

# Tribological properties of carbon nanotubes as lubricant additive

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## ABSTRACT

Tribological performances of innovative lubricant additives based on IF-WS<sub>2</sub> and other transition metal dichalcogenides like MoS<sub>2</sub> nanoparticles have been widely investigated in recent years. The boundary lubrication regime is the main target for the benefits of well-tested or potential additives, since the film thickness of the lubricating base is no longer sufficient to preserve separation of the opposing metal surfaces. Among the various investigated materials, nanocarbons such as fullerenes and nanotubes have proven attractive and promising tribological properties in terms of friction reduction and anti-wear action. In this work experiments have been carried out on a pin-on-disc tribometer to get assessment about the effectiveness of such additives as friction reducers in boundary and mixed lubrication regimes. Multiwalled carbon nanotubes of different geometric characteristics (diameter, length, thickness) were obtained by catalytic CVD. Several tests, performed on arrays of operating conditions in terms of speeds and loads, have aimed to underline the friction loss saving of the lubricated pair by varying nanoadditive concentration in the oil formulation. AISI 316 steel pins with different surface finish have been used to consider the effect of roughness parameters, while the counterpart surface is an X155Cr13MoKu steel disc, 60 HRC.

**Keywords:** nanolubricant, carbon nanotubes, tribological properties

## 1 INTRODUCTION

The most known natural carbon structures are graphite and diamond. Since 1950 graphite has been studied for its tribological properties and utilised as solid lubricant for a long time. Diamond is known as the hardest material in nature, while diamond like carbon (DLC) coatings, considered as amorphous or nanocrystalline diamond, are widely studied for their excellent tribological properties.

The discovery of fullerene and carbon nanotubes (CNT) opened a new field of research also for carbon compound in tribology [1]. Considering the microstructure of CNT, the superior tribological properties predicted, and the expected

weak intermolecular bonding with counterparts, tribology application can become an important application for CNT.

## 2 EXPERIMENTAL

### 2.1 Materials and methods

#### *Carbon nanotubes*

Multiwalled carbon nanotubes (MWNT) have been prepared by catalytic ethylene chemical vapor deposition (CCVD) [2-3] on Co/Fe supported Al<sub>2</sub>O<sub>3</sub> and NaY powders. Co, Fe catalysts (2.5 wt% of each metal) were prepared by dry impregnation with a cobalt acetate and iron acetate solution of gibbsite and NaY-zeolite. The catalysts were dried at 393 K for 720 min and preheated before synthesis at 70 K/min up to 973 K under N<sub>2</sub> flow. For the CNT synthesis a mixture of ethylene in nitrogen was fed to a continuous flow microreactor at 973 K, with a runtime of 30 min. Gas flow rate, controlled by Brooks mass flow controllers, and catalyst mass were 120 (stp)cm<sup>3</sup>/min (10% v/v of C<sub>2</sub>H<sub>4</sub> in N<sub>2</sub>) and 400 mg, respectively. Two types of MWNTs, differing in the aspect ratio L/D (Length/Diameter), have been prepared. In particular, high aspect ratio (L/D=14000) MWNT (HA) and low aspect ratio (L/D=2000) MWNT (LA), see Table 1, have been synthesized on Co/Fe-Al<sub>2</sub>O<sub>3</sub> and Co/Fe-NaY, respectively. To remove the catalyst the synthesized samples were treated with HF (46% aqueous solution), and the solid residue was washed with distilled water, centrifuged and finally dried at 353 K for 12 h, resulting in high purity (> 97%) MWNTs. After purification HA has been sonicated for 5 h (HAS) to obtain shortened carbon nanotubes with a length of few microns and an aspect ratio comparable with that of LA.

MWNTs have been characterized by transmission (TEM) and scanning (SEM) electron microscopy. TEM images were performed with a Philips CM30T instrument with a LaB<sub>6</sub> filament as source of electrons operated at 300 kV. Scanning electron microscopy (SEM) pictures were obtained with a LEO 420 microscope.

Raman spectra were obtained at room temperature with a microRaman spectrometer Renishaw inVia (514 nm excitation wavelength).

