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Fabrication and properties of dense thin films containing functionalized carbon nanofibers

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ABSTRACT

In this study, dense thin films containing carboxylic acid-functionalized carbon nanofibers (O-CNFs) are fabricated by a two-step approach involving solution filtering and mechanical compression through a rolling process. Optical images reveal a notable change from porous to dense in the surface morphology of the rolled O-CNF thin film. Moreover, test results show that the tensile strength and electrical conductivity of the rolled thin film are improved by approximately 400% in comparison to the non-rolled thin film. Upon fracture, electron microscope image shows significant pull-out and alignment of O-CNFs parallel to the direction of the applied load due to interlocking mechanism within the highly entangled O-CNF network.

1. Introduction

Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) are well known for their unique combination of mechanical and electrical properties and have been demonstrated as effective nanofillers to improve properties of polymeric composites [1,2]. One of the direct uses of CNTs or CNFs is in the form of a buckypaper, which is a thin film that consists of CNT or CNF entangled network [3,4]. From the microscopic point of view, CNTs or CNFs in the buckypaper are discontinuous filaments that are entangled together as opposed to commercial fabrics which form a continuous filament network. According to previous investigations, the discontinuity among CNTs in the buckypaper leads to the presence of inter-filler junctions that could negatively affect the transport properties of buckypaper (e.g., electrical and thermal conductivity) [5,6]. In fact, the electrical conductivity of the CNT-based buckypapers was found to decrease by at least two orders of magnitude in comparison to the theoretical conductivity of a single CNT [7] due to the inter-filler junctions.

To overcome this problem, the buckypapers have previously been subjected to different modification schemes such as mechanical [6–8], chemical [9], plasma sintering [10], and hydroentangling [11] methods to alter their bulk density. These methods have been demonstrated to effectively improve the mechanical, electrical, and thermal properties of buckypapers as a result of higher bulk density and reduction of inter-filler junctions. Furthermore, the fabrications of buckypaper containing aligned CNTs have been reported and its mechanical, electrical, and thermal properties have also been shown to be promising [12,13]. While successfully performed at the laboratory scale, some of these methods are not cost-effective and are limited by chemical incompatibility between pristine nanofillers and polymer matrix. In this work, a scalable methodology involving solution filtering and mechanical compression is used to produce dense carboxylic acid-functionalized CNF (O-CNF) thin films with enhanced mechanical and electrical properties.

2. Experiments

As-received CNFs (AR-CNFs) used in this study were Pyrograf PR-24-XT-PS from Applied Sciences, Inc. According to the vendor, the CNFs' average diameter and length were in the range of 60–150 nm and 30–100 μm, respectively, and iron content is approximately 14,000 ppm. AR-CNFs were chemically modified according to the procedure previously reported [14] but with a treatment time of only two hours to obtain the O-CNFs. Two types of non-rolled CNF thin films were fabricated in this study: non-rolled O-CNF thin film (NR-OCNF) and non-rolled surfactant-treated AR-CNF thin film (NR-SCNF). For the preparation of the NR-OCNF, 250 mg of O-CNFs were sonicated with ultrapure deionized water in a water bath for one hour and the resulting solution was filtered through a nylon membrane. The NR-SCNF was made by tip-sonicating 250 mg of AR-CNFs with a mixture of surfactant/acetone in a water bath for 30 min, filtering the mixture through a nylon membrane, and continuously rinsed with excess acetone to remove trapped surfactant. Both NR-SCNF and NR-OCNF were obtained by peeling them from the membrane after drying.

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Table 1
Average thickness and bulk density of thin films.

Sample name	Process, material type	Thickness [standard deviation] (μm)	Bulk density (g/cm^3)
NR-SCNF	Non-rolled, surfactant treated CNF	356 [±18]	0.150
R-SCNF	Rolled, surfactant treated CNF	173 [±9]	0.247
NR-OCNF	Non-rolled, functionalized CNF	175 [±12]	0.280
R-OCNF-90	Rolled to 90 μm, functionalized CNF	102 [±3]	0.431
R-OCNF-60	Rolled to 60 μm, functionalized CNF	79 [±3]	0.583
R-OCNF-30	Rolled to 30 μm, functionalized CNF	65 [±3]	0.681

