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Hyperelasticity of three-dimensional carbon nanotube sponge controlled by the stiffness of covalent junctions

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ABSTRACT

To expand the applications of carbon nanotubes (CNTs) at macroscale, a heteroatom doping technique has been employed to fabricate isotropic 3-D CNT architectures by inducing elbow-like covalent junctions into multiwalled CNTs. As the junctions modify the topology of each CNT by favoring the stable bends in CNTs, junction stiffness and the consequence of junction-related morphology changes in sponge's hyperelasticity remain largely elusive. In this study, two types of 3-D multiwalled CNT sponges were fabricated by inducing boron-doped or nitrogen-doped covalent junctions into CNTs. Hyperelastic properties of the sponges were experimentally quantified as the functions of CNT morphology. A novel microstructure informed continuum constitutive law was developed specifically for such isotropic CNT sponges with junctions. Analyzing the experimental data with the new theory demonstrated that, for the first time, the effective modulus of boron-doped junctions (~100 GPa) is higher than that of nitrogen-doped junctions (~20 GPa), and the junction stiffness is a key factor in regulating the hyperelastic compressive modulus of the material. Theoretical analysis further revealed that increased number of junctions and shorter segments on each individual CNT chain would result in stronger hyperelastic 3-D CNT networks. This study has established a fundamental knowledge base to provide guidance for the future design and fabrication of 3-D CNT macrostructures.

1. Introduction

Carbon nanotubes (CNTs) possess extraordinary mechanical properties, structural stability, thermal conductivity, and electrical properties [1]. In order to promote the applications of the CNTs at macroscale, fabrication of high performance 3-D CNT-based architectures (i.e. sponges, forms and aerogels) attracts a lot of interests recently [2,3]. Different from uniformly aligned CNT bundles or CNT films, 3-D sponges composed of randomly oriented CNTs have been fabricated to achieve isotropic material properties [4–6]. The 3D CNT sponges with hierarchical structures were observed to exhibit excellent mechanical properties such as controllable viscoelasticity and high electrical conductivity as a result of increased surface area [7,8]. Their multifunctional characteristics have been exploited for a number of applications, such as hydrogen storage, tissue engineering and environmental-friendly reusable sorbent [4,9,10]. However, it remains a great challenge to fabricate CNT sponges that reflect the mechanical properties of individual CNTs. Previous

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studies have shown compressive modulus values of these sponges fall in the range of kPa [6]. In human body, through the control of topology and organization, collagen fibers can form into various tissues with drastically different mechanical functions, such as cartilage, ligament, and skin, by controlling their topology [11]. This fact encourages a natural hypothesis that optimizing the topology and ultrastructure of CNTs may generate unprecedented functional 3-D sponges for various applications.

An effective technique to tailor the CNT morphology and organization in forming 3-D sponges is to introduce non-hexagon structures into CNT graphitic layers through heteroatom doping, such as boron and/or nitrogen [12]. We have used this technique successfully in generating a 3-D boron-doped multi-walled CNT (CBxMWCNT) sponge, in which the formation of atomic-scale "elbow-like" junctions in CNT reforms the nanotube into a 3-D multi-segment architecture [4]. Recently, we also synthesized 3-D nitrogen-doped CNT (N-MWCNT) sponges by introducing nitrogen into the CNT structures [6]. Although both 3-D CNT sponges demonstrate prominent hyperelastic properties with nonlinear stress–strain relationship, which makes them good candidates for load support with a shock absorption capability, they showed entirely different hyperelastic behaviors. Moreover, we found that the MWCNT sponges with covalent junctions have drastically different mechanical behaviors with the pristine (undoped) sponges, including the plastic, elastic, viscoelastic, and dynamic properties. CBxMWCNT sponge is demonstrated as a more predictable and stable material than the undoped-MWCNT sponge [8]. This difference implies that covalent junctions may play a critical role in shaping the mechanical behaviors of 3D CNT sponges. Since the CNTs are modeled as multi-segment chains, the present constitutive model may not be suitable for the undoped CNT sponges [8]. It is also important to note that the time-dependent viscoelastic behaviors and plastic properties of the sponges are not incorporated in this model.

