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A pressurized filtration technique for fabricating carbon nanotube buckypaper: Structure, mechanical and conductive properties

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ABSTRACT

Self-supporting carbon nanotube (CNT) buckypaper has unique structural and conductive properties which can be utilized in various applications. A pressurized filtration technique was developed to fabricate the buckypaper, and tailor its porous structures and properties. Compared with the conventional vacuum filtration technique, the pressure applied in the pressurized filtration process increased from 1 atm to as high as 12 atm. Filtration behaviors of the CNT solutions during the vacuum and pressurized filtration processes were studied. The results indicated that the filtration behaviors were largely dependent of the applied pressure. Micro-morphologies of the buckypaper were also characterized and appeared to be corresponding to the filtration behaviors well. Upon applying high pressure during the filtration, porosity of the buckypaper was reduced slightly by ~1.9% due to the flexibility of the porous CNT network structure. Dimensions of the gaps within the interior of highly intermingled CNT bundles or junctions also decreased, resulting in higher intertube interactions. The higher intertube interactions improved the overall mechanical properties, as well as electrical and thermal conductivities of the buckypaper significantly.

1. Introduction

Since their discovery in 1991 [1], carbon nanotubes (CNTs) have been considered as ideal candidate materials for both structural and functional applications in various fields, owing to their inherent high surface area, unique chemical properties, and outstanding thermal and electric properties combined with the high specific stiffness and strength. Yet, many such applications can only be attained by developing appropriate approaches that can translate the properties of the CNTs into the macroscopic scale. One of the most important successes in this area was the fabrication of CNT film. Free-standing CNT film, commonly referred to as buckypaper, is a macroscopic paper-like material composed of CNTs which form continuous and porous entangled network structures. Its porous structure opens up a new avenue for a wide range of potential applications in the field of membrane science, from water desalination [2], to gas separation, purification and storage [3]. Buckypaper is also an ideal candidate for providing a new technical approach toward realizing structural/multifunctional material, due to the lightweight, high mechanical property and high electrical/thermal conductivities [4]. By infusing polymer into its porous structure, buckypaper can be fabricated into advanced composites, which can be potentially applied in the airspace industry, and to achieve this goal, buckypaper with better mechanical and conductive properties are needed.

For the industrial applications, the fabrication techniques and properties of the buckypaper are of key interest. Currently, techniques for fabricating buckypaper can be conveniently categorized into dry and wet approaches. The dry approaches include the direct in situ CVD growing [5], as well as several post-synthetic techniques, such as contact transfer printing [6], domino pushing [7], solid-state drawing [8] and shear pressing [9]. The buckypaper produced by dry approach commonly consists of CNTs with high level of structural perfection and less degree of tube agglomeration. However, the pristine buckypaper usually contains impurities including catalyst and amorphous carbon, which are un-desirable for the membrane applications. Other problems lie in the difficulty in achieving relative high thickness and density of the film, the inconveniency for scaling to large area, as well as the purification or functionalization of CNTs, which are important for the composite applications. On the other hand, the wet approaches, such as membrane filtration [4,10–12], drop casting [13–15], air-spraying [16,17], dip-coating [18], rod-coating [19], spin-coating [20], controlled flocculation [21], Langmuir–Blodgett deposition [22], and electrophoresis deposition [23,24], are more attractive from the viewpoint of production engineering, for that they can be cost-effectively scaled up and are compatible with a wide variety of

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substrates. Among them, the membrane filtration method is the most widely used, as it can (1) adjust the homogeneity of the buckypaper by the filtration process itself [10], (2) precisely control thickness of the film by the CNT solution concentration and volume, (3) be easily applied to various or even mixed types of CNTs, carbon nano-fibers and graphene [25], and (4) provide large room for modification of these nano-components [26]. A successful strategy of the wet approach generally involves a reliable means, such as surfactant wrapping, sonication and/or centrifugation, to form a stable CNT solution, and then a robust mechanism to remove the CNTs from the solution, such as through evaporation of solvent, or specific interactions between CNTs. Hence, besides the various factors relating to the solution preparing process, such as the nanotube type and quality, the processing parameters, including CNT solution concentration and surfactant type, the mechanism to remove CNTs from the solution is another critical factor affecting the properties of the buckypaper.