To mechanically compress thin films, both NR-OCNF and NR-SCNF were subjected to a rolling process using a three-roll-mill. Each thin film was placed on the feed roll and rolled at approximately 3 rpm, with each side of the thin film rolled for 10 repetitions per gap size (defined as the distance between the two rollers). It is important to mention that only two out of the three rollers in the calendering machine were used to perform the rolling process. To fabricate rolled O-CNF thin film, three layers of NR-OCNF were rolled to gap size of 90, 60, and 30 μm, respectively. These samples are referred to as R-OCNF-90, R-OCNF-60, and R-OCNF-30, respectively. Each NR-OCNF was rolled from 120 μm to the desired gap size at a reduction of

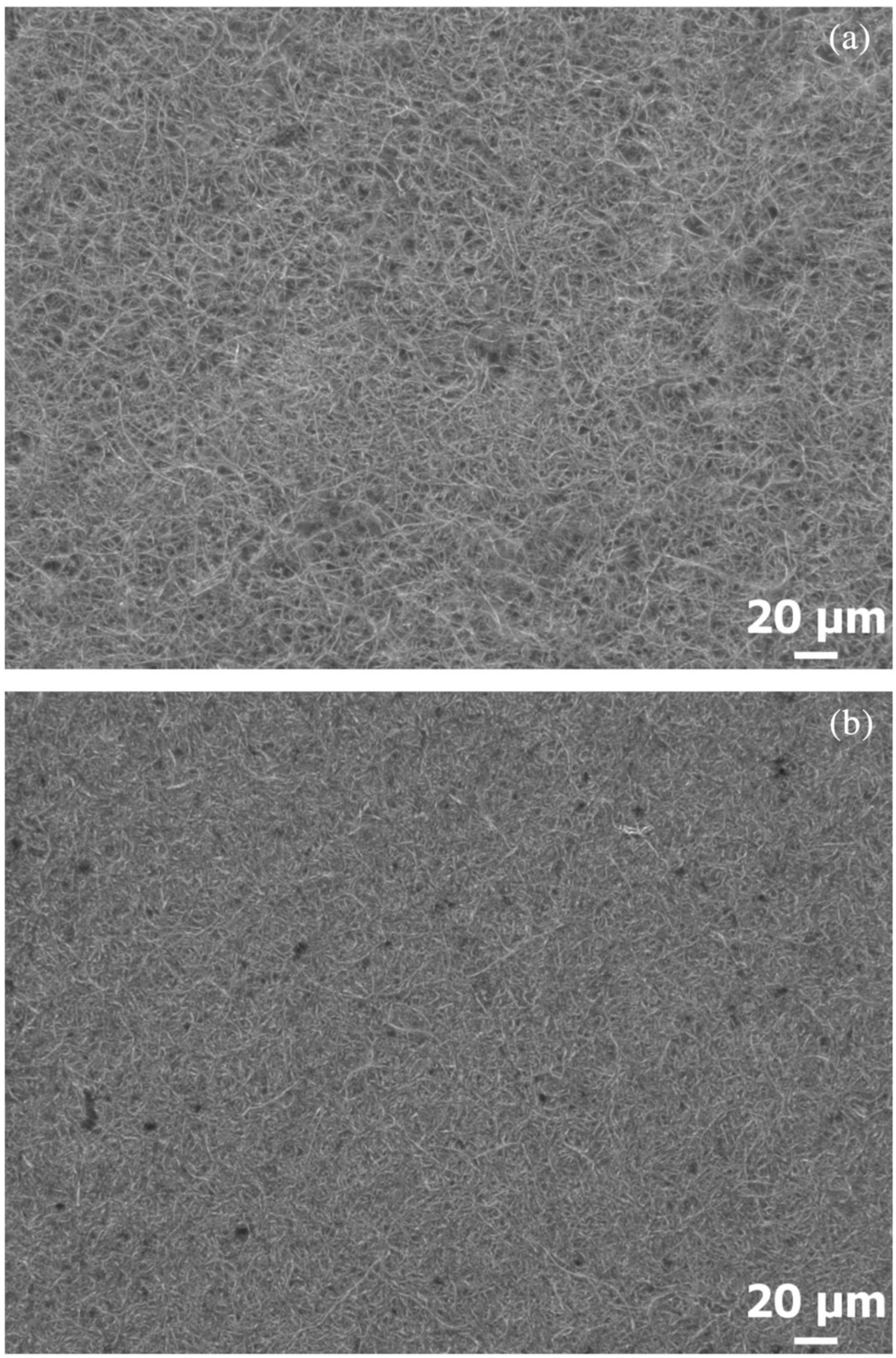

Fig. 1. Optical images of the surface of (a) NR-OCNF and (b) R-OCNF-30 thin films. The images were captured at 200× magnification.