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Mechanics of filled carbon nanotubes

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ABSTRACT

The benefits of filling carbon nanotubes (CNTs) with assorted molecular and crystalline substances have been investigated for the past two decades. Amongst the study of new structural phases, defects, chemical reactions and varied types of host–guest interactions, there is one fundamental characterisation aspect of these systems that continues to be overlooked: the mechanical behaviour of filled CNTs. In contrast to their empty counterparts, the mechanics of filled CNTs is a subject where reports appear far and apart, this despite being key to the application of these materials in technological devices. In the following paragraphs, we review the work that has been carried out up to the present on the mechanics of filled CNTs. The studies discussed range from experimental resonant frequency essays performed within electron microscopes to modelling, via molecular dynamics, of three-point bending of nanotubes filled with gases.

Contents

1. Introduction

Ever since the existence of the fullerene molecule (C_{60}) was reported in 1985 [1], a large community of researchers have focused their effort on studying carbon allotropes. Due to its outstanding physical and chemical properties, one particular nanostructure that has stimulated research activities all over the world is the carbon nanotube (CNT) [2]. Since two decades ago, a large number of potential applications for CNTs have been proposed, ranging from electronic devices to drug delivery systems [3]. However, the timeline to bring them to the marketplace has been highly underestimated and the majority of the proposed applications have not yet passed the laboratory stage (in particular for products that represent disruptive technologies). Still, market penetration is starting to grow with two examples being the use of CNTs in lithium-ion batteries [4–7] or in polymer composites for electrostatic discharge applications [8,9].

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Amongst the peculiar features of CNTs, there is one that represents a trump over other carbon allotropes (including graphene): their high aspect-ratio cavities. These can be used to incorporate molecules and compounds in order to generate novel host–guest materials [10]. Encapsulation of organic and inorganic entities within CNTs has been studied since 1993 [11]. The interest behind these structures lies in the possibility to study new structural phases [12] and associated defects [13] as well as to tailor the functional properties of either the carbon host or the guest filling. Eventually one may use them as storage/transport vehicles for nanoscaled matter [14]. Up to the present, several procedures have been used to fill the inner space of nanotubes. They can be classified in three types: the in situ method, wherein both the filling and carbon nanotube are produced in a single-step process, the chemical method, which takes advantage of simple and well-tested wet chemistry procedures and the physical method, where the tube is filled via prolonged exposure to a molten material [10,15]. In the in situ method, either the arc discharge [16] or chemical vapour deposition [17] growth processes are employed. Particularly for the latter, the transition metal catalysts that are used to grow the nanotubes end up being confined in the carbon shell such as in the thermal decomposition of metallocenes [18,19]. In the chemical method, nanotubes are commonly refluxed in a nitric acid bath in order to first open their tips. When a metal salt is added to the bath, it is possible to obtain, after due processing, encapsulated oxides [20] or pure metal particles [10,21] (for instance). In the physical method, no solvent is used as the CNTs are directly immersed in a melt of the selected filling material. Provided its physical properties are within appropriate limits (e.g. surface tension $< 180\ \mathrm{mN\ m^{-1}}$ [22]), this substance will then be driven into the tube by capillarity forces. Whilst with the chemical method a wider range of materials can be introduced into the nanotubes, the effective quantity of enclosed matter remains rather low and, invariably, in the form of isolated particles. In the case of the physical method, the filling material choices are restricted but the amount of enclosed matter is significantly larger and, commonly, in the form of continuous filaments (i.e. nanowires) [10].

With the list of filled CNT systems increasing yearly, it is essential to study their physicochemical characteristics. For instance, knowing their mechanical properties and response to applied forces is particularly crucial for filled-CNTs applications such as magnetic force microscopy probes [23] or nanopipettes [24]. Today, there is a wealth of information on the mechanics of empty CNTs. We know, for instance, that single-walled CNTs should possess extremely high Young's modulus values, around 1 TPa [25], and that these are a result of the strong sp^2 C–C bonds. We are also aware that the presence of defects in their structure considerably alters this value [26]. By contrast, there are relatively few studies that have focused on the mechanical properties and response of filled-CNTs. The following summarizes the work carried out on filled-CNTs nanomechanics. The listed studies range from physical tests conducted with highly sophisticated instrumentation to modelling using molecular dynamics or finite element analysis computational tools.

