CARBON 50 (2012) 5618–5630

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Letters to the Editor

Deformation and capillary self-repair of carbon nanotube brushes

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ARTICLE INFO

Article history:
Received 8 March 2012
Accepted 15 June 2012
Available online 26 June 2012

ABSTRACT

Brushes with nanoscale bristles, such as nanotube arrays held together by van der Waals forces, have applications as compliant electrical switches, probes and micro-scale cleaning tools. Repeated use exposes the brushes to contact and impact at high strains resulting in the bristles undergoing exfoliation, deformation and damage. We show that the damages incurred can be nearly recovered by capillary evaporation of solvents from the free standing aligned nanotube brushes.

Brushes are simple inhomogeneous, anisotropic structures that are indispensable to our everyday chores that include brushing, grooming, polishing, and cleaning of teeth, hair, shoes, vessels, floors and sidewalks. Their ubiquity in these applications derives from their functional ability to smoothly interpolate between the behavior of an individual bristle to clean a crevice and the collective behavior of a brush to sweep a surface. Indeed, as a function of their geometry and loading, they can maintain a large range of intermittent contact with surfaces, which gives wide and easy tenability of electrical, thermal and mechanical transport/contact properties [1]. For example, in cleaning and grooming applications, the individual behavior of the bristles prevent the brush from jamming or clogging easily, while in conducting applications such as in electric motor armatures, brushes are the best way to maintain low-resistance and low-friction contact between moving parts [2,3]. Since it is the geometry of the assembled brush structure that leads to its unique properties, an obvious question is if similar advantages might accrue with brushes at much smaller scales. A natural direction towards this is afforded by self-assembled carbon nanotube structures consisting of tens of thousands of nanotubes oriented in parallel that can be synthesized quite readily over areas of square millimeters with length reaching millimeters [4]. Since the structure of these aligned arrays of nanotubes resembles that of macroscopic brushes that we use in daily life; we will use the terminology of *nanobrushes* from now on to characterize these structures. The differences between macroscale brushes and the nanotube brushes are in the dimensions of individual bristles and how they are held together. Macroscale brushes have macroscale bristles that are held together or embedded in a common support. In nanobrushes, the individual nanotubes are weakly entangled physically along their entire length and the intermittent contact if any, rises from the presence of short range van der Waals forces holds them together (Fig. 1a), hence nanobrushes are free standing structures.

In the structure we describe here, the bristles are made of multiwalled nanotubes that have a distribution of diameters depending on the conditions used during growth. The

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0008-6223/$ - see front matter
http://dx.doi.org/10.1016/j.carbon.2012.06.025

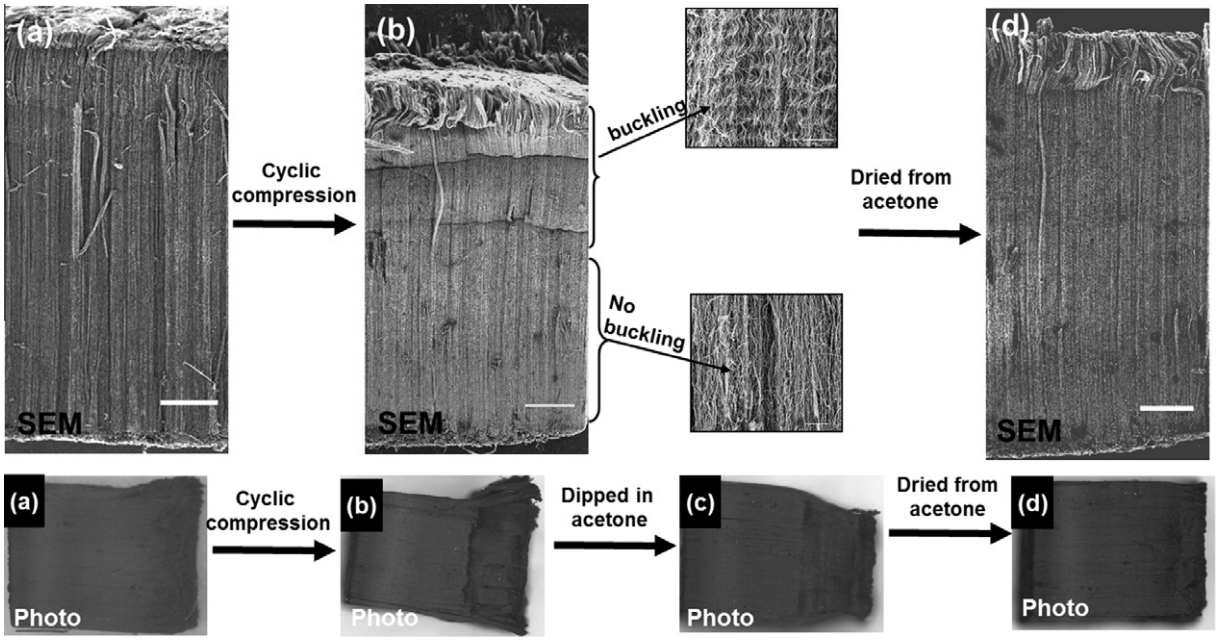

Fig. 1 – Top portion and bottom portion are the SEM (scale ~0.5 mm) and optical micrograph photo images of the MWTs in different state respectively. (a) Carbon nanotubes block, as prepared (b) carbon nanotubes which underwent cyclic compression loading at 35% strain for 10^5 cycles. The nanotubes are seen exfoliated at the upper portion of the block, where the density of the naontubes is lower. (c) The nanotube block is immersed in the acetone for 10 min and removed. (d) Once the nanotube block is dried it recovers to its nearly original state.

