MECHANICAL PROPERTIES OF MULTI-WALLED CARBON NANOTUBE BUCKYPAPER BY POLYVINYL PYRROLIDONE ADHESIVES

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1 Introduction

Due to its characteristic structure and excellent functional performance, buckypaper (BP), a self-supported carbon nanotube (CNT) network, is promising for many application domains for their excellent functional properties. However, their applications in structural materials have been hindered by the weak Van der Waals interaction at junction points. The Young’s modulus and tensile strength of conventionally produced random multiwalled carbon nanotube (MWCNT) BPs have lied in 0.05-1.2GPa and 0.4-4.0MPa, which are far below that of individual nanotube [1-3].

In recent years, many different methods were carried out to strengthen BPs. Air burning treatment can remove the residual surfactant in BP, but it also introduce defects to the nanotubes [4]. Electron irradiation has been demonstrated to be an effective technique to create strong and stiff covalent bonds between the adjacent CNTs and between the internal walls of MWCNTs, which lead to great improvements in the mechanical performance of BPs [5]. The CNT alignment degree also has profound impact on the mechanical properties of BPs, and the researches manifested that BPs fabricated by magnetic field process [4] or mechanical stretching methods perform superior mechanical properties than random CNT stacking BP [6]. Polymer intercalation is another effective method to enhance load transfer between nanotubes which is always obtained by soaking the BPs in polymer solutions [7]. Among these methods, the last method is the most
uncomplicated with little damage to the CNT structure. However, the polymer intercalation method can’t get rid of the negative effect of micromolecular surfactant, meanwhile the hard impregnation of polymer is the critical factor that restrain further enhancement for the BP mechanical performance.

In this study, PVP replaced traditional micromolecular surfactant during the dispersion process for preparing MWCNT BP. The macromolecular structure of PVP was expected to enhance tube-tube interaction. The effects of tube-dispersant interaction and PVP content on tensile properties of obtained BPs were investigated. Additionally, three commercially functionalized CNTs were adopted to fabricate the corresponding BPs with aid of PVP. The presence of functional groups was expected to further enhance intertubular interaction through hydrogen bonding. The influences of functional group and CNT morphology on the mechanical performance of BPs were discussed in detail.

2 Experimental

2.1 Experiment Materials

Pristine carbon nanotubes (Pri-CNTs) and three kinds of functionalized MWCNTs with carboxyl groups, hydroxyl groups and amino groups (referred as COOH-CNTs, OH-CNTs and NH₂-CNTs, respectively) were fabricated and supplied by Chengdu Organic Chemicals Co., Ltd. These MWCNTs have the diameter about 20-30 nm with the length between 0.2 to 4μm, and the CNT content is larger than 95%. The dispersant PVP-k30 (Molecular weight 40,000) and Triton X-100 were purchased from Beijing Yili Fine Chemical Co., Ltd. and Xilong Chemical Co., Ltd., respectively. The microporous membranes with a pore diameter of 0.45μm were obtained from Hangzhou ANOW Microfiltration Co., Ltd.

2.2 Preparation of MWCNT buckypapers

The MWCNT buckypapers were prepared by vacuum filtration of aqueous CNT suspension. CNTs were ultrasonicated in deionized water for two hours with the aid of dispersants, i.e. Triton X-100 and PVP. The dispersed CNT solution was filtrated through a microporous membrane with positive pressure. The buckypaper fabricated with the aid of Triton X-100
was then rinsed by isopropyl alcohol to remove the surfactant. After drying at 80°C for two hours in a vacuum oven, buckypaper could be easily peeled off from microporous membrane.

2.3. Characterization

Field emission scanning electron microscope (FESEM, CamScan-Apollo300) with the acceleration voltage of 15 kV was employed to characterize the surface and cross-section morphology of various buckypapers. Thermogravimetric analysis (TGA, STA449F3) was performed to evaluate the PVP content of buckypaper. XPS experiments were carried out with an ESCA-Lab220i-XL electron spectrometer provided by VG Scientific using 300W AlKα radiation. The binding energies were referenced to the C1s line at 284.8eV from adventitious carbon. Raman spectra were collected from samples using HR800Uv with a 785 nm laser source. Mechanical properties were performed using Instron 3344 with a tensile speed of 0.2 mm/min at room temperature. The tensile specimens were cut into rectangle shape (35×6 mm²) with a clamping distance of 15mm, and at least eight specimens were tested for each.

