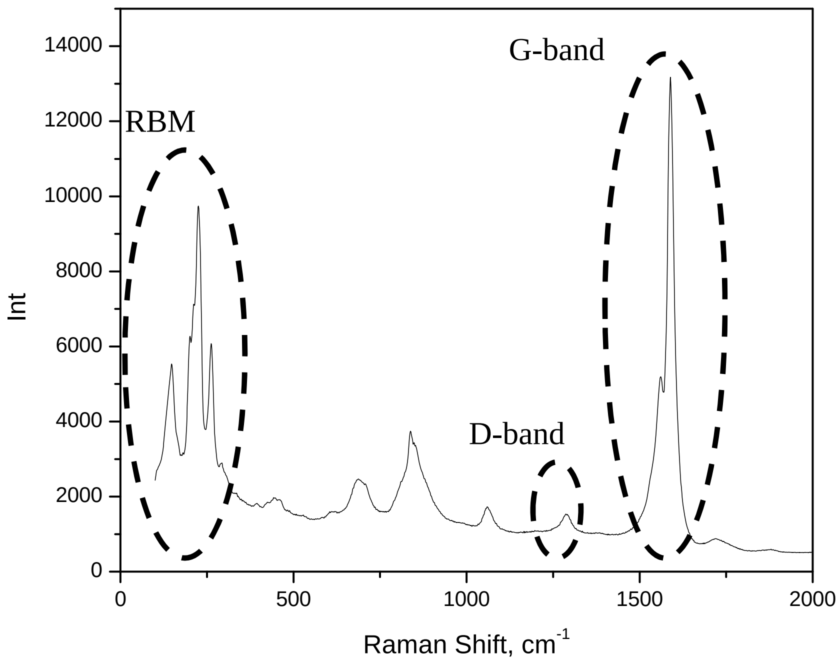


Fig. 1 Raman shift recorded after SWNT growth (at 785 nm wavelength)

By using the Raman shift from the RBM region, together with the equation developed by Araujo and coworkers [15], it was possible to calculate the diameters of the single wall carbon nanotubes (table 2). The low intensity of the D-band centered at 1292 cm^{-1}, characterized for disorder carbon species coupled with a supra unitary purity index

(G-band/D-band ratio) suggests a very good selectivity for SWNTs synthesized.

Table 2: The diameter distribution of the single wall carbon nanotubes

Sample	Diameter, nm			G-band/D-band
Co-MCM-41	1.65	1.01	0.91	1.11

Morphological and structural characterization of single wall carbon nanotubes obtained by vapor phase catalytic deposition was performed by using Tecnai F 12 200 kV microscope from Yale University. Prior to TEM investigations, SWNTs samples were sonicated in ethanol and then dispersed previous to imagine the carbon framework.

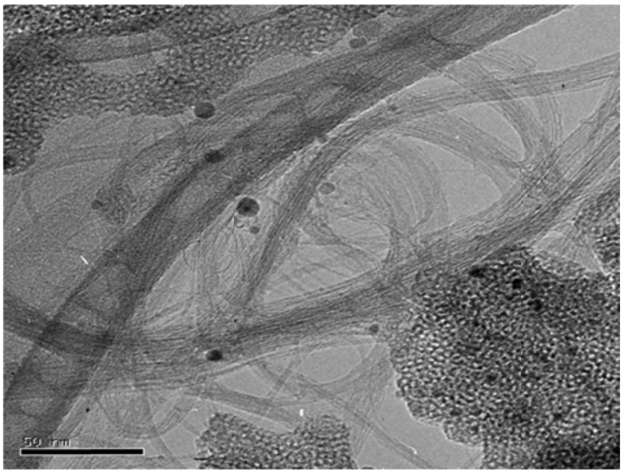


Fig. 2 TEM images of the as-reacted SWNTs

2.1.4. Carbonaceous nanomaterials

Functionalized single wall carbon nanotubes, multiwall carbon nanotubes, fullerene and graphene used as antiwear additives in our investigations were provided by Iolitec.

