

Friction of partially embedded vertically aligned carbon nanofibers inside elastomers

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Vertically aligned carbon nanofibers partially embedded inside polyurethane (eVACNFs) are proposed as a robust high friction fibrillar material with a compliant backing. Carbon nanofibers with 50–150 nm in diameter and 20–30 μm in length are vertically grown on silicon and transferred completely inside an elastomer by vacuum molding. By using time controlled and selective oxygen plasma etching, fibers are partially released up to 5 μm length. Macroscale friction experiments show that eVACNFs exhibit reproducible effective friction coefficients up to 1. Besides high friction, the proposed fabrication method improves fiber-substrate bond strength, and enables uniform height nanofibers with a compliant backing. © 2007 American Institute of Physics. [DOI: 10.1063/1.2767997]

Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have been very promising nanomaterials for a wide range of applications due to their exceptional thermal, electrical, and mechanical properties. Using plasma enhanced chemical vapor deposition (PECVD),¹ vertically aligned CNFs (VACNFs) can be produced on 4 in. diameter substrates. Although VACNFs exhibit excellent performance in a wide variety of applications, it is essential to prove their durability for applications requiring mechanical stability. VACNFs exhibit very favorable mechanical properties and are relatively tough. However, this toughness does not necessarily relate to the bond between the fibers and the backing substrate. For any application that includes a mechanical contact, the fiber is likely to break at the base where the maximum stress occurs. Furthermore, due to the nested-cup-like structure of the VACNFs,² a single VACNF is weak under side impacts and tends to break or plastically deform at its base in the presence of a shear force or any force which can create the same effect. Previous work by Dickrell *et al.*³ which investigates the friction properties of multiwalled carbon nanotubes (MWCNTs) showed that the effective friction coefficient of a MWCNT array decreased as much as 30% with number of cycles due to the flattening of the fibers. A similar study by Zhao *et al.*⁴ on the use of a MWCNT array as a synthetic gecko dry adhesive showed that the friction of the array decreased drastically following successive adhesion tests due to the breaking and/or lateral matting of fibers after each run. This prevents the use of MWCNTs as a robust friction material for such applications.

Extensive studies have been reported in developing CNF composites to improve the robustness of the assembly while making use of the intrinsic high mechanical properties of individual nanofiber elements.^{5,6} Researchers embedded vertically aligned MWCNTs into relatively harder polymers

such as poly(methyl methacrylate) for enhanced backing-fiber bond.⁷ However, it is important to embed fibers in soft materials for maximum fiber-backing bond strength as in the case of contact, a softer backing will minimize the strain therefore the stress on a single fiber. Harder backing also limits the applications of VACNFs where the flexibility of the substrate is necessary or beneficial as in flexible electronics and curved surface applications. Previous work includes growing CNTs on plastic substrates,⁸ transferring CNTs in polymer for fully embedding the fibers in polymer,^{5,6} and contact transfer of CNTs on various substrates.⁹

This work focuses on combining the high friction obtained from nanofibrillar surfaces with the advantage of compliant backing in terms of mechanical stability and flexibility to create a robust high friction material and study its friction characteristics. In general, high friction is obtained from soft materials such as rubber such that soft materials achieve intimate contact with the opposing surface due to their compliance. Fibrillar surfaces achieve a similar compliance due to the ability of each individual fiber to deform freely upon contact. This compliance could form millions of contact points with the opposing surface and the resistance from each contact adds up to create significant friction.¹⁰ Let the friction coefficient be the ratio of the friction force (V) to the normal compressive load (P). Then, assuming that the contact area of each fiber (A_f) is the same, an effective friction coefficient of a fibrillar surface ($\bar{\mu}$) could be defined in terms of the friction coefficient of a smooth surface of the same material (μ) as

$$V = \bar{\mu}P,$$

$$\bar{\mu} = \mu + \frac{N\tau A_f}{P}, \quad (1)$$

where N is number of fibers in contact and τ is the interfacial shear strength per unit area. Equation (1) implies that in ad-

