

Development of Nanodevices, Nanostructures, Nanocomposites, and Hierarchical Nanocomposites at Hawaii Nanotechnology Laboratory

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ABSTRACT

Development of nanodevices, nanostructures, nanocomposites, and hierarchical nanocomposites at the Hawaii Nanotechnology Laboratory of the Department of Mechanical Engineering of the University of Hawaii at Manoa is explained here. On nanodevices, a multifunctional nanobrush using carbon nanotubes is discussed. On nanostructures, a high-performance nanofoam using carbon nanotubes is explained. On nanocomposites, developments on toughening of polymeric materials employing nanoparticles and carbon nanotubes are reported. On hierarchical nanocomposites, first, mechanical properties improvements for continuous fiber ceramic composites using nanoparticles are discussed. Finally, the multifunctional properties improvement of a novel three-dimensional hierarchical nanocomposite employing carbon nanotubes is explained. In closing, the effects of chirality of single-walled nanotubes on their thermomechanical properties evaluated analytically using asymptotic homogenization method and numerically employing finite element method are discussed, and analytical closed form solutions for matrix filled nanotube nanocomposites, also verified numerically, assuming generally cylindrical orthotropic properties will be reported.

Keywords: Nanodevices, nanostructures, nanocomposites, hierarchical nanocomposites, nanobrush, nanofoam, nanoforests, nanoparticles, carbon nanotubes.

1 INTRODUCTION

Carbon nanotubes (CNTs) are well known for their superior mechanical, electrical, and thermal properties as they have been research topics in recent years. CNTs are quasi-one dimensional, nearly single crystalline (axially), hollow, graphitic carbon structures [1, 2]. The combination of high aspect ratio, small size, excellent mechanical properties [3, 4], low density, and high electrical conductivity [5] make them perfect candidates as basic building blocks for nano-devices and systems. Experimental as well as theoretical predictions [6] on nanotubes suggest axial Young's modulus of 1 TPa [7]. It is frequently reported that CNTs [8] are one of the excellent reinforcement candidates for mechanical and physical property enhancement of the composite materials and structures leading to a new class of composite materials,

i.e., nanocomposites, in which at least one of the constituents is in nano-size. Such nanocomposites can be integrated with reinforcing fibers to give hierarchical nanocomposites.

2 NANODEVICES: Multifunctional Carbon Nanotube-based Nanobrush

This section of the paper explains carbon nanotube-based nanodevices; namely, micro-brush [9]. Several applications of carbon nanotubes have been demonstrated in recent times, taking advantage of their small size, and exceptional mechanical, chemical and electrical properties [10-13]. This remarkable range of physical properties of nanotubes allows the design of yet several novel multifunctional architectures with new applications in mind [1, 2]. Here, we used a simple synthesis procedure that combines conventional chemical vapor deposition and selective substrate area growth, to fabricate multifunctional nanobrushes from aligned carbon nanotube arrays and demonstrated applications in several new tasks [9]. The high aspect ratio and small dimension, mechanical stability and flexibility [7, 14], surface chemical and adhesive characteristics and high electrical conductivity [15, 16] provide a wide range of functionalities and uniqueness to the nanotube nanobrush. The brushes are made from aligned nanotube bristles grafted onto long SiC fiber handles in various designs and can easily be manipulated physically, either manually or with the aid of motors. We demonstrated the multifunctionality of these brushes by applying these in the manipulation and removal of nanoparticles on planar as well as microstructured surfaces (e.g. terrains with microscale trenches and elevations), selective surface cleaning via chemical/physical adsorption, painting and coating in normally inaccessible spaces such as inside micro-capillaries, and as movable brush-contacts which could act also as electro-mechanical switches that can work swiftly in both air and liquid environments. With surface modification and functionalization [17, 18] the nanotube brushes could become a versatile micro-tool in many chemical and biological applications and in the creation of novel electro-mechanical devices with excellent thermo-mechanical stability and endurance. Figure 1 shows the developed nanobrushes. This work was a collaboration between UHM and RPI [9].