2.2. Antiwear procedure

The friction of vegetable oil and vegetable oil additivated with different carbonaceous nanomaterials were investigated on Pin on Disk tribometer. The Pin on Disk tribometer covers procedures for determining the coefficient of friction of a lubricating oil and its ability to protect against wear, as well as the wear rate and the sliding friction with rolling under dry friction or lubrication.

The Pin on Disk test consist 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 33%, while the ambient temperature was between 20-23°C.

2.3. XPS analysis of the worn and steel surfaces

X-Ray photoelectron spectroscopy is a surface chemical analysis technique that can be used to analyze the surface chemistry of different materials in unrefined state or after some treatments, in our case, sliding friction. XPS analysis was performed using a K-Alpha by Thermo Scientific multifunctional X-ray photoelectron spectrometer. The AlKα radiation (1486.6 eV) was used as the exciting source. The spot size in XPS studies was 100 µm and the binding energies of the target elements were determined at pass energy of 20 eV, with a resolution of about 0.3 eV.

2.4. SEM investigations

The morphology of the rubbed surfaces was investigated by using a Hitachi S-3400N scanning electron microscope working with 30 kV and maximum resolution of 5 nm.

2.5. AFM investigations

The AFM investigations were done with Park Systems XE-100 instrument (maximum horizontal scan range of 50 µm×50 µm and maximum vertical movement of 12µm), and the measurements were done in tapping mode.

3. Results and discussion

The tribological behavior of SWNTs as an antiwear additive for sunflower oil was investigated on a Pin on Disk tribometer. In order to establish the optimal antiwear and friction reduction, five specimens were compared under the same conditions: sunflower oil (SF) without any additives and with four different SWNTs concentrations (0.05, 0.1, 0.2 and 0.5 wt %). SWNTs have been dispersed into vegetable oil by utrasonication for 30 min. Single wall carbon nanotubes have proved good dispersibility in vegetable oil, the sample with various mass concentrations of SWNTs dispersed in oil being stable up to 72 hours. Unfortunately, after 72 hours from the startup of the dispersing process the suspension become unstable and it was observed the tendency of SWNTs to drop to the bottom of the flask. The aim for further experiments is utilization of functionalized single wall carbon nanotubes or ionic liquids to stabilize the suspension [20,22, 23]. Pin on Disk tribometer results in figure 3 show the behavior of friction coefficient as a function of SWNTs concentrations.

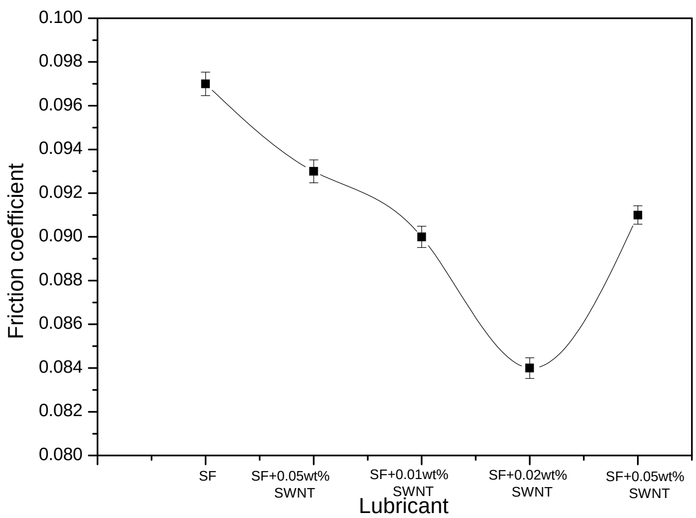


Fig. 3 Friction coefficients for vegetable oil with different SWNTs concentrations

Dispersion of different concentrations of SWNTs in sunflower oil seems to be beneficial for the evolution of the friction coefficient. From figure 3 it is obvious that the friction coefficient had the highest value for the pure vegetable oil and by raising the additive concentration from 0.05 wt.% up to 0.2 wt.%, the friction coefficient decreases monotonically. Higher additive concentration did not result in a friction reduction effect probably because, at this concentration level, the vegetable oil is saturated with nanotubes; a part from the SWNTs are already physically or chemically adsorbed on the surface and the remaining SWNTs are agglomerated and gradually destroyed, leading to an increase of the friction coefficient and the wear rate. Similar behavior was noticed in our previous study when mineral oil was used instead vegetable oil [2].

