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Tribological properties of fluorinated nanocarbons with different shape factors

N. Nomède-Martyr [a,b,c], E. Disa [a,b], P. Thomas [c], L. Romana [c], Jean-Louis Mansot [c,d,**], M. Dubois [a,b,*], K. Guérin [a,b], W. Zhang [a,b,e], A. Hamwi [a,b]

[a] Clermont Université, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand (ICCF, UMR 6296), Inorganic Materials team, 63171 Aubière, France
[b] CNRS, UMR 6296, 63170 Aubière, France
[c] Groupe de Technologie des Surfaces et Interfaces (GTSI, EA 2432), Faculté des Sciences Exactes et Naturelles, Université des Antilles et de la Guyane, 97159 Pointe à Pitre Cedex, France
[d] Centre Commun de Caractérisation des Matériaux des Antilles et de la Guyane (C^3MAG), Faculté des Sciences Exactes et Naturelles, Université des Antilles et de la Guyane, 97159 Pointe à Pitre Cedex, France
[e] Ecole Centrale de Pékin, Beijing University of Aeronautics and Astronautics (BUAA), Road 37, HaiDian District, Beijing 100191, China

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ABSTRACT

The structural parameters of fluorinated nanocarbons presenting different shapes, i.e. spherical, tubular and discotic are investigated and correlated to their tribological properties. Different fluorination rates of graphitized carbon blacks (0D), carbon nanofibres (1D) and a mixture of carbon nanodiscs and nanocones (2D) were achieved under pure molecular fluorine gas flow (direct fluorination). Raman spectrometry, X-ray diffraction and ^{19}F solid state nuclear magnetic resonance underline similar structure and nature of the C–F bonds (covalent) for equivalent fluorine contents. In spite of the similarities of physical–chemical properties at equivalent fluorine contents, the tribological properties of the fluorinated nanocarbons differ. Those properties are discussed taking into account the role of the fluorine content and location of the fluorine atoms in the decrease of the interparticle interactions and in the cleavage of the external fluorocarbon layers to form the tribofilm. Finally, the effect of the shape is discussed.

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1. Introduction

During the last three decades, the increase of severity of lubrication conditions in engines and environment protection purpose are at the origin of the development of new additivation strategies for lubrication in the boundary regime. These developments are mainly investigated to overcome the insufficiency of conventional lubricant additives which protective efficiency depends on their reactivity with the sliding surfaces, associated to the occurrence of formation of a protective tribofilm and which present high sulfur and phosphorus contents [1–4]. These new strategies of lubrication consist in the introduction of either solid nanoparticles of tribo-active phases [2] or precursor of tribo-active phases [3,4] in the lubricant base. These new nano-additives are subjected to form the protective tribofilm, in the physical–chemical conditions of a sliding boundary contact, without any chemical reactions with the sliding surfaces. Nano-particles of lamellar compounds or precursors of lamellar compounds such as carbonaceous nanomaterials (carbon nanotubes, onions, nanohorns, peapods...) are promising candidates as far as carbon lamellar compounds (graphite) already present good intrinsic friction properties [1,5]. These good properties are associated to the layered structure of graphite type phases where graphene layers are separated by van der Waals gaps through which interactions between graphene layers are extremely weak [6]. Previous studies also showed that the tribological properties of graphite strongly depend on the environmental conditions [7–10] which are able to significantly modify the surface energy of the particles and then the interparticular interactions leading in many cases to an improvement of the intrinsic properties recorded under vacuum or in dry air.

In the present work two strategies are investigated to improve the tribological properties of nanocarbon phases [11–13]:

- The modification of nanoparticle surface energies by chemical covalent functionalization with fluorine atoms.
- The optimization of the shape/dimensional factors (spherical = 0D, cylindrical = 1D, discotic = 2D).