2. Experimental essays

Nanomechanics studies of discrete CNTs require high precision manipulation of nanostructures and, usually, vibration-inducing or force-sensing instrumentation. These should be coupled to built-in capabilities to observe in high-resolution (and ideally in real-time) the deformation of 1D materials. Methods employed are mainly based on atomic force microscopy (AFM), scanning tunnelling microscopy (STM) or electron microscopy (either in scanning, SEM, or transmission, TEM, mode). Within the microscope chamber, force sensors may be integrated that allow the operator to perform indentation, stretching or compression of the CNTs. Other often used methods are the thermal [27] or electric-field induced resonance techniques wherein the harmonics of a nanotube are correlated with the Young's modulus [28]. Generally, the nanostructures are dispersed on substrates bearing excavated trenches (for three-point analysis) or attached to micro-electromechanical (MEMS) devices. Surprisingly, the number of experimental data reported up to the present in relation to filled-CNTs is remarkably small. From a literature search, we only found three systems that were analysed.

2.1. C_{60}-filled CNTs

One of the best known examples of filled CNTs is the so-called peapods which consist of nanotubes filled with long chains of buckyballs. The mechanical resonant characterisation of bundles of C_{60}-filled SWCNTs was performed by Jaroenapibal and colleagues [29]. This experimental study employed a TEM and a custom-built sample holder allowing the injection of electrical signals via a function generator. Upon the application of an AC signal, the resonant frequencies and amplitudes were recorded as a function of the bundle dimensions (Table 1), similar to the method initially developed by Poncharal and colleagues [28]. The aim of using nanotubes filled with C_{60} was both to investigate whether the intra- and inter-tube interactions would not only just increase the overall bending modulus but also reduce the eventual sliding of SWCNTs in a bundle under deformation.

Assuming round cross-sections for the bundles and taking in consideration the Euler–Bernoulli analysis of a cantilevered beam [30], the authors derived a relationship between the resonant frequency and the dimensions of the bundles:

$$f_i = \frac{B_i^2}{8\pi L^2} D \sqrt{\frac{E_b}{\rho}} \tag{1}$$

where f_i is the resonant frequency, L and D correspond to the bundle's length and diameter, respectively, I is the moment of inertia, A is the cross-sectional area, E_b is the effective bending modulus, ρ is the density, and B_i is a constant for the ith harmonic oscillation: for instance, $B1 = 1.875$ and $B2 = 4.694$. From Table 1, one observes that the average value for $(E_b/\rho)^{1/2}$ is 19,002 m/s for the peapods. For the empty bundles this was noticeably lower, at 13,230 m/s. The effective densities employed were $\rho\ (empty) = 1.3 \times 10^3\ \mathrm{kg/m^3}$ and $\rho\ (filled) = 1.78 \times 10^3\ \mathrm{kg/m^3}$ which led to the extraction of an average bending modulus of $E_b\ (empty) = 240 \pm 105$ GPa and $E_b\ (filled) = 650 \pm 156$ GPa, respectively. Plotting the E_b of each bundle as a function of its diameter further illustrated the enhanced structural stiffness provided by the C_{60}-filling action (Fig. 1). Importantly, their results showed that the mechanical properties of SWCNT bundles may be modified without sacrificing the structural integrity of the nanotubes. The authors proposed that the E_b/ρ increase for the peapods is related to the additional strain energy in the filled tubes as the tube inner surface and C_{60} chains interact. In fact, bending of filled bundles alters the tube–C_{60} equilibrium gap. The authors further dismissed suggestions that interface properties and inter-tube interactions could change with the filling process and thus

Table 1
Length L, diameter D, resonant frequency f, and $(E_b/\rho)^{1/2}$ of filled SWCNT bundles [29]. Reprinted with permission. Copyright 2005, AIP Publishing LLC.

D (nm)	L (nm)	f (MHz)	$(E_b/\rho)^{1/2}$ (m/s)
14	1693	13.20	19,465
16	2405	7.96	20,962
18	2616	8.04	22,603
19	1556	21.56	19,847
20	2682	6.32	16,607
20	2733	7.66	20,766
21	3442	4.56	18,215
23	5916	1.52	16,796
35	6831	1.64	15,757