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Frictional anisotropy of oriented carbon nanotube surfaces

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This report examines highly anisotropic tribological behavior of multi-walled nanotube films oriented in mutually orthogonal directions. The average values of coefficient of friction varied from extremely high values ($\mu = 0.795$) for vertically aligned nanotubes grown on rigid substrates to very low values ($\mu = 0.090$) for nanotubes dispersed flat on the same substrates. The results were insensitive to humidity, in contrast to graphite materials, and indicate that nanotubes could be utilized as both low and high frictional surfaces.

KEY WORDS: carbon nanotubes, coefficient of friction, micro-tribology, engineered surfaces

Carbon nanotubes have unique properties, such as high tensile and flexural strengths, high elastic modulus and a high aspect ratio, that make them attractive for tribological applications [1–6]. Particularly, films up to several microns in thickness can be easily deposited on select substrates by chemical vapor deposition (CVD) [7], to configure novel nanostructured surfaces in tribology. Nanotube filled polymer [8,9], ceramic [10–12], and metal nanocomposites [13–15] have already been considered. In these composites, it was observed that the friction and wear rates were reduced through the addition of nanotubes. In a study with arrays of vertically aligned amorphous carbon nanofibers, low friction coefficients ($\mu < 0.1$) were measured in a humid laboratory air environment, consistent with a graphitic surface [16]. However, the overwhelming argument for the reduction of friction in nanotube reinforced composite structures has been based on the hypothesis of an intrinsic self-lubricity of nanotubes [9,14] at the tribological interface. The ability of individual carbon nanotubes to both slide and roll on their surfaces has been demonstrated in both atomic force microscopy-based experiments [17,18] and atomistic simulations [19,20] and their use as low friction nanoscopic bearings has been proposed [21].

Considering the highly anisotropic geometric structure of individual carbon nanotubes, it is expected that the tribological properties of nanotubes are orientation dependent. In the present study, the coefficient of friction for a bed of vertically aligned capped multi-walled nanotubes and a layer of multi-walled nanotubes randomly oriented in the plane of the substrate (transversely aligned) is experimentally evaluated. The coefficient of friction was measured under a glass pin where the circular contact area contains many nanotubes. The experiments were run under both humid air and an inert gas environment of argon.

Homogeneous arrays of vertically aligned multi-walled carbon nanotubes were grown on a quartz (SiO_2) substrate using CVD [7,22] having average lengths of $\sim 50 \mu m$. To manufacture the transversely aligned sample, nanotubes from the vertically aligned sample were scraped off and distributed onto a fresh quartz substrate. A scanning white-light interferometer with a 20× objective was used to measure the layer thicknesses of the films, which were between 40–80 μm and 2–10 μm for the vertically aligned and the transversely aligned samples respectively. Figure 1 shows both the tribology setup and scanning electron microscopy images of the vertically and transversely aligned sample.

To verify that the carbon nanotubes in the transversely aligned sample retain their character after removal and rearrangement, Raman spectra of the two films were recorded using a confocal micro-Raman spectrometer with a ~10 mW 632.8 nm excitation source and 100× objective. The Raman spectra of both films had pronounced features at $\sim 1350 cm^{-1}$ (D-mode), ~ 1580 cm^{-1} (G-mode), and ~ 2700 cm^{-1} (2D-mode) indicative of multi-wall nanotubes with a highly graphitic order [23]. The intensity ratio of the D- to G-bands was 0.56 for both spectra corresponding to a microcrystalline planar size of ~8 nm [24]. The only noticeable difference between the two spectra is the appearance of a weak shoulder ~ 1618 cm^{-1} in the transversely aligned sample spectrum, which

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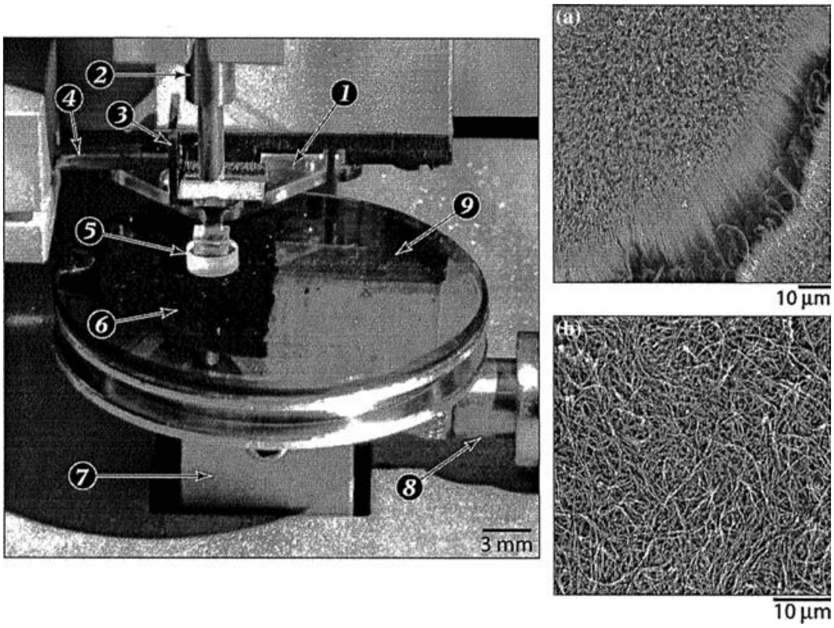