Table 1. MWNT geometrical characteristics

	L*	D*
HA	200 $\mu\text{m}$	14 nm
LA	50 $\mu\text{m}$	25 nm
HAS	20-30 $\mu\text{m}$	14 nm
* mean values		

### Lubricant formulation and tests

Tested lubricants are base mineral oils classified as ISO32 and ISO50. Particularly, ISO50 is mineral base oil for engines in a broad area of requirements. Main data are listed in Table 2. This analysis aims to get assessment about friction loss modification due to the specific additive, since other commercial additive compound are absent, e.g., dispersant.

Table 2: Oil properties

	ISO32	ISO50
$v_{40^\circ\text{C}}$ (cSt)	30.9	55.0
$v_{100^\circ\text{C}}$ (cSt)	5.4	8.0
$\rho$ ( $\text{kg/m}^3$ )	862	870
V.I.	111	105

The mixture carbon nanotubes/oils has been obtained through sonication at  $80^\circ\text{C}$  in a low power sonic bath to obtain a stable suspension. LA/ISO32 and HAS/ISO50 mixtures have been prepared.

### Tribological experimental-setup

Friction tests on a pin/disc frictional pair in ambient air have been performed through a tribometer setup (Fig. 1). Several contact conditions have been analyzed in order to achieve boundary and mixed lubrication regimes. The experimental study has been carried out on two different mineral base oils and the effect of nanoparticles size and concentration has been investigated, for each material.

### Experimental device

The tribometer setup is a friction test bench which allows different motion conditions, such as rotations, ramps, oscillations, etc.. According to the standard test principle a stationary test specimen (pin, ball, ring) with a defined normal force is pressed against the surface of a rotational disc. Normal force is applied by a lever system and can be varied in the range  $0 \text{ N} \div 100 \text{ N}$ . The tribometer is driven by a brushless motor with speed from 0.1 to 3000 rpm. The measurement of the normal force is assured by a force sensor arranged between load lever and lower specimen restraint. The oil temperature is measured by a NiCr-Ni-thermocouple in the tank and the friction torque is measured by a torque sensor.

The test equipment depicted in Figure 1 is composed by (i) the test rig with frictional pairs, (ii) the control cabinet and all sensors amplifiers as well as the drive module, (iii) the PC interface for controlling the operating conditions (iv) the acquiring boards. Several tests, performed on arrays of operating conditions in terms of speeds and loads, have aimed to underline the friction loss saving of the lubricated pair by varying nanoadditive concentration in the oil formulation. AISI 316 steel pins with different surface finish have been used to take into account the effect of roughness parameters, while the counterpart surface is an X155Cr13MoKu steel disc, 60 HRC. The friction reduction ability of nanoparticles is shown as generalized Stribeck curve. The abscissa in these diagrams is a dimensionless parameter, lubrication number  $\Lambda$ , given as  $\mu UD/W$ , where  $\mu$  is the oil dynamic viscosity,  $U$  is the sliding speed,  $D$  is pin diameter and  $W$  is the normal imposed load.

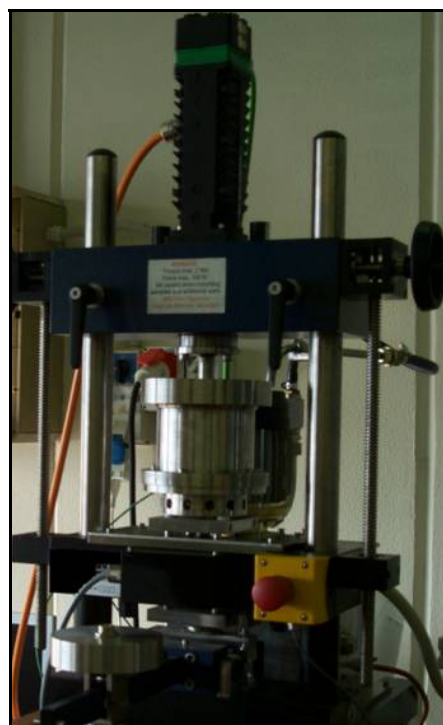


Figure 1: Tribometer for pin - disc contact tests

### Experimental procedure

The friction experiments were performed using a pin on disc frictional pair, as distributed contact condition. Main properties material end test conditions are listed in Table 1. Disc surface was polished with  $R_a 0.05 \mu\text{m}$  while pin finish surfaces varies from  $R_a 0.30$  to  $0.60 \mu\text{m}$ . The load conditions brings the pressure in the order of magnitude of 1 MPa. Sliding velocity range was covered performing friction tests at constant speed values, from 0.01 m/s to maximum 1 m/s.

