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Stiffness threshold of randomly distributed carbon nanotube networks

Yuli Chen [a,b,*], Fei Pan [a], Zaoyang Guo [a,b], Bin Liu [c], Jianyu Zhang [d]

[a] *Institute of Solid Mechanics, Beihang University (BUAA), Beijing 100191, PR China*
[b] *International Research Institute for Multidisciplinary Science, Beihang University (BUAA), Beijing 100191, PR China*
[c] *AML, CNMM, Department of Engineering Mechanics, Tsinghua University, Beijing 100084, PR China*
[d] *College of Aerospace Engineering, Chongqing University, Chongqing 400044, PR China*

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A B S T R A C T

For carbon nanotube (CNT) networks, with increasing network density, there may be sudden changes in the properties, such as the sudden change in electrical conductivity at the electrical percolation threshold. In this paper, the change in stiffness of the CNT networks is studied and especially the existence of stiffness threshold is revealed. Two critical network densities are found to divide the stiffness behavior into three stages: zero stiffness, bending dominated and stretching dominated stages. The first critical network density is a criterion to judge whether or not the network is capable of carrying load, defined as the stiffness threshold. The second critical network density is a criterion to measure whether or not most of the CNTs in network are utilized effectively to carry load, defined as bending–stretching transitional threshold. Based on the geometric probability analysis, a theoretical methodology is set up to predict the two thresholds and explain their underlying mechanisms. The stiffness threshold is revealed to be determined by the statical determinacy of CNTs in the network, and can be estimated quantitatively by the stabilization fraction of network, a newly proposed parameter in this paper. The other threshold, bending–stretching transitional threshold, which signs the conversion of dominant deformation mode, is verified to be well evaluated by the proposed defect fraction of network. According to the theoretical analysis as well as the numerical simulation, the average intersection number on each CNT is revealed as the only dominant factor for the electrical percolation and the stiffness thresholds, it is approximately 3.7 for electrical percolation threshold, and 5.2 for the stiffness threshold of 2D networks. For 3D networks, they are 1.4 and 4.4. And it also affects the bending–stretching transitional threshold, together with the CNT aspect ratio. The average intersection number divided by the fourth root of CNT aspect ratio is found to be an invariant at the bending–stretching transitional threshold, which is 6.7 and 6.3 for 2D and 3D networks, respectively. Based on this study, a simple piecewise expression is summarized to describe the relative stiffness of CNT networks, in which the relative stiffness of networks depends on the relative network density as well as the CNT aspect ratio. This formula provides a solid theoretical foundation for the design optimization and property prediction of CNT networks.

* Corresponding author at: Institute of Solid Mechanics, Beihang University (BUAA), Beijing 100191, PR China.
E-mail address: yulichen@buaa.edu.cn (Y. Chen).

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1. Introduction

Researchers have been seeking a way to transfer the excellent properties of Carbon Nanotubes (CNTs) in nanoscale to macro-materials (Bryning et al., 2007; Kim et al., 2011; Lu et al., 2012; Wang et al., 2012; Xie et al., 2011; Xu et al., 2010). It has been found that isolated CNTs can hardly make great improvements in mechanical properties of macroscale materials (Ma et al., 2009; Moniruzzaman and Winey, 2006). Recent studies show that CNT constructed networks, such as films (Wu et al., 2004; Zhang et al., 2005), sponges (Gui et al., 2010) and foams (Cao et al., 2005), are probably an effective material structure form to utilize CNTs in macroscale applications, hence drawing many attentions.

CNT constructed networks process many unique properties (e.g. low density and high porosity) and therefore have wide potential applications, such as CNT conductive coatings for lightning protection and electromagnetic interference shielding (Gagné and Therriault, 2014; Gou et al., 2010; Yang et al., 2005), CNT membrane filters for water and air purification (Brady-Estévez et al., 2008; Cooper et al., 2003; Halonen et al., 2010; Li et al., 2013; Smajda et al., 2007; Viswanathan et al., 2004), catalyst supports (Halonen et al., 2010; Zhu et al., 2010), artificial muscles (Aliev et al., 2009; Foroughi et al., 2011; Vohrer et al., 2004) and gas sensor (Sayago et al., 2008; Slobodian et al., 2011).