The evolution of the friction coefficients is similar to the evolution of the wear rate on ball and disk calculated and depicted in table 3. Minimum wear rate on ball and disk was achieved for 0.2 wt% SWNTs dispersed in sunflower oil and increasing of the concentration of carbon nanotubes in oil lead to an increasing of the wear rate.

Table 3:Wear rate on ball and disk

Sample	**Max. Hertzian Pressure [GPa]**	**Wear rate on ball [mm^3/N/m]**	**Wear rate on disk [mm^3/N/m]**
Sunflower oil (SF)	1.031	8.21E-008	1.96E-005
SF+0.05 wt.% SWNTs		7.98E-008	1.48E-005
SF+0.1 wt.% SWNTs		5.84E-008	0.87E-005
SF+0.2 wt.% SWNTs		4.36E-008	0.72E-005
SF+0.5 wt.% SWNTs		6.14E-008	1.11E-005

The influence of different carbon based nanomaterials on the friction coefficients is depicted in figure 4. Addition of 0.2 wt.% SWNTs, SWNTf, MWNTs and fullerene has a positive effect over the friction coefficient, all carbon-based nanomaterials are contributing to decreasing of the friction coefficient with about 5% MWNTs, 13% SWNTs, 18% fullerene and 22% SWNTf compared to the friction coefficient of non additivated sunflower oil.

It is clearly observed that the friction coefficient for sunflower oil with functionalized single wall carbon nanotubes has the lowest value than for the other carbonaceous species

investigated in the present study. A potential explanation for this behavior can be made based on the surface modification of the carbon nanotubes. In other studies, it was assumed that by modification of the surface of the carbon nanotubes it is possible to decrease the friction coefficients because the functionalization of the tubes can introduce defects within the SWNTs sidewalls, resulting in a degradation of the tubular structure thus, reactive edge sites will be created leading to binding between the lubricant and adjacent surfaces [10]. However, a chemical adsorption on the metallic surface might occur or SWNTs can fill in pits and scratches and between surface asperities or between sliding surfaces by this decreasing the friction coefficient and the wear rate.

A low value for the friction coefficient was achieved for fullerene dispersed in sunflower oil, most likely because of their specific quasi-spherical shapes. These spherical nanoparticles fill the irregularities of different scale size from nano to micro-defects on the surface; improving the lubricating properties of the lubricant they are dispersed.

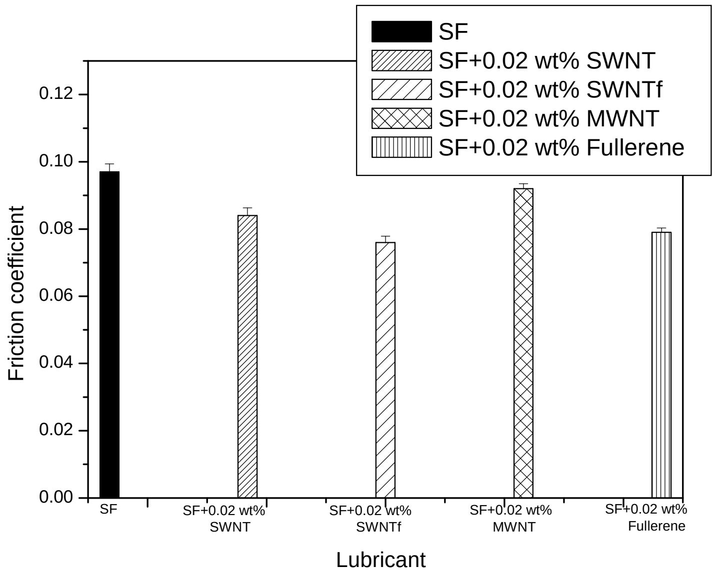


Fig. 4 Friction coefficients of vegetable oil with different carbon nanomaterials such antiwear additives