Test conditions and materials	
Velocity range (m/s)	0.01 – 1
Disc material	X155Cr13MoKu
Pin material	AISI 316
Surface finish $R_a$ ( $\mu\text{m}$ )	0.3 – 0.6

The variation of friction force and oil temperature as function of time were registered continuously during the test. Preliminary experiment was performed on all pins to evaluate the test length and repeatability of friction measures. For each condition five experiment have been performed, the time period for each test being ten minutes both on pure and additivated oil. A common problem of nanoparticles is the aggregation of the particles during their manufacture and in the fluid media within which they are dispersed. Both mixing mode and mixing time influence remarkably the stability of dispersion.

## 2.2 Results and discussion

### Carbon nanotubes

Figure 2 shows typical SEM pictures of the as produced bundles of nanotubes HA and LA as grown from catalyst, with a length of about 200  $\mu\text{m}$  and 50  $\mu\text{m}$ , respectively. Nanotubes are multiwalled, with a mean external and internal diameter of 14 nm and 6 nm for HA (Figure 3) and 25 nm and 8 nm for LA.

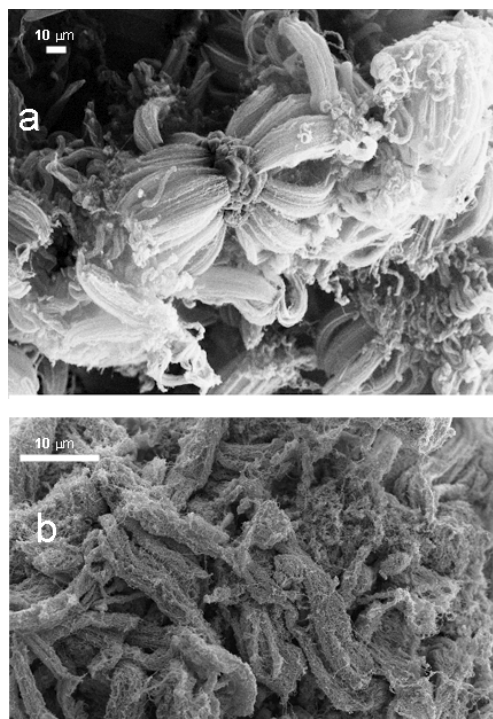


Figure 2: SEM images: (a) as produced HA, (b) as produced LA

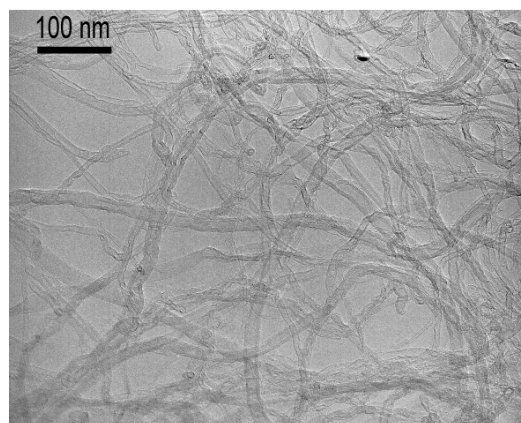


Figure 3: TEM image of as produced HA

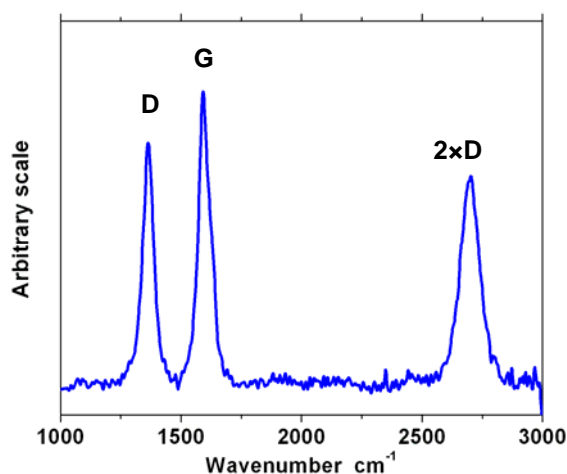


Figure 4: Raman spectrum of as produced HA

Raman spectra of nanotubes (see Figure 4 for HA) show the typical D, G, 2D peaks, centred at 1364, 1594 and 2702  $\text{cm}^{-1}$ , respectively. The intense G peak indicates the presence of crystalline graphite carbon, while the D peak is attributed to amorphous carbon, defects in curved graphene sheet and finite size of tubes crystalline domains. The 2D peak, which is an indication for clean sample, is at the position of doubling frequency of the D-line peak.

