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Co-SWNTs-like Material as Antiwear and Extreme Pressure Additive for Biodegradable Lubricants

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Abstract

This paper describes the antiwear (AW) and extreme pressure (EP) potential of Co-based single wall carbon nanotubes (SWNTs) for a biodegradable oil, in comparison with two commercial antiwear and extreme pressure additives, commonly used as additives for mineral oils. Friction coefficients and the thickness of lubricant layer were determinate by using HFRR equipment, while a four ball tester was used to evaluate the extreme pressure properties. The single wall carbon nanotubes were produce by chemical carbon vapor deposition (CCVD) and were characterized by transmission electron microscopy (TEM) and the diameter of the tubes were determinate by RAMAN spectroscopy. According to our experimental results, SWNTs is more efficient antiwear additive rather than commercial AW additives but is less efficient extreme pressure additive.

Key words: *SWNTs, AW and EP additives, biodegradable lubricants*

Introduction

Nowadays, about 95% of lubricants are synthesized from mineral base oils derived from petroleum resources. The rapidly exhausted fossil sources coupled with increasing price of petroleum together with the public awareness concerning the environmental protection, are the main reasons that have made many scientists to search for alternative, renewable and biodegradable sources.

Vegetable oils are potential sources of raw material for lubricants, more than that; there are some applications that imposes utilization of lubricating oils with high biodegradability such as mechanisms lubrication system using “total loss of lubricant”, which require a low degree of toxicity or for two-stroke engine used for small boats.

Unfortunately, the vegetable oil used as raw materials for lubricants is an area less exploited and the domain of specific additives for vegetable oils is less developed.

In our experimental study, evaluation of antiwear and extreme pressure properties of single wall carbon nanotubes for vegetable oils was made by comparing our results with the results obtained by additivation of sunflower oil with two commercial AW and EP additives, successfully used for mineral oil.

Experimental Study

In our study the SWNTs were synthesized by CCVD (chemical carbon vapor deposition) method, presented below. For comparison the AW and EP potential of SWNTs were compared with two AW and EP additives (AW1-an additive package with dialkyl dithiophosphate and calcium sulfonate and AW2-based on Zn-dialkyl dithiophosphate) commonly used for additivation of mineral oils.

Co-SWNTs synthesis

SWNTs were synthesized by carbon monoxide (CO) disproportionation method using the catalysts produced by the sol-gel method at 3 wt% total cobalt (Co) loading according to a method presented elsewhere [1-3]. The laboratory plant used for SWNTs synthesis is depicted in figure 1 while the temperature program used in the synthesis steps is presented in figure 2.

