Fluorinated nanocarbons as promising additives for lubrication

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A few words about tribology

Tribology: part of science concerned with friction, wear and lubrication processes → involved in many natural and industrial domains

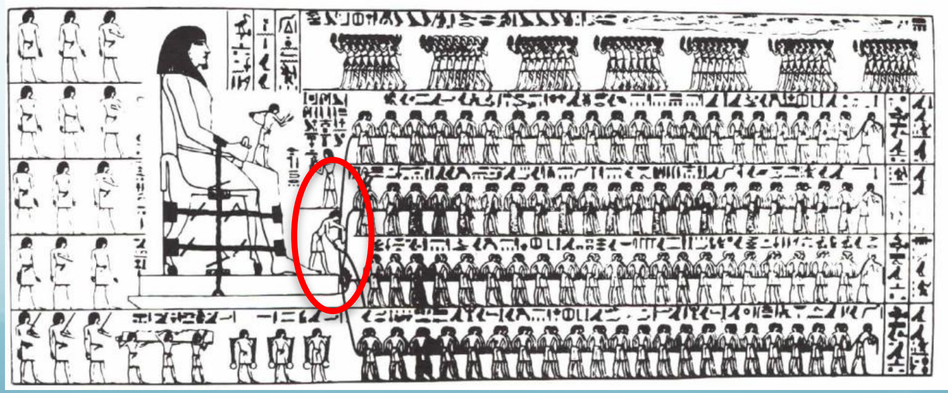
⇓

Relative movement of two contacting surfaces: friction and wear

↙ Energy losses
30% of produced energy in the world is lost by friction

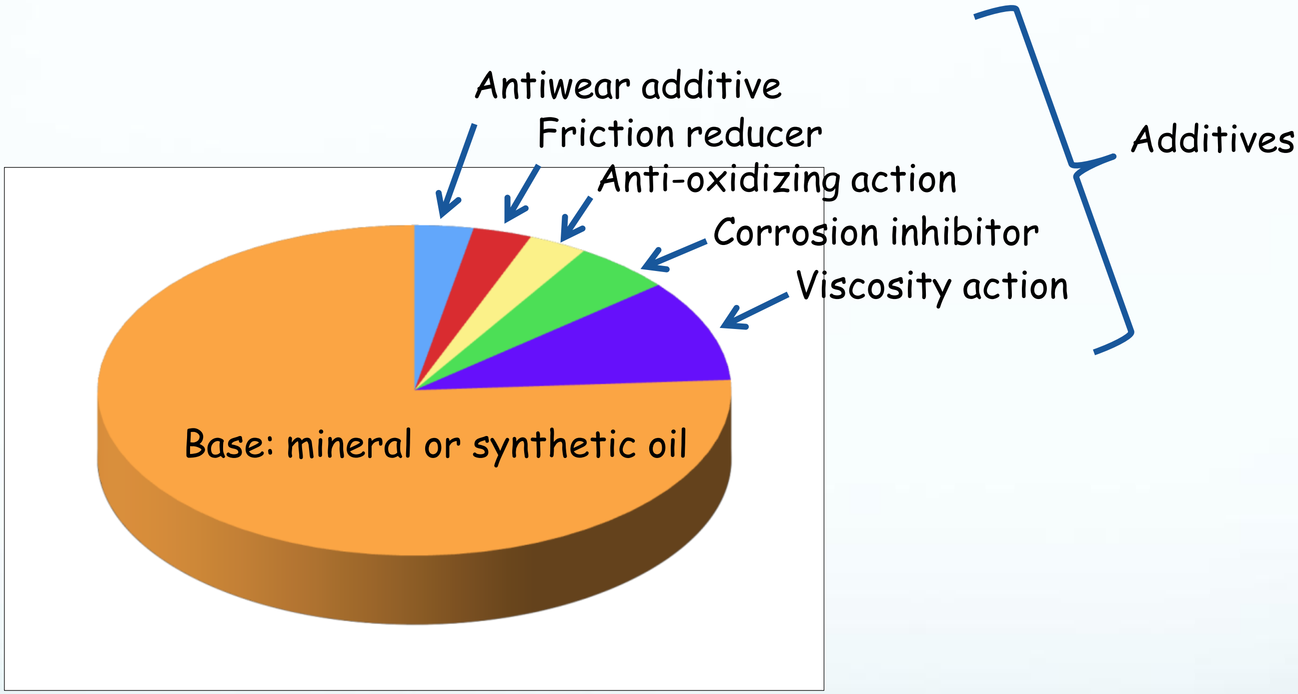
↘ Materials losses
66 million euros/year in France

Lubrication: prevents contact between sliding surfaces



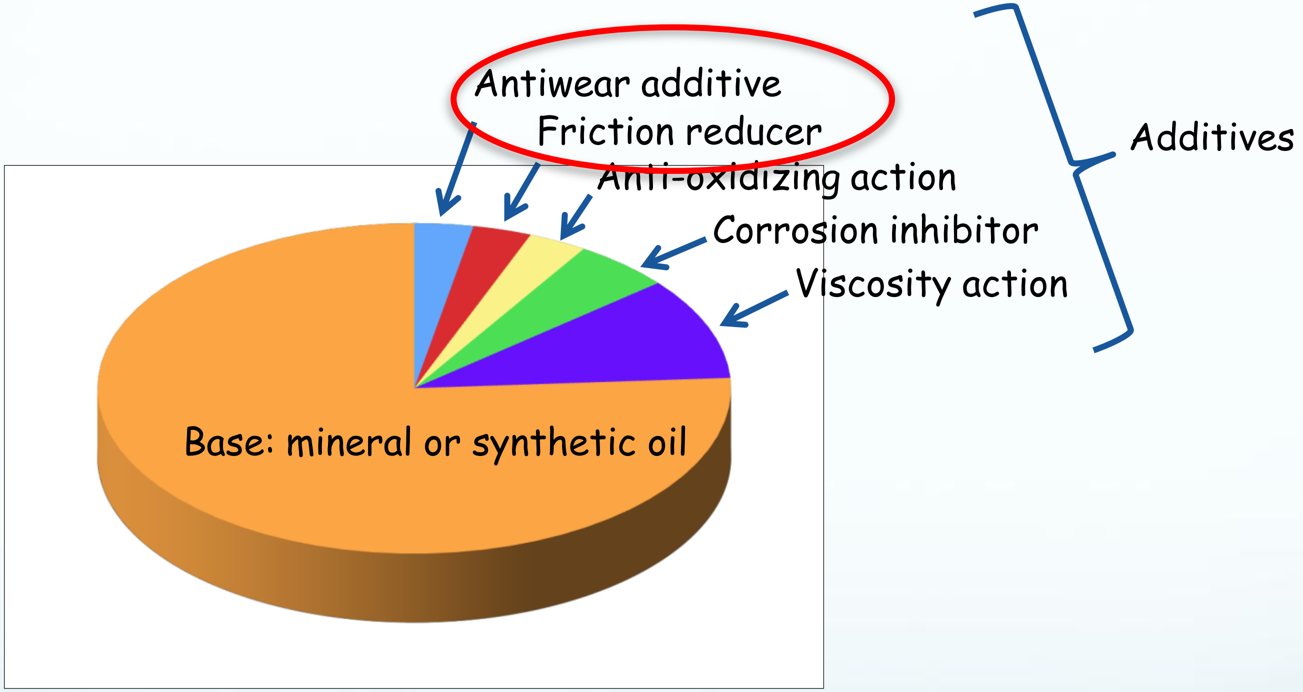
Lubrication regimes

Liquid lubricant: base + additives



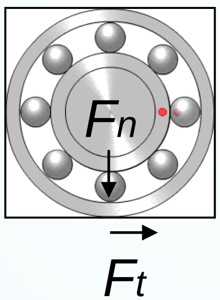
Lubrication regimes

Liquid lubricant: base + additives

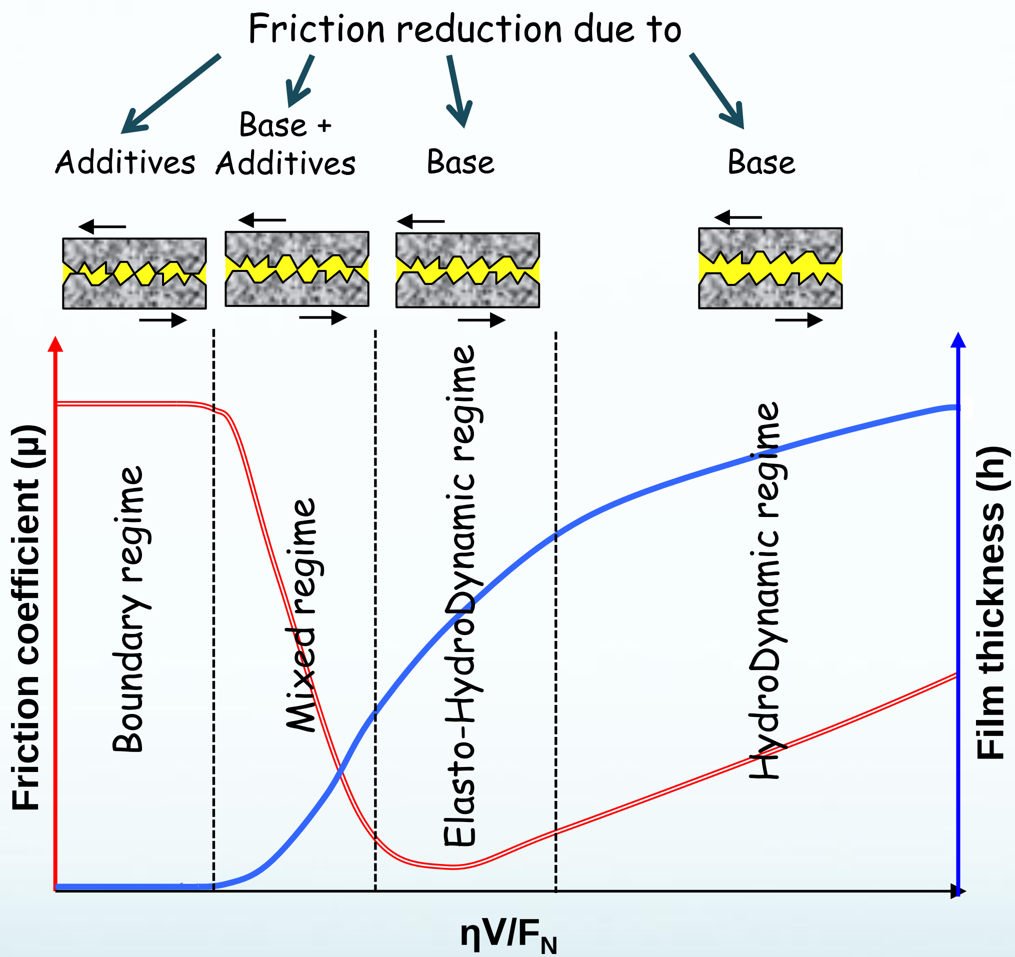


4 lubrication regimes → Sliding speed of moving surfaces
→ Lubricant viscosity
→ Normal load

