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Load dependent frictional response of vertically aligned single-walled carbon nanotube films

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ABSTRACT

Here we use microscratch testing to demonstrate how a single-walled carbon nanotube (SWCNT) forest material can exhibit variable adhesion properties with solid surfaces ranging from negligible adhesion at low loading due to the normal alignment of SWCNTs to maximum adhesion at high loading that exploits the extraordinary sidewall adhesion of SWCNTs. This observation, which exhibits no analog in conventional bulk materials, is correlated to loading-induced structural modification of the low-density SWCNT-substrate interface morphology. This observation opens new pathways to use structural modification of low density materials to engineer and control a wide range of adhesion properties with solid surfaces.

Nanostructured material interfaces with solid surfaces represent a platform for technologies ranging from batteries, flexible electronics, and solar cells, to transparent conductive thin films [1–3]. Despite the widespread application of these systems, the interfacial mechanics associated with such nanostructured material interfaces remains poorly understood [4–6]. Building from a vast body of literature on the mechanical properties of interfaces of inorganic and organic films, characteristics such as the microstructure, crystal structure, grain size, material homogeneity, and defects [7] in inorganic films and crystallinity, polymer chain length, chain orientation, and plasticizer content [8–10] in organic films can describe the film-dependent mechanical properties. In contrast, nanomaterial interfaces exhibit mechanical properties entirely distinct from these previous studies that arise from characteristics such as nanomaterial density, nanomaterial morphology, and individual chemical/physical properties of the nanomaterials [11–13]. Whereas mechanical behavior of individual nanostructures is a dynamic area of research due to observations of superlubrication and other phenomena at the nanoscale, studies extending fundamental ideas observed at single-particle scales to complex film assemblies are only starting to recently emerge [14–18].

Of particular interest to such applications are carbon nanotubes, which are readily grown or processed into complex networks that can exhibit unique frictional characteristics, such as strong shear-on binding response up to 100 N/cm^2 and easy normal lift off [19–21]. These unique carbon nanotube networks have been shown to exhibit frictional properties 10× improved from a natural gecko foot, and further enable contact transfer of complex stacks of organized carbon nanotubes to arbitrary substrates [22,23]. Other recent advances have focused on *in-situ* TEM and SEM compression and tensile testing of nanomaterial pillars and films [12,24,25], and nanoindentation of CNT films to understand and engineer the hardness and compressive behavior [13,26]. Whereas early studies have indicated the ability to apply scratch testing approaches to complex CNT-based networks [27,28], studies intersecting the exciting applications of the CNT-based frictional characteristics, such as forming functional adhesives, and more conventional techniques for testing mechanical properties of inorganic and organic film interfaces remain mostly unexplored.

Here we adapt a microscratch technique traditionally used to determine the adhesion of thin films to substrates [29,30] to study the load-dependent frictional response of vertically aligned single-walled carbon nanotube (SWCNT) thin films grown by alcohol-assisted catalytic chemical vapor deposition (ACCVD) [31–33]. Our experiments indicate a load-dependent frictional response where coupling of mechanical energy into the SWCNT material modifies the interfacial morphology of

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the SWCNTs and leads to increased adhesion properties until reaching a load threshold where maximum frictional response is obtained. Our work highlights how external loading can be used to actuate frictional properties in low density networks of SWCNTs in a manner generalizable to other low density materials composed of nanostructured building blocks.

SWCNT films were synthesized using ACCVD as detailed in the supplementary information. Microscratch tests in this study were performed using a RHESCA CSR-02 microscratch testing system with a 100 μm diameter diamond tipped stylus. The testing apparatus (Fig. 1) consists of a traditional audio cartridge typically used for record players, where a magnetic stylus is connected to a magnetic sensing coil. The scratch tests involve two motions in a single x-y plane: (1) an oscillatory motion in the x-direction described by $X = X_0\ Cos(\omega t)$ (Fig. 1a), and (2) a linear lateral motion normal to the oscillatory motion (y-direction). To induce a constantly increasing force on the SWCNT film, the film was maintained at a slight angle of 1° relative to the lateral motion in the y direction (Fig. 1b). With this angle and tip the microscratch measurement has a loading rate of 17.64 μN/μm in the y-direction of motion while oscillatory motion in the x-direction enables the measurement of friction. In this system, the frictional force between the stylus and the film causes the stylus to lag behind the cartridge motion, generating a voltage response. This voltage response is proportional to the frictional response of the thin film, and is conventionally represented in units of V or in arbitrary units due to known calibration challenges [34]. Following fast Fourier transform (FFT) noise correction, the measured response is proportional to the frictional force measured by the stylus. In a traditional microscratch measurement on a conventional thin film, the stylus is maintained at a z-distance above the thin film and there is an initial period with no measured response. Once the stylus engages the thin film through movement in the y-axis direction, mechanical energy is coupled into the film. The normal component of this applied load increases with the displacement and a linearly increasing frictional response is observed until the thin film detaches from the substrate at a critical load which corresponds to a rapid jump in the frictional response followed by large fluctuations (see Fig. 1c) [29]. A comparison of the raw signal and the FFT signal for the data in the main text is presented in Fig. S1. Notably, the microscratch data in Fig. 1c is representative of a measurement using this technique from a conventional coating, and only included for a generalized comparison between a conventional scratch test and our microscratch data on a SWCNT film.

