OXIDIZED MULTI-WALLED CARBON NANOTUBE FILM FABRICATION AND CHARACTERIZATION

Kastanis D.¹, Tasis D.²*, Papagelis K.³, Parthenios J.¹, Tsakiroglou C.¹,
Galiotis C.¹²

¹FORTH/ICE-HT, Stadiou Str., 26504 Rion Patras, Greece
²Department of Materials Science, University of Patras, 26504 Patras, Greece

*Author to whom correspondence should be addressed
dtassis@upatras.gr

Received 17 October 2007; accepted 30 December 2007

ABSTRACT

The topological and mechanical properties of carbon nanotube films prepared by different oxidized treatments have been studied. Tensile parameters have been found to be strongly correlated with topological parameters such as porosity and bundle size. It was found that low porosity films prepared from highly oxidized CNTs result in the enhancement of their mechanical properties.

1. INTRODUCTION

The discovery of carbon nanotubes (CNTs) by Iijima in 1991 [1] has initiated a large number of scientific investigations in an attempt to explore their superb mechanical, electrical and thermal properties. Experimental studies [2,3] have shown that longitudinal elastic moduli of the order of 1Tpa and tensile strengths in excess of 45 GPa can be achieved for small ropes of single-walled CNTs.

However, potential macroscale applications have been hindered as bulk nanotube material consists mainly of aggregated bundles bound together by weak van der Waals interactions. This results in a massive reduction in the bulk mechanical properties when compared to that of individual tubes. Recently, some progress has been made using a solid state process to organize CNT-containing aligned arrays into functional macroscale superstructures in the form of yarns and thin sheets [4]. In an alternative approach, researchers have fabricated self-supporting mats of entangled tubes by a solution-based protocol involving filtration of stable CNT suspension [5].

Such nanoporous preforms, the so called buckypapers, have already been proposed as reinforcements in polymer composites [6], actuators [7], catalyst supports [8] and scaffolds for biomaterialization assays [9]. Concerning their structural integrity, a considerable effort has been made into measuring the mechanical properties of species containing single-wall CNT material. Moduli and breaking strengths were reported to fall into the 1-8 GPa and 6-33 MPa range, respectively [10]. Since the mechanical properties of buckypapers are primarily determined by the tube-tube interactions, chemical functionalization of the CNT sidewalls and tips could be utilized to increase the modulus and strength of the CNT buckypapers. To our knowledge, a detailed study about the mechanical integrity and porous structure of buckypapers consisting of functionalized multi-walled CNTs (MWCNTs) has not been applied yet. In a recent study, Kukovecz and co-workers [11] have studied the morphology and the gas permeability of multi-walled CNT mats by electron microscopy and gas adsorption analysis.

In this work a systematic experimental campaign has been attempted to study the effect of surface oxidation of MWCNTs on the mechanical properties—tensile modulus, strength and ductility of CNT films fabricated via vacuum filtration. Furthermore, the correlation between the pore size distribution and the homogeneity of the CNT network with each oxidation scheme is also discussed.

2. EXPERIMENTAL AND MATERIALS

The material used in this work was thin MWCNTs supplied by Nanocyl SA. Their average diameter was 15 nm with purity around 80% as claimed by the sup-
plier. As-received MWCNTs were further purified using concentrated hydrochloric acid (37%).
MWCNTs were then oxidized using three different chemical treatments namely, ammonium hydroxide/
hydrogen peroxide mixture, sulfuric acid/ hydrogen peroxide (piranha) and hot nitric acid. Details for the
oxidation protocols and the characterization of the treated MWCNTs have been reported previously [12].

Concerning the fabrication of MWCNT buckypapers stable aqueous CNT suspensions at a concentration
of 0.125 mg/ml were prepared by tip sonication for 30 min. These dispersions were then vacuum filtered
through polycarbonate membrane filters of 450 nm pore size. After drying at room temperature in a
vacuum oven for 24 hours the CNT films were peeled off from the filtration membrane. The average thick-
ness of the produced buckypapers is approximately 100 μm and their diameter about 9 cm.

Scanning electron microscopy (SEM) was performed using a LEO SUPRA 35 VP scanning electron
microscope. Mercury intrusion curves of the studied CNT sheets were obtained using a Quantachrome
PoreMaster 60 Hg Porosimeter. Rectangular pieces of 10 x 30 mm were cut from all the CNT films. The
capillary pressure, \( P_c \), has been replaced by the di-

\[ P_c = 4\gamma \cos \theta / D \]

where \( \gamma \) is the surface tension of Hg (= 0.48 N m\(^{-1}\))
and \( \theta \) is the contact angle (= 40°). Mechanical test-
ing was performed in a TA Instruments Dynamic Me-
chanical Analyzer Q800 with a displacement rate of
10 μm/min on strips of dimensions 24 x 8 mm\(^2\). For
each film type, stress-strain curves were measured for five strips.

