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Short communication

Friction properties of surface-fluorinated carbon nanotubes

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Abstract

Surface modification of the tubular or sphere-shaped carbon nanoparticles through chemical treatment, e.g., fluorination, is expected to significantly affect their friction properties. In this study, a direct fluorination of the graphene-built tubular (single-walled carbon nanotubes) structures has been carried out to obtain a series of fluorinated nanotubes (fluoronanotubes) with variable C_nF ($n = 2–20$) stoichiometries. The friction coefficients for fluoronanotubes, as well as pristine and chemically cut nanotubes, were found to reach values as low as 0.002–0.07, according to evaluation tests run in contact with sapphire in air of about 40% relative humidity on a ball-on-disk tribometer which provided an unidirectional sliding friction motion. These preliminary results demonstrate ultra-low friction properties and show a promise in applications of surface modified nanocarbons as a solid lubricant.

Keywords: Friction; Carbon nanotubes; Fluorination; Fluoronanotubes

1. Introduction

The performance of solid lubricants largely depends upon the particle size and their shape at the nanoscale level [1–6]. The modeling and experimental studies suggest that the cage-like nanosize particles having either spherical or tubular morphology will provide great application advantages in the field of tribology [4]. Their seamless structure helps to inhibit the sticking and burnishing of the nanoparticles by the rubbing metal or other surfaces. These tubular particles slide and roll in part during sliding contact, resulting in a low friction and wear. The primary structures may also crack open during contact between the tribocouples leading to small graphitic low surface energy layers, which behave similar to graphite. The spherical nanoparticles can also serve as effective spacers, prohibiting contact and wear of the metal surfaces under heavy loads where fluid lubricants are normally squeezed out. Other advantages include the superior oxidation and thermal stability of the tubular and spherical nanoparticles, prolonging their wear life. For example, the hollow spheres of MoS_2 and WS_2 exhibit ultra-low friction and wear (by an order of magnitude) in comparison with the macro-scale materials because the curved S–M–S (M = Mo, W) planes significantly reduce the oxidation and preserve the layered structure [5,6].

The discovery of synthetic methods to produce carbon nanotubes, structurally built of graphene cylinders, opened the research opportunities for a variety of applications [7–10], including lubricants. Surface modification of the carbon nanotubes as well as other carbon nanoparticles, nano-onions [11] and nanodiamonds [12], through chemical treatment [13], e.g., fluorination [14,15], is expected to affect their friction and degradation behavior in lubricant application. This expectation is supported by the

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experimental studies of graphite fluoride $(CF)_x$ powder films that demonstrate longer wear lives, low friction coefficients and superior load-carrying capacities in comparison with graphite both in humid air and at elevated temperatures due to weakened interlamellar van der Waals forces [16,17]. The intent of this work is to examine the effect of surface modification of SWNTs on their tribological properties. In the present work, we report the evaluation data on friction coefficients and wear life of neat lubricating films prepared from fluorinated single-walled carbon nanotubes (fluoronanotubes) with variable C_nF ($n = 2$–20) stoichiometries. The samples of pristine and oxidative acid treated nanotubes, and the nanotubes which were short cut by the fluorination-pyrolysis method [18] were also tested for comparison.

2. Experimental

2.1. Materials

Single-walled carbon nanotubes (SWNTs), prepared by the HiPCO process, were purified prior to use by wet air oxidation and subsequent hydrochloric acid treatment followed by washing and vacuum drying to remove all nontubular forms of carbon and iron catalyst according to a documented detailed procedure developed at Rice's CNST [19]. The iron content in so purified SWNTs was found to be lower than 1 wt.% according to TGA. The fluoronanotubes of the C_2F and C_5F stoichiometry were prepared by direct fluorination of purified SWNTs under controlled conditions well established in the earlier work [14,18]. Hydrazine treatment of the C_2F sample was used to reduce the fluoronanotubes to approximately a $C_{20}F$ composition [13,14]. Cut-SWNTs of 100–300 nm lengths were prepared by treatment of SWNTs in 2 M HNO_3 by 30 min sonication [13]. Pyrolysis of C_5F fluoronanotubes in argon produced shorter nanotubes (F-cut-SWNTs) of predominantly 20–80 nm length distribution [18].

2.2. Friction property testing

The evaluation tests were run on a ball-on-disk tribometer (Fig. 1). A 6 mm sapphire ball was loaded (1.4 N) and put in contact with a rotating (120 rpm) quartz disk of 12.7 mm diameter to provide the average Hertzian contact pressure of about 0.3 GPa. The force of the ball on the disk and tangential force were used to determine the friction coefficient. All experiments were performed at a track diameter of 6 mm and a sliding velocity of 38 mm/s. The wear life of the lubricant was estimated by the number of rotating passes at which the friction coefficient increased to 0.15.

The films were prepared by deposition of nanotube sample suspensions either in toluene (SWNTs, cut-SWNTs, and $C_{20}F$) or isopropanol (C_2F, C_5F, and F-cut-SWNTs) on the quartz disk followed by evaporation of solvent under dry nitrogen flow. Films of four different relative thicknesses (0.63, 1.26, 1.89, and 2.52 $\mu g/mm^2$) were fabricated and tested. The most unambiguous measure of thickness is weight per unit area, which we use to define the coating load. Bonding between a coating and the substrate is due to van der Waals' forces. The nanotubes are mechanically tangled with each other. All tests were run in air environment of about 40% relative humidity at room temperature (~23 °C).

3. Results and discussion

3.1. TEM studies

High-resolution TEM images (Fig. 2) show significantly different surface morphologies for all chemically treated nanotube samples in comparison with the pristine SWNTs. Smooth sidewall surfaces of thick SWNT bundles (Fig. 2a) generate slight protrusions as a result of oxidative acid (HNO_3) treatment under mild conditions which creates minor defects on the sidewalls of nanotubes, cuts them into shorter lengths and opens their ends, as shown by the image

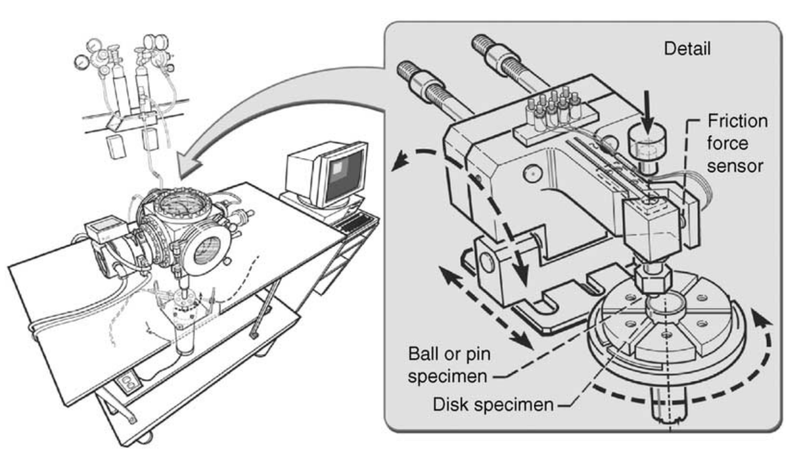

Fig. 1. The ball-on-disk tribometer (the disk surface was coated by a thin film of a neat nanotube sample prior to testing).