For the conventional membrane filtration method, the mechanism to remove CNTs from the solution is typically the vacuum induced negative pressure. The pressure is relatively low, without exceeding one atmospheric pressure (1 atm, about 101 kPa). However, though researchers have characterized the quality of buckypaper with different fabrication parameter combinations [27,28], no research has been carried out to investigate the quality of the buckypaper fabricated from a higher pressure to the best of our knowledge. To address this issue, here we report the fabrication of buckypaper by a pressurized syringe filtration technique, as schematically shown in Fig. 1. Although the fundamental principle for the vacuum filtration and the pressurized filtration processes is similar, much higher transmembrane pressures can be employed by applying constant load on the syringe-filter. Filtration behaviors of the CNT solution at different transmembrane pressures were investigated. Micro-morphologies, mechanical and conductive performances of the buckypaper generated from different transmembrane pressures were also studied.

2. Experimental

2.1. CNT solution filtration processes

Multi-walled CNTs, with diameters ranging from 8 to 15 nm and lengths ranging from 10 to 50 μm, were supplied by Cheap Tubes Inc. CNT solution with a concentration of 500 mg/L was prepared with 1 wt% Triton X-100 by sonication. The pressurized filtration was realized by syringe-filtering the CNT solution through a cellulose acetate (CA) syringe filter (Supatop Syringe Filter, 0.45 μm, 33 mm, Anachem) using a programmable syringe-pump (Aladdin AL-100, World Precision Instruments). The applied pressures during the syringe filtration were 4, 8 and 12 atm, respectively. For comparison, buckypaper was also fabricated by the common vacuum filtration process using the vacuum filtration apparatus (Millipore) with a 0.45 μm CA filter membrane. After the solution filtration, plenty of water was subsequently filtered through the filter to wash away the residual surfactant. Then the buckypaper was dried and immersed into acetone bathes for several times to ensure complete removal of the CA filter. The obtained free-standing buckypaper was vacuum dried at 80 °C overnight, before cutting into rectangular strips for the mechanical and conductive tests.

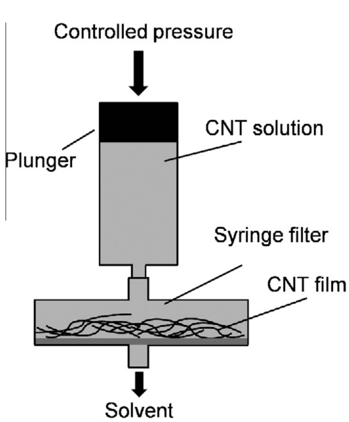

Fig. 1. Schematic of the pressurized filtration process.

2.2. Micro-morphology characterizations

Micro-morphologies of the buckypaper were investigated using a field emission scanning electron microscopy (SEM, JEOL JSM-6330F) operated at an accelerating voltage of 10 kV. Pore diameter distributions of the buckypaper were obtained by analyzing the SEM images [4], using an image analysis program (Image-Pro Plus 6.0). It should be noted that the SEM images do not contain any quantitative depth information, and the image analysis results should be only regarded as apparent pore structure measurements. More detailed pore size information was also collected from the N_2 adsorption isotherms at 77 K on a Quanta-chrome QuadraSorb Station 3 instrument. A wide range of pore size distribution could be obtained by the Barret–Joyner–Halenda (BJH) method from the adsorption branch of the N_2 adsorption isotherm.

2.3. Mechanical and conductive measurements

Tensile tests for the buckypaper strips were carried out using an Instron 3343 tensile apparatus with a load cell of 10 N, at a constant loading speed of 0.1 mm/min. Electrical conductivities of the buckypaper strips were obtained using a Keithley 2410 1100 V source meter and a commercial four probe test plate. Thermal conductivities of the buckypaper strips were measured using an instrument (LFA 447 Nanoflash, Netsch).

2.4. Molecular simulation

The molecular simulation was conducted at 300 K using an NVT ensemble with a time-step of 1 fs, with the commercial software Materials Studio® (Accelrys Inc.) employing a COMPASS (Condensed-phase Optimized Molecular Potentials for Atomic Simulations Studies) force field to describe the inter-atomic chemical bonds and non-bonding potential energy [29].

3. Results and discussion

3.1. Filtration behavior

It is customary in chemical engineering to characterize the dead-end filtration process by measuring the so-called filtration curve, the amount of solvent transported through a filter as a function of time. In this study, CNT filtration curves were measured and shown in Fig. 2a. All the filtration curves are half parabolas starting from the origin of the *time* (t) *vs. permeation volume per unit filtration area* (v) Cartesian coordinate system. Hence, the filtration behavior of the dilute CNT solution can be adequately described as a special case of the generic Carman equation for constant pressure dead-end filtration. In the filtration of dilute suspensions, the time (t) necessary to accumulate certain permeation volume through a unit filtration area is given by:

$$t = \frac{\mu}{P}\left[R_m v + \frac{\alpha C v^2}{2}\right] \quad (1)$$