The friction properties of the pristine carbon nanophases and fluorinated ones obtained via the two strategies are investigated in

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[*] Corresponding author at: Clermont Université, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand (ICCF, UMR 6296), Inorganic Materials team, 63171 Aubière, France. Tel.: +33 473407105; fax: +33 473407933.

[**] Corresponding author at: Groupe de Technologie des Surfaces et Interfaces (GTSI, EA 2432), Faculté des Sciences Exactes et Naturelles, Université des Antilles et de la Guyane, 97159 Pointe à Pitre Cedex, France. Tel.: +33 590483097.

E-mail addresses: jean-louis.mansot@univ-ag.fr (J.-L. Mansot), Marc.DUBOIS@univ-bpclermont.fr (M. Dubois).

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order to evaluate the influence and benefits associated to each structural/chemical parameters.

0D materials (spherical carbon blacks), 1D nanocarbons (carbon nanofibres) and 2D ones (carbon nanodiscs) with similar crystalline order (graphitized materials) were selected and fluorinated using molecular fluorine F_2. The tribological properties of the resulting derivatives were then investigated. As a matter of fact, the C–F bonding is highly versatile in fluorinated carbons. The nature of the interactions between the fluorine and the carbon atoms can considerably vary: in the case of the fluorine adsorption on the surface of carbonaceous materials, these interactions are very weak. On the other hand, a covalent, semi-ionic or ionic character can be obtained [14,15]. In particular, intermediate states are observed in compounds where fluorinated carbon atoms, with sp^3 hybridization, and non-fluorinated sp^2 ones coexist in the layers (hyperconjugation) [16,17]. The nature of the C–F bonds depends on the synthesis conditions; for covalent compounds, namely graphite fluorides $(C_2F)_n$ and $(CF)_n$, prepared with molecular fluorine at 350 °C and 600 °C [17,18], respectively, the carbon skeleton consists of trans-linked cyclohexane chairs or cis-trans linked cyclohexane boats with sp^3 hybridization. In the case of fluorine–graphite intercalation compounds (C_xF), obtained at temperature lower than 100 °C, the planar configuration of graphite is partially preserved; the nature of the C–F bond evolves from ionic for low fluorine contents to covalent for higher fluorine contents. Moreover, due to the high number of walls, the curvature of nanofibres is low and does not affect the C–F bonding contrary to the cases of single, double or low diameter multiwalled nanotubes or fullerenes [19].

In the first part of the present paper, the physical–chemical characterization of the fluorinated carbons using ^{19}F solid state nuclear magnetic resonance (NMR), X-ray diffraction (XRD) and Raman spectroscopy will be discussed in order to underline the structural order and the nature of the C–F bonds. The tribological properties will be then compared for the 0D, 1D and 2D fluorinated nanocarbons.

2. Experimental

2.1. Carbonaceous nanomaterials

The 0D compounds were prepared from carbon blacks provided by Superior Graphite, graphitized by high temperature treatment (2000 °C under argon) and denoted as GCBs in the paper. Transmission electron microscopy (TEM) showed for the same commercial product that highly graphitized layers surround the core of the particles; this outer shell of about 10 nm thickness results from the graphitization process [20].

The 1D materials were synthesized from high purity (>90%) carbon nanofibres (CNFs), of 2–20 microns length, supplied by MER Corporation, Tucson, Arizona. They were obtained by chemical vapor deposition (CVD) and heat treated at 1800 °C in an argon atmosphere to enhance their graphitization degree.

The 2D samples consist in a mixture of carbon nanodiscs (70 weight %), carbon nanocones (20 weight %) and amorphous carbon (10 weight %), provided by NTec Norway [21,22] annealed under argon at 2700 °C for graphitization. Because of the large amount of discs, the mixture will be denoted CNDs. CNDs were produced by pyrolysis of heavy oil using the Kvaerner Carbon Black and Hydrogen Process (CBH) [23].