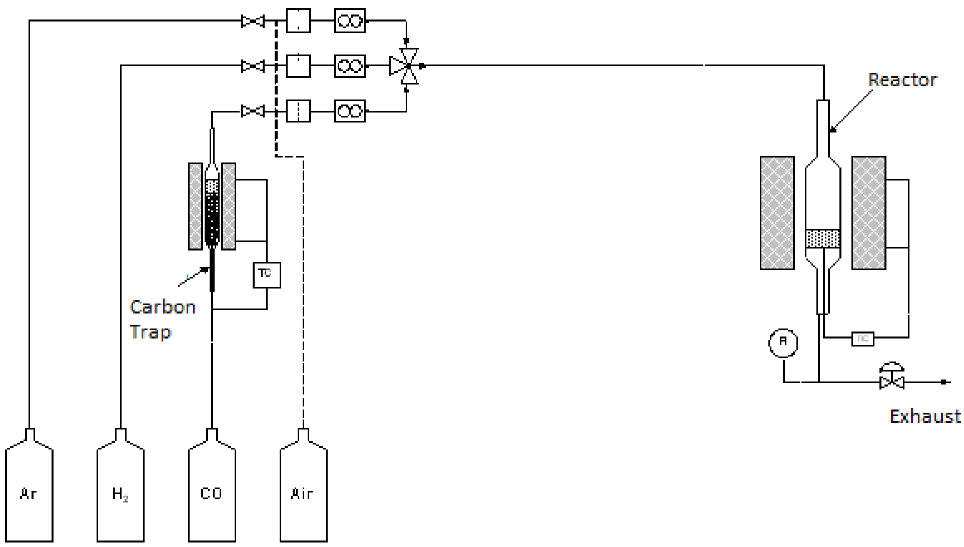

Fig. 1. Laboratory plant for SWNTs synthesis

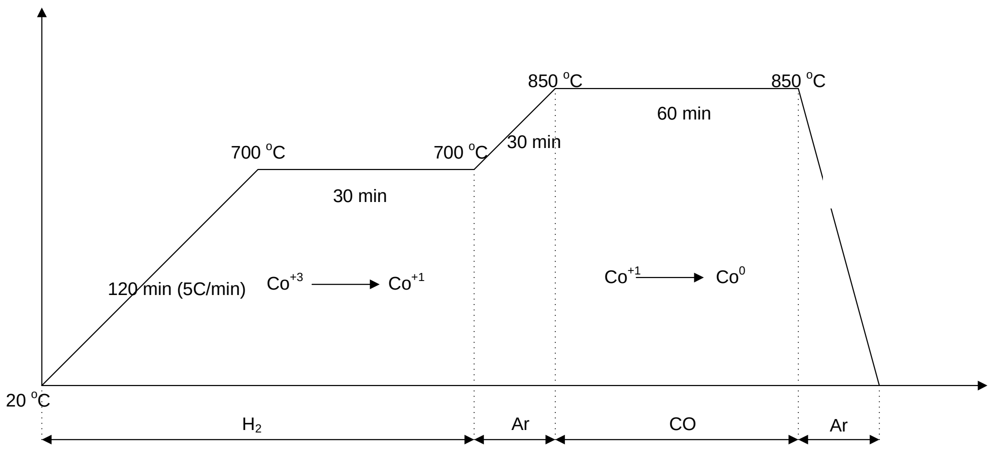

Fig. 2. Temperature program for SWNTs synthesis

Prior to the utilization of SWNTs as additive for vegetable oil, after the synthesis step of SWNTs it was essential to purify them in order to remove the silica, amorphous carbon and metal particles. SWNTs were initially put in a 3-neck flask containing 500 ml solution of NaOH 1M. The flask was heated with a reflux attachment for 1 h. This hydrothermal treatment is useful to remove the silica source of the catalyst. The SWNTs treated hydrothermally were dried and put back in the 3-neck flask containing 200 ml solution of HCl (36.5%). The flask was heated at 60-70^{0}C with a reflux attachment for 12 h. This second procedure is helpful to remove metal particles. After this procedure SWNTs were filtrated and then dried in a convection oven at 60^{0}C for 6 h and then heated at 300^{0}C in a furnace for 30 min to burn the amorphous carbon.

Co-SWNTs characterization

TEM investigations

High resolution transmission electron microscopy (TEM) is the most powerful tool to image nanoscale materials, to evaluate the diameter of SWNTs and the pore structure of MCM-41. TEM images of the SWNTs were recorded using a Tecnai F 12 200 kV microscope (figure 3).