It is natural to speculate that the presence of junctions is a key factor in controlling the sponges' mechanical properties. For example, when musculoskeletal tissues in the human body fail under a traumatic overloading, such as ligament tear or meniscus rupture, they are mostly induced by the failure of interfibrillar junctions, not the collagen fibers themselves [13]. In particular, the collective behaviors of the CNT assemblies should be dependent on parameters such as the density of junctions along each nanotube, number of zigzag nanotubes in a unit volume, and the stiffness of the junctions [14]. However, actual roles of these parameters and their mechanical contributions remain largely elusive. The stress–strain curves of CNT sponges were mostly explained using linear elastic or viscoelastic models [5,8]. No proper constitutive model is available to correlate the mechanical behaviors of CNT sponges with the CNT morphology or junction properties. Due to the challenges involved in performing a bending test at the junction site, little information about the junction modulus is available. Thus, understanding the CNT sponge properties as functions of covalent junction-related characteristics would determine which junction-related parameters should be regulated, during the design and fabrication of 3-D CNT sponges, to achieve the desired mechanical properties.

In this work, the CBxMWCNT and N-MWCNT sponges were fabricated via boron and nitrogen doping during chemical vapor deposition processes, respectively. Mechanical behaviors of both 3-D CNT materials as well as their correlations with the sponge densities and various CNT morphology parameters were systematically characterized. Inspired by the similarity between the hierarchical structures of CNT sponges and many natural biopolymer networks [15,16], we further proposed a hyperelastic constitutive model for 3-D CNT sponges in which each fiber can deform independently and move with the macroscopic deformation. The new constitutive laws are expressed in the form of a hyperelastic strain-energy function as an indication of the nonlinear stress–-strain behaviors of each single nanotube and overall CNT sponges [17]. The model accurately describes the nonlinear stress–strain relationship observed in the mechanical testing of both CBxMWCNT and N-MWCNT sponges. It also captures the dependency between the hyperelasticity and apparent density of the materials. The correlation between the CNT diameter and compressive modulus of the N-MWCNT sponges matches perfectly with the theoretical prediction and curve-fitting is not necessary. More importantly, for the first time, the effective modulus of junctions was predicted based on the morphology of CNTs and the bulk mechanical behaviors of sponges. Covalent junctions in CBxMWCNT (~100 GPa) are much stronger than those in the N-MWCNT (~20 GPa), which partially contributes to the higher compressive modulus of CBxMWCNT sponge. This finding also matches the theoretical conjecture that the boron-carbon bond is stronger than the nitrogen–carbon bond, which remains technically challenging to measure. The constitutive model further reveals that increased concentration and enhanced stiffness of CNT junctions, and shorter CNT segments on each individual CNT chain can generate stronger hyperelastic 3-D CNT networks. Therefore, with fabrication, mechanical testing, and constitutive modeling, this study revealed the junction properties in 3-D CNT sponges and further quantified the effects of junction stiffness and junction-related morphological variations in the hyperelasticity of materials. The results provide a fundamental knowledge base and benchmark to guide future design and fabrication of 3-D CNT architectures.

2. Experimental section

2.1. 3-D CNT sponges preparation

CBxMWCNT sponges were grown onto the walls of a quartz tube furnace using ferrocene, toluene, and triethylborane under Ar gas at 860 °C via an aerosol-assisted catalytic CVD method [4]. N-MWCNT sponges were synthesized in a CVD system, where a mixture of ferrocene, thiophene and pyridine was injected into the furnace using a syringe pump [6]. The diameters of the N-MWCNTs were controlled by varying the concentration of thiophene. N-MWCNT sponges with CNT diameters of 40–110 nm, 60–140 nm, and 80–180 nm were synthesized in the presence of thiophene at concentrations of 0.25, 0.5, and 0.75 vol%, respectively. The morphology of CBxMWCNT was characterized by the field emission scanning electron microscopy (FESEM) using a LEO1530 and an FEI Nova NanoSEM630, both operated at 5 kV. The N-MWCNT sponges were characterized by SEM mode of focus ion beam (Zeiss, Auriga 60). The sample analysis chamber was operated at a pressure of 10-9 Torr. The diameters of the CNTs inside the N-MWCNT samples were measured using SEM images.

2.2. Mechanical characterizations of 3-D CNT sponges

Monotonic compressive testing was performed on CBxMWCNT and N-MWCNT sponges. Both types of samples were cut into 3 mm diameter cylinders using a Harris Micro-Punch (Ted Pella, INC.). Since both types of sponges after fabrication showed plastic deformation under compression, all samples were preconditioned before testing by repetitive compressive loading until the plasticity vanishes. The thicknesses of the samples were then measured on a dynamic mechanical analyzer (DMA, Q800, TA Instruments) with a 0.01 N preload and ranged from 0.8 to 2 mm. Weights of the samples were measured on an XP6 microbalance (Mettler–Toledo,