The effect of oxidation treatment on the properties of multi-walled carbon nanotube thin films

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**A R T I C L E  I N F O**

Article history:
Received 31 August 2008
Received in revised form 25 August 2009
Accepted 23 September 2009

Keywords:
Carbon
Oxidation
Thin films
Mechanical properties

**A B S T R A C T**

Carbon nanotube thin sheets – buckypapers – were prepared from multi-walled carbon nanotubes oxidised with different oxidation agents. Prepared buckypapers were characterized by mechanical testing, surface conductivity and mercury porosimetry. It was found that their mechanical properties were increased by increasing the power of oxidation agents. Nitric acid-treated buckypapers showed the highest structural integrity and surface conductivity.

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**1. Introduction**

Since the landmark paper by Iijima [1], carbon nanotubes (CNTs) have attracted considerable research interest due to their unique combination of mechanical, electrical and thermal properties. Forms of CNTs in the macroscopic level, such as forests, yarns and films have been reported providing a practical venue to utilize and manipulate the remarkable properties of CNTs for broad applications [2,3]. Paper-like CNT films, also called buckypapers, are self-supporting networks of entangled CNT assemblies arranged in a random fashion and held together by van der Waals interactions at the tube–tube junctions.

Buckypapers are prepared by vacuum filtration of well-dispersed CNT solution [4] or compression method [5]. The final properties of buckypapers can be affected by various factors, such as concentration of CNT solution, sonication time, vacuum pressure [6], solvent medium [5], growth method of nanotubes and/or surface functionalization [7]. Such CNT-based sheets and their composites have become a hot topic in CNT research and have been widely reported in the literature [8,9]. The intrinsic properties of CNT films make them useful candidate for radio frequency filters, cold-field cathode emitters, capacitors or battery electrodes as well as thermal and electrical conductive materials. Recently, highly oriented CNT papers made of aligned tube arrays (forests) have been prepared by a simple and effective method called ‘domino pushing’ [9]. These buckypapers have shown better performance in thermal and electrical conductance.

Concerning their structural integrity, a considerable effort has been made into measuring the mechanical properties of species containing single-walled carbon nanotubes (SWCNTs). Moduli and breaking strengths were reported to fall into the 1–8 GPa and 6–33 MPa range, respectively [10,11]. 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 [12] have studied the morphology and the gas permeability of multi-walled CNT mats by electron microscopy and gas adsorption analysis. Interestingly, buckypapers comprising of different mixtures of single- and multi-walled CNTs showed an unexpected...
tunability of the in-plane Poisson’s ratio from positive to negative values [13].

This work is a continuation of our previous work regarding the effect of chemical oxidation on the structural integrity of multiwalled carbon nanotubes (MWCNTs) with reagents of different oxidation power [14]. Buckypapers were prepared by MWCNT material oxidised by various reagents such as hydrochloric acid (HCl), piranha (H2SO4/H2O2), nitric acid (HNO3), acidic permanganate (H2SO4/KMnO4) and NH4OH/H2O2 mixture. The effect of different oxidation treatment on the mechanical and electrical properties of the resulting MWCNT thin sheets is demonstrated in detail. In addition, the correlation of the aforementioned properties with the porosity of the CNT networks is also discussed.

2. Experimental details

2.1. Materials

The MWCNT employed in this work was supplied by Nanocyl (Belgium). The nanotubes were synthesized by catalytic carbon vapour deposition (CCVD) and had a purity of around 80%. The CNT diameter ranged between 10 and 20 nm. Purification and chemical oxidation of MWCNTs [14,15] was carried out with different oxidation agents supplied by Aldrich.

2.2. Buckypaper fabrication procedure

Concerning the fabrication of MWCNT buckypapers, stable aqueous CNT suspensions at a concentration of 1 mg/ml were prepared by tip sonication for 60 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 h the CNT films were peeled off from the filtration membrane. The average thickness of the produced buckypapers is approximately 200 μm and their diameter about 9 cm.