2.2. Fluorination conditions

Direct fluorination was carried out with pure fluorine gas flow in a Monel reactor. Different fluorine contents were obtained according to the fluorination temperatures T_F with constant duration of 3 h and F_2 gas flux of 10 mL min^{-1}. The fluorine content "x" of the fluorinated nanocarbons, expressed as the atomic F/C ratio, was determined first by gravimetry upon fluorination (weight uptake method) and confirmed by quantitative ^{19}F NMR analyses. Details on synthesis and direct fluorination mechanism have been already published elsewhere [22,24]. Four different fluorine contents for every fluorinated carbons were selected close to $x = 0.15$, 0.65, 0.75 and 1. The accuracy of F/C is ±0.02.

Carbon nanofibres were placed under a pure fluorine gas flow (1 atm) at temperatures T_F ranging between 405 and 480 °C; the resulting samples are denoted CNF-T_F. Fluorinated carbon nanodiscs were obtained at temperatures ranging between 450 and 520 °C (CND-T_F). For graphitized carbon blacks, three samples were obtained by fluorination in the 360–410 °C range for 3 h, the highest fluorination rate (F/C = 1.04) being prepared at 400 °C for 48 h. The resulting samples are called GCB-T_F.

2.3. Physical–chemical characterizations

^{19}F NMR experiments were carried out using a Bruker Avance spectrometer, with a working frequency of 282.2 MHz. A magic angle spinning (MAS) probe (Bruker) operating with a 4 mm rotor was used. For MAS experiments, a simple sequence was performed with a single $\pi/2$ pulse length of 4.0 μs. ^{19}F chemical shifts were externally referenced to $CFCl_3$. To confirm the molar ratio F/C obtained by weight uptake method, quantitative ^{19}F NMR measurements were carried out using the same conditions for each sample, i.e. similar receiver gain, scan number and recycling time D_1 ($D_1 > 5T_1$ where T_1 is the spin–lattice relaxation time T_1, usually $T_1 < 500$ ms in air [25,26] so D_1 was equal to 3 s). The intensities are divided by the sample mass. Polyvinyldifluoride $(CF_2–CH_2)_n$ was used as a standard for the fluorine content quantification.

Secondary electron images were recorded on a ZEISS Supra 55VP Scanning electron microscopy (SEM) operating in high vacuum at accelerating voltage between 4 and 15 kV, using an Everhart–Thornley detector. Specimens were prepared by sticking powder on the surface of an adhesive carbon film.

X-ray diffraction diagrams were obtained using a X Pert Pro Philips diffractometer with a Cu anode (Cu Kα radiation, $\lambda = 1.5406$ Å).

Raman spectrometry was performed at room temperature using a Jobin Yvon T64000 with a charge coupled device multichannel detector. The excitation light was the 514.5 nm wavelength line delivered by an Argon ion laser. The laser power was tuned at 10 mW.

The tribological properties of the nanocarbons were evaluated using a ball-on-plane reciprocal tribometer consisting of an AISI 52100 steel ball rubbing against an AISI 52100 steel plane. The surfaces were polished in order to obtain roughness of the ball and the plane of 20 nm and 200 nm RMS, respectively. The high roughness of the plane is needed to improve the adhesion of the tested materials which were deposited onto the plane by a burnishing method; the latter consists of the crushing of nanomaterial powder between two planes leading to surface films of thicknesses in the 1–3 μm range. The sliding speed of the ball on the plane was 6 mm s^{-1} and the normal applied load F_N of 10 N leaded to a contact area with a diameter of 140 μm and a mean contact pressure of 0.65 GPa (according to Hertz theory). The tangential force F_T was measured with a computer-based data acquisition system. The friction coefficient is defined as $\mu = F_T/F_N$.

At the beginning of the tribological experiment, when the loaded sphere on plane contact was established, one drop of pentane (boiling point of 36 °C) was added in order to improve the feeding of the sliding contact with nanoparticles and then to

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