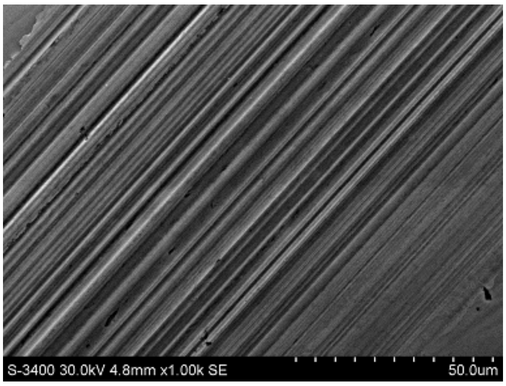
The investigations of the friction coefficient were completed by the results of the wear rates on ball and disk presented in table 4. The smallest values for the wear rate were obtained for vegetable oil additivated with SWNTf while the highest wear rate was observed for vegetable oil additivated with MWNTs.

Table 4:Wear rate on ball and disk

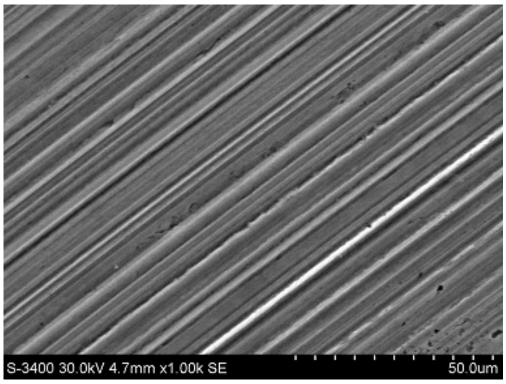
Sample	**Max. Hertzian Pressure [GPa]**	**Wear rate on ball [mm^3/N/m]**	**Wear rate on disk [mm^3/N/m]**
Sunflower oil (SF)	1.031	8.21E-008	1.96E-005
SF+0.2 wt.% SWNTs		4.36E-008	0.72E-005
SF+0.2 wt.% SWNTf		2.98E-008	0.61E-005
SF+0.2 wt.% MWNTs		7.65E-008	1.37E-005
SF+0.2 wt.% Fullerene		3.45E-008	1.67E-005

Figure 5 shows the wear scar images of the pin on disk test taken with SEM. In figure 5a the worn surface of the steel disk lubricated with non additivated sunflower oil shows wide and deep parallel grooves in the wear track. By dispersing carbon-based nanomaterials in vegetable oil it is noticeable an improvement of the tribological properties.

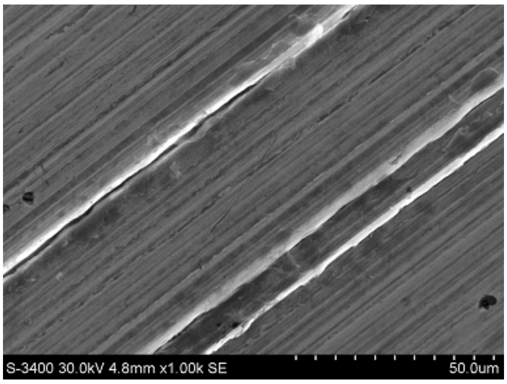
Figures 5c and 5e show relatively smaller, narrower and smoother wear scratches on the friction surfaces.



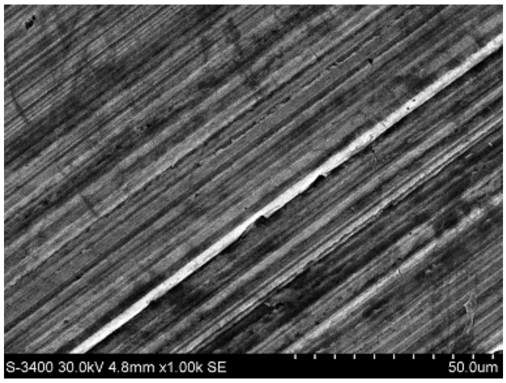
(a)