2.3. Characterization

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 mm × 30 mm were cut from all the CNT films. The capillary pressure, Pp, has been replaced by the diameter of an equivalent cylindrical tube, D, according to the relation:

\[ P_p = \frac{4\gamma \cos \theta}{D} \]  

where \( \gamma \) is the surface tension of Hg (0.48 N m\(^{-1}\)) and \( \theta \) is the contact angle (40°). The tensile properties such as modulus, strength, and % elongation were carried out using a TA Instruments Dynamic Mechanical Analyzer Q800 with a strain rate of 0.02 min\(^{-1}\) on strips of dimensions 24 mm × 8 mm. For each film type, stress–strain curves were measured for five strips.

The electrical resistivity \( \rho \) (reciprocal value conductivity \( \sigma \)) of the samples was measured by using the well established van der Pauw method. Four electrical contacts were made by bonding thin copper wires on the circumference of the samples using electrically conductive silver paste. The samples were mounted in a cryostat and measurements were performed at a constant temperature (20°C) in an inert nitrogen atmosphere. All samples were checked for voltage–current linearity.

3. Results and discussion

Buckypapers prepared by vacuum filtration of well-dispersed CNT aqueous suspensions were found to be uniform, smooth and crack-free disks exhibiting significant structural integrity, as confirmed by SEM images (Fig. 1). The produced thin films consist of randomly interconnected CNTs forming a porous structure as it is apparent from Fig. 1a. The SEM image of a cross-section of a representative sheet (Fig. 1b) indicates an almost homogeneous CNT deposition through the thickness giving rise to a dense morphology.

Fig. 2 reveals typical pore diameter distribution profiles obtained from mercury intrusion analysis for the studied samples. In general, excluding surface porosity which are irregularities of the external surface and are not representative of the internal porosity, two types of porosity can be found namely the inter- and intra-bundle one. The latter porosity corresponds to channels in the interior of the bundles which is expected to be comparable to mean diameter of the MWCNTs (~15 nm). The sharp peak located at 12–15 nm corresponds to the distribution of intra-bundle pores. The inter-bundle porosity is formed between MWCNT bundles criss-crossing through the sample and is indicative of the density and homogeneity of the network created by the nanotube bundles. This porosity type is of high importance for the mechanical properties of the films (see below). As can be clearly seen in Fig. 2, the inter-bundle porosity spans a very broad range of pore sizes (10\(^{-2}\) to 10\(^{-1}\)). Interestingly, the mean value of the pore diameters shifts to larger sizes and the width of the aforementioned distribution increases in the order piranha < HNO3 < NH4OH/H2O2 < HCl. The smaller mean pore diameter and the narrower pore size distribution of the inter-bundle porosity indicate homogeneous and dense CNT films. Indeed, the relatively small width of the pore diameter distribution of inter-bundle porosity as shown in the case of piranha- and nitric acid-treated films is associated with well-organized and homogeneous structures. Therefore, the formation of a narrow pore size distribution is strongly related to the etching capability of the oxidation agents. In addition, the HCl buckypaper treated with surfactant seems to be more uniform compared to the
Fig. 2. Pore diameter distribution profiles obtained from Hg intrusion analysis.

Table 1
Tensile parameters of oxidized MWCNT films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>E (GPa)</th>
<th>σ (MPa)</th>
<th>ε (%)</th>
</tr>
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<tbody>
<tr>
<td>HCl</td>
<td>0.08 ± 0.03</td>
<td>0.42 ± 0.13</td>
<td>1.09 ± 0.42</td>
</tr>
<tr>
<td>HCl + surfactant</td>
<td>0.11 ± 0.03</td>
<td>0.95 ± 0.29</td>
<td>5.05 ± 0.45</td>
</tr>
<tr>
<td>NH₄OH/H₂O₂</td>
<td>0.09 ± 0.03</td>
<td>0.49 ± 0.08</td>
<td>1.05 ± 0.19</td>
</tr>
<tr>
<td>H₂SO₄/H₂O₂</td>
<td>0.20 ± 0.02</td>
<td>1.39 ± 0.20</td>
<td>2.11 ± 0.58</td>
</tr>
<tr>
<td>H₂SO₄/KMnO₄</td>
<td>0.22 ± 0.05</td>
<td>1.77 ± 0.50</td>
<td>2.10 ± 0.90</td>
</tr>
<tr>
<td>HNO₃</td>
<td>1.16 ± 0.16</td>
<td>3.88 ± 1.12</td>
<td>0.53 ± 0.17</td>
</tr>
</tbody>
</table>

neat HCl one, indicating better tube dispersion in the suspension during the filtration process.