3 Results and discussion

3.1 Tensile properties of BP by PVP adhesion

The typical surface images of PVP-BP and Trit X-BP are presented in Fig. 1. The surface image in Fig. 1a manifests relatively homogenous and loose CNT skeleton of PVP-BP. In addition, the surface image in Fig. 1b indicates that a CNT network formed by curly tubes for Trit X-BP, and the diameters of the individual CNT are much thinner than that of PVP-BP. The volume density of Trit X-BP is 0.53 g/cm³, approximately 1.7 times as that of PVP-BP.

The typical tensile stress-strain curves are measured for the two kinds of buckypapers are presented in Fig. 1c. The BP samples show low fracture elongation, in the range of 0.5% to 0.6%. The tensile strength and modulus of PVP-BP are respectively 6.08 and 1430 MPa, 227% and 295% higher than those of Trit X-BP, even comparable to the tensile performance of SWCNT BPs. The data imply that the PVP-BPs with looser CNT stacking possess higher tensile performances than the conventionally Trit X-BP. We believe that, owing to
the high molecular weight and amphiphilicity of the PVP dispersant, the interfacial interaction between CNT and PVP plays a crucial role in improving the mechanical properties of the PVP-BP. Tallury [8] proposed that the flexible backbone polymer, like PVP, tends to wrap around the CNT by inter-chain coiling. The hydrophobic alkyl chain in Triton X-100 can physically adsorb onto the tube surface and block direct contacts of inter-tubes. Due to the high molecular weight of PVP, the density of PVP-BP is smaller than Trit X-BP. However, the specific polymer wrapping coat tends to generate enhanced interactions of CNT-PVP, and the contact area of adjacent tube-tube conjunctions are simultaneously increases. Subsequently, the stronger interactions of CNT-PVP-CNT (due to polymer bonding effect) result in superior mechanical properties for PVP-BP.

Further studies were conducted to analyze the influence of PVP content on the tensile properties of PVP-BPs. Three kinds of pristine BPs were prepared, i.e. PVP-BP, PVP-BP-1 and PVP-BP-5 with no rinse, one time rinse and five times rinse respectively. TGA was used to evaluate the PVP content in the three BPs. According to weight residue of CNTs and the BP at 600°C, the weight fraction of PVP were estimated as in Eq. (1).

\[ w_{f_{PVP}} = \frac{m_{CNT}-m_{BP}}{m_{CNT}-m_{PVP}} \quad (1) \]

Where \( m_{CNT} \), \( m_{BP} \) and \( m_{PVP} \) are the weight residue of carbon nanotubes, PVP-BP and PVP, respectively.

The PVP-BP presents the highest content of PVP (29wt%). After one-time washing, the PVP content is reduced to 25wt% for PVP-BP-1, meanwhile the BP density slightly increases from 0.31 to 0.34 g/cm\(^3\). The tensile strength and Young’s modulus of PVP-BP are 6.08 MPa and 1.43 GPa, while those of PVP-BP-1 are 7.01 MPa and 1.81 GPa, increased by 15.3% and 26.6% respectively, as shown in Fig. 2. The improvement of the BP tensile properties is ascribed to partial removal of PVP leading to the densification of CNT network. The PVP content is decreased to 23wt% for PVP-BP-5, simultaneously, the tensile strength is increased to 7.24 MPa but the modulus is reduced to 1.68 GPa (see Fig.2).

The tensile fracture morphologies of the BPs with different PVP content are presented in Fig.3.
The CNT skeletons are complete impregnated by PVP and abundant resin-rich region and few CNT pull-outs in PVP-BP can be observed in Fig.3a. Mishra reported that the PVP film, with molecular weight of 40000, is 1.4 MPa in strength [9]. Hence, extra-high content of PVP is not conducive to obtain high property of the BP, e.g. PVP-BP without rinse. After one-time rinse, the mechanical properties of PVP-BP-1 are increased, and the morphology in Fig.3b indicates a mixed failure mode of CNT pull-out and polymer fracture. After five-time rinse, PVP-BP-5 reveals a unitary failure mode of CNT pull-out in Fig.3c, and resin-starve defects can be observed. This implies that appropriate content of PVP is favorable for improving the mechanical properties of BP, but excessive removal of PVP will decrease the contact area of inter-tubes weakening stress transfer efficiency within the CNT network.