Lubrication regimes

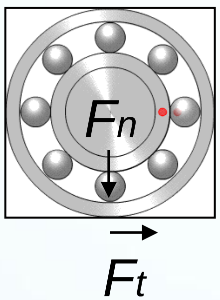


$$\mu = \frac{F_t}{F_n}$$

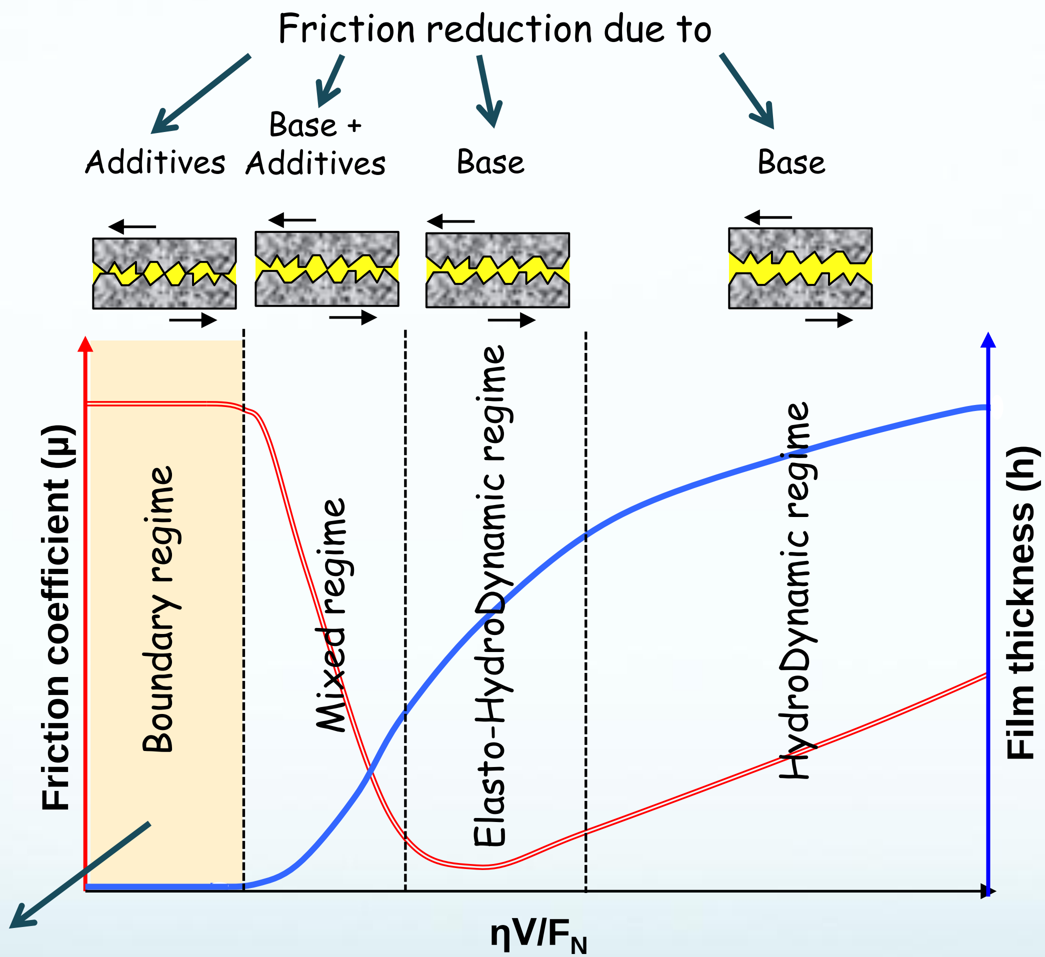


η : Lubricant viscosity
F_N : Normal load
V : Sliding speed

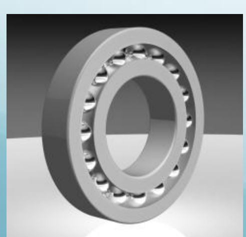
Lubrication regimes



$$\mu = \frac{Ft}{Fn}$$

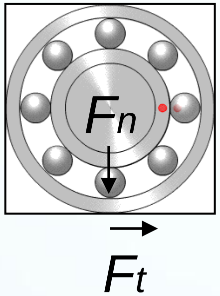


η : Lubricant viscosity
F_N : Normal load
V : Sliding speed

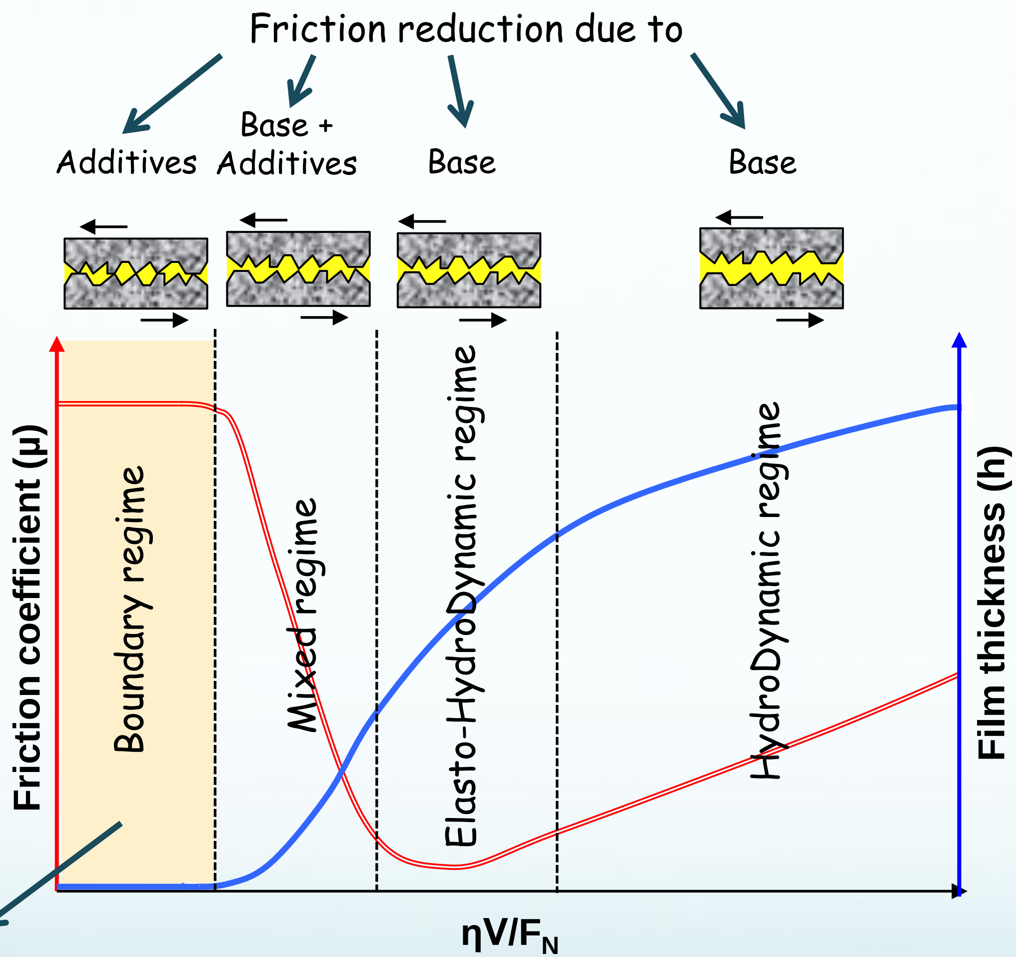

Ball bearings

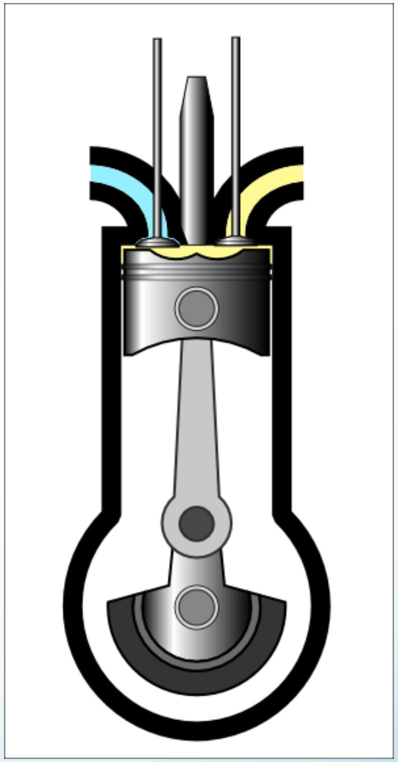
High friction coefficient
Severe wear

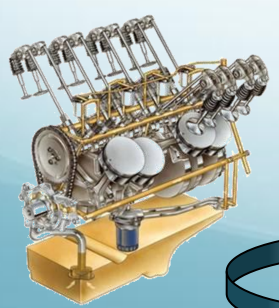
Lubrication regimes



$$m = \frac{Ft}{Fn}$$







Engines

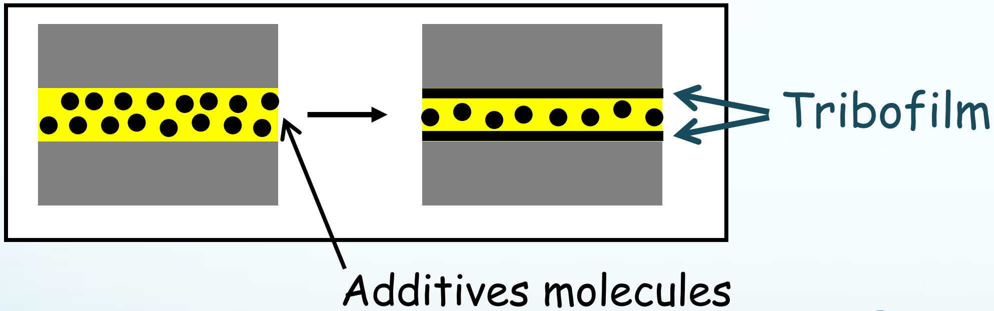
High friction coefficient
Severe wear

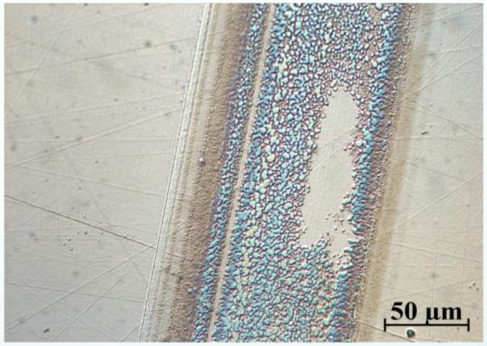
Performances due to antiwear and friction reduction additives

Conventional friction reduction and antiwear additives

Conventional additives: Zinc DialkylDithiophosphate (ZDDP), Molybdenum Dithiophosphate (MoDTP) or Dithiocarbamate (MoDTC)

Built up of a protective tribofilm resulting from chemical reactions between additives molecules and surfaces





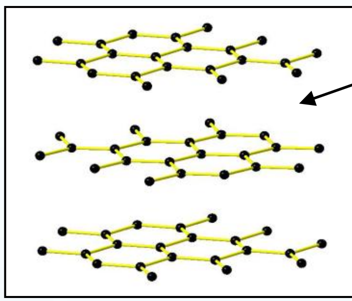
But

- The tribofilm is not immediately built (induction period) → severe wear undergone by the substrates
- The protective action is not efficient in the case of non-reactive sliding surfaces (ceramics,…)

New lubrication strategies

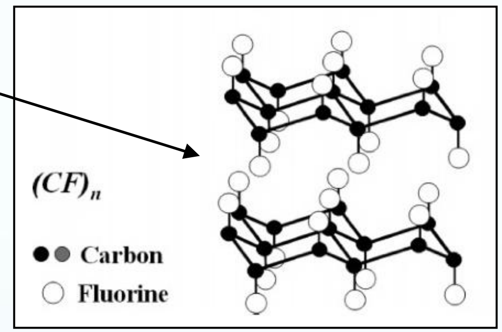
