Materials and Design 101 (2016) 236–244

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Tunable morphology and its influence on electrical, thermal and mechanical properties of carbon nanostructure-buckypaper

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ARTICLE INFO

Article history:
Received 1 December 2015
Received in revised form 22 March 2016
Accepted 23 March 2016
Available online 4 April 2016

Keywords:
Buckypapers
CNTs
Mechanical properties
Electrical conductivity
Thermal conductivity

ABSTRACT

In this study, free-standing buckypapers (BPs) made up of a three-dimensional network of multi-walled carbon nanotubes (MWCNTs) that are branched, cross-linked, and share common walls, defined henceforth as multi-walled carbon nanostructures (MWCNSs) are characterized to obtain their electrical, thermal and mechanical properties. Two types of free-standing sheets are studied, namely uncompressed buckypapers (UBPs) and compressed buckypapers (CBPs). Both are processed via a vacuum filtration method, with subsequent compressive force applied between platen presses to obtain CBP. CBPs are found to exhibit improved thermal and electrical conductivities since higher density of CNT networks leads to more conductive pathways. However, mechanical properties of CBPs and UBPs are approximately the same. Local anisotropic behavior of both BPs allows them to have either positive or negative Poisson's ratio. While UBP is suitable for membrane applications due to its mechanical stability and well-defined pore characteristics, the CBP offers a compact structure that can reduce penetration of the polymer matrix in composite applications such as for integrated circuit packaging and EMI shielding.

1. Introduction

Carbon nanotubes (CNTs) have attracted remarkable attention due to their excellent mechanical, thermal and electrical properties [1]. They have been utilized to fabricate macroscopic CNT sheets, commonly referred to as 'buckypapers' (BPs). These BPs are suitable for both lightweight structural and functional applications. These free-standing sheets are cohesively bound by van der Waals' interactions among entangled CNTs. The central idea behind the fabrication of BP is to utilize the outstanding properties of individual CNTs in macroscopic form. This macroscale CNT sheet is advantageous to facilitate easier handling of CNTs and to improve the safety of using CNTs in industrial scale. Although the performance of BPs is lower than that of individual CNTs due to the low interaction energy, densely-packed and inter-entangled structures of CNTs offer multi-functional capabilities owing to their mechanical stability, flexibility, high electrical and thermal conductivity [2–5]. These characteristics make BPs suitable for membranes [6–8], electrodes [3,9,10], actuators [4,11–14], sensors [15–18], heat conductors [19–21] and for structural reinforcement in polymer composites [5,22–27].

BPs are commonly prepared by dispersing CNTs or chemically modified CNTs in a solvent medium followed by vacuum filtration process through a microporous membrane [5,28]. Through this process, CNTs are generally oriented randomly in the BP unless specific techniques such as the application of strong magnetic fields are used to align them [29,30]. Mechanical spinning of CNT from the CNT arrays or flakes may also result in a BP with aligned CNTs [21,31]. It has been demonstrated that properties of BPs are affected by many parameters such as CNT type (single- or multi-walled) [32], dimension (length and diameter) [19], purity [14,33,34], chemical modification of CNTs [28] and degree of alignment [21]. Smaller diameter and higher purity of CNT usually lead to BP with higher tensile strength, whereas larger CNT diameter results in BP with higher porosity and lower tensile strength [8]. Functionalization of CNT can improve inter-CNT interactions in the BP and thus improves their mechanical performance and conductivity to a certain extent [28,35,36]. The solvent medium used for the CNT dispersion and the synthesis conditions as well as post-treatments have a significant effect on the pore size distribution and nanotube packing density and hence on the final properties of the BP [21,24,37].

Through careful selection of CNT types and processing conditions, desired characteristics and properties of the resulting BPs can be achieved. However, fabricating macroscopic form of CNT networks with controlled geometry, porosity and properties is challenging. In addition to the experimental efforts, computational modeling strategies are important to develop tools so as to optimally design the CNT

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http://dx.doi.org/10.1016/j.matdes.2016.03.122
0264-1275/

systems and configurations for specific targeted behavior and properties. Modeling of BPs based on a coarse-grain model of carbon nanotubes, with possible variation in parameters including initial CNT density and ratio of CNT type (single- and double-walled) was performed by Cranford and Buehler [38]. Through manipulation of the parameters, the porosity and Young's modulus of the BP can be tuned over a range of 0.3–0.9 and 0.2–3.1 GPa, respectively. Yang Li et al. [39] have developed an algorithm that combines molecular dynamics and Monte Carlo methods to equilibrate initial structure of BP. Initial structure of BP was generated by applying random walk theory. Entanglement and bundling mechanisms are found to influence the pore size and mechanical properties of the BP.

In this paper, both UBPs and CBPs are characterized in terms of its surface morphology, pore characteristics, thermal, electrical and mechanical properties. These BPs are synthesized from MWCNS. The MWCNS are produced in an industrial scale using chemical vapor deposition (CVD) method, capable of making nanotubes in high-throughput. Both BPs are processed by vacuum filtration method, with subsequent compressive force applied between platen presses to obtain CBP.