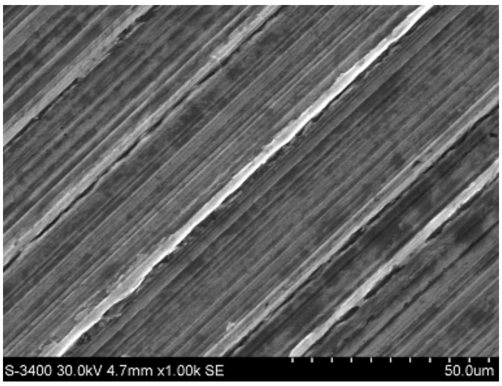
(b)



(c)



(d)

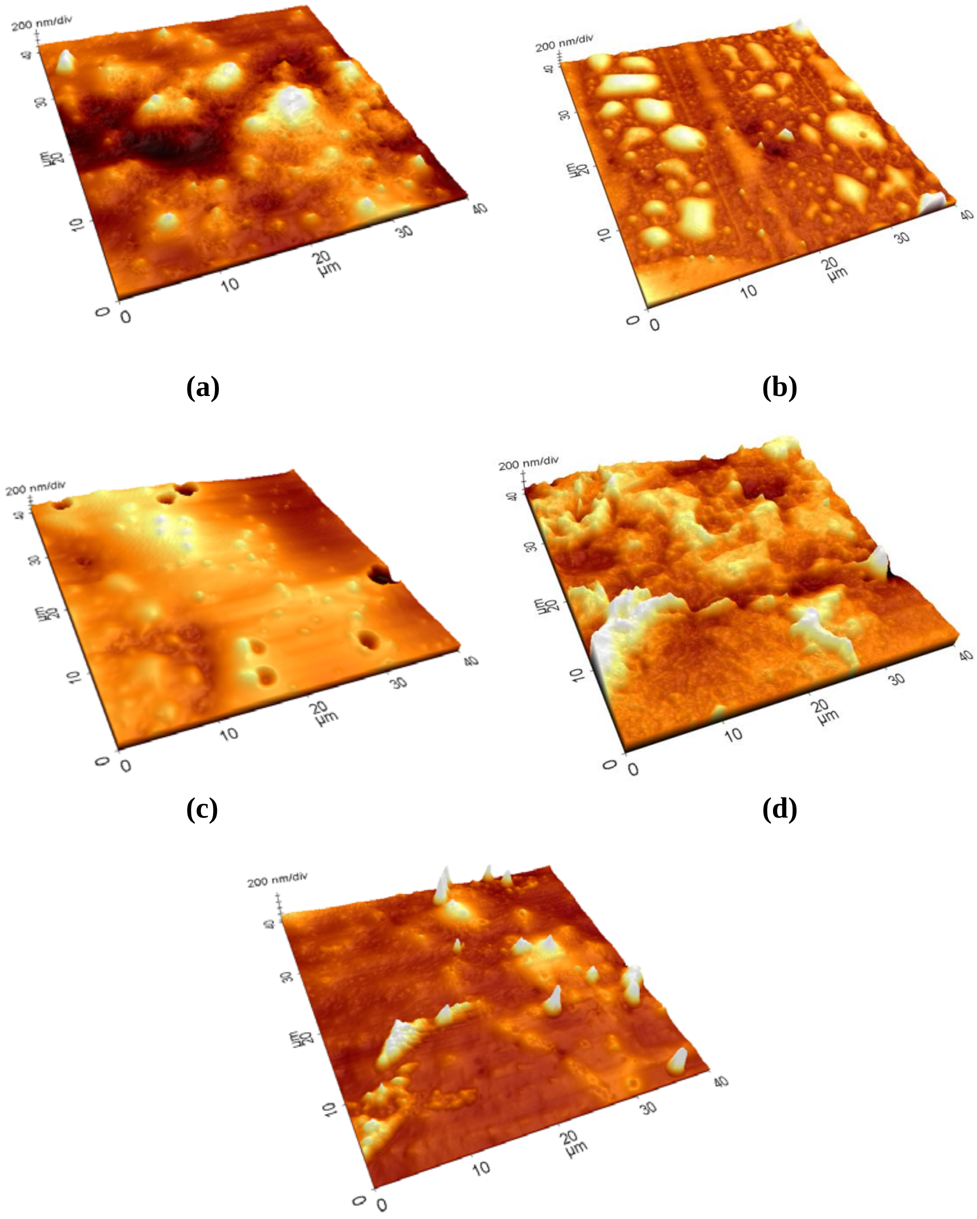


(e)

