Some tribological properties of Ni/Y Based Single Wall Carbon Nanotubes (SWNT)

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Introduction

Since their discovery in 1991 [1], carbon nanotubes have attracted much interest. Their structure confers them interesting properties and many potential applications have already been studied such as field emitters [2] and nanoscale electronic device [3]. Another potential of nanotubes is in connection with their mechanical properties. The resistance of carbon nanotubes to bending has already been observed and studied [4]. Nanotubes can also have interesting tribological properties: with their nanometric size, they can easily be active in the contact area, their structure without dangling bonds confers them a chemical inertness. Moreover, the use of carbon materials in tribological applications is a field of research increasingly investigated and many carbon compounds have already been extensively studied for their tribological properties (diamond, graphite, amorphous carbon and C60) [5].

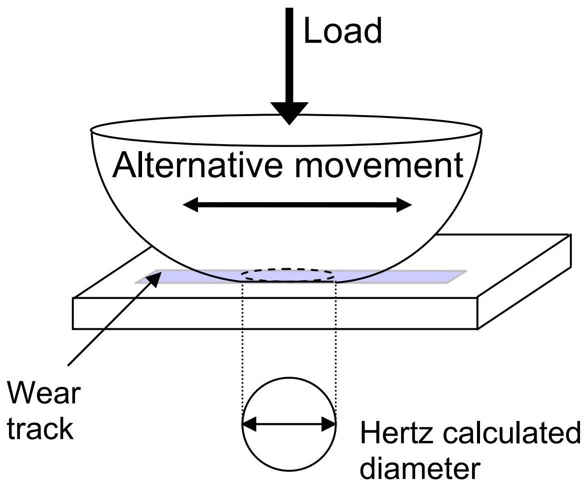
The only studies reported in the literature concerning the tribological behaviour of composite layers of materials containing carbon nanotubes use carbon as reinforcement. Chen et al. [6] have demonstrated that a Ni-P-CNT composite coating exhibits higher wear resistance and lower friction coefficient in comparison with traditional electroless composite coatings such as Ni-P-SiC and Ni-P-graphite. Few simulations have also investigated the response of carbon nanotubes during their friction between two sliding surfaces [7, 8]. The movement of carbon nanotubes align on graphite have been examined and showed that nanotubes roll along the surface and at other times slide instead [7]. The response of a nanotube bundle to applied shear forces is sliding or a combination of rolling and sliding [8].

In this work, we report preliminary results on the tribological properties at ambient temperature of Ni/Y-based single wall carbon nanotubes (SWNT) used as an additive to synthetic polyalphaolefin base oil (PAO). The nanotubes were tested in a boundary lubrication regime. Morphological observations made with transmission electron microscopy (TEM) and carried out before and after friction tests were used to correlate tribological properties and structural evolution of nanotubes. Analytical analyses were also performed by energy dispersive X-ray spectroscopy (EDX) and energy loss electron spectroscopy (EELS) in order to get information about the chemical composition of the material and to follow some eventual structural modification of the carbon nanotubes.

Experimentals

SWNTs were synthesized by electric arc discharge [9]. The arc is generated between two electrodes (size 6x6x100 mm) under a helium atmosphere (40 kPa). The cathode is in graphite and the anode in graphite containing a mixture of catalyst Ni/Y (4.2 at% and 0.9 at%). Presence of catalyst particles in the cathode permits formation of only single wall nanotubes.

Carbon nanotubes were tested in a lubricated contact using a pin-on-flat tribometer. Pin and flat are made of AISI 52100 steel. Figure 1 explains the principle on which the tribometer works. During the friction, the pin is elastically deformed and the real contact surface of the pin is circular. The diameter of this contact area corresponds to the calculated Hertz diameter. It depends on several parameters: material of both antagonist surfaces, pin diameter and contact pressure. An observation by optical microscopy of the pin after friction informs on the wear. If it is not important, there are only some scratches on the pin. At the opposite, if the wear is important, the wear scar has a diameter larger than the calculated Hertz diameter and the pin is flattened.