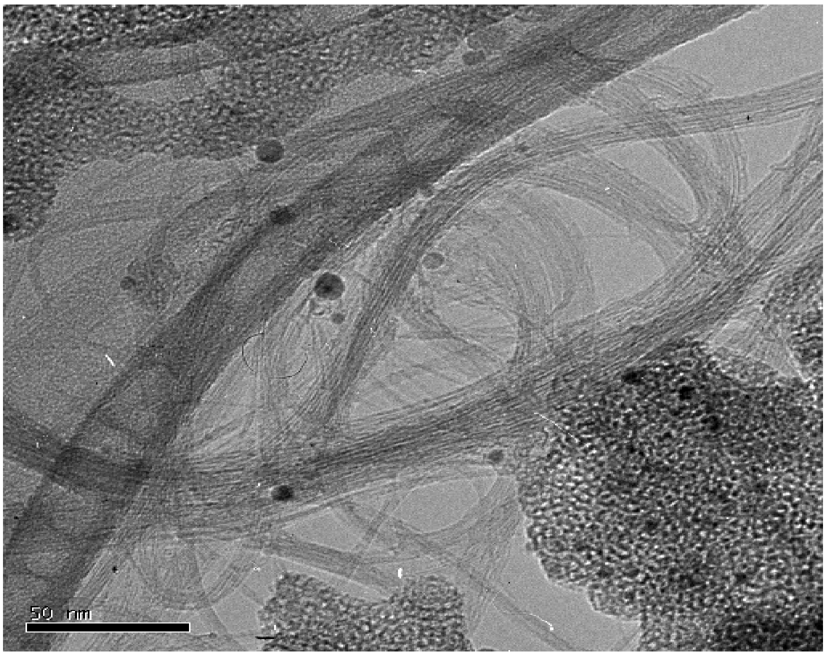

Fig. 3. TEM images of the as-reacted SWNTs

RAMAN spectroscopy

The diameters of the tubes of SWNTs were evaluated base on RAMAN spectroscopy. RAMAN spectra were recorded using a Jasco LASER Raman Spectrophotometer NRS-3100 Series. The RAMAN spectrum was recorded using one excitation laser wavelengths 785 nm (1.58 eV). Raman spectra of SWNTs show three characteristics peaks: The Radial Breathing Mode (RBM) below 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} (figure 4).

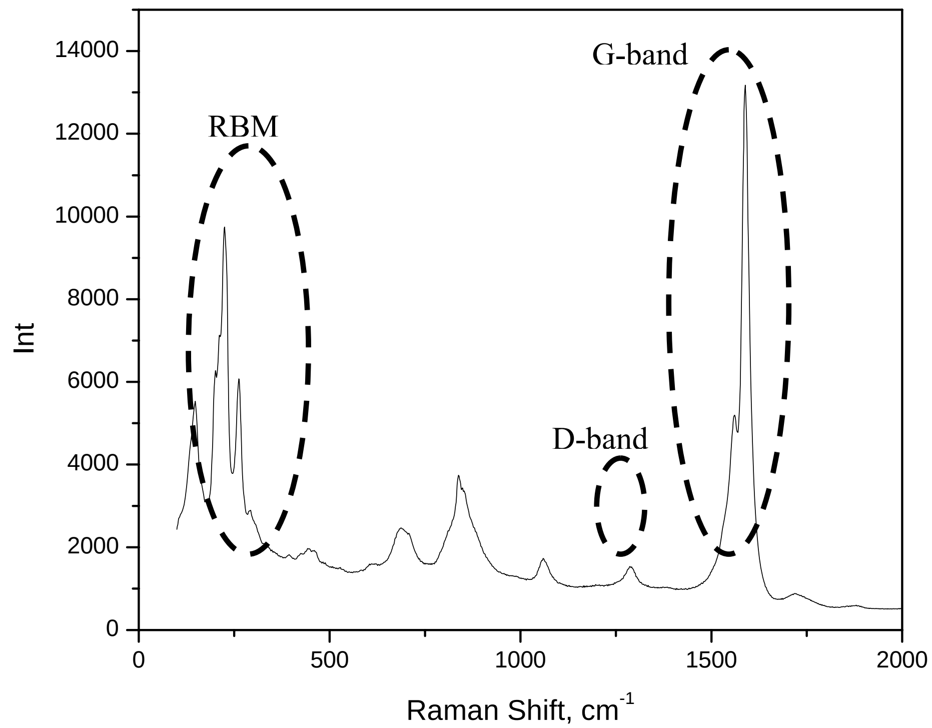

Fig. 4. Raman shift recorded after SWNT growth (at 785 nm wavelength)

The peaks from RBM zone are useful for calculation of SWNTs diameters.

The three peaks from RBM region suggest a wide distribution of the tube diameters. In table 1 are depicted the diameters of SWNTs calculated with an equation developed by Araujo and coworkers [4]. The range of the calculated diameters is between 0.88-1.69 nm and a supra unitary purity index (G-band/D-band ratio) coupled with a low intensity of the D-band, characteristic for the disorder carbon species, are indicators for an excellent selectivity for synthesized SWNTs.

Table 1. The diameter distribution of the single wall carbon nanotubes

Sample	Diameter, nm			G-band/D-band
Co-MCM-41	1.69	1.03	0.88	1.12

Selection of vegetable oil

In order to test the AW and EP potential of SWNTs four vegetable oils (sunflower, rapeseed, soybean and palm) were characterized to select the oil with the best features. The results are presented in table 2.

All four vegetable oils show very good viscosity indexes, high values for flash points, adequate copper corrosion behavior but poor oxidation stability and inappropriate pour points. Taking into account the drawback characteristics of these oils, for our investigations sunflower oil was selected as base oil.

