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A nonlinear mechanical model for the fatigue life of thin-film carbon nanotube supercapacitors

Giovanni Formica [a], Walter Lacarbonara [b, *]

[a] Dipartimento di Architettura, University of Roma Tre, 00184 Rome, Italy
[b] Dipartimento di Ingegneria Strutturale e Geotecnica, University of Roma La Sapienza, 00184 Rome, Italy

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ABSTRACT

The effects of cyclic loading on the mechanical performance and fatigue life of a novel carbon nanotube supercapacitor are investigated. The highly flexible supercapacitor is a monolithic, pre-fabricated, fully functional film made of a nanostructured free-standing layer in which ions are stored within two vertically aligned multi-walled carbon nanotube (MWCNs) electrodes that are monolithically interspaced by a solution of microcrystalline cellulose in a room temperature ionic liquid electrolyte. To study the cyclic mechanical response of such nanostructured multilayer composite, an original framework is adopted by combining the equivalent continuum approach of Eshelby–Mory–Tanaka and a Weibull-like approach for the evolution of debonding carbon nanotubes electrodes. One- and three-layer models of the supercapacitor are proposed. Cyclic tests are numerically carried out in strain control. A fatigue life limit is determined by considering a confidence interval for the number of cycles corresponding to the states at which the effective elastic modulus of the partially debonded nanostructured portion of the supercapacitor is reduced by a percentage between 20% and 30%. The simulated cyclic tests yield Wholer-type fatigue curves showing the fatigue life limit as the maximum number of cycles N for each strain amplitude.

The sensitivity of the fatigue life with respect to meaningful parameters such as the interfacial strength between the MWCNs and cellulose is investigated. Frequency-response functions of the multilayer nanostructured composite are further computed as function of the strain amplitude during cyclic tests.

1. Introduction

In recent years, substantial improvements in the functionality of a wide spectrum of high-tech engineering applications, such as hybrid electric vehicles, laptops, biomedical devices, unmanned aerial vehicles (UAVs), airships, have been sought resorting to the incorporation of pre-fabricated and free-standing functional composite films that, once connected to current collectors, become lightweight, flexible energy storage devices also known as supercapacitors [1,2]. In some of these applications (e.g., stratospheric airships, air vehicles), the severe weight constraints are such that this type of energy storage system is the only viable approach.

Standard film-based supercapacitors are typically fabricated by assembling two electrodes and a separator impregnated with electrolyte, all sandwiched between two current collectors. The separator is devised to avoid electrical contact between the electrodes. However, it causes a significant degradation in the supercapacitor performance during its in-service life because the undesirable initiation/propagation of interfacial debonding between the stacked layers determines a disturbance to ions mobility preventing free travels towards the electrodes. The interfacial problems are solved by making all the key components in the form of a single monolithic layer engineered so as to host inter-spaced multiwalled carbon nanotube electrodes impregnated with electrolyte (see Fig. 1) [1,2]. Vertically aligned MWCNs with their percolated pore structure due to their high specific area were optimized in terms of their length and enhanced by an innovative nanoparticle surface coating leading to excellent electrochemical performance, high maximum power density (108.2 kW/kg) and high reaction speed.

While the monolithic fabrication of the above mentioned supercapacitor overcomes the separator discontinuity of standard film-based sandwiched supercapacitors, the vertically aligned carbon nanotube electrodes introduce a new challenge associated with the mechanical performance. When subject to cyclic loading,

* Corresponding author.
E-mail addresses: formica@uniroma3.it (G. Formica), walter.lacarbonara@uniroma1.it (W. Lacarbonara).

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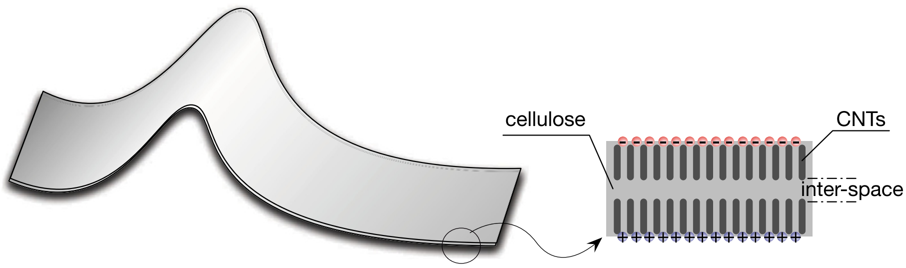

Fig. 1. Schematic geometry of the flexible supercapacitor with the two multi-walled carbon nanotube electrodes immersed in cellulose separated by an inter-space.