Figure 1. Photograph of the micro-tribometer setup showing: (1) the glass flexure to react normal load and friction forces, (2) optical sensor for vertical deflections, (3) mirrors, (4) optical sensor for horizontal deflections, (5) borosilicate crown glass pin, (6) vertically aligned MWNT layer, (7) reciprocating stage, (8) LVDT for stage position measurements, and (9) quartz substrate. Right: scanning electron microscopy images of (a) vertically aligned multi-walled carbon nanotube arrays (near a scratch so that the nanotubes can be more directly observed and measured, (b) the transversely aligned nanotubes.

suggests an increase in terminating or defective graphene sheets [25]. Overall, the Raman data and electron microscopy data support the conclusion that the transversely aligned multi-walled nanotubes retain their character and structural integrity upon removal.

Tribology experiments were run on a microtribometer that uses dual flexures. One flexure is used to apply the normal load and the other is used in the measurement of friction forces [26]. The entire tribometer is located on an active vibration isolation granite table inside a softwall cleanroom with an acrylic chamber that encloses the entire tribometer enabling experiments to be run in controlled environments.

A pin sample with a 7.78 mm radius of curvature was made from borosilicate crown glass (manufacturer-reported elastic modulus is 82 GPa). The pin was bonded to the end of the glass flexure using cyanoacrylate. The contacting area and contact pressure were not measured. The quartz substrate on which the multi-walled nanotube samples were prepared was mounted onto a 25 mm aluminum microscopy stub that was held in a receiving post of the tribometer. The samples were then linearly reciprocated under the pin. The reciprocating path length was 0.6 mm, which was measured using a linear variable differential transformer (LVDT). The reciprocating frequency was 0.16 Hz and experiments were run for 60 complete cycles. Normal loads were varied over 0.5, 2, 5, and 10 mN. Experiments were run in laboratory air (average Relative Humidity 25–50%) as well as in argon gas (purity of 5 ppm for O_2 and 3 ppm for H_2O). The acrylic enclosure (120 L) was purged with argon at a flow rate of $\sim$7 Lmin^{-1} for 12 hours prior to testing, under a positive pressure of $\sim$500 Pa.

The average coefficient of friction values of the vertically and transversely aligned nanotube layers for both air and argon tests are summarized in figure 2(a). These values were obtained by taking the arithmetic average of the absolute values of the reported coefficient of friction during the entire sixty cycles of sliding, ignoring the pin reversal locations. In laboratory air, the average coefficient of friction over all of the loads was $\mu = 0.795$ with a standard deviation of $\sigma = 0.067$ for the vertically aligned sample and $\mu = 0.090$ with $\sigma = 0.015$ for the transversely aligned sample. Similarly, in argon $\mu = 0.676$ with $\sigma = 0.074$ for the vertically aligned sample and $\mu = 0.104$ with $\sigma = 0.015$ for the transversely aligned sample. Additionally, 6 repeat tests under the 2 mN load and 0.16 Hz reciprocating frequency were run, and the standard deviation in the friction coefficient was $\sim$10%.

Figure 2(b) shows the coefficient of friction versus the track position for cycle 30/60. The reduced coefficient of friction for the transversely aligned sample under the same conditions and cycle number can be readily seen. The progression of average coefficient of friction with cycle number for the forward and reverse portions of the sliding path are shown in figure 3(a). The coefficient of friction decreased monotonically for the vertically aligned sample but was relatively flat for the transversely aligned sample. These trends show remarkable agreement with the results of molecular

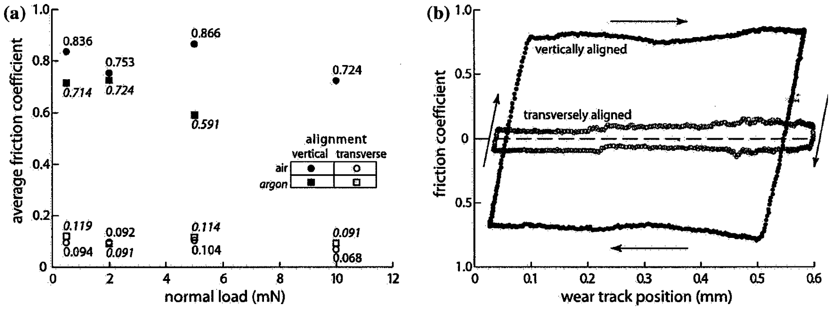

Figure 2. (a) Average coefficient of friction values over an entire test for 60 cycles with reversal locations removed, (b) coefficient of friction data versus track position, collected for one full cycle of reciprocating sliding: normal load = 2 mN, reciprocating frequency = 0.16 Hz, laboratory air, cycle 30 of 60, and reciprocating path length was approximately 0.6 mm.