Load (N)	Contact pressure (GPa)	Calculated Hertz diameter (µm)
1	0,66	54
2	0,83	68
5	1,12	92
10	1,42	116

Figure1 : Pin-on-flat tribometer principle

Nanotubes were dispersed in a synthetic base oil, a polyalphaolefin. Various concentrations (0.5, 1 or 2wt%) were tested. Without the use of a dispersant, the colloidal solution of SWNTs/PAO is stable over four hours. Two droplets of the lubricant were deposited on the flat before starting the experiments. All measurements were performed in ambient atmosphere (30-35 RH) and ambient temperature (25°C), and the value of sliding velocity was 2.5 mm/s. Effect of contact pressure was studied using: 0.66, 0.83, 1.12, 1.42 GPa (corresponding to normal loads of 1, 2, 5 and 10 N). Note that with these conditions, experiments are made under boundary lubrication.

Characterisation of nanotubes before and after friction was performed by TEM. Analytical TEM was performed on a JEOL 2010 FEG microscope operating at 200kV accelerating voltage equipped with a ISIS EDS spectrometer (probe size of 5 nm) and a

Gatan 666 PEELS (resolution 1.2 eV). A LEO 912 microscope operating at 120 kV equipped with an omega filter was also used to perform Electron Spectroscopy Imaging in energy-filtered TEM. This technique is very useful to get map of the distribution of the species in the sample (Y, Ni, C).

Results

TEM characterisation of nanotubes before friction (figure 2) shows the presence of different structures in the sample: nanotubes bundles, catalyst particles and pseudo-graphitic carbon around catalyst particles. Figure 2 clearly shows that the single wall nanotubes grow from catalyst particles (figure 2a) whose size is between 5 and 15 nm. The atomic Ni/Y ratio is equal to 85/15. It is well known that the morphology of nanotubes is related to the Ni/Y composition [10]. With a proportion Ni/Y: 85/15, nanotubes are in long bundles (figure 2b). Each bundle contains approximately 20 SWNTs. The mean diameter of a bundle is 10 nm.

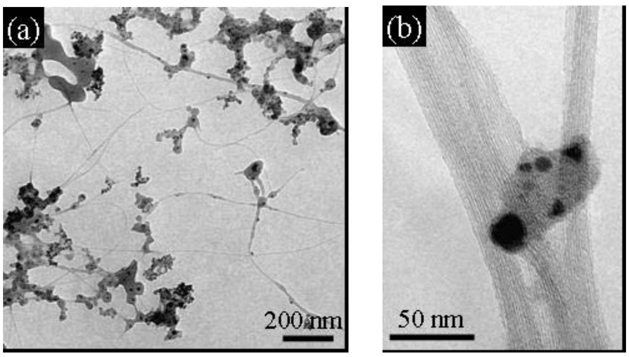


Figure 2: TEM images of SWNTs synthesised by electric arc discharge

The study of nanotubes concentration was performed using a contact pressure of 0,83 GPa. Three concentrations were tested: 0.5, 1 and 2wt%. Figure 3 shows the evolution of the friction coefficient with the nanotubes concentration. If a small effect can already be observed from 0.5wt%, the strongest reduction of the friction coefficient occurs for a concentration of at least 1wt% of nanotubes (70% less compared to that of the pure PAO). These results give the evidence of the friction reducing properties of this material.

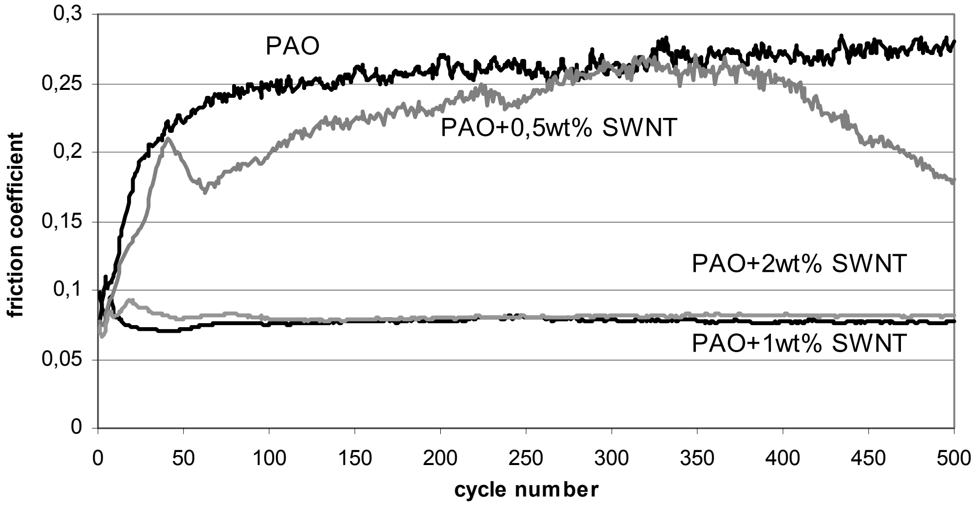


Figure 3: Evolution of friction coefficient in a lubricated contact: influence of nanotubes concentration in PAO