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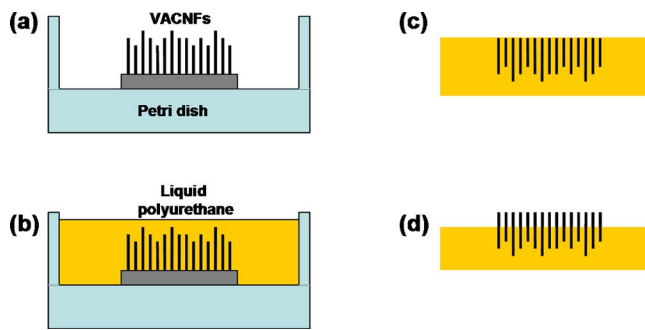


FIG. 1. (Color online) Process flow for the fabrication of partially embedded VACNFs inside a polyurethane elastomer: (a) PECVD grown VACNFs on a silicon substrate is glued to a Petri dish with the fibers facing up. (b) The liquid polyurethane is poured onto the sample under vacuum. (c) The polyurethane is peeled off from the silicon substrate upon curing, transferring the VACNFs inside the polyurethane. (d) Around $5\ \mu\text{m}$ thick polyurethane is selectively etched away from the surface using oxygen plasma leaving the VACNFs partially released.

dition to τ and A_f , which are determined by the material properties and fiber diameter, respectively, enhancement in friction is obtained by increasing N . N could be increased by increasing the fiber density (number of fibers per unit area) and the fiber compliance.^{11,12}

To fabricate high friction fibrillar surfaces with a compliant backing, a VACNF array grown on a silicon wafer is transferred to the elastomer by molding and the top of the elastomer surface is etched to partially release the VACNFs. The fabrication steps of partially embedded VACNFs inside an elastomer (eVACNFs) are illustrated in Fig. 1. VACNFs were grown on a silicon wafer using PECVD. Fibers are $50\text{--}150\ \text{nm}$ in diameter and $25\ \mu\text{m}$ in average length with 20% length variation due to the fabrication process. The nominal length of the fiber can be varied from 3 to $35\ \mu\text{m}$ by tuning the reaction time. The density of the VACNFs is approximately 2.5×10^8 fibers/ cm^2 , which corresponds to about $630\ \text{nm}$ center-to-center fiber spacing. Having grown the VACNFs on a silicon substrate, the next step is transferring the fibers into the elastomer by molding. A high tensile strength and soft polyurethane elastomer (ST-1060, BJB Enterprise) with $3\ \text{MPa}$ Young's modulus was selected as the molding media because of its high tear resistance, and particularly for its high etch rate under oxygen plasma. The wafer with VACNFs is glued to a Petri dish with fibers facing up. Then, liquid polyurethane is poured next to the VACNFs. This step is followed by placing the Petri dish in a vacuum chamber for 5 min to remove all the trapped air in the liquid polyurethane. After the trapped air was removed from the liquid polyurethane, the vacuum chamber is tilted to make the polyurethane flow slowly onto the VACNFs until it reaches the base of all the fibers. After this vacuum molding process, the polyurethane is cured at room temperature for 24 h in air, and the cured polyurethane with fully embedded VACNFs is mechanically peeled off from the silicon substrate. A Technics PE-II parallel plate plasma etcher is used to selectively etch the polyurethane with oxygen plasma at $150\ \text{W}$ for 50 min. The etch process yielded $5\ \mu\text{m}$ etch depth leaving the VACNFs partially released from the polyurethane surface, as shown in Fig. 2. For this specific polyurethane, etch depths larger than $5\ \mu\text{m}$ are not possible as the etch rate slows down drastically after $5\ \mu\text{m}$ depth is reached and further processing leads to extensive damage to the VACNFs. This fabrication process not only improves the