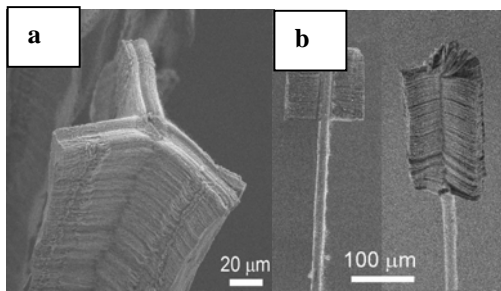


Figure 1. Carbon Nanotube-Based Nano-Brushes [9].

3 NANOSTRUCTURES: Multifunctional Carbon Nanotube-based Nano-brush

It was reported [19] that freestanding films of vertically aligned carbon nanotubes exhibit super-compressible, foam-like behavior, and could be repeatedly compressed to more than 85% of film thickness. Under compression, nanotubes collectively formed zigzag buckles that could fully fold themselves and unfold to free length elastically upon load release. Comparing to conventional low density flexible foams, the “nanotube foams” show much higher (two orders of magnitude) compressive strength, recovery rate (>2000 $\mu\text{m}/\text{sec}$), sag factor (>4), and the open-cell nature of nanotube arrays gives excellent breathability. The nanotube films present a new class of open-cell foam structure, consisting of well arranged one-dimensional units (nanotube struts). The light-weight, highly resilient nanotube films could be useful as compliant and energy absorbing coatings.

Structural foams have a variety of applications in modern society such as in construction, energy dissipation, cushioning and packaging. Mechanical strength (compressive stress) and compressibility (strain) are two important factors that determine the performance and applications of foams; however, these two properties are of opposing nature. Increasing the volume fraction of cells (void area) in a foam results in higher compressibility (up to 75%), but at the expense of rapidly decreasing strength [20]. For the foam at a fixed chemical composition, its modulus decreases with increasing relative cell volume [19]. The elastic segments (struts) between adjacent cells form the architecture of a foam, and it is the bending and buckling of these struts that allow the foam to be compressed. A carbon nanotube [1, 2] is perhaps the ultimate strut to make ultra-light yet strong foams, considering its exceptional mechanical strength, low density and elasticity. In particular, the nanotube exhibits extreme structural flexibility [21, 22], and can be repeatedly bent through large angles and strains without structural failure [14]. The ability of nanotubes to adopt various buckled morphologies reversibly makes them capable of accommodating and sustaining large local strains without failure [23, 24].

Vertically aligned multi-walled carbon nanotube (MWCNT) arrays were produced by chemical vapor deposition (CVD) [19]. Freestanding nanotube films peeled off from the substrate (with typical areas ranging from 0.5 to 2 cm^2) were compressed along the film thickness direction (along nanotube axes) at a set constant strain, repeatedly for thousands of cycles at a frequency of 0.1 to 1 Hz (see schematic in Fig. 3). Snapshots show that the nanotube film does not fracture, tear or collapse under compression, but remains at constant width during the cycles, that is, Poisson’s ratio = 0. The porosity of the (as-grown) nanotube films was ~87% [19], potentially allowing a large volume reduction (up to 85%) when being compressed. The near full thickness recovery lasts until hundreds of cycles before a small reduction in thickness; however, the gap was stabilized at <20% of the total film thickness even after ten thousands of cycles.

The process of nanotube film thickness recovery back to its original thickness during each cycle, during compression release period, happens very fast. The compression head was set to retreat at a speed of 120 mm/min (upper limit of the instrument), and the film was observed to follow the returning head closely without any gap between the head and the top surface of the film. Therefore, the film expansion rate, on recovery, can be considered (lower limit) as at least the same as the speed of the receding head (120 mm/min, or 2000 $\mu\text{m}/\text{sec}$). This is much faster than typical recovery rate for compressed conventional foams and spongy structures. This work was a collaboration between the UHM and the RPI [19].

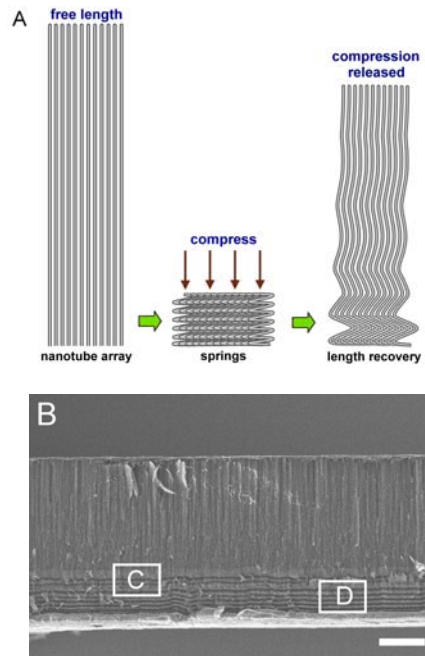


Figure 2. Super-compressible nano-foam [19].