Others forms of carbon (graphite, C60) added at 1wt% to PAO were tested in the same conditions. The comparison of the results (figure 4) shows clearly that nanotubes are the best anti friction additives.

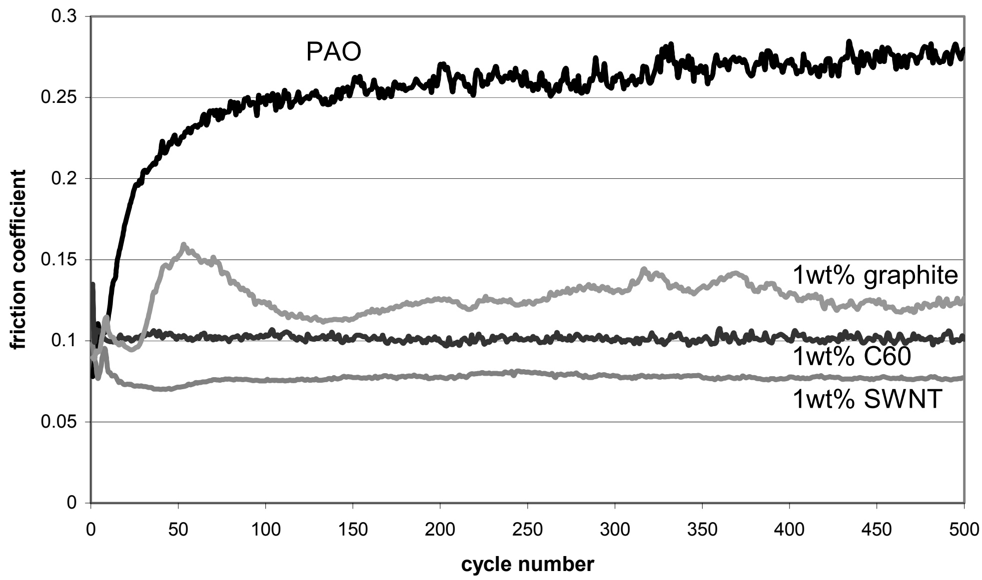


Figure 4: Comparison of different carbon forms added at 1wt% to PAO

The study of the wear on the pin obtained for all these experiments indicates that nanotubes present interesting anti-wear properties. With pure PAO, the diameter of the wear scar is larger (170µm) than the Hertz calculated diameter (68µm). This is characteristic of an important wear. The pin is also flattened. At the opposite, with SWNTs, only some scratches can be observed in contact area. These observations indicate that nanotubes have both friction reducing and anti wear properties. These results are interesting for potential applications of nanotubes as additive, since those actually used are either friction reducing or anti wear, two additives have so to be used.

By changing the contact pressure from 0.66 GPa to 1.42 GPa, efficiency of nanotubes can be tested. Friction coefficients obtained from the 1 wt% concentration of nanotubes sample with four different contact pressures are reported on figure 5. We can note that the higher the contact pressure, the smaller the friction coefficient is. This suggests that some structural changes may be responsible for the efficiency of SWNTs.