Fig. 2 shows three microscratch experiments on a SWCNT film showing the measured frictional response of the SWCNT film as a function of displacement (bottom) and applied load (top). By comparing the measured frictional response with the traces of the scratches (Fig. S2), three general regimes are identified. The first regime is highlighted in blue in Fig. 2, and corresponds to a range of displacements where the stylus had engaged the SWCNT film and removed it from the surface without any measureable frictional response (from 0 to 0.6 mN). We attribute this regime to the weak normal binding of SWCNTs oriented perpendicular to a solid substrate in a low density SWCNT material. With increasing lateral displacement in the y-direction, a second regime highlighted in red is encountered where both the stylus is engaged with the SWCNT film and a small frictional response is recorded (from 0.6 to 2.3 mN). The onset of this regime (~0.6 mN) represents the point where external loading starts to disrupt the normal orientation of SWCNTs at the SWCNT-substrate interface, and increased adhesion is measured. Finally, a third regime is highlighted in gold where a greater slope is observed in the frictional response indicating a significantly enhanced coefficient of friction (from 2.3 mN to 5.7 mN). At the very end of this regime, a maximum value of the frictional response is achieved at a point attributed to a condition where increasing mechanical energy leads to no further increase in the frictional response. With exception of minor variance between measurements, it is notable that this same pattern was measured in all three of the microscratch experiments shown in Fig. 2. Beyond the point of maximum frictional response from the CNT film, a stick-slip response is measured that is attributed to the convoluted frictional response between the stylus, the SWCNT film, and the underlying substrate.

Closer examination of the SEM trace from the scratches (Fig. 3 and Fig. S2) indicates full removal of the SWCNT film in the first regime, with only partial removal of the SWCNT film in the subsequent regimes. Removal of the film indicates that the adhesion of the SWCNT film to the stylus is greater than to the substrate. As more of the CNT film remains after the microscratch tests when a greater force is applied to the substrate, we can deduce that the SWCNT film has increased adhesion to the substrate when greater forces are applied. In order to better

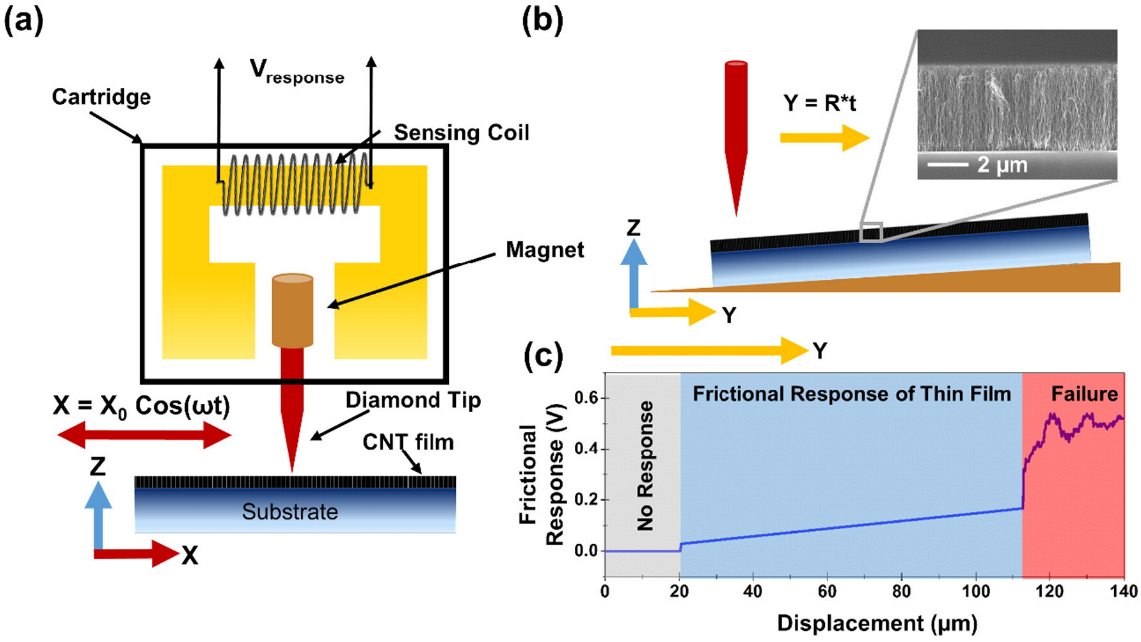

Fig. 1. Microscratch testing approach used for this study with the experimental apparatus and oscillatory motion depicted in (a) and the lateral motion depicted in (b) with an inset SEM image of the alcohol catalytic CVD grown SWCNT film tested. (c) A typical response using this technique with a conventional thin film coating.