4 NANOPARTICLE AND CARBON NANOTUBES NANOCOMPOSITES

Works are in progress in the Hawaii Nanotechnology Laboratory (HNL) to enhance the multifunctional mechanical properties of nanocomposites based on nanoparticles and carbon nanotubes in terms of their stiffness/compliance, strength, strain to failure, fracture toughness, thermomechanical responses, structural damping, and electrical and thermal conductivities. In these studies, issues such as dispersion, alignments, and interface/interphase properties are important parameters affecting the above-mentioned multifunctional properties.

5 HIERARCHICAL NANOCOMPOSITES

This section explains two hierarchical nanocomposites; namely, CFCC-based SiC nanoparticle nanocomposites [25] and 3-D carbon nanotube-grown nanoforests hierarchical multifunctional nanocomposites [26].

5.1 Continuous Fiber Ceramic Nanocomposites with Nanoparticles

The preceramic polymer pyrolysis route to ceramic chemistry has attracted much attention as it offers a promising and cost-effective way to manufacture CMCs/CFCCs with little to no final machining and parts with greater compositional homogeneity [27-28]. Preceramic polymers are organo-metallic polymers which, after curing, are chemically transformed during their pyrolysis step to yield a contributing ceramic phase(s) in the final ceramic part. In this form of hierarchical nanocomposites, we report on the integration of the concept of CFCC with that of nanocomposites with nanoparticles. Nanoparticle reinforced CFCC samples consistently showed marked improvements in flexural strength compared to their samples without nanoparticle reinforcement.

Details on the manufacturing process is reported by Ghasemi-Nejhad and co-workers [25]. The inorganic polymer used in this study was KiON CERASET® preceramic polymer [29]. The final composition of the composite depends on the pyrolysis cycle and inert gas used; e.g., nitrogen gas produced silicon carbide matrix. Nicalon™ ceramic fiber was the fiber system reinforcement. The nano-sized inclusions were ceramic and metal nanoparticles. Five different nanoparticles were used: silicon carbide (SiC), carbon (C), titanium oxide (TiO₂), yttrium oxide (Y₂O₃), and zinc oxide (ZnO). All these particles are insoluble in water and stable in air.

In the following, Ni/CE refers to a CFCC that is not reinforced with nanoparticles and is considered as a base material. Ni/CE-n refers to a base composite reinforced with any Nanoparticle, say “n”, manufactured with

preceramic polymer pyrolysis/reinfiltration route where the initial matrix has nanoparticles but reinfiltration matrix does not. Ni/CE-n-R-n refers to a Ni/CE composite that uses matrix reinforced nanoparticle “n” for both fabrication and subsequent reinfiltrations. The void content of the samples were found to be well below 4% indicating a good part quality. All CFCC samples manufactured without and with nanoparticles took the same number of pyrolysis/reinfiltration cycles to achieve the weight convergence [25]. This suggests that the nanoparticle reinforcements do not cause premature closures. The four-point bending test [30] was used to evaluate the flexural strength and modulus of the CFCC specimens. The flexural strength and modulus of the Ni/CE were 31.85 MPa and 95.14 GPa, respectively. While the strength of nanocomposites increase (see Figure 3), their modulus drops anywhere between 90 GPa and 70 GPa.

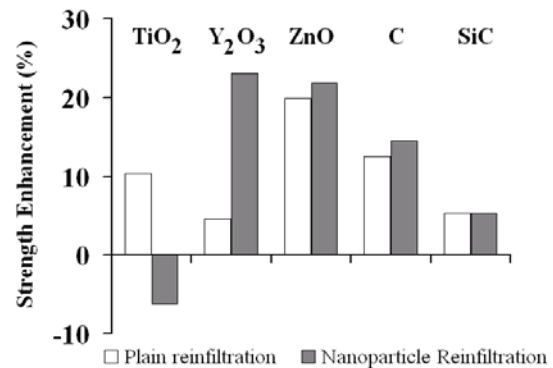


Figure 3. CFCC strength enhancement for various types of nanocomposites [25].