Fig. 5 SEM images of the friction surface of the disk after the friction test
a) Sample 1: Sunflower oil (SF), b) Sample 2: SF +0.2 wt.% SWNT, c) Sample 3: SF +0.2 wt.% SWNTf, d) Sample 4: SF+0.2 wt.% MWNT, e) Sample 5: SF+0.2 wt.% Fullerene

From fig. 5c and 5e it is obvious the antiwear potential of functionalized single wall carbon nanotubes and fullerene, these compounds are contributing to the friction reduction, the scratches derived from the friction being more reduced rather than the scratches observed for the samples lubricated with raw sunflower oil (fig.5a) or sunflower oil additivated with SWNTs (fig. 5b) or MWNTs (fig. 5d). Moreover, these observations are in agreement with the friction results which promote the functionalized carbon nanotubes such as the best antiwear carbon-based nanomaterial additive, of the materials analyzed.

Figure 6 presents AFM images obtained for the friction area of fig. 5 a-e.



(a) (b) (c) (d) (e)

Fig. 6 AFM images of the friction surface test
a) Sample 1: Sunflower oil (SF), b) Sample 2: SF +0.2 wt.% SWNTs, c) Sample 3: SF +0.2 wt.% SWNTf, d) Sample 4: SF+0.2 wt.% MWNTs, e) Sample 5: SF+0.2 wt.% Fullerene

The AFM investigations come in addition to the preliminary results of the tribological tests. The AFM study revealed the presence of carbon-based materials on stainless steel surface after the friction tests, as well as the topography of the samples. Friction surfaces for the samples additivated with SWNTf (fig. 6c) and fullerene (fig. 6e) present wide smooth regions while the friction surfaces for the samples additivated with SWNTs (fig. 6b) or MWNTs (fig. 6d) or without any additives (fig. 6a) expose rough surfaces with slight scratches.

Figure 7 shows high resolution XPS spectra of C1s on worn steel surface lubricated by vegetable oil additivated with different carbonaceous nanomaterials.

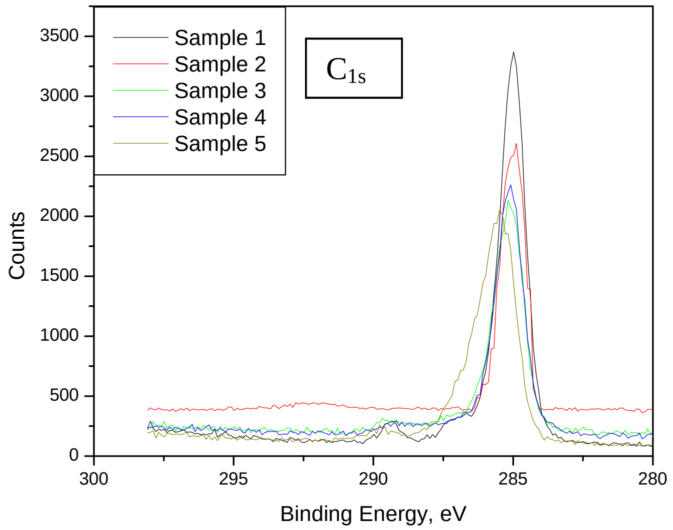


Fig. 7 XPS spectra of the carbon on the worn surface
Sample 1: Sunflower oil (SF), Sample 2: SF +0.2 wt.% SWNTs, Sample 3: SF +0.2 wt.% SWNTf, Sample 4: SF+0.2 wt.% MWNTs, Sample 5: SF+0.2 wt.% Fullerene

The C signal for the first sample originates from the presence of accidental C (284.8 eV) from exposure to air. For samples from 2-5 the C signal at 285.08-286.48 eV is due to the C-C. From the XPS analysis is assumed that carbonaceous nanomaterials, during friction tests, are adsorbed on the metallic surface and make the frictional area flat and smooth, resulting in a decreasing of frictional force.