New additives: micro/nanoparticles of tribo-active phases (graphite, MoS_2) or precursors of tribo-active phases (C and inorganic nanotubes or fullerenes) dispersed in the lubricant base

Phases are selected according to their intrinsic friction properties



Graphite: μ = 0,1

van der Waals gap



CFx: μ = 0,09

Good lubricant if $\mu \leq 0{,}1$

Fluorinated carbons

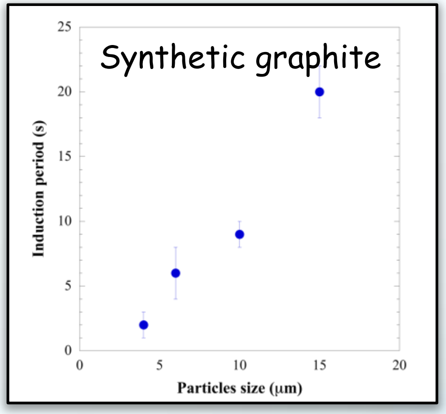
- Good friction properties
- High chemical stability
- Good thermal stability
- Anticorrosive and hydrophobic properties

New lubrication strategies

New additives: micro/nanoparticles of tribo-active phases (graphite, MoS_2) or precursors of tribo-active phases (C and inorganic nanotubes or fullerenes) dispersed in the lubricant base

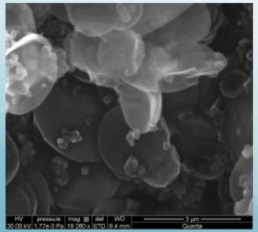
Immediate formation of the tribofilm in the sliding contact conditions without any chemical reactions with the substrates

The induction period strongly depends on the size of the particles: feeding of the sliding interface



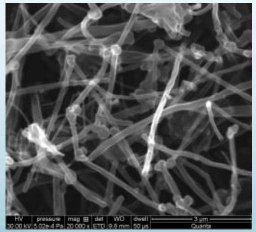
Study of fluorinated nanocarbons

2D structure



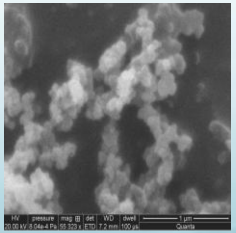
Carbon Nanodiscs (CNDs)

Tubular 1D structure



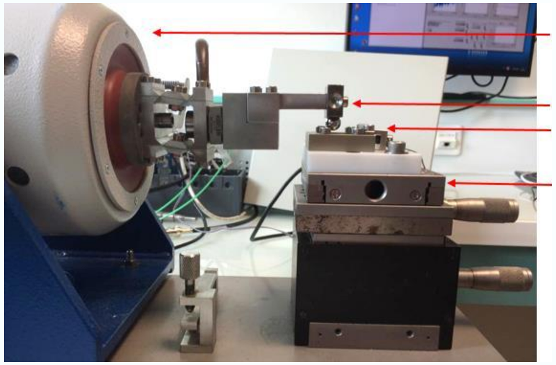
Carbon Nanofibers (CNFs)

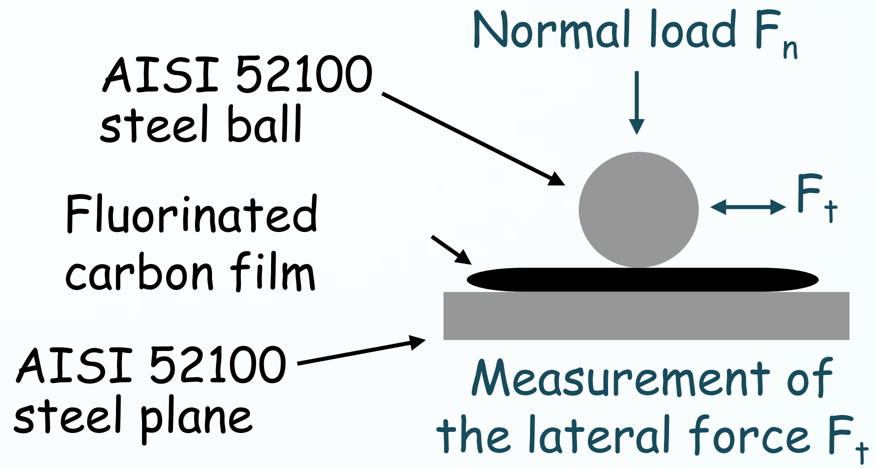
Spherical 0D structure



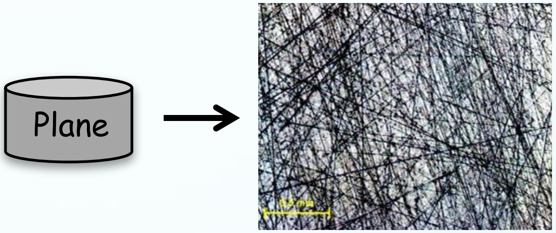
Graphitized Carbon Blacks (GCBs)