It should be noted here that the pore volume distribution for the H₂SO₄/KMnO₄ treated tubes differs significantly from all others. Although the sharp peak at 12–15 nm is prominent in all bucky-paper samples, it appears suppressed in the case of H₂SO₄/KMnO₄ oxidation. This clearly demonstrates that efficient elimination of CNT bundles has taken place within the corresponding sheets. The inter-bundle porosity consists of two well separated peaks centered at ∼0.03 and ∼1 μm. These results give us the opportunity to perform further studies in order to achieve structures with tailored pore size distributions.

Stress–strain curves obtained from the studied bucky-paper samples are shown in Fig. 3. The extracted tensile properties such as Young’s modulus E, breaking strength σ and % elongation-to-fracture are summarized in Table 1. The errors correspond to the standard deviation of five measurements on each specimen. Concerning the E and σ values, nitric acid–treated bucky-papers exhibit the highest values while the HCl and H₂O₂/NH₄OH treated samples exhibit the lower ones. The addition of a surfactant slightly enhances mainly the breaking strength while it affects considerably the elongation property value. The latter value is comparable to that reported for SWCNT films [16]. It is important to stress that the average modulus for HNO₃–treated buckypaper is comparable to the reported values for neat SWCNT films in the literature ranging between 0.3 and 2.2 GPa [17–20]. Also, the strong oxidative reagent piranha and the H₂SO₄/KMnO₄ treatment shows enhancement of the tensile strength and elongation.

A closer inspection of the porosimetry results and the mechanical parameters in Table 1 reveals a clear correlation between the inter-bundle network porosity and the tensile parameters of the films. Indeed, it is expected that the various chemical treatments applied affect significantly the MWCNT stacking motif and degree of homogeneity within the films and, as a result, the stress transfer efficiency. As a matter of fact, the use of acidic agents such as nitric acid and piranha produces CNT material with high oxygen content which gives rise to enhanced modulus and strength values due to hydrogen bonding interactions. The relatively small elongation-to-fracture for the HNO₃-treated film can be related to the severe fragmentation (the average length was estimated to be 700 nm) of the MWCNTs after the strong oxidative treatment [14].

Concerning the electrical conductivity of bucky-papers, corresponding values are presented in Table 2. The highest conductivity is reached for HNO₃–treated films. This can be related to the increased density of CNT interconnects within the buckypaper structure. The overall picture is that there is no clear trend between the mechanical and the electrical data. This can be explained by the fact that the electrical measurements are sensitive to the surface morphology of the sheets whereas the mechanical ones depend on the stress transfer efficiency between the interconnected tubes within the bucky-papers.

4. Conclusions

By increasing the density of polar functional groups on the CNT surface through oxidation, the porosity of the prepared buck-

Fig. 3. Representative stress–strain curves for MWCNT buckypapers treated with different oxidation agents.

Table 2
Surface conductivity σs for buckypapers oxidised with different oxidation agents.

<table>
<thead>
<tr>
<th>Sample</th>
<th>σs (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>12.73</td>
</tr>
<tr>
<td>NH₄OH/H₂O₂</td>
<td>9.81</td>
</tr>
<tr>
<td>H₂SO₄/H₂O₂</td>
<td>12.99</td>
</tr>
<tr>
<td>H₂SO₄/KMnO₄</td>
<td>6.53</td>
</tr>
<tr>
<td>HNO₃</td>
<td>18.18</td>
</tr>
</tbody>
</table>
Films having narrow pore size distribution have shown an increase of their mechanical properties and surface conductivity. The H$_2$SO$_4$/KMnO$_4$ based sheets exhibit a different porosity profile compared to the oxidative agents. These films can be ideal candidates as structural materials for fabricating high volume fraction nanocomposites.

**Acknowledgements**

The authors acknowledge the financial support of the Marie-Curie MTKD-CT-2005-029876 grant (CNTCOMP) and Dr. V. Drakoopoulos for helping with the SEM measurements. K.P. acknowledges financial support by a “K. KARATHEODORIS” grant from the University of Patras Research Committee.

**References**