### Tribological experiments

It has been reported that very low concentrations of MWNT are sufficient to observe a positive effect on friction behavior [1]. The MWNTs investigated by us have been tested under boundary and mixed lubrication regimes through the tribometer setup. In comparison with pure oil, the addition of 0.1 wt.% of MWNT produced a friction coefficient decreasing in both cases [4].

More in details, by adding LA to base oil ISO 32 (Figure 5), a weak reduction of friction coefficient up to 15% was

observed in boundary lubrication regime, i.e. lubrication number less than  $1.0 \div 1.5$ ; above this threshold, in mixed lubrication regime a marked beneficial effect was observed with average friction reduction around 25%.

In the same operating conditions, the HAS-CNT added to base oil ISO 50 generally allowed enhanced friction reducer properties on the whole lubrication number scale (Figure 6).

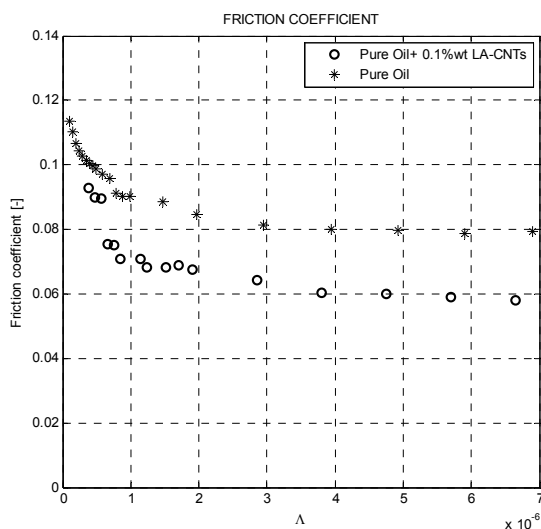


Figure 5: Friction coefficient vs. lubrication number for ISO32+0.1wt LA-CNT

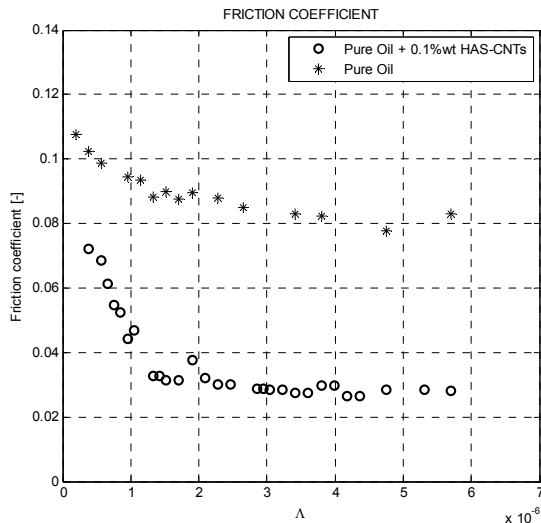


Figure 6: Friction coefficient vs. lubrication number for ISO50+0.1%wt HAS-CNT

### 3 CONCLUSION

CNT used as additive for lubricating base oil have been tested under boundary and mixed lubrication regimes through a tribometer setup. These first tests show a drastically reduced sliding friction loss under the mentioned operating conditions with both the CNT additives.

This encouraging experimental outcome is the necessary milestone before further investigations aimed to isolate the oil viscosity effect on dispersion stability, and to optimise the CNT aspect ratio (length, diameter, thickness) with respect the tribological performance.

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