Tribologic experimental device

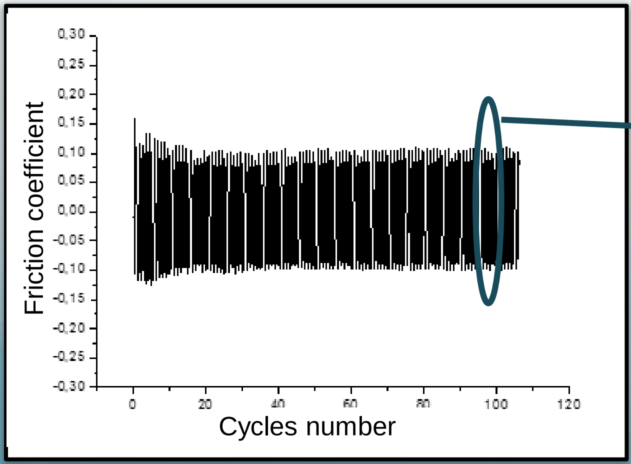


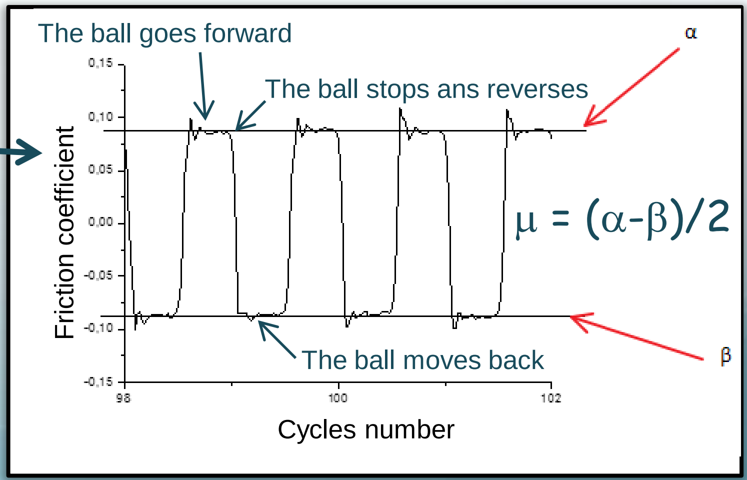


- Normal load: 10 N
- Contact area diameter: 140 μm
- Maximum contact Pressure: 1 GPa
- Sliding speed: 6 mm/s



Friction coefficient $\mu = F_t / F_n$

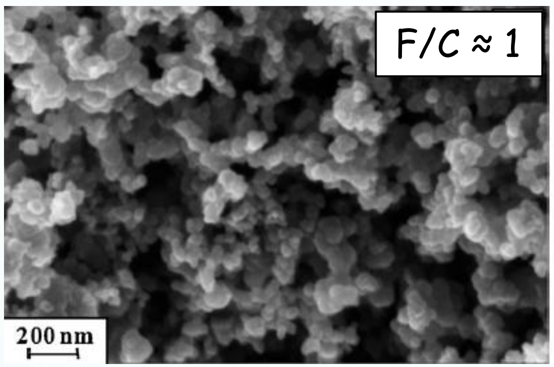




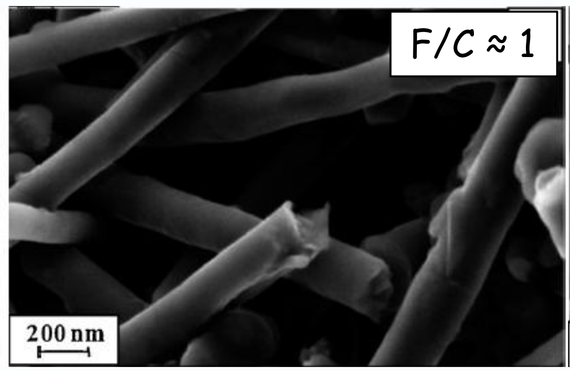
Cycle = reciprocal travel of the ball on the static plane

Nanocarbons fluorination

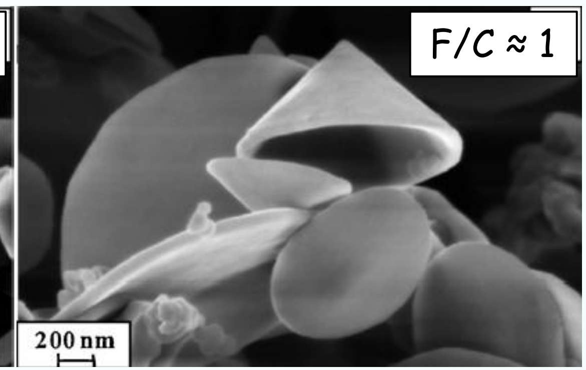
Fluorination under F_2 atmosphere at selected temperatures in order to obtain controlled fluorine contents (expressed as atomic F/C ratio)



Graphitized Carbon Blacks (GCBs)



Carbon Nanofibers (CNFs)



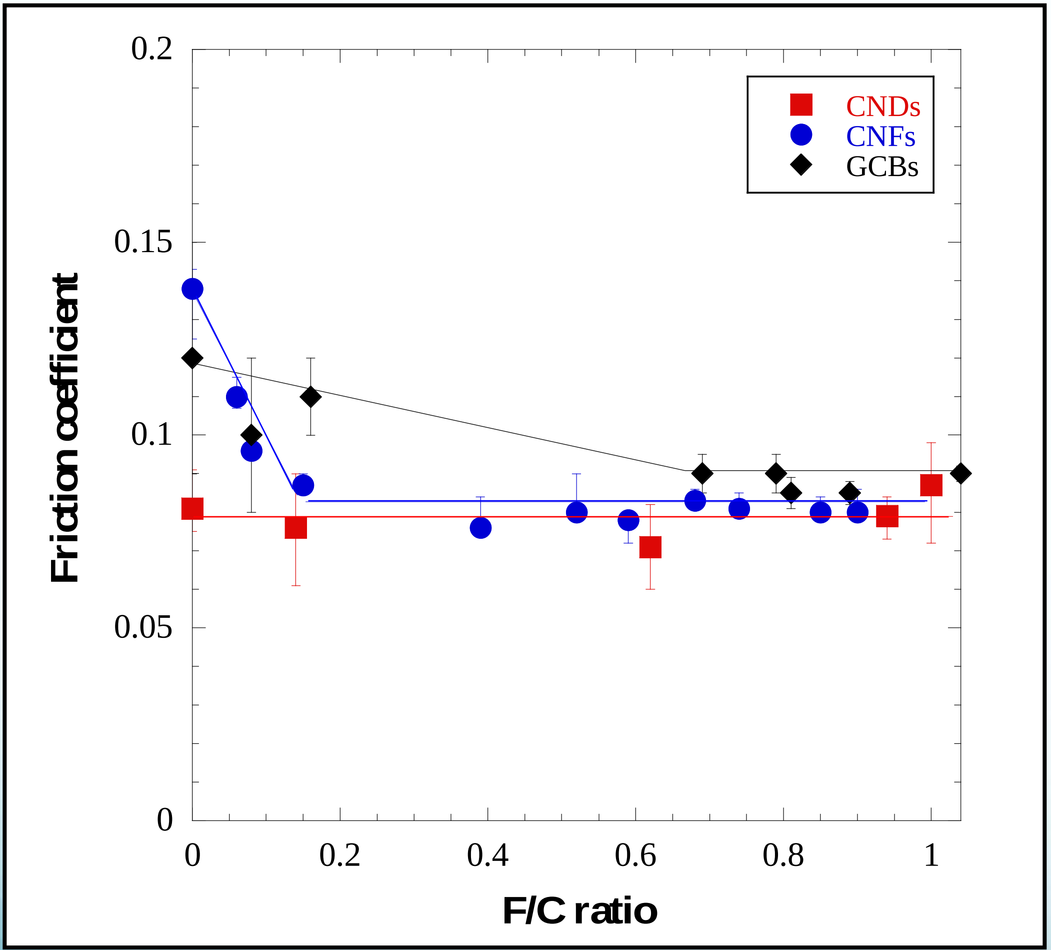
Carbon Nanodiscs (CNDs)

Starting material	T_F range (°C)	F/C range*
CNDs	450-520	0.14-1.0
CNFs	380-480	0.06-1.04
GCBs	320-340	0.08-1.04