2. Experimental procedures

2.1. Synthesis of multi-walled carbon nanostructures and buckypapers

Multi-walled carbon nanostructures (MWCNSs) have been developed by Applied Nanostructured Solutions, LLC through a unique CVD process specifically characterized by their low cost/high volume production process [40]. Unlike the conventional CNT processes that mostly focus on production of high purity CNT, the MWCNS process allows rapid and continuous growth of CNT on a moving substrate. While the conventional CNT growth rate is typically in the order of several microns per minute, the MWCNS process can achieve a growth rate of several microns per second. As a result, the nanotubes within the MWCNS are more defective than those in a conventional CNT flakes. MWCNSs consist of bundles of aligned MWCNTs. Inner walls are intact, but the outer most wall that has 5 or 7 member of "C" rings which are covalently bonded with adjacent similar structure of other MWCNTs are defective. These defective features are characterized by its highly entangled, branched, cross-linked, and wall-sharing architecture.

The vacuum filtration method was used to fabricate the BPs. The UBP was prepared by adding the MWCNS flakes into an ethanol/distilled water mixture, with subsequent gentle stirring and sonication with ½″ tip diameter at maximum amplitude for 10 min. The ethanol/distilled water volume ratio and the MWCNS suspension concentration were set to 1:1 and 0.175 g/L, respectively. Afterwards, the MWCNS suspension was vacuum-filtered through a glass fiber filter. After the free-flowing liquid was vacuumed and a damp MWCNS sheet was formed, the BP was peeled off from the filter and then put in a convection oven and dried fully. The CBP was fabricated using the same filtration method, with subsequent application of mechanical pressure between platen presses at 750 psi after peeling it off from the filter. The MWCNS suspension concentration was adjusted to obtain a uniform thickness of 30–40 μm for both BPs. Since MWCNSs are branched and covalently bonded with adjacent nanotubes, applied pressure of 750 psi was found to be optimum to obtain good consolidation of CBPs. Lower pressures didn't yield a good consolidation of CBPs while higher pressures mechanically damaged the resultant BPs.

2.2. Characterization of multi-walled carbon nanostructures and buckypapers

Two different scanning electron microscopes (SEMs), namely Quanta 250 and Nova NanoSEM were used to elucidate the surface morphology of the BPs. Quanta 250 examines the sample at 10 mm working distance, whereas Nova NanoSEM which utilizes 5 mm working distance is capable of observing the sample at higher magnification. Transmission electron microscope (TEM) Technai TF20 was used to characterize the MWCNS. Quanta 3D dual beam SEM/FIB was used to evaluate the cross section morphology of the BPs. To obtain cross-sectional image of the BP, the sample was firstly tilted at 52°. Afterwards, the cross section was milled by focused ion beam (FIB) using a high beam current (7 nA) followed by several smoothing steps using lower beam current (0.3 nA). Finally, the resulting smooth cross-sectional area was observed by SEM.

Pore size distribution of the BPs was measured by two different methods; SEM image analysis and capillary flow porometer (CFP). Image analysis of the top surface of SEM image of the BPs was conducted by image segmentation of the pores and MWCNS via gray level thresholding technique using ImageJ software. The areas of all pores were obtained and the diameters of the pores were calculated by considering the pores as circular pores. The CFP measurement (Porous Materials, Inc.) was performed based on wet/dry flow method. The circular sample of the BP was wetted with Galwick, a wetting liquid with low surface tension of 15.9 dyn/cm, and then placed into the porometer sealed chamber through which a gas flows. Subsequently, the pressure of the gas was increased gradually and the through flow was recorded. The pressure needed for gas to flow through the wet sample and to remove the wetting liquid completely was used to measure the pore size. In wet/dry flow method, the porometer only considers one diameter per pore, which is the throat (most constricted) diameter across the through-thickness path of the BP. In the current work, the maximum applied pressure was 200 psi, which is adequate for detecting smallest pore diameter of 33 nm.

The electrical resistivity of the BPs was measured using a four point probe (LakeShore, USA) according to the Van der Pauw method. The electrical contact was made by placing the contact needles onto the four corners of the 1.1×1.1 cm^2 size of the BP sample. To facilitate the electrical contact, silver conductive ink was manually painted onto the four corners of the sample. The electrical conductivity (σ) was computed by $\sigma = 1/\rho$, where ρ is the electrical resistivity of the sample.

The Netzsch LFA 457 Microflash was used to determine the through-thickness thermal diffusivity (α) of the BPs according to ASTM E-1461 [41]. Each sample was tested with a reference sample for the specific heat (C_ρ) calculation. The density (ρ) was evaluated from the measured weight and volume of the sample. From α, ρ and C_ρ measurements, the thermal conductivity (κ) was determined by $\kappa = \alpha \times \rho \times C_\rho$.

2.3. Mechanical tests

Quasi-static tensile tests of the BPs with rectangular dimension of $60 \times 6 \times$ (thickness) mm^3 were conducted in displacement mode with a crosshead speed of 20 μm/min in Zwick Roel Z005 universal tensile machine with 20 N load cell. The thickness of both BPs ranges from 30 to 40 μm. The average thickness at three locations of each tensile sample was used for the stress evaluation. Unloading-reloading tests were performed with the same crosshead speed. To avoid high stress concentration in the grip zone and to ensure effective clamping, adhesive foam tape was used as a specimen tab.

The evolution of the strain field on the surface of the BP during loading was evaluated by digital image correlation (DIC) technique. Similar to the use of extensometer, the DIC technique is important to obtain valid strain measurements. Micro deformation in the grip zones can under-/overestimate the measured strain depending on the shape of the test sample and the material behavior. This effect can be eliminated from the measurement using DIC technique. Moreover, Poisson's ratio and strain contour during the test can be evaluated.