3. RESULTS AND DISCUSSION

In Fig. 1 a typical batch of the produced MWCNT films are presented. Regarding their morphology, the
samples appeared as uniform, smooth and crack-free disks exhibiting significant structural integrity. In
order to assess the structural topology of the CNT films SEM images and mercury porosimetry mea-
surements have been obtained for each oxidation
treated sample. By comparing the top views in Fig. 2
of the presented samples, it is evident that for piran-
ha and nitric acid-treated samples the pore struc-
ture seems to be more uniform indicating better tube dispersion in the suspension during the filtration pro-
cess. This is further supported from the edge cross
sectional low resolution SEM images (insets in Fig.2)
where a more homogeneous and dense morphology
is clearly observed. In sharp contrast, basic (ammo-
nium hydroxide/hydrogen peroxide mixture) and HCl-
treated materials are deposited as large agglomer-
ates forming voids some of them having dimensions
in the micrometer scale.

In Fig. 3a the Hg intrusion curves are shown, where
three different types of porosity can be clearly dis-
tinguished:

1. The surface porosity (\( D > 10 \) μm) consists of large
and fully accessible to Hg pores which are irreg-
ularities of the external surface of the film and are
not representative of the internal porosity. Because
of the small thickness of the films, surface pores
comprise an important fraction of the total pore
volume. The contribution fraction of surface po-
rosity to total porosity is expected to decrease
significantly as the thickness of the film increases.

2. The inter-bundle porosity (10 μm< \( D < 0.01 \) μm)
is the pore space left between the bundles of
nano-tubes, spans a very broad range of pore
Fig. 2: SEM images of the surface of the fabricated MWCNT films for different treatment types: (a) HCl, (b) Ammonia, (c) piranha and (d) nitric acid treated. Inset images come from the cross section of the film.
For the complete analysis of the pore structure of such multi-scale porous materials, sophisticated methods based on the combination of the datasets from various experimental techniques (e.g. BSEM images, Hg porosimetry, N₂ sorption, NMR, etc) with numerical modelling are required [13, 14, 15]. However, even a simple analysis based on the conventional model of parallel cylindrical tubes allows us to get an insight into the pore structure of films. So, the complete volume-based pore-diameter distributions were obtained by differentiating the Hg intrusion curves (Fig.3b). In order to distribute total porosity to the aforementioned sub-porosities, each pore diameter distribution was fitted with a tri-modal distribution function composed of log-normal component distribution functions. The results of the fitting are shown in Table 1 and Fig.3b.

For all films, the intra-bundle porosity has a mean pore diameter (Table 1) ranging from ~12 nm to ~15 nm, values which are comparable to the mean diameter of nanotubes. The mean value of the inter-bundle pore diameter distribution shifts to larger sizes and its width increases as one goes from piranha- to nitric acid- to Ammonia- to HCl-treated films (Table 1). The smaller the mean pore diameter, and the narrower the pore-diameter distribution of the inter-bundle porosity, the more homogeneous and denser the film. The higher density of piranha- and nitric acid-treated films, compared to Ammonia- and HCl-treated films, is reflected in the lower sum of the specific pore volumes of inter- and intra-bundle porosities ($V_{1i} + V_{1b}$ in Table 2). On the other hand, the relatively small width of the pore diameter distribution of inter-bundle porosity for piranha- and nitric acid-treated films is associated with well-organized and homogeneous structures (Table 1).

Stress - strain curves obtained from the four samples tested are shown in Fig. 4. Numerical values of Young’s moduli, tensile and breaking strength are presented in Table 3. By comparing the mechanical parameters of each film type, the nitric acid and piranha treated nanotube films exhibit the highest mechanical properties.

It is expected that the colloidal stability of the aqueous suspensions would affect considerably the CNTs stacking motif and degree of homogeneity within the
Table 1: Mean value (μ), standard deviation (σ) and contribution fraction (c) of the log-normal component of pore-diameter distribution (i=1, 2, 3 for surface, inter-bundle, and intra-bundle porosity, respectively).