5.2 Multifunctional Nanocomposites using Reinforced Laminae with Carbon Nanotube Nanoforests

While the in-plane loading and stresses can be handled by various configurations of fiber architectures in conventional composites, such as 1-D (i.e., unidirectional tapes) and 2-D (i.e., woven fabrics), the intralaminar and interlaminar stresses have remained major issues resulting in relatively weak interlaminar fracture toughness. This weakness often leads to interlaminar failures, such as delamination, in composites under various loading conditions. To solve these significant challenges, researchers have developed 3-D braided fibers as well as through thickness stitching [31, 32]. These have problems such as low in-plane strengths for the 3-D braided fibers [32] and shorter tensile fatigue life [33] and lower compression strengths for the stitched fiber laminates [34].

Different works using carbon nanotube reinforcements in polymer composites [35-39] have reported small improvements in the bulk mechanical properties compared to traditional fiber reinforced composites. However, the real use of nanotubes in composites for structural

applications has been disappointing, despite huge promises, due to the issues such as dispersion, alignment, and interfacial strength [35-36]. Ghasemi-Nejhad and co-workers [26] have recently developed big opportunity for nanotubes in composites, to influence and increase the 3-D composite interlaminar properties, using unique reinforced laminate with carbon nanotube nanoforests grown on fabric cloths as building blocks for 3-D hierarchical nanocomposites.

Traditional fiber-reinforced composite materials with excellent in-plane properties fare poorly when out of plane through thickness properties are important [31]. Composite architectures with fibers designed orthogonal to the 2-D layout in traditional composites could alleviate this weakness in transverse direction, but all the efforts [31, 32] so far have only produced limited success. Ghasemi-Nejhad and co-workers [26] unveiled a novel approach to the 3-D composite challenge, without altering the 2-D stack design, based on the concept of interlaminar carbon nanotube nanoforests that provides enhanced multifunctional properties along the thickness direction. The carbon nanotube nanoforests allow the fastening of adjacent plies in the 3-D composite. Multiwalled carbon nanotubes were grown on the surface of micro-fiber fabric cloth layouts, normal to the fiber lengths, using a CVD process [40], resulting in a 3-D effect between plies under loading. These nanotube coated fabric cloths serve as building blocks for the multi-layered 3-D hierarchical nanocomposites with the nanotubes nanoforests providing much needed interlaminar strength and toughness under various loading conditions. These fabrics were then infiltrated by high temperature epoxy matrix and subsequently stacked [26, 41] to form multi-layered 3-D composites with remarkable improvements in the interlaminar fracture toughness, hardness, delamination resistance, in-plane mechanical properties, damping, thermoelastic behavior, and thermal and electrical conductivities making these structures truly multifunctional. Figure 4 give the schematics of 3-D carbon nanotube nanoforest hierarchical nanocomposites fabrication. This work was a collaboration between the UHM and RPI [26].

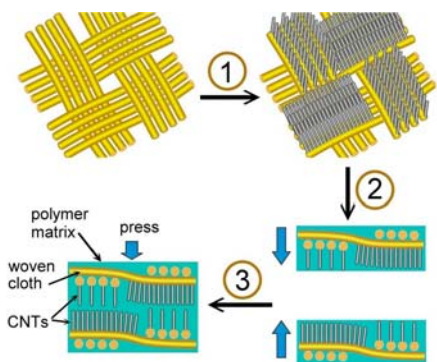


Figure 4. Schematics of 3-D Carbon Nanotube-based Nanoforests Hierarchical Nanocomposites Fabrication [43].

The developed 3-D carbon nanotube nanoforests hierarchical nanocomposites [26] show remarkable multifunctionalities and properties improvements, i.e., four times better performance in fracture tests and five-fold increase in their ability to dissipate energy by structural damping over the original ceramic composites without nanotubes forests. The new nanocomposite material has three times better dimensional stability compared to the base material without nanotubes. This could well be the most preferred composite structure for the future structural applications. The novel 3-D hierarchical nanocomposite [26] performs much better in terms of thermal and electrical conductivities. This essentially gives an indication that the carbon nanotube nanoforests have the capacity to participate in the structural system thermal managements as well as to perform as electrical sensors through-the-thickness [26].

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