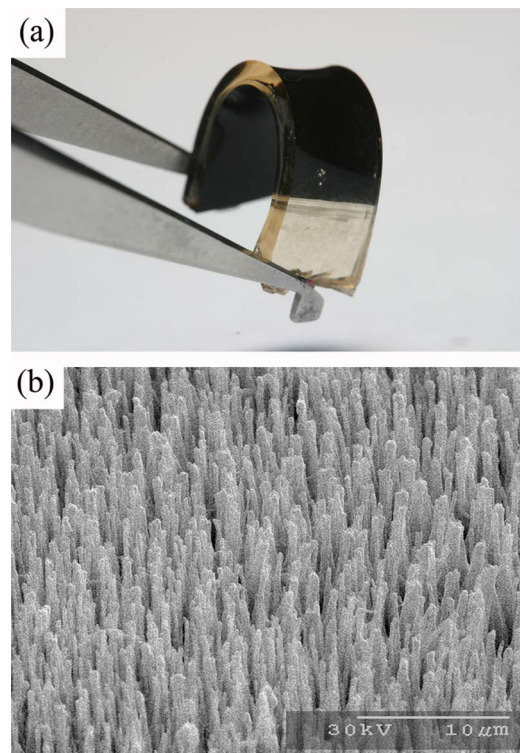


FIG. 2. (Color online) (a) Photo and (b) scanning electron microscope images of the partially embedded (around $5\ \mu\text{m}$ length of nanofibers is released outside) vertically aligned carbon nanofibers ($20\text{--}30\ \mu\text{m}$ length and $50\text{--}150\ \text{nm}$ diameter) with a flexible polyurethane backing.

bond between VACNFs and its compliant backing, it also eliminates the length variation because the tip of the fibers in the polyurethane backing corresponds to the base of the same fiber on silicon substrate. Furthermore, the backing material can be any elastomer that could be etched using oxygen plasma.

Friction experiments were performed on a custom friction and adhesion measurement system which enables movement and simultaneous force measurement in two axes. Two motorized high precision linear actuators (MFA-CC; Newport) provide movement in lateral and normal directions while the load cells (GSO-50 and GSO-25; Transducer Techniques) simultaneously record the friction and normal forces between the sample and a $6\ \text{mm}$ diameter glass hemisphere (QU-HS-6; ISP Optics). Custom real-time software controls the actuator to move the hemisphere into contact with the sample at $5\ \mu\text{m}/\text{s}$ until a prespecified preload is reached. After a 1 s pause, the sample is then moved in the lateral direction at $5\ \mu\text{m}/\text{s}$ fixed velocity for $200\ \mu\text{m}$ distance followed by the retraction of the hemisphere from the sample until the detachment occurs. The software continually captures the normal force and the friction force data from the load cells with $0.1\ \text{mN}$ resolution. Hemispherical geometry is preferred over the flat for the glass probe to eliminate possible edge effects and measurement deviations due to misalignment.

Prior to testing, the glass sphere was cleaned in an ultrasonic bath with ethanol for 5 min and dried in a vacuum oven. Initial friction measurements were performed at three different locations on the eVACNFs for preloads (P) ranging from 1 to $50\ \text{mN}$ with $5\ \text{mN}$ increments. The highest friction force (V) and effective friction coefficient ($\bar{\mu}$) are plotted with respect to the applied preload (P) in Fig. 3(a) where $\bar{\mu}$

