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Effect of fluorination on the stability of carbon nanofibres in organic solvents

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ABSTRACT

Beneficial effects of fluorination on the stability of carbon nanofibre (CNF) dispersion in organic solvents as a function of time are evidenced. Because of their excellent friction properties, fluorinated CNFs (CF_{0.85}) can be used as nanoparticles of tribo-active phase in lubrication; however, they have to be added into a matrix. We have shown that mixtures of CF_{0.85} are more stable than CNF solutions. Investigations by ultraviolet–visible spectroscopy have been carried out 2 h after sonication and after an ageing of 4 months. Hansen solubility theory was used, and after ageing, tribological and Raman spectroscopy experiments showed no significant modification of physicochemical properties of the CF_{0.85}.

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R É S U M É

L'avantage de la fluoration sur la stabilité dans le temps des nanofibres de carbone (CNF) en dispersion dans des solvants organiques a été démontré. Les nanofibres de carbone fluorées (CF_{0.85}) ont d'excellentes propriétés de frottement et peuvent donc être utilisées pour la lubrification. Nous montrons que les CF_{0.85} ont une meilleure stabilité que les CNF. Des analyses par spectrométrie ultraviolet–visible ont été réalisées deux heures après la dispersion, également après un vieillissement de quatre mois. La théorie de solubilité de Hansen a été utilisée et, après vieillissement, des expériences tribologiques et au Raman n'ont montré aucune modification des propriétés physicochimiques des CF_{0.85}.

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Mots-clés:

Fluorination

Nanofibres de carbone

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Solubilité de Hansen

Propriétés tribologiques

Abbreviations: CNFs, Carbon nanofibres; CF_{0.8}, fluorinated carbon nanofibres with F/C atomic ratio 0.85.

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1. Introduction

Fluorination is one of the most effective methods to modify and control physicochemical properties of carbon materials [1–3]. Numerous studies have been mainly devoted to fluorination of graphite or graphitized carbons and to the characterization of the fluorinated compounds, which have found important practical applications, as electrode materials for primary lithium batteries or solid lubricants [4–7]. The nature of the interaction between fluorine and carbon atoms can be varied considerably and modulated as a result of the fluorination route, the morphological and structural types of the carbon precursor [8–11]. Indeed, because of the versatility of the C–F bonding and the distribution of fluorine atoms within the carbon network, the physicochemical properties of carbonaceous materials are drastically changed and controlled. In the case of fluorine adsorption on the surface of carbonaceous materials, these interactions are very weak. On the contrary, a covalent, semi-ionic or ionic character can be obtained according to the fluorination condition and nature of the starting carbonaceous material [12–14]. A significant advance concerns fluorinated carbon nanofibres (CNFs) regarding their excellent electrochemical and tribological properties have been shown [15,16].

To decrease wear and loss due to increasing severity of lubrication conditions in engines, new strategies of lubrication consist of introducing either solid nanoparticles of tribo-active phases or precursors of tribo-active phases into the lubricant base [17]. Different studies have shown that fluorinated carbonaceous nanomaterials (carbon blacks, CNFs and carbon nanodiscs) exhibit good tribological properties and can act as excellent precursors of tribo-active phase for lubrication [7,18,19]. The present work focuses on CNFs and their fluorinated analogues (F-CNFs). They are similar to multi-walled carbon nanotubes (MWCNTs) with ill-defined core and a larger diameter. The method of fluorination using F_2 (direct fluorination) at an optimal reaction temperature close to 465 °C leads to a high fluorination content F/C of 0.85.

Tribological properties of fluorinated CNFs have been evaluated according to the fluorine content and show that $CF_{0.85}$ are excellent candidates for lubrication. Indeed, the friction coefficient about 0.080 ± 0.001 is lower than that of nonfluorinated CNFs ($\mu = 0.14 \pm 0.01$) and also lower than the most popular solid lubricants, that is, graphite ($\mu = 0.12 \pm 0.01$). Moreover, the thermal stability of $CF_{0.85}$ is extended up to 480 °C due to homogenous distribution of the fluorinated parts in the whole volume of nanofibres [20]. The comparison of various samples clearly underlined that the tubular nanostructuring of both the raw carbon and the fluorinated part plays a key role for the stability of fluorinated CNFs. Good thermal and chemical stabilities are then achieved. According to their excellent properties, fluorinated CNFs can be expected to serve as structural reinforcement for lightweight composite systems with the further promise of multifunctionality. However, specifically in polymer composites, the mechanical properties depend on the ability to transfer load from the matrix to the nanotubes [21,22].

In the case of fluorinated nanolubricants, they must be integrated either into an organic media or into a composite to be sprayed onto a mechanical component. Nevertheless, commonly used organic solvents can modulate their properties. Dispersion state, friction properties and damage of the $CF_{0.85}$ can be modified in the presence of an organic solvent as a function of time. Mickelson et al. [23] have shown that fluorinated single-walled carbon nanotubes (F-SWCNTs) were well dispersed in alcohol solvents to give long-living metastable dispersion. Hansen solubility parameters have been useful in explaining the dispersion state and to determine which solubility parameter is the most influential [24–26]. Nomède-Martyr et al. [27] have shown that fluorinated CNFs ($CF_{0.85}$) have a higher dispersion state than the nonfluorinated CNFs in ethanol, isopropanol, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *N*-methylpyrrolidone, chloroform and 1,2-dichlorobenzene. The best result has been obtained in *N*-methylpyrrolidone for a dispersion limit value of 570 mg/L, whereas 310 mg/L was the maximum for CNFs. Then fluorination appears as an efficient functionalization method to increase the dispersion limit of such dispersible nano-objects. The presence of fluorine atoms on the surface of carbonaceous nanomaterials increased the hydrogen bonding with CNFs and consequently the three Hansen parameters became all important to estimate the dispersion state in organic solvents.

The main objective of this study was to estimate the time dependence of fluorinated and nonfluorinated CNF concentration in different organic solvents. The nanofibres have been dispersed without surfactant or additive with an ultrasonic probe in ethanol, DMF, DMSO and chloroform. UV–visible spectroscopy has been used to determine the percentage of nanofibres in dispersion after a first sonication and after an ageing of 4 months of the dispersions. Hildebrand and Hansen parameters of solvents were used to evaluate the stability of the mixtures and to understand modifications of surface properties of the nanofibres in dispersion. The fluorinated CNFs were then dried to study changes in their physicochemical properties after a long ageing into the different solvents. It has been reported that sonication cannot only exfoliate the nanotube bundles but also induce defects and even scission of the tubes [28]. The tribological properties of these fluorinated nanofibres have been compared with initial $CF_{0.85}$ powder. Then, the damage of the $CF_{0.85}$ was monitored by Raman spectroscopy. The increase in the defect (or D) band compared with the corresponding graphitic (or G) band intensity was considered as an indication of the damage to the nanofibres [29,30].

2. Experimental section

2.1. Materials

High purity (>90%) CNFs, 2–20 μm in length and 150 ± 30 nm in average diameter, were supplied by courtesy of the MER Corporation (Tucson, Arizona). They were obtained by chemical vapour deposition and treated at 1800 °C in an argon atmosphere to enhance their graphitization degree. The graphitization post-treatment insures

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