<table>
<thead>
<tr>
<th>Film type</th>
<th>c₁</th>
<th>μ₁ (μm)</th>
<th>σ₁ (μm)</th>
<th>c₂</th>
<th>μ₂ (μm)</th>
<th>σ₂ (μm)</th>
<th>c₃</th>
<th>μ₃ (μm)</th>
<th>σ₃ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT- Piranha</td>
<td>0.222</td>
<td>102.5</td>
<td>75.26</td>
<td>0.682</td>
<td>0.167</td>
<td>0.303</td>
<td>0.096</td>
<td>0.0127</td>
<td>0.0023</td>
</tr>
<tr>
<td>MWCNT - Nitric</td>
<td>0.257</td>
<td>70.74</td>
<td>93.84</td>
<td>0.660</td>
<td>0.224</td>
<td>0.504</td>
<td>0.083</td>
<td>0.0138</td>
<td>0.0030</td>
</tr>
<tr>
<td>MWCNT - Ammonia</td>
<td>0.272</td>
<td>128.9</td>
<td>111.8</td>
<td>0.669</td>
<td>0.641</td>
<td>2.177</td>
<td>0.059</td>
<td>0.0127</td>
<td>0.0029</td>
</tr>
<tr>
<td>MWCNT - HCl</td>
<td>0.245</td>
<td>125.3</td>
<td>93.64</td>
<td>0.708</td>
<td>2.714</td>
<td>17.95</td>
<td>0.047</td>
<td>0.0139</td>
<td>0.0035</td>
</tr>
</tbody>
</table>

Table 2: Pore volume distribution of films corresponding to surface, inter-bundle and intra-bundle porosity.

<table>
<thead>
<tr>
<th>Film type</th>
<th>Total pore volume, V_p (cm³/g)</th>
<th>Surface pore volume (V_s=c₁V_p) (cm³/g)</th>
<th>Inter-bundle pore volume (V_i=c₂V_p) (cm³/g)</th>
<th>Intra-bundle pore volume (V_e=c₃V_p) (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT- Piranha</td>
<td>2.213</td>
<td>0.491</td>
<td>1.509</td>
<td>0.212</td>
</tr>
<tr>
<td>MWCNT - Nitric</td>
<td>2.207</td>
<td>0.566</td>
<td>1.456</td>
<td>0.184</td>
</tr>
<tr>
<td>MWCNT - Ammonia</td>
<td>2.607</td>
<td>0.708</td>
<td>1.744</td>
<td>0.154</td>
</tr>
<tr>
<td>MWCNT - HCl</td>
<td>3.675</td>
<td>0.901</td>
<td>2.602</td>
<td>0.171</td>
</tr>
</tbody>
</table>

Table 3: Tensile parameters of oxidized MWCNT films.

<table>
<thead>
<tr>
<th>Film type</th>
<th>Young Modulus (GPa)</th>
<th>Strength (MPa)</th>
<th>Ductility (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT - HCl</td>
<td>0.87±0.02</td>
<td>0.50±0.12</td>
<td>0.63±0.11</td>
</tr>
<tr>
<td>MWCNT - Ammonia</td>
<td>0.88±0.03</td>
<td>1.11±0.04</td>
<td>1.47±0.17</td>
</tr>
<tr>
<td>MWCNT - Piranha</td>
<td>1.73±0.02</td>
<td>2.66±0.05</td>
<td>1.32±0.19</td>
</tr>
<tr>
<td>MWCNT - Nitric</td>
<td>4.86±0.02</td>
<td>2.77±0.08</td>
<td>0.78±0.12</td>
</tr>
</tbody>
</table>

On the other hand, there is a clear correlation between the inter-bundle network porosity and the tensile parameters of the film. While the nitric acid treated films exhibit the highest Young’s modulus and strength, its porosity is the minimum one. This can be explained by the efficient packing of individually deposited tubes during the filtration process, leading to enhanced stress transfer due to a higher density of inter-tube junctions.

4. CONCLUSIONS

By increasing the density of carboxylic and hydroxyl group on the CNT surface, high quality dispersions and low porosity buckypaper films are produced. It is observed that low porosity films from highly oxidized CNTs result in the enhancement of their mechanical properties. These films can be ideal candidates as structural materials for fabrication high CNT volume fraction nanocomposites.

ACKNOWLEDGEMENTS

Financial support from the Marie Curie Transfer of Knowledge program CNTCOMP [Contract No.: MTKD-CT-2005-029876] is gratefully acknowledged.
References:

Advanced Composites Letters, Vol. 16, Iss. 6, 2007