Table 2. Physical-chemical characteristics for vegetable oils

Physical-chemical characteristics	Sunflower oil	Rapeseed oil	Soybean oil	Palm oil	Methods
Kinematic Viscosity at 40 °C, cSt	32.93	34.44	34.85	40.45	ASTM D-455
Kinematic Viscosity at 100 °C, cSt	7.72	7.85	8.04	8.51	ASTM D-455
Viscosity index	216	211	215	193	ASTM D-445
Pour point, °C	-9	- 21	- 9	+ 30	ASTM D 97
Flash point, °C	264	298	300	264	ASTM D 92
Copper corrosion (3h, 100 °C)	1a	1a	1b	1b	ASTM D-130
Oxidation stability (RBOT), min	20	5	5	20	ASTM D-2272
Resistance at high pressure on 4 Ball Test - Wear scar diameter (20daN/100min), mm; - Weld point, daN	 0.7 100	 0.7 100	 0.7 100	 0.65 120	ASTM D-4172

Results

Antiwear investigations

In this paper, the friction coefficients and the thickness of the lubricant layers of vegetable oil additivated with different SWNTs concentrations or with commercial AW and EP additives were investigated on HFRR equipment. Commonly, the HFRR equipment enables rapid, repeatable assessment of the performance of fuels and lubricants. This equipment is particularly suitable for wear-testing poor lubricants and has the big advantage of using small quantities of lubricants [5]. In addition, HFRR allows determination of the coefficient of friction, wear scar diameter and the thickness of the lubricant layer.

In figure 5 are presented the friction coefficients for sunflower oil with different concentrations of additives. It is obviously that the addition of classic additives for mineral oils (AW1 and AW2) is not beneficial for sunflower oil for all, thus the additives suitable for mineral oils are not appropriate for vegetable oils. However, much lower concentrations of single wall carbon nanotubes seems to have an antiwear potential, the friction coefficients decreases with increasing of SWNTs concentrations.

These interesting results are completed by the thickness values of lubricant layers for sunflower oil with different additives concentrations (figure 6).

The lubricant film thickness has a higher value and is constant in the case of additivation with different concentrations of SWNTs than for additivation with classic AW additives.

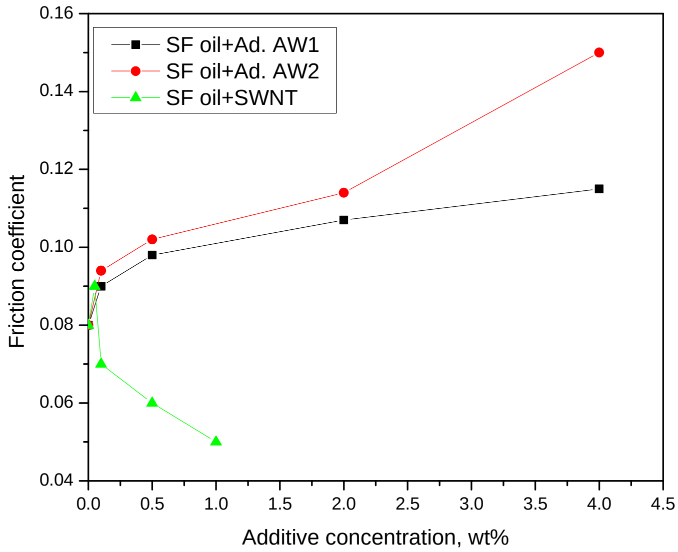

Fig. 5. Friction coefficients for sunflower oil with different additives concentrations

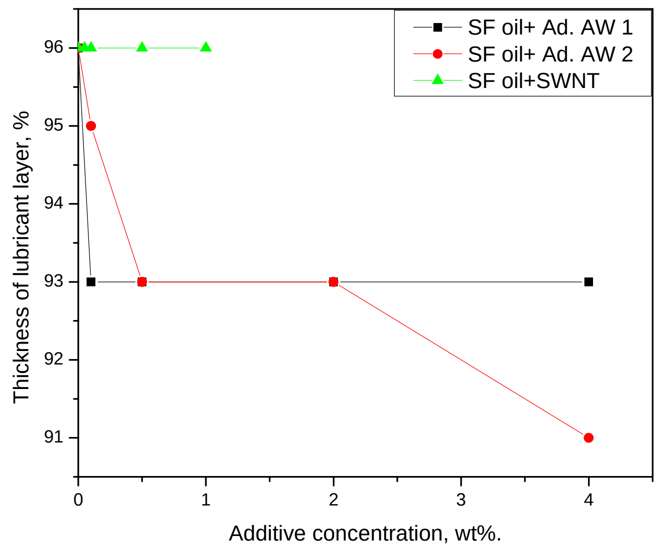

Fig. 6. Thickness of lubricant layer for sunflower oil with different additives concentrations