3.2 Tensile properties of functionalized BPs

Three kinds of MWCNTs (COOH-CNTs, OH-CNTs and NH2-CNTs) were used to fabricate the functionalized BPs in comparison with the pristine BP. Firstly, chemical compositions of the CNTs were analyzed by XPS. The data in Table 1 show that C and O elements are detected in Pri-CNTs and functionalized CNTs, while N element can only be detected in NH2-CNTs, with the atomic content of 1.44%. For all the CNTs, the O atomic contents are more than 5%, in which Pri-CNT shows the lowest value of 5.18% and COOH-CNT possess the highest of 7.53%. Subsequently, the deconvolutions of C 1s spectra were conducted to estimate the functionalities of the CNTs, as illustrated in Fig.4. Values of the binding energy and the percent contribution of each curve fit to the total C 1s are listed in Table 2. Carbon atoms conjunct with oxygen and nitrogen (including C-O, C-N, C=O, and O-C=O groups) are defined as activated carbon atoms, which can be achieved from the sum of peak 2 to peak 4.

Pri-CNTs have the lowest content of activated carbon atom of 31.24%, and the functionalized CNTs possess higher content from 33.64 to 38.60% (seen in Table 2). According the data of the activated carbon atom, the functionalization degree of the CNTs is: Pri-CNT< COOH-CNT< OH-CNT< NH2-CNT. The types of functional groups can affect interactions of
CNT-water solvent and CNT-PVP dispersant, influencing dispersity and stability of the CNT aqueous suspensions, which will finally influence the stacking structure of the BPs [10].

Three functionalized BPs were fabricated from COOH-CNTs, OH-CNTs and NH$_2$-CNTs with the aid of PVP. Volume density and tensile properties of the BPs are summarized in Table 3. All types the BPs were rinsed by five times to eliminate superfluous PVP dispersant in the pores of the CNT network. The data in Table 3 show that the PVP content in COOH-BP is the lowest (21 wt%), while the content is highest (32 wt%) in NH$_2$-BP and the contents in Pri-BP and OH-BP are moderate. Note that properties of Pri-BP are listed in Table 1(denoted as PVP-BP-5). For the volume densities of the four BPs, OH-BP has the highest volume density of 0.55 g/cm$^3$ and the density of Pri-BP is the lowest (0.33 g/cm$^3$). Furthermore, the ranking sequence of the tensile properties is quite similar to that of the volume density, both of which are: Pri-BP$<$ NH$_2$-BP$<$ COOH-BP$<$ OH-BP. This strongly demonstrates that the CNT stacking density plays a prominent role in determining the BP mechanical performance. The CNT functionalization can improve compatibility between the CNT and the aqueous solvent and interactions between the CNT and the PVP dispersant. Hence, tensile properties of the functionalized BPs are higher than Pri-BP. From a comparative point of view, acidified CNTs, e.g. OH-CNTs and COOH-CNTs, tend to form stronger BPs than those fabricated from alkalinized CNTs (i.e. NH$_2$-CNTs).

Specific tensile strength and modulus are always calculated for better comparison by taking into the account of the porosity of buckypaper and eliminating the density. As shown in Fig. 5, NH$_2$-BP reveals the highest specific tensile strength of 29.5×10$^3$ N•m/kg, then the value of OH-BP and COOH-BP is 27.7×10$^3$ N•m/kg and 23.1×10$^3$ N•m/kg, respectively. By contrast, Pri-BP possesses the lowest specific tensile strength. In general, the specific tensile strengths steadily increase with more activated carbon content of the MWCNTs in Fig.5. Hydrogen bonding can be formed between the –OH, –COOH and –NH$_2$ with C=O in the PVP molecular enhancing the interfacial adhesive between functionalized
MWCNT and PVP. However, values of the specific modulus display no-significant trend with the activated carbon content of the MWCNTs, especially for NH$_2$-BP.