*F/C ratios were determined by weight uptake or ^{13}C and ^{19}F NMR

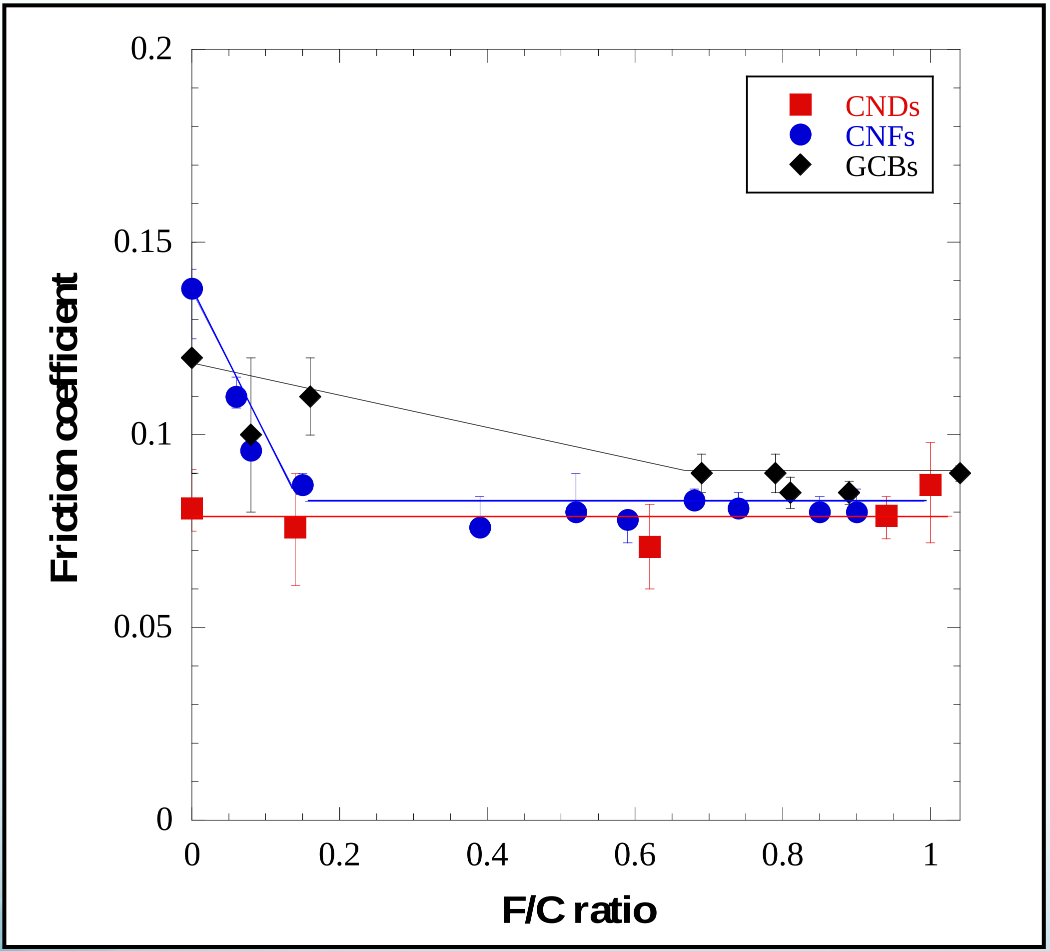
Covalent C-F bonds

Tribologic properties of fluorinated nanocarbons



- Fluorination improves the friction properties
  - ➡ $\mu_{\text{fluorinated materials}} < \mu_{\text{pristine compounds}}$
- Carbon nanodiscs (CNDs): the friction properties do not depend on the fluorine content
  - ➡ $\mu \approx 0.08$ for all the tested compounds
- Carbon nanofibers (CNFs) and graphitized carbon blacks (GCBs): the friction properties depend on the fluorine content
  - ➡ Linear decrease of μ for $0 < F/C < 0.15$ for CNFs and $0 < F/C < 0.6$ for CBGs
  - ➡ Stabilization at $\mu \approx 0.08$ for higher F/C ratios

Tribologic properties of fluorinated nanocarbons



- Very low values of μ

Fluorinated nanocarbons present excellent friction reduction properties

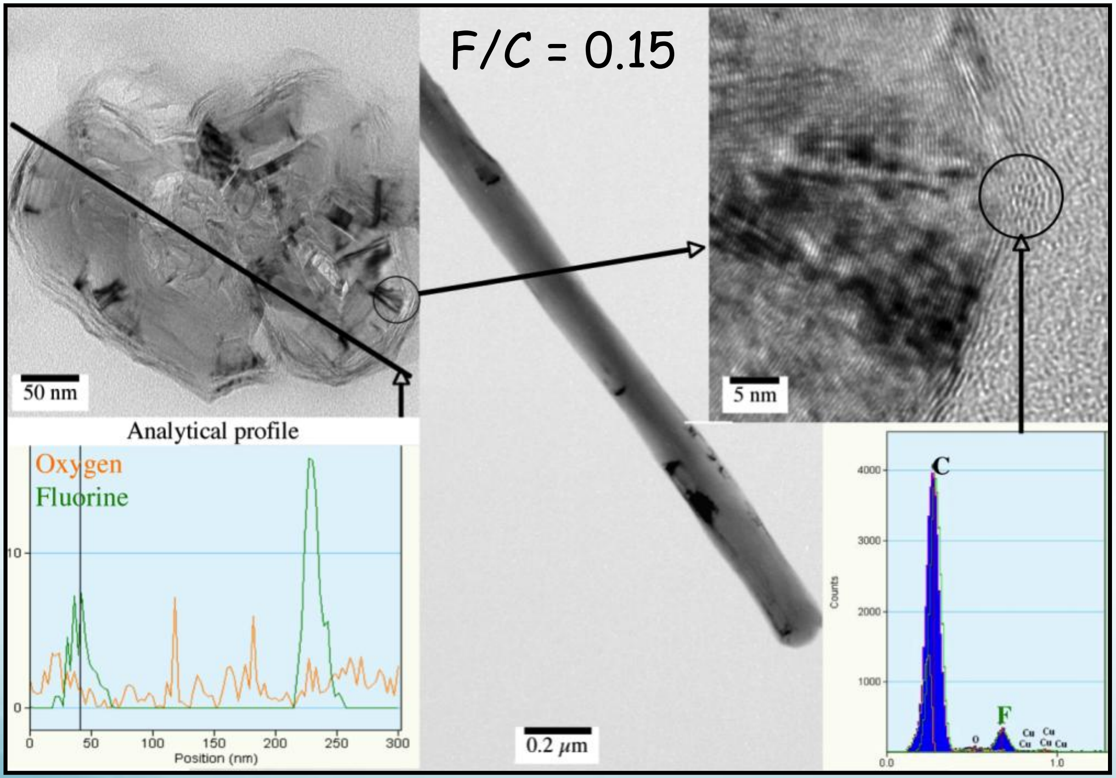
- Different tribologic behaviour depending on the morphology of the particles

Different friction reduction mechanisms

Friction reduction mechanisms

Friction reduction mechanisms of CNFs: correlation between friction properties and structural characterizations

TEM investigation of a cross section of a fluorinated CNF



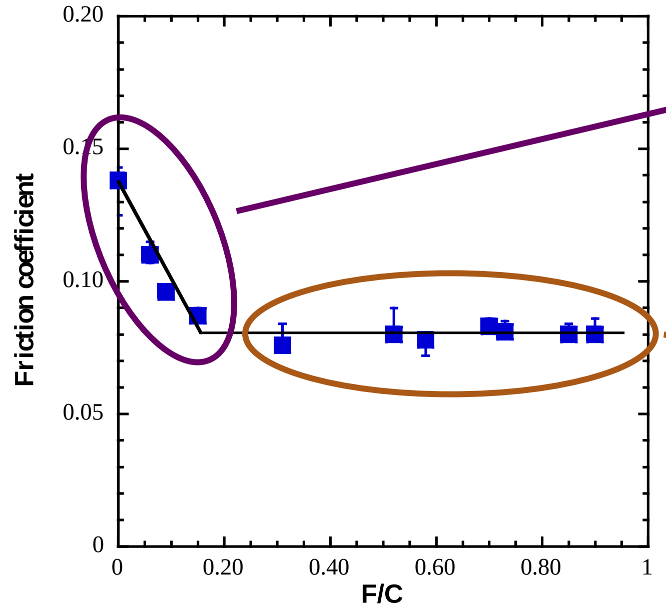
- Lattice fringes corresponding to graphitic structure are visible in the internal part of the fiber

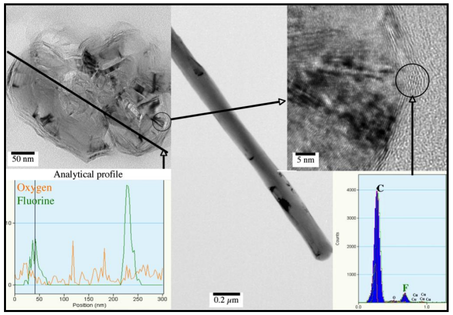
- Presence of fluorine at the periphery

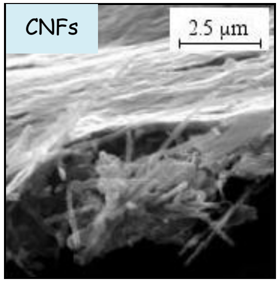
Progressive fluorination proceeding from the outer part of the carbon nanofiber towards its core as far as the fluorination temperature increases

Friction reduction mechanisms

Friction reduction mechanisms of CNFs: correlation between friction properties and structural characterizations







- μ ↘ for $F/C < 0.15$

Fluorination → Decrease of surface free energy: minimum obtained for $F/C \approx 0.15$

- $\mu \approx 0.08$ for $F/C > 0.15$

Fluorination progresses towards the fibres core : no significant evolution of the surface free energy

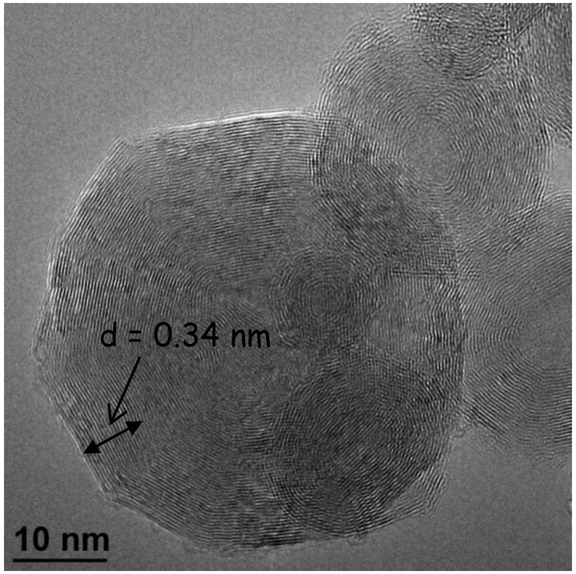
Friction reduction mechanism involving surface effects (individual nanofibers interactions)

Friction reduction mechanisms

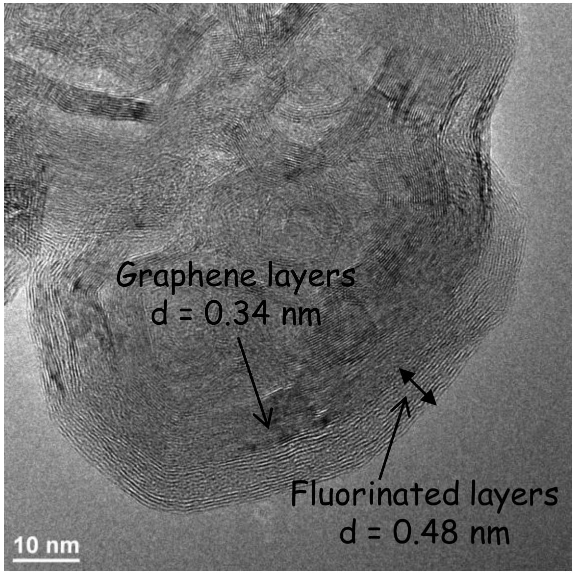
Friction reduction mechanisms of GCBs: correlation between friction properties and structural characterizations