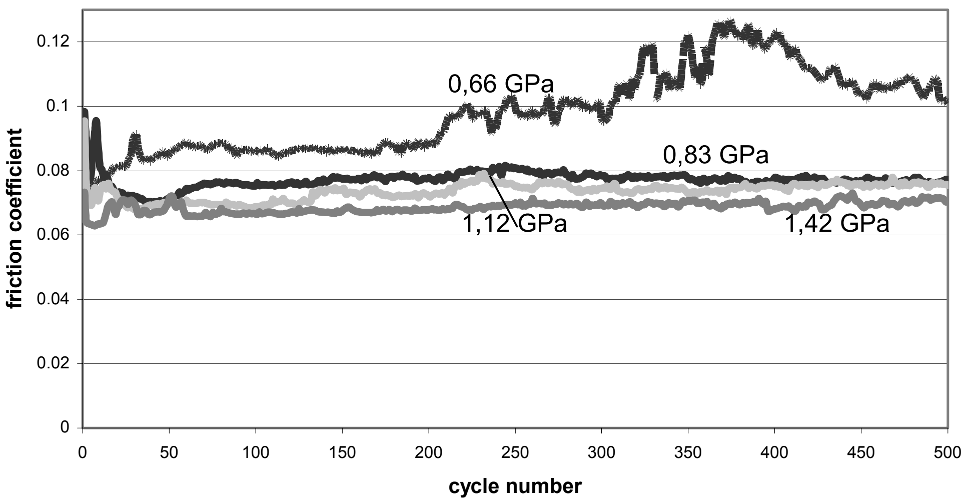


Figure 5: Evolution of friction coefficient for 1wt% SWNTs in PAO - Influence of contact pressure

The characterisation by TEM of the wear particles was performed on the 1 wt% nanotube sample tested with a load of 0.83 GPa. Wear particles were collected on the pin and observed by analytical TEM. Pictures show the presence of typical carpet-like wear debris (figure 6a and b) containing well dispersed catalyst particles (see EDX spectrum). These carpets are also observed for the three pressures (0.83 to 1.42 GPa) for which a decrease of the friction coefficient has been observed. Note that they were not present in the as-synthesised SWNT powder. For the matrix, EELS analysis at the carbon K-edge was carried out from the area shown on the figure 6b. The experimental spectrum was compared to those obtained from pure amorphous carbon, graphite and nanotubes before friction. These analyses prove the amorphous structure of the carbon matrix, supporting the strong alteration of the SWNT structure during friction. This structural modification can undoubtedly be attributed to the high pressure exerted on the nanotubes in the contact. These carpets of carbon are either due to SWNT crushed in the contact or to flattened nanotubes which could slide when the two antagonist steel surface are in movement. This could explain the good anti-friction properties of the nanotubes.

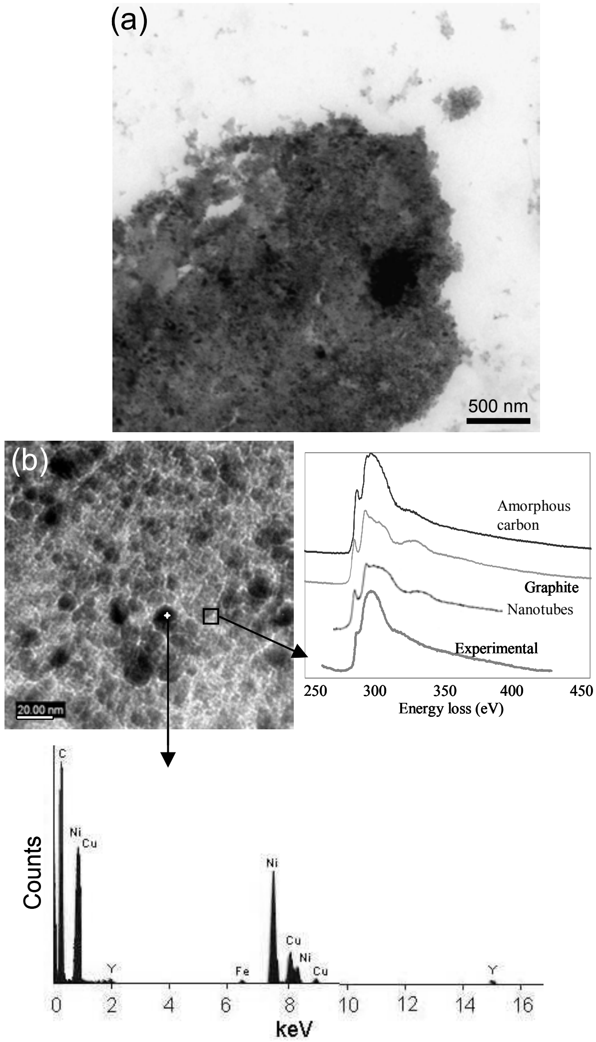


Figure 6 : TEM image of carpet-like wear debris collected from the pin: a) low magnification, b) higher magnification with corresponding EELS and X-Ray analysis performed in the black frame and on the arrowed particle, respectively