4. Conclusions

This paper presents the results of our investigation on the tribological properties of Co-based single wall carbon nanotubes, functionalized single wall carbon nanotubes, multi wall carbon nanotubes and fullerene. Based on the results of the present study, the following conclusions can be drawn:

1. The friction and wear properties during the ball on disk sliding contact in the presence of sunflower oil used as lubricant depend strongly on the material used as antiwear additive.

2. Addition of only 0.2 wt% SWNTs leads to a decrease with about 13% of the friction coefficient and a reduction with 47% of wear rate on ball and 63% wear rate on disk.

The optimum concentration of SWNTs was found to be around 0.2 wt%, higher concentration lead to increasing of the friction coefficient as well as the wear rate on ball and disk. The most probable hypothesis is that nanotubes are agglomerated and then destroyed during the friction leading to an increase of the friction coefficient and the wear rate.

3. SWNTf, fullerene and MWNTs demonstrate also their potential such as antiwear additives for a vegetable oil. The lowest friction coefficient and wear rate was observed for SWNTf while the highest value was noticed for MWNTs.

4. According to SEM, AFM and XPS analyses it was found that SWNTf, fullerene and SWNTs are contributing to the reduction of the friction being potential antiwear additives for future formulation of biolubricants. For formulation of biolubricants 0.2 wt.% SWNTf would be a reasonable functionalized single wall carbon nanotubes concentration.

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References

[1] T. Mang, W. Dresel, Lubricants and Lubrication, Wiley-VCH, 2nd Ed., (2007).
[2] D.L. Cursaru, C. Andronescu, C. Pirvu, R. Ripeanu, Wear, **290-291,** 133 (2012).
[3] R. Chou, A. Hernandez Battez, J.J. Cabello, J.L. Viesca, A. Osario, A. Sagastume, Tribology International (2010), doi:10.1016/j.triboint.2010.08.006.
[4] E. Fernandez Rico, I. Minondo, D. Garcia Cuervo, Wear **262**, 1399 (2007).
[5] Y. Choi, C. Lee, Y. Hwang, M. Park, J. Lee, C. Choi, M.Jung, Current Applied Physics **9**, 124 (2009).
[6] L. Rapoport, O. Nepomnyashchy, I. Lapsker, A. Verdyan, A. Moshkovich, Y. Feldman, R. Tenne, Wear **259**, 703 (2005).
[7] Q. Wang, X. Zhang, X. Pei, Materials and Design **31**, 3761 (2010).
[8] S. Vizireanu, L. Nistor, M. Haupt, V. Katzenmaier, C. Oehr, G. Dinescu, Plasma Processes and Polymers **5** (3), 263 (2008).
[9] S. Vizireanu, M. D. Ionita, G. Dinescu, I. Enculescu, M. Baibarac, I. Baltog, Plasma Processes and Polymers **9**, 363 (2012)
[10] R.L.V. Wal, K. Miyoshi, K.W. Street, A.J. Tomasek, H. Peng, Y. Liu, J.L. Margrave, V.N. Khabashesku, Wear **259,** 738 (2005).
[11] R. Vail, D.L. Burris, W.G. Sawyer, Wear **267,** 619 (2009).
[12] L. Joly-Pottuz, F. Dassenoy, B. Vacher, J.M. Martin, T. Mieno, Tribology International **37**, 1013 (2004).
[13] D.L. Cursaru, D. Enescu, D. Ciuparu, Revista de Chimie **62** (7) (2011)
[14] M. Stancu, D. Cursaru, A.M. Manta, R. Grigore, I. Stamatin, D. Ciuparu, Revista de Chimie **61** (6) (2010).
[15] P.T. Araujo, S. Doorn, S. Kilina, S. Tretiak, E. Einarsson, S. Maruyama, H. Chadram, M. Pimenta, A. Jorio, Physical Review Letters **98**, 06740 (2007).