TEM characterization of fluorinated GCBs

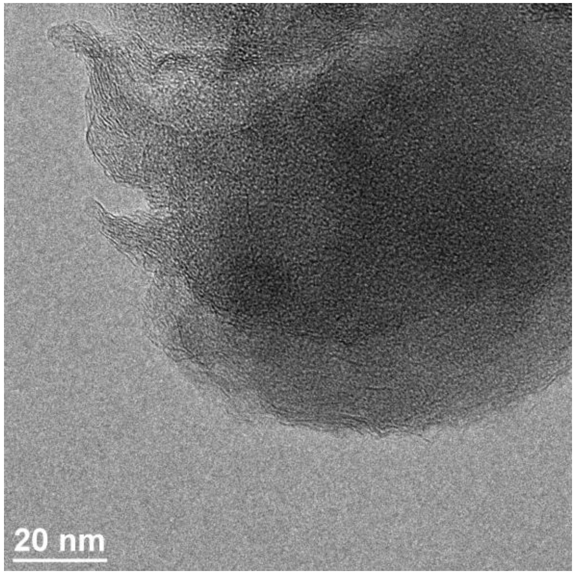
Pristine CBGs



CF0.16



CF0.89



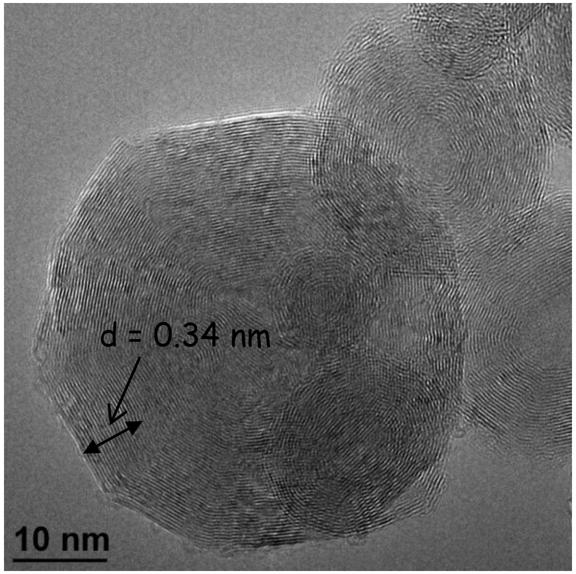
- Pristine materials present a graphitic structure
- The fluorinated parts are characterized by an increase of the interplanar distance (d = 0.48 nm) compared to graphite one (d = 0.34 nm)

Friction reduction mechanisms

Friction reduction mechanisms of GCBs: correlation between friction properties and structural characterizations

TEM characterization of fluorinated GCBs

Pristine CBGs



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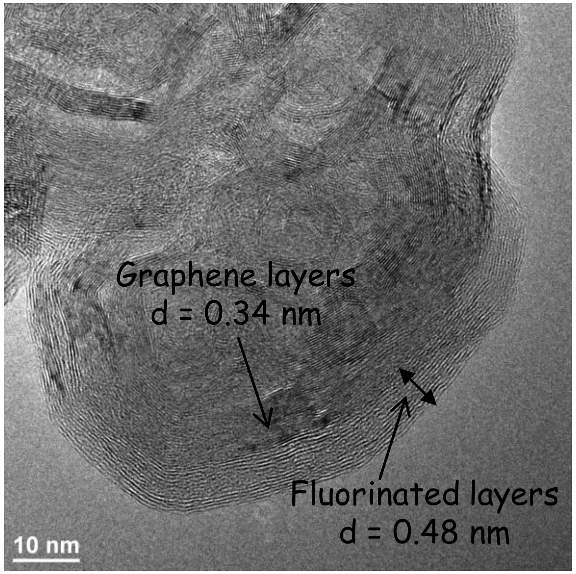

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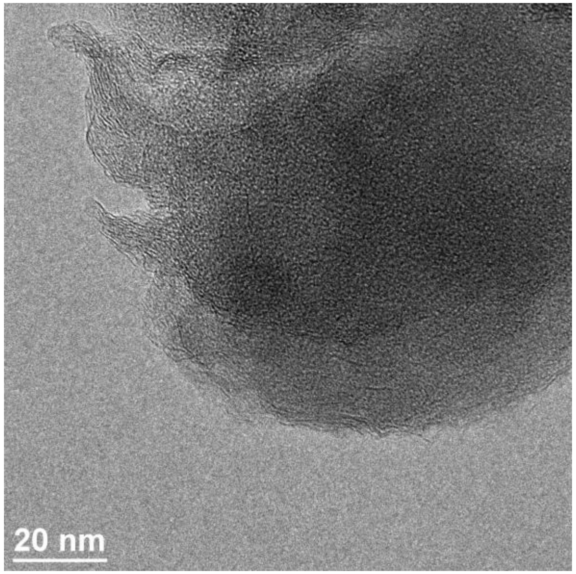
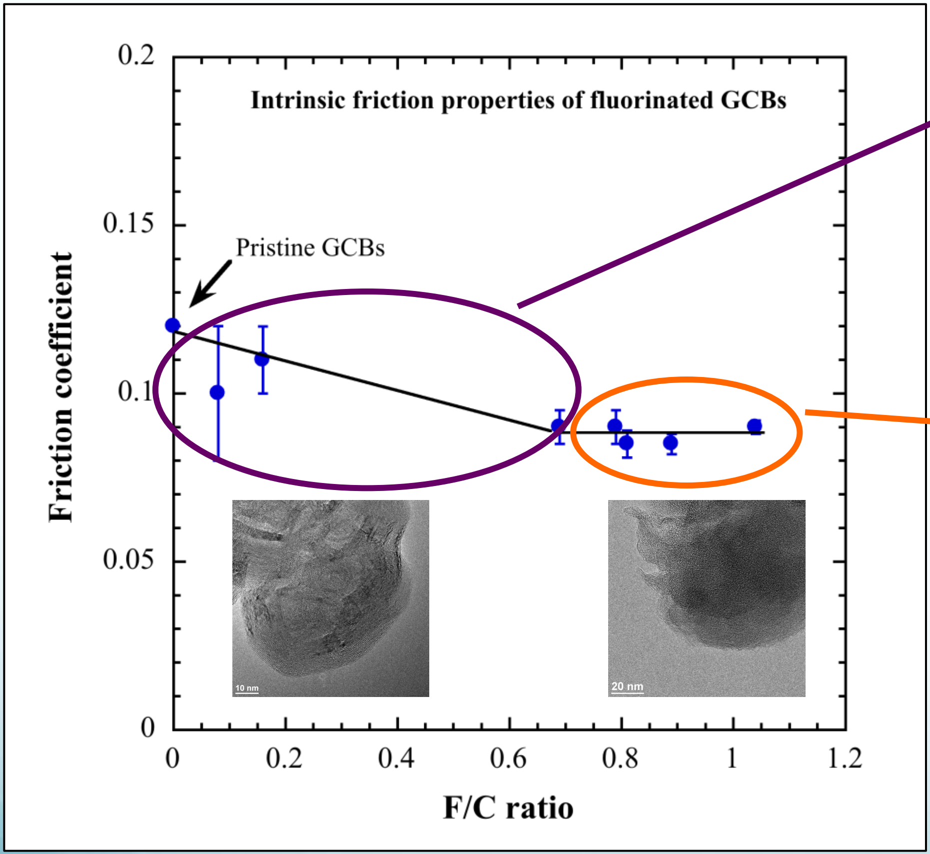


The fluorination process progresses from external layers towards inner ones

Friction reduction mechanisms

Friction reduction mechanisms of GCBs: correlation between friction properties and structural characterizations



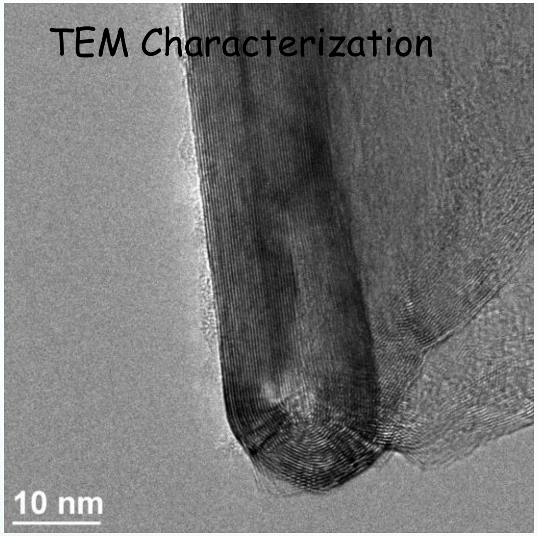
- Decrease of μ associated to the lowering of surface energy of the particles due to the thickening of the fluorinated layer
- The thickness of the surrounding fluorinated layer is sufficient to stabilize the surface energy of the particles