Experimental studies have exhibited that the formation of CNT networks may lead to sudden changes in properties of their macro-materials. For example, the electrical percolation threshold of CNT/polymer composites is observed experimentally (Allaoui et al., 2002; Gojny et al., 2006; Koerner et al., 2005; Kovacs et al., 2007; Moisala et al., 2006). The composites are conductive only when the volume fraction of CNTs in the composites is higher than the threshold. And furthermore, once the CNT volume fraction reaches the threshold, the conductivity of the composites increases rapidly. This sudden change as well as the electrical percolation threshold is predicted by studying the topology of the network (Chen et al., 2015a; Lu et al., 2010). The question then arises: does this threshold behavior also exist in mechanical properties of CNT networks? As for mechanical properties, a similar stepwise sudden change is found in the fracture toughness study on CNT reinforced composites: the main failure mode is converted from CNT pull-out to CNT break with an increase in interface strength, and the fracture toughness also declines suddenly during this transition (Chen et al., 2010, 2015b). This phenomenon is also identified experimentally by other researchers (Tang et al., 2011a, 2011b). Besides, a sudden increase in stiffness of compressed exfoliated graphite as well as nanocomposites is captured in experiments and simulations (Baxter and Robinson, 2011; Celzard et al., 2005). The critical value for this sudden increase is considered to be consistent with the electrical percolation threshold, although the sudden increase in stiffness can hardly explained by the mechanism of electrical percolation threshold.

Therefore, it is reasonable to guess that increasing CNT volume fraction in CNT networks may lead to sudden change in their mechanical properties. The aims of this paper are to reveal the stiffness threshold mechanism for randomly distributed CNT networks, and to establish the relation between topology and stiffness of CNT networks, which may be readily used to guide the design optimization and strength analysis in practical applications. This paper is structured as follows. First, the topology analysis on load-transfer paths and defect fraction of 2-dimensional (2D) CNT networks is carried out to reveal the mechanism of load-carrying capacity of CNT networks and the existence of stiffness threshold and bending–stretching transitional threshold in Sections 2 and 3, respectively. The invariants at the two thresholds are derived based on the geometric probability analysis on the average intersection number of each CNT in the network, and validated by the numerical simulations. Subsequently, in Section 4, the expression to describe the three-stage behavior of CNT network stiffness is established based on the two thresholds. The methodology to estimate the stiffness and thresholds of CNT networks are extended to 3-dimensional (3D) CNT networks in Section 4.4 and a brief summary is given in Section 5.

2. Stiffness threshold versus electrical percolation threshold

Based on the previous studies and the subsequent simulations, considering both the electrical and mechanical properties, the CNT networks may present 4 different types of behaviors with increasing network density, as illustrated in Fig. 1: (1) neither electrical conductive nor able to carry load; (2) electrical conductive but not able to carry load; (3) electrical conductive and able to carry load by bending dominated deformation; and (4) electrical conductive and able to carry load by stretching dominated deformation. The critical value between type 1 and type 2 is the electrical percolation threshold, and the critical value between type 2 and type 3 is defined as the stiffness threshold in this paper. In this section, we will focus on these two values, and the last critical value will be studied in Section 3.

2.1. Qualitative analysis on stiffness threshold

The electrical percolation threshold has been intensively studied by both theoretical and experimental approaches (Balberg et al., 1984; Bauhofer and Kovacs, 2009), and most researchers have reached a consensus that the composite is conductive only when the conductive path is formed. The lowest CNT volume fraction to form the conductive path is defined as the electrical percolation threshold.

Similarly, the load-transfer path must be constructed so that the CNT networks can carry load; otherwise, without load-transfer path, the network cannot carry load, and the stiffness of the network is zero. Therefore, for the CNT networks with low density, there should be a critical CNT volume fraction at which the stiffness becomes nonvanishing. This critical CNT