Extreme pressure investigations

A SETA Shell Four-Ball Machine producing sliding motion under high pressure with a drive shaft speed of 1475 rpm was used to evaluate extreme pressure and antiwear properties of sunflower oil additivated with different additives. The test ball used have a 12.7 mm diameter and a roughness of R_a=0.035 mm and are made from AISI E 52100 steel. The EP tests were performed according to ASTM D-2783 standard. The results are presented in figure 7.

For the four ball test, the additive efficiency is correlated with the weld point, i.e. a high value of the weld point indicates that the lubricant provides lubrication for a longer period of time under extreme pressure conditions.

From figure 7 we observe that SWNTs has extreme pressure potential but is less efficient than both classic AW and EP additives. Actually, these results confirm the trends observed in similar tests when AW and EP additives often have a "shielding" action for the mutual specific functions.

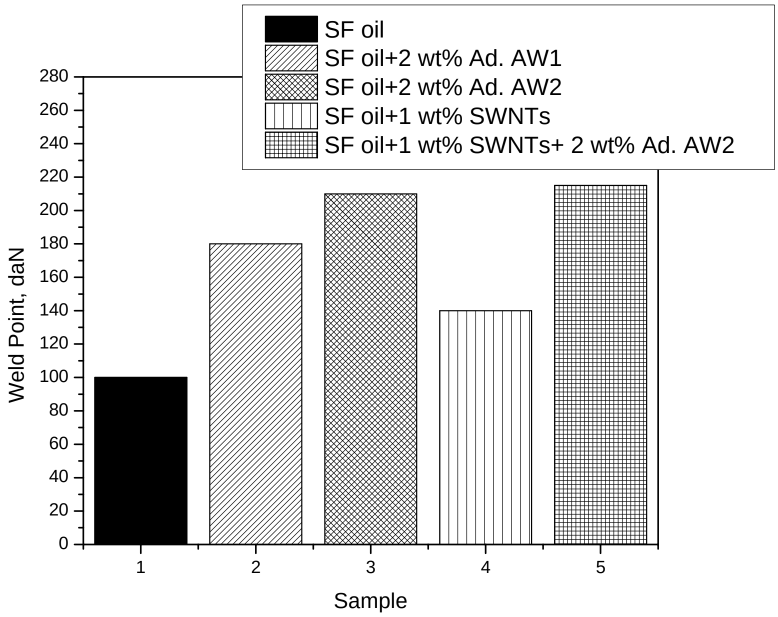

Fig. 7. Plot of Weld points for sunflower oil with different additives concentrations

Conclusions

This paper reports useful information about antiwear and extreme pressure properties of Co-based single wall carbon nanotubes. The antiwear investigations have shown that SWNTs is more efficient antiwear additive for vegetable oils than classic antiwear additives, successfully used for mineral oils but is less efficient as extreme pressure additive than classics. In order to determine the mechanism that governs the friction in the presence of single wall carbon nanotubes is essential to study the chemical and morphological of rubbed surfaces after friction.

Acknowledgements

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Co-SWNTs-ca aditiv antiuzură şi extremă presiune pentru lubrifianți biodegradabili

Rezumat

Această lucrare descrie potențialul antiuzură(AW) şi extremă presiune (EP) al nanotuburilor de carbon cu un singur perete (SWNTs) pentru un ulei biodegradabil, prin comparație cu doi aditivi antiuzură şi extremă presiune comerciali, utilizați cu succes ca aditivi pentru uleiurile minerale. Coeficienții de frecare şî grosimea peliculei de lubrifiant au fost determinate cu ajutorul echipamentului HFRR în timp ce o maşina cu 4 bile a fost utilizată pentru a evalua proprietățile de extremă presiune. Nanotuburile de carbon au fost sintetizate prin metoda de depunere chimică a vaporilor de carbon şi au fost caracterizate prin microscopie electronică de transmisie iar diametrul tuburilor au fost determinate prin spectroscopie RAMAN. Conform rezultatelor experimentale, SWNTs este un aditiv antiuzura mai eficient decât aditivii AW comerciali dar este un aditiv de extremă presiune mai puțin eficient.