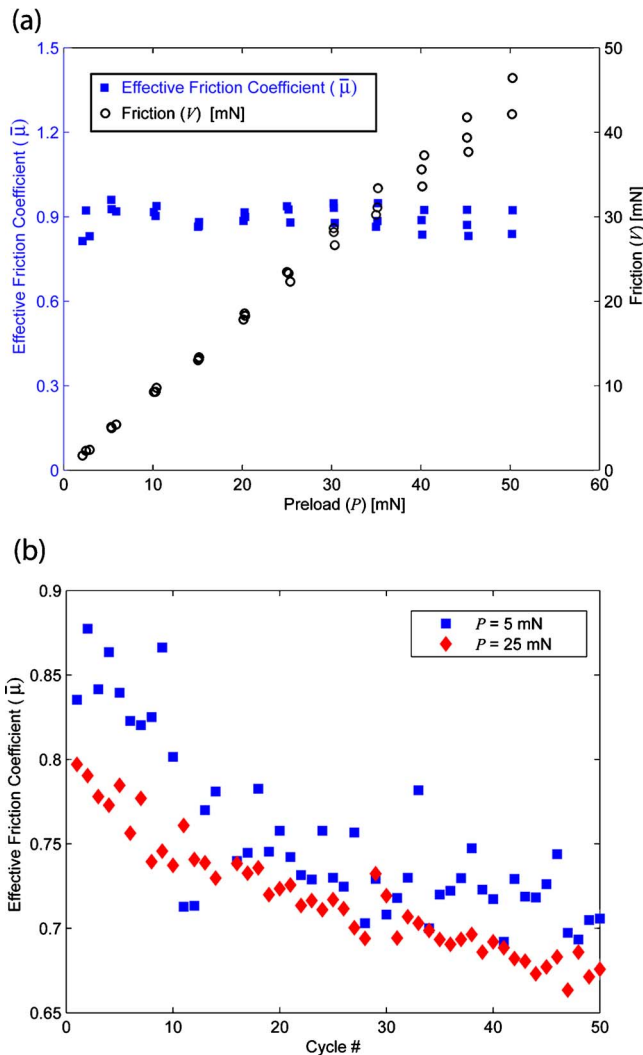


FIG. 3. (Color online) Experimental friction and effective friction coefficient results obtained from the partially embedded vertically aligned carbon nanofiber sample: (a) for varying preloads at three different nanofiber locations on the same sample and (b) for varying cycles on the same nanofiber location for each preload at 5 and 25 mN preloads. All experiments were performed with a 6 mm diameter glass hemisphere at a constant speed of 5 $\mu\text{m/s}$.

ranges from 0.8 to 1 and decreases slightly with higher preloads. The same experiments performed on the VACNFs that were grown on silicon substrate with averages of 3 and 25 μm lengths and similar density yielded $\bar{\mu}=0.4$ and $\bar{\mu}=2.2$, respectively. The difference in friction between the two as-grown VACNF samples could be explained by referring to Eq. (1). Since the fiber material and the diameter are the same for both as-grown VACNF samples (i.e., τ , A_f and μ are the same), $\bar{\mu}$ could only be enhanced by increasing N for a constant P . But increasing N is only possible through the enhancement of compliance as the fiber densities are the same for both samples. Therefore, for 25 μm long fibers, the excess length makes the fiber array more compliant effectively, which increases N for a given preload and thus the overall friction coefficient. However, this argument fails to explain the difference between the effective friction coefficients of eVACNFs and 3 μm VACNFs grown on silicon substrate, which have similar fiber lengths. This discrepancy is believed to arise from the difference in fiber tip structures

and possibly the added compliance of eVACNFs due to the soft polyurethane backing. Due to the fabrication method, the tip (free end) of an individual fiber in eVACNF corresponds to the base of a fiber in as-grown VACNF. Therefore, in addition to the cone angle, there might be some catalyst on the tip of the eVACNF fibers that makes not only the tip structure but also the tip material different. Despite the enhanced friction obtained from the 25 μm long VACNFs grown on silicon, both 25 and 3 μm long fibers tend to be flattened or break during the experiments.

For the second type of experiments, friction measurements were performed on eVACNFs at the same location for each preload for 50 times at $P=5$ mN and $P=25$ mN to determine the change in friction with cycle number. The results in Fig. 3(b) show that $\bar{\mu}$ decreased by about 15% after 50 cycles for both preloads. However, the decrease in friction is less compared to the previous work by Dickrell *et al.*³ in which the experiments were conducted at significantly smaller preloads. This result and the investigation of the sample under the optical microscope show that the damage to the fibers is minimal. In addition to friction experiments, adhesion experiments were also performed between the 6 mm diameter glass hemisphere and the eVACNF sample using the same experimental setup. However, no measurable adhesion was recorded. This suggests that the eVACNF sample is a high friction material with low adhesion, which could be advantageous for specific applications such as tires and shoes.¹⁰

In conclusion, vertically aligned carbon nanofibers embedded in polyurethane elastomer were proposed as a robust high friction fibrillar material. Vertically aligned carbon nanofibers with 50–150 nm in diameter and 20–30 μm in length were embedded in polyurethane elastomer by vacuum molding and partially released up to 5 μm length using oxygen plasma etching. Macroscale friction experiments showed that eVACNFs exhibit effective friction coefficients up to 1. The friction decreased only by around 15% after 50 cycles at 5 and 25 mN preloads, which showed enhanced friction reproducibility for eVACNFs. In addition to high friction, the proposed fabrication method also improved the fiber-substrate bond strength and enabled uniform height fibers with a compliant backing.

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