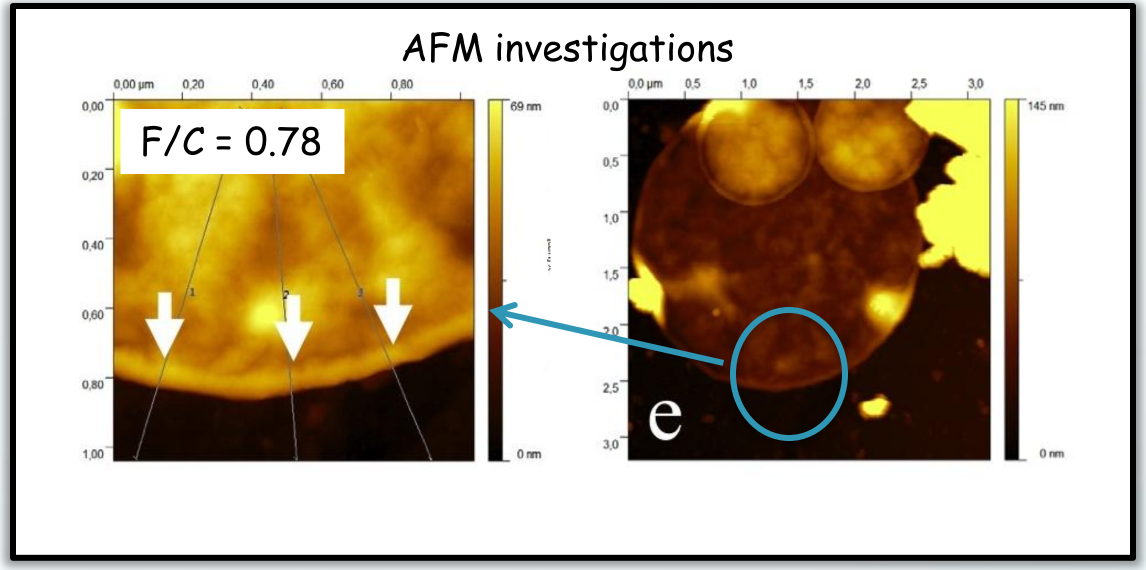
No more surface effects: stabilization of the friction coefficient

Friction reduction mechanism involving surface effects

Friction reduction mechanisms

Friction reduction mechanisms of CNDs: correlation between friction properties and structural characterizations



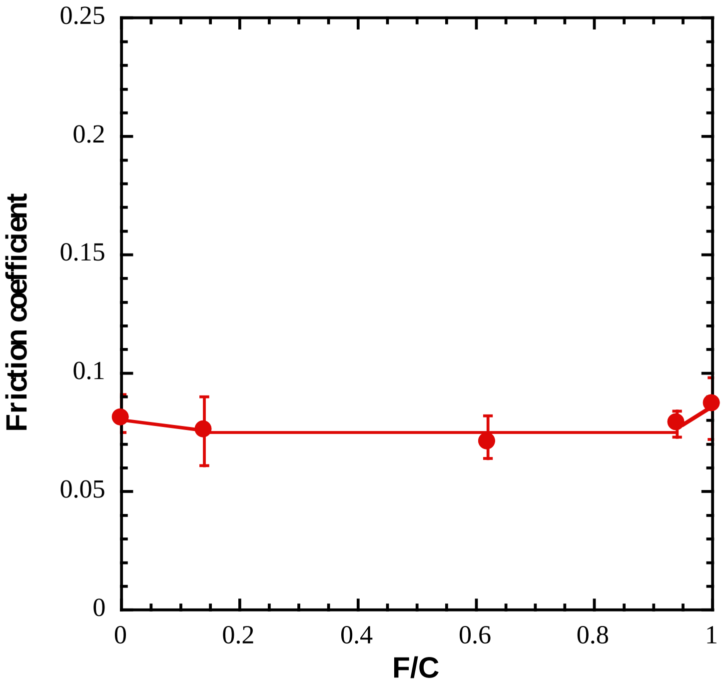


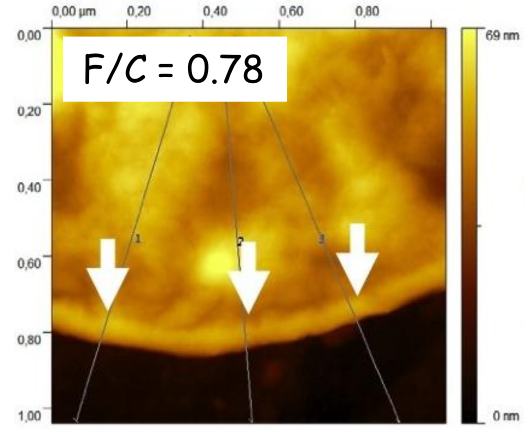
- Swelling is more pronounced at the edges of the nanodiscs
- Swelling of the edges is visible in the overall perimeter

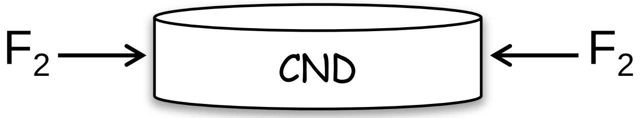
The fluorination process mainly occurs via the edges of the CNDs

Friction reduction mechanisms

Friction reduction mechanisms of CNDs: correlation between friction properties and structural characterizations



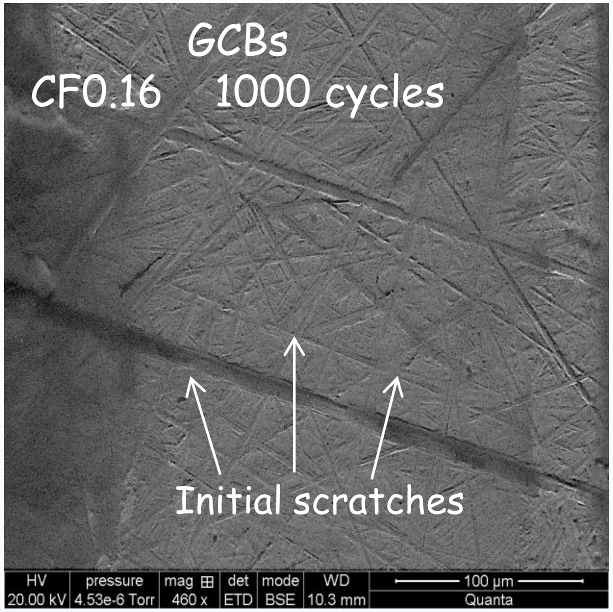


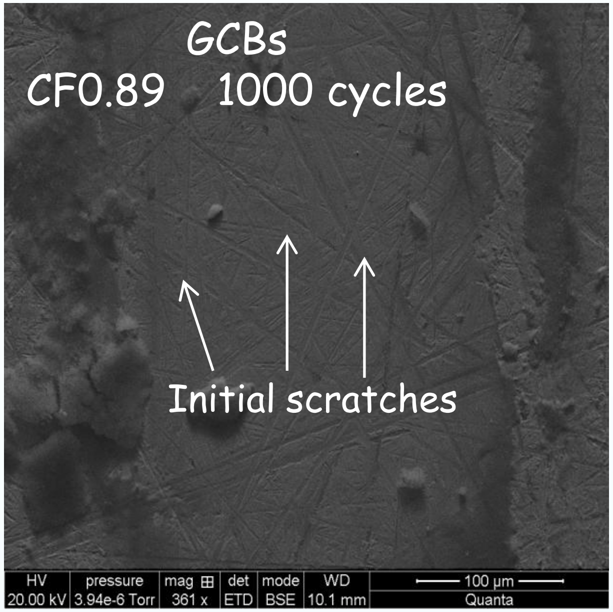


- Fluorination occurs via the edges: the fluorine atoms diffuse in the whole volume

The friction coefficient does not depend on the fluorine content: friction reduction mecanisms implying bulk effects

Antiwear properties of fluorinated nanocarbons





- Initial scratches are still visible after 1000 cycles of friction: very weak wear
- Same observations for all the tested compounds

Fluorinated nanocarbons present good antiwear properties

Conclusions

- Fluorination improves the friction performances of nanocarbons

- Friction reduction mechanisms depend on the morphology of the particles

Bulk effects
Carbon nanodiscs (2D)

Surface effects
Carbon nanofibers (1D)
graphitized carbon blacks (0D)

- Promising new nano-additives for liquid or gel lubricants

  - Very low friction coefficient: $\mu \approx 0.08$
  - Very good durability of the friction performances
  - Instantaneous protective action: no induction period
  - Good antiwear properties
  - Sizes and geometries well adapted for a good feeding of the sliding interface

Thank you for your attention

ACKNOWLEDGEMENTS: The authors acknowledge the CNRS, the Conseil Régional de la Guadeloupe, the Fond Social Européen (FSE) and Fonds Européens de Développement Régional (FEDER) for their financial supports.

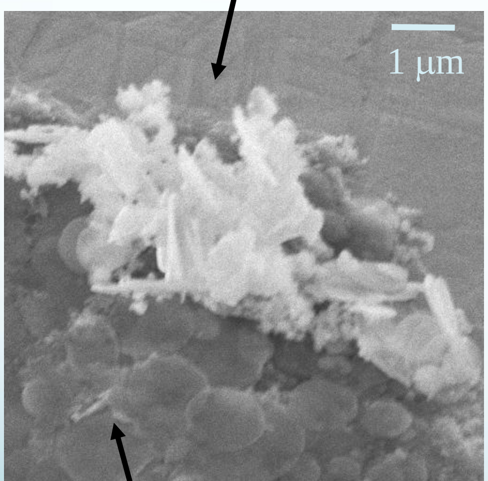
Friction reduction mechanisms

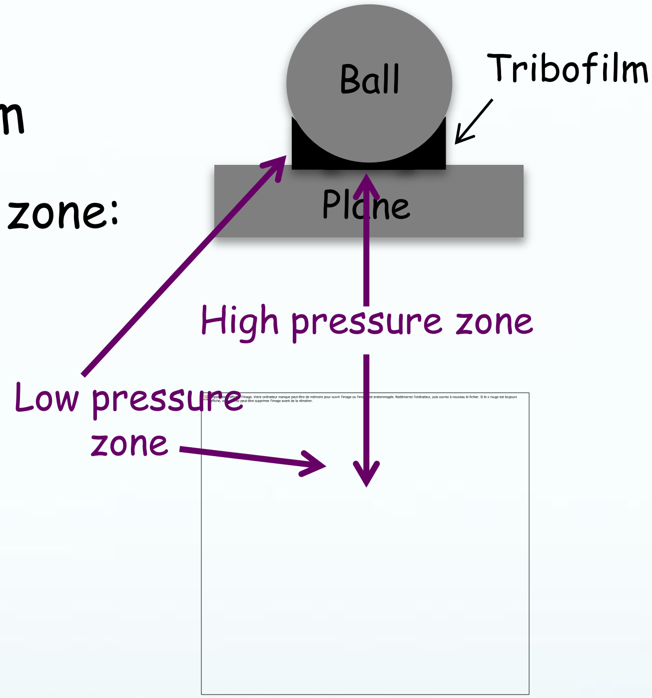
Study of the tribofilms: SEM investigations