Chemical mapping of Ni, O, Y and Fe were performed on one of these carpets to get details on the distribution of these species in the carbon structure. This result indicates a high content of catalyst particles and the presence of only few oxidised iron particles. From this observation, an hypothesis can be proposed to explain the very good anti-wear properties of the nanotubes. The wear particles made up of amorphous carbon containing catalyst particles forms a protective material in which the few wear debris are confined. These wear debris are thus no more abrasive for the surfaces. The presence of Ni/Y particles in the amorphous carbon can also strongly contribute to the decrease of the wear. This so formed layer on substrate surface can be assimilate to a

Ni-doped DLC like material. It is effectively well known that such materials are quite hard and are usually used to protect surfaces against abrasion [11, 12].

Conclusion

Carbon nanotubes used as additive to lubricating base oil have been tested in a regime of boundary lubrication. Addition of only 1 wt% leads to a drastic decrease of friction and a reduction of wear of both antagonist surfaces. A contact pressure of at least 0.83 GPa is necessary to obtain these results indicating that a structural modification of the material is necessary. These properties seem to be related to the formation of carpet-like wear debris made up of amorphous carbon and containing catalyst particles. The mechanism of formation of these carpets is for the moment ambiguous. The most probable hypothesis is that nanotubes are flattened and/or crushed in the contact. The low amount of iron particles and the high fraction of catalyst particles after friction indicates the formation of a protective layer during the test which could be similar to a Ni-doped DLC-like material, well known for its good tribological properties.

References

[1] S. Iijima. Helical microtubules of graphitic carbon. Nature 1991; 354: 56-58.

[2] A.G. Rinzler, J.H. Hafner, P. Nikolaev, L. Lou, S.G. Kim, D. Tomanek, P. Nordlander, D.T.Colbert and R.E. Smalley. Unraveling nanotubes : Field emission from an atomic wire. Science 1995; 269: 1550-1553.

[3] P.G. Collins, A. Zettl, H. Bando, A. Thess and R.E. Smalley. Nanotube Nanodevice. Science 1997; 278: 100-103.

[4] M. Buongiorno-Nardelli, J.L. Fattebert, D. Orlikowski, C. Roland, Q. Zhao and J. Bernholc. Mechanical properties, defects and electronic behavior of carbon nanotubes. Carbon 2000; 38 (11-12): 1703-1711.

[5] U.D. Schwarz, O.Zwörner, P. Köster and R. Wiesendanger. Quantitative analysis of the frictional properties of solid materials at low loads. Physical review B 1997; 56 (11): 6987-6995.

[6] W.X. Chen, J.P. Tu, L.Y. Wang, H.Y. Gan, Z.D. Xu and X.B. Zhang. Tribological application of carbon nanotubes in a metal-based composite coating and composites. Carbon 2003; 41: 215-222.

[7] A. Buldum and J.P. Lu. Atomic scale sliding and rolling of carbon nanotubes. Physical Review Letters 1999; 83: 5050–5053.

[8] B. Ni and S.B. Sinnott. Tribological properties of carbon nanotubes bundles predicted from atomistic simulations. Surface Science 2001; 487: 87-96.

[9] C. Journet, W.K. Maser, P. Bernier, A. Loiseau, M. Lamy-de-la-Chapelle, S. Lefrant, P. Deniard, R. Lee and J.E. Fisher. Large-scale production of single-walled carbon nanotubes by the electric-arc technique. Nature 1997; 388: 756-758.

[10] J. Gavillet, A. Loiseau, F. Ducastelle, S. Thair, P. Bernier, O. Stephan, J. Thibault and J.C. Charlier. Microscopic mechanisms for the catalyst assisted growth of single-wall carbon nanotubes. Carbon 2002; 40: 1649-1663.

[11] Q. Wei, R.J. Narayan, J. Narayan, J. Sankar and A.K. Sharma. Improvement of wear resistance of pulsed laser deposited diamond-like carbon films through incorporation of metals. Materails Science and Engineering 1998; B53: 262-266.
[12] Y.Y. Chang, D.Y. Wang and W.T. Wu. Catalysis effects of metal doping on wear properties of diamond-like carbon films deposited by a cathodic-arc activated deposition process. Thin Solid Films 2002; 420: 241-247.