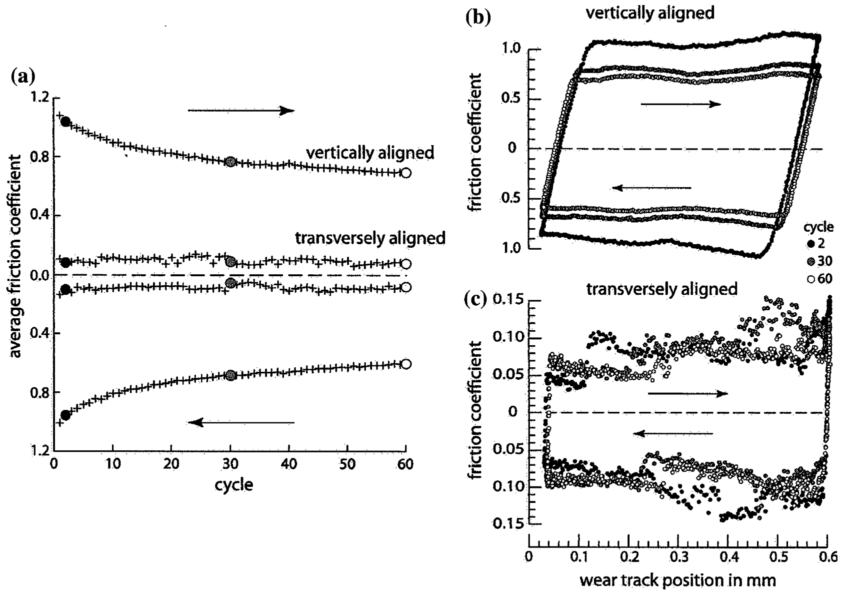

Figure 3. (a) the average coefficient of friction data excluding reversal zones versus cycle number, (b) coefficient of friction data versus track position, collected for one full cycle of reciprocating sliding for the vertically aligned nanotubes and (c) the transversely aligned. The experimental conditions were normal load = 2 mN, reciprocating frequency = 0.16 Hz, laboratory air.

dynamics simulations [27]. Atomistic modeling was used to investigate multiple configurations of groups of six and nine single walled nanotubes, 25 Å in length, sliding between two hydrogen-terminated diamond (111) surfaces. The simulations showed how the transversely aligned carbon nanotubes can slide over one another relatively easily at low loads, or engage in complex motions that combine sliding and rolling at higher loads in response to applied shear forces. This accounts for the flatness of the measured friction coefficients for the transversely aligned sample. In contrast, aligned carbon nanotubes elastically flattened and buckled in response to applied normal and shear forces suggestive of the observed monotonic decrease in friction coefficients with cycle number.

The measured values of average coefficient of friction of ~0.795 in air and ~0.676 in argon compare reasonably well with coefficient of frictions of groups of vertically aligned carbon nanotubes found using molecular dynamics simulations [27]. The configuration in the simulations consisted of vertically aligned capped nanotubes under 11.5 GPa compressive pressure that resulted in a coefficient of friction of 0.87. The value of the average coefficient of friction for the transversely aligned surface is significantly lower than the vertically aligned surface. One explanation for this is suggested by simulations [27] of transversely arranged nanotubes under 13.7 GPa compressive pressure that demonstrate high mobility with elastic and reversible sliding over one another, even when severely compressed. The origin of the lubricous nature of the unaligned nanotubes is interesting, especially the ability to provide low friction in inert environments. This is in stark contrast to graphite where the intercalation of water or other species between the graphene layers is believed to be responsible for lubricity, and the friction coefficients are high in inert environments.

In closure, multi-walled nanotubes show consistently high friction when aligned normal to the contact plane and very low friction when laying flat along the contact plane. This frictional behavior is robust to dry and humid environments, and is consistent with the tribological mechanisms posed by molecular dynamics simulations of nanotube arrays. The order of magnitude variations in friction coefficient is shown to be a function of the nanotube orientation in the films. This offers the potential to engineer surface domains to be either low friction or high friction through control of nanotube orientation alone.

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