Carbon nanodiscs

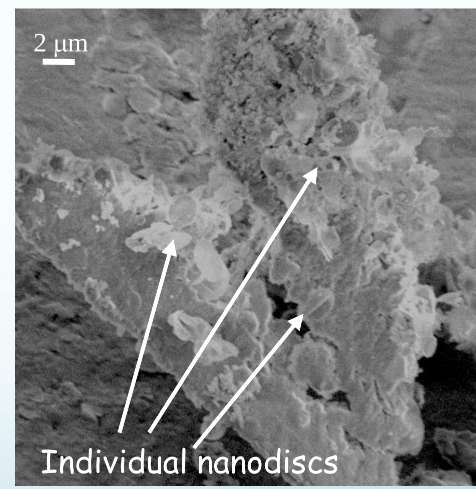
Aspect of the tribofilm

High contact pressure zone: very smooth aspect





Particles extracted from the wear scar



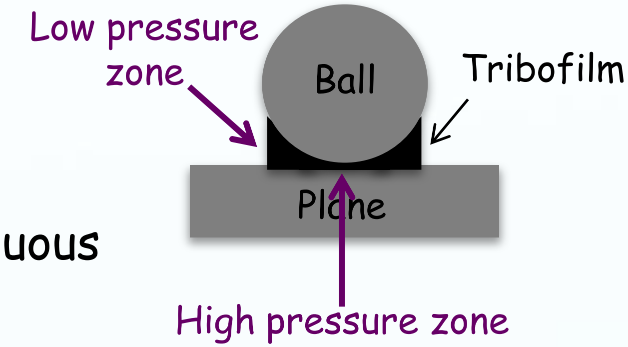
Low contact pressure zone: the discs are oriented parallel to the sliding direction

The tribofilm is mainly amorphous with some individual discs embedded in the disordered phase

Friction reduction mechanisms

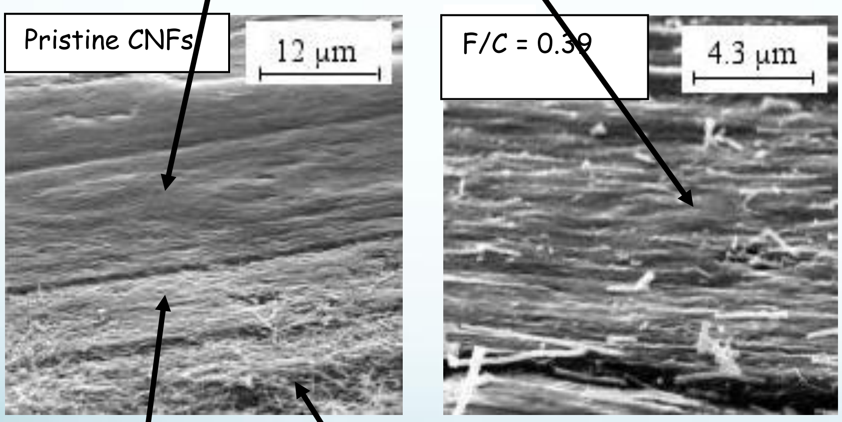
Study of the tribofilms: SEM investigations

Carbon nanofibers



Aspect of the tribofilm

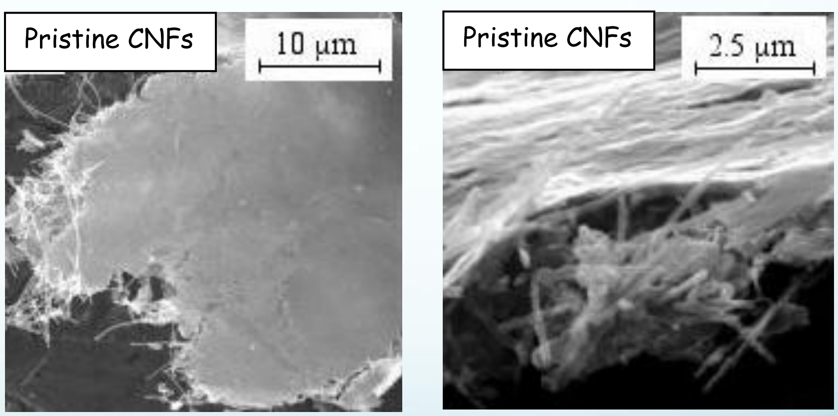
High pressure zone: continuous aspect with ondulations



Tangled fibers

Low contact pressure zone: orientation of the fibers along the sliding direction

Particles extracted from the wear scar

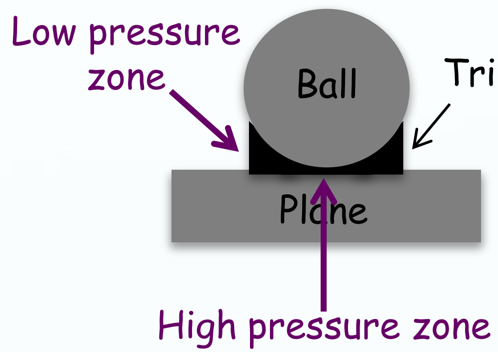


Tribofilms constituted of individual nanofibers covered by an ill organized layer (0.3 µm thickness)

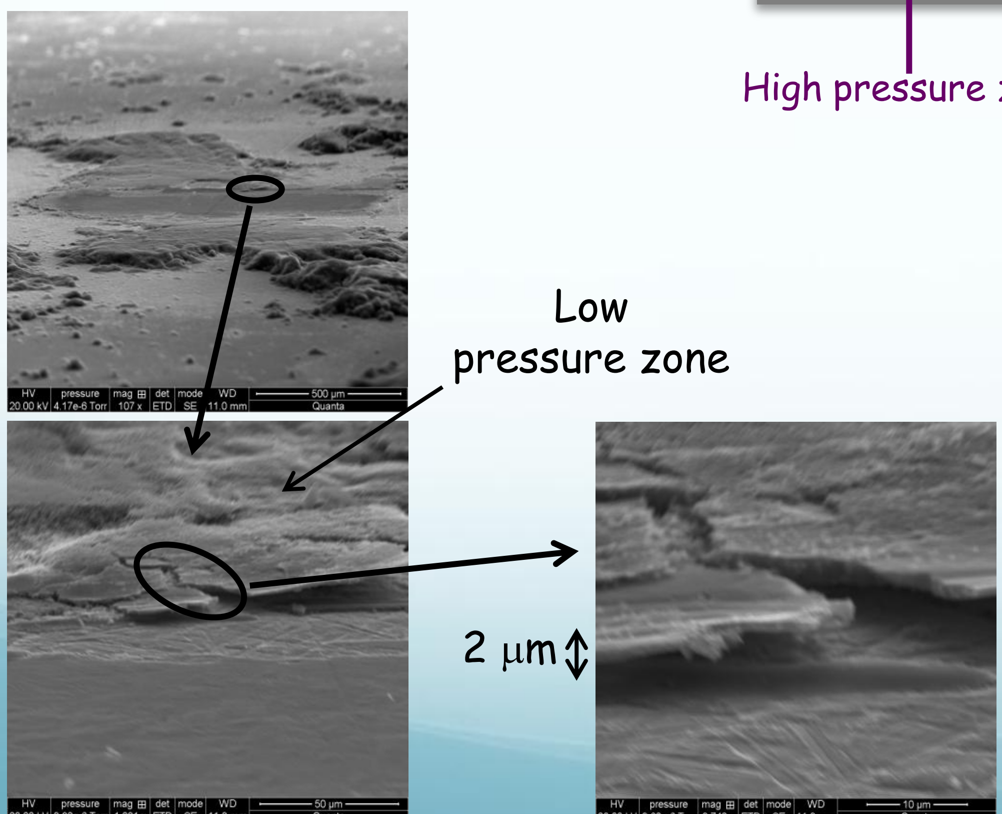
Friction reduction mechanisms

Study of the tribofilms: SEM investigations

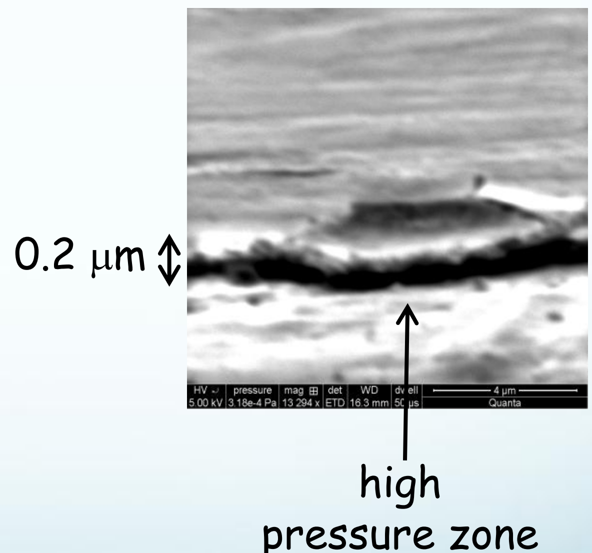
Graphitized carbon blacks



Aspect of the tribofilm



Wear scar



Tribofilms seems to be constituted of individual CBGs embedded in a disordered phase