MWCNs can suffer debonding from the hosting cellulose matrix if the hydrostatic stress states in the plane normal to the CNTs reach the interfacial strength. Therefore, the interfacial discontinuity which is truly local in nature can influence the macroscopic behavior when a nonnegligible volume fraction of MWCNs is subject to such a limit state. Indeed, from a strictly mechanical point of view, the fatigue life of the nanostructured film can be reached when the extent of debonding phenomenon causes a significant loss of average stiffness of the composite. Whether this mechanical limit state can compromise the electrochemical performance of the supercapacitor is still an open question. Certainly, the physical discontinuity between the MWCNs external walls and the electrolyte has the potential to affect the charge mobility and distribution within the percolated pore structure.

To investigate the progressive debonding of this class of nanostructured composite films leading to the estimation of their fatigue life, the nonlinear model proposed by Ref. [3] is here employed. In the literature, various theories have been proposed to describe damage evolution in composites embedding different types of inclusions, including CNTs [4–10]. The literature on linear and nonlinear models of carbon nanotube nanocomposite materials employed for micro-nano plates or beams is wide and covers diverse fields such as homogenization [14], gradient/nonlocal elasticity [16–19], elasto-plasticity [20].

In the present work, the dynamical formulation presented jn [3] for the macroscopic response of carbon nanotube composites accounting for the cumulative debonding of CNTs due to weakening of the interface is particularly suitable. It relies on a thermodynamically consistent phase flow law for the evolution of the volume fraction of debonded CNTs treated as cylindrical inclusions in a rate form amenable to a full dynamical formulation which enables parametric studies and fatigue life assessment. This flow law is the combination of the Weibull statistics and a law giving the rate of the effective stress measure which drives the debonding progression. As a result of progressive debonding, stiffness degradation occurs in the nanostructured composite up to a state in which the fatigue life is reached. In the literature, various works addressed theoretically and experimentally fatigue loading in composite laminates by employing stiffness degradation models for graphite/epoxy laminates [11], for cross-ply laminates using a suitable fatigue life measure and shear-lag analysis [12], or for adhesively-bonded double- and stepped-lap joints [13]. The common objective of these approaches was to establish a correlation between the evolution of the residual stiffness (i.e., generalized stiffness degradation) and the number of cycles for a given loading amplitude. When the residual stiffness attains a threshold value called failure stiffness, fatigue life is conventionally assumed to be reached. A typical outcome is the evolution of the modulus reduction ratio with the number of cycles. Such a characterization allows to correlate the loading magnitude with the number of cycles at the fatigue limit (i.e., F–N Wohler-type curves).

In the present work, we employ a similar approach for the multilayer nanostructured supercapacitor film to investigate such fatigue limit scenarios. We illustrate the nonlinear mechanical model in Section 2 and the numerical results in Section 3.

2. Nanostructured composite subject to progressive debonding

The multilayer thin film supercapacitor is made of three domains, the interspace composed of cellulose (isotropic elastic material) and the two adjoining MWNTs electrodes immersed in cellulose (see Fig. 1). The latter is a nanostructured layer which is modeled as a three-phase material (see Fig. 2): hosting matrix (cellulose), perfectly bonded CNTs, and debonded CNTs. The three phases are described by the associated volume fractions.

The nanostructured layer with the perfectly bonded CNTs is described by the equivalent linear elastic tensor obtained via the Eshelby–Mory–Tanaka homogenization method. On the other hand, following [3] a suitable phase law together with a Weibull statistics-like approach is proposed to describe the evolution of the volume fraction of debonded CNTs.

Let ϕ_1 denote the volume fraction of perfectly bonded CNTs, ϕ_2 denote debonded CNTs, and $\phi_0 = 1 - \phi_1 - \phi_2$ be the elastic hosting

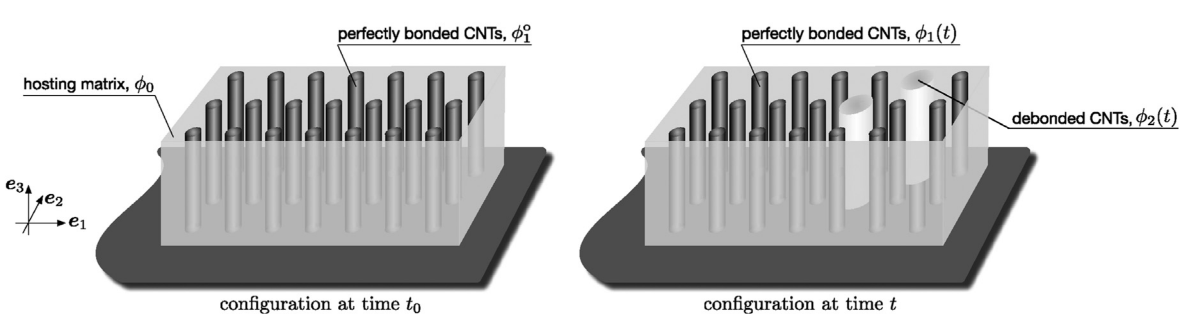

Fig. 2. Three-phase nanostructured material: hosting matrix, bonded CNTs and debonded CNTs.