**Conclusion**

PVP was used to fabricate enhanced BPs in the dispersion process, which is proved to be an effective dispersant to obtain homogeneous CNT skeleton. The morphological analysis indicates that the MWCNT diameter is considerably thickened due to the wrapping of PVP molecules on the CNT surface. For the increased interaction of CNT-PVP and contact area of tube-tube conjunctions, the tensile strength and modulus of PVP-BP are 227% and 295% higher than that of Trit X-BP. However, superabundant PVP is unfavorable for mechanical property improvement. Mechanical tests on pristine and functionalized BPs reveal that the latter possess higher tensile properties than the former. Moreover, acidified CNTs tend to form denser CNT skeletons and stronger BPs than those fabricated from alkalinized CNTs. The highest tensile properties are observed in OH-BP with tensile strength and modulus of 15.24 MPa and 3.22 GPa, respectively. The density normalized tensile results reveal that the specific tensile strengths of BPs steadily increased with the activated carbon content of MWCNTs, but the specific tensile moduli are rarely affected by the degree of functionalization.

**References**


Fig. 1. Surface morphologies of BP fabricated with aid of (a) PVP and (b) Triton X-100; (c) Representative stress-strain curves from tensile tests of BPs with aid of Triton X-100 and PVP.

Fig. 2. The mechanical properties of buckypaper fabricated with aid of Triton X-100 and PVP, respectively.

Fig. 3. The cross-section morphologies of BPs with different PVP content: (a) PVP-BP; (b) PVP-BP-1; (c) PVP-BP-5.

Table 1. The element composition of various MWCNTs

<table>
<thead>
<tr>
<th>Treatment</th>
<th>C1s (%)</th>
<th>O1s (%)</th>
<th>N1s (%)</th>
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<tbody>
<tr>
<td>Pri-CNTs</td>
<td>94.82</td>
<td>5.18</td>
<td>-</td>
</tr>
<tr>
<td>COOH-CNTs</td>
<td>92.47</td>
<td>7.53</td>
<td>-</td>
</tr>
<tr>
<td>OH-CNTs</td>
<td>94.09</td>
<td>5.91</td>
<td>-</td>
</tr>
<tr>
<td>NH2-CNTs</td>
<td>93.13</td>
<td>5.43</td>
<td>1.44</td>
</tr>
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</table>
Fig. 4. Deconvolution of XPS C1s peaks for: a) Pri-CNTs; b) COOH-CNTs; c) OH-CNTs; d) NH₂-CNTs

Table 2. The element composition according to the overall spectra and the C1s peak fitting results for different MWCNTs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak1 (%)</th>
<th>Peak2-4 (%)</th>
<th>Peak5 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C-C (284.8 eV)</td>
<td>C-O (286.0 eV), C-N (286.1 eV); π-π* (287.2 eV)</td>
<td>C=O (287.2 eV); O-C=O (289.0 eV) (291.0 eV)</td>
</tr>
<tr>
<td>Pri-CNT</td>
<td>63.05</td>
<td>31.24</td>
<td>5.71</td>
</tr>
<tr>
<td>COOH-CNT</td>
<td>63.97</td>
<td>33.64</td>
<td>2.39</td>
</tr>
<tr>
<td>OH-CNT</td>
<td>59.07</td>
<td>37.86</td>
<td>3.07</td>
</tr>
<tr>
<td>NH₂-CNT</td>
<td>57.97</td>
<td>38.60</td>
<td>3.43</td>
</tr>
</tbody>
</table>
Table 3. PVP content, volume density and tensile properties of different functionalized BPs, and the data of the corresponding Pri-BP are listed in Table 1 and denoted as PVP-BP-5.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Structural parameters</th>
<th>Tensile properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PVP content (wt%)</td>
<td>Density (g/cm³)</td>
</tr>
<tr>
<td>COOH-BP</td>
<td>21.4</td>
<td>0.49±0.03</td>
</tr>
<tr>
<td>OH-BP</td>
<td>26.1</td>
<td>0.55±0.04</td>
</tr>
<tr>
<td>NH₂-BP</td>
<td>32.4</td>
<td>0.35±0.03</td>
</tr>
</tbody>
</table>

Fig. 5 (a) Specific tensile strength vs. activated carbon content and (b) specific tensile modulus vs. activated carbon content, for different functionalized MWCNT BPs.