nanotubes are formed by the catalytic chemical vapor deposition of hydrocarbon precursor (xylene) and metallorganic catalyst (ferrocene), where both are fed into the reaction chamber in the vapor phase. At higher temperatures (optimized at ~770 °C) the nanotubes self-assemble on certain substrates (e.g. quartz) [5,6]. When the structures are grown to lengths exceeding millimeters they can be easily peeled off from the substrate, enabling handling and testing of these nanotube brushes. In the sample we describe here the average nanotube diameter is ~53 nm, length ~3.45 mm. These individual nanotubes are not perfectly straight but reflect a wavy shape, with the pitch of the waviness typically in the submicron length scales. Hence when they are aligned parallel to each other the actual contact area between nanotubes is small compared to an ideal case where the nanotubes are touching along their entire lengths. The brush is of extremely low density and the occupational density of nanotubes in the brush, calculated by the weight of the CNT block/(volume of the brush) is only ~5% of the density of parent graphite (~2.2 g/cc) material. There are large gaps between individual nanotubes (~100 nm) in the brush and limited contact and entanglement between the nanotubes produces sufficient van der Waals force to keep them together as a brush.

The alignment of nanotubes in the entire brush is also not perfect as there is a small fraction of the nanotubes (<5%) that are not aligned. Careful microscopic examination reveals that the density of nanotubes remains uniform for the initial part of the growth (approximately for the first ~1 mm growth) but continuously decreases for the rest of the growth duration, resulting in decreasing density towards the growth end. This has a strong impact on how the nanotube brushes would behave under cyclic compressive loading [4].

The individual bristles (nanotubes) in the brush are elastic and flexible. Carbon nanotubes are well known for their excellent mechanical properties especially for their super compressibility and elongation [7,8]. Unlike conventional materials [9] used in mechanical applications, nanotubes can withstand extreme stress and strain. It has been recently shown that the brushes can be repeatedly compressed to very high strains over thousands of cycles [4]. Under a strain of 25%, the brush structure can be compressed and released over for more than half a million cycles, without any visible damage to the structure. The nanotubes generally buckle on applying compressive stress and straighten when the load is released, although the stress strain curves under compression of the brushes show some hysteresis due to interfacial frictional forces between nanotubes as they get compressed collectively. However, under higher strains (~35%) the nanotube brush (of non-uniform density, as pointed earlier) undergoes buckling relatively early without complete recovery thereby leading to shrinkage of the original brush length. In the experiment we report here, the nanotube brush was subjected to compressive strain (~35%, Supplementary Fig. 1) for a period of 10^5 cycles at a strain rate of 0.1 mm/s. The length of CNTs and hence of the brush was decreased (from 3.45 to 3.021 mm) by 13% (Fig. 1b). This geometric damage looks quite dramatic, especially in the top regions of the brush, where the density of nanotubes is lower (Fig. 1c). The overall damage has a mushroom-like appearance, caused by the separation of the nanotube arrays in the top region. We note that no damage is seen for such high strains if shorter bristles (nanotubes) were used (<1 mm length), which also has uniform nanotube density for the entire length. It is obvious that under the repeated compression cycles, the individual

nanotubes are not permanently damaged, but have been exfoliated from the arrays as the local contacts between individual tubes became progressively disconnected during cyclic loading in the case of long nanotubes. The structure has not been completely exfoliated due to the fact that the nanotubes in these brushes are not aligned along with the majority of the tubes but are in different orientations with the majority, leading to restoring forces that keep the whole structure from collapsing.

Since the individual nanotubes are not permanently damaged, but their structure has been changed, one might ask if this structural damage can be repaired. We discovered that this is possible using capillary effects [10] during infiltration and evaporation of a solvent into the brush structure. In a typical experiment, the damaged nanotube brush was immersed in acetone for ~10 min, removed from acetone and left in air at room temperature to dry out for 15 min. The nanotube brush initially shrinks (Supplementary movie) because of the capillary forces associated with liquid imbibition. Quantitatively, this follows a kinetic relation with the length of the shrunk region l growing diffusively following the law $l \sim (\sigma r/\mu\varphi^{1/2})^{1/2}t^{1/2}$, where σ is the surface tension of the acetone–air interface, r is the average radius of the nanotubes, $\varphi \sim r^2/\delta^2$ is the volume fraction of nanotubes of radius r separated by an average distance δ in the brush, and μ is the viscosity of the acetone. During this process of imbibition, the nanotubes come together due to the interfacial forces. While a quantitative theory would require detailed information about the structure of the brush, here we use simple scaling notions to delineate the various regimes following Kim and Mahadevan [11]. If the average distance between contacts is denoted by D, balancing elastic and capillary forces yields the relation $B\delta/D^3 \sim \sigma D$ where B is the stiffness of an individual nanotube, so that there is a minimum distance between contacts $D \sim (B\delta/\sigma)^{1/4} \sim (Br/\varphi^{1/2}\sigma)^{1/4}$ for capillary interactions to completely collapse the porous brush with a volume fraction $\varphi \sim r^2/\delta^2$ of material. It can be clearly seen from this experiment that the density of the nanotubes in the brush is different at both ends; indeed the differential shrinkage (Fig. 1c) is a direct reflection of this. On drying in air after solvent immersion, the length of the nanotube brush is recovered to 98.5% (Fig. 1d) of its original length; we note however that the dynamics of drying is very different and much slower than that of wetting/imbibition because drying occurs diffusively and not due to flow. The capillarity induced self-healing process is both a simple and robust way to anneal out the global buckling and delamination of individual nanotubes, that had resulted in the brush damage. Practically the nanotube brush length was reduced during the cyclic compression, and on using the above mentioned capillary evaporation method the length can be regained. This could be an effective way to anneal the mechanical damage in nanotube brushes which could one day find application as contact brushes which would undergo repeated mechanical force during contact cycles.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2012.06.025.

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