Accepted Manuscript

Mechanical and electrical properties of cross-linked carbon nanotubes

Seung I. Cha, Kyung T. Kim, Kyong H. Lee, Chan B. Mo, Yong J. Jeong, Soon H. Hong

PII: S0008-6223(07)00660-4
DOI: 10.1016/j.carbon.2007.12.023
Reference: CARBON 4745

To appear in: Carbon

Received Date: 4 July 2007
Revised Date: 14 November 2007
Accepted Date: 13 December 2007


This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.
Mechanical and electrical properties of cross-linked carbon nanotubes

Seung I. Cha, Kyung T. Kim, Kyong H. Lee, Chan B. Mo, Yong J. Jeong, Soon H. Hong

Abstract

Several macroscopic assemblies of carbon nanotubes (CNTs), consisting only of CNTs, have been developed for the maximum utilization of their characteristic properties for macroscale structures. These include bucky paper, freestanding films, and fibres. However, these materials have limited performance because the CNTs are assembled via weak interactions, such as van der Waals forces, or the entanglement of CNTs. Here, we report an isotropic bulk form of randomly oriented CNTs in which they are cross-linked with each other through chemical reaction between functional groups on them. The reaction is included by spark plasma sintering. This chemical cross-linking provides a strength of 100 MPa with improved electrical conduction. Compared to a CNT pellet before sintering, the electric conductivity of cross-linked CNT increases by one order from 2 S/cm to 24 S/cm at room temperature and at the same time, the activation energy for electric conduction is decreased. The increased electrical conductivity is related to increased inter-CNT transport of charge carriers, with the cross-links providing bridges for them. The enhancement of mechanical strength and electric conduction by this cross-linking allows wider applications of macroscopic assemblies of CNTs as sensors, transistors, electrodes, actuators and fibres.
1. Introduction

Recently, many attentions are given to macroscopic assemblies of carbon nanotubes (CNTs), including bucky-papers, fibers, pellets and thin films, in order to utilize the characteristic properties of a single CNT in macroscopic scale. They have huge potential applications for structural and functional components such as hybrid solar cells, supercapacitors, transparent electrodes, chemical sensors, artificial muscles and high-surface-area electrodes.[1–12] These attempts are inspired by successful fabrication of carbon nanotube nanocomposites, which enhanced the performance of polymer, ceramic and metal matrix considerably by addition of relatively small amount of CNTs.[13,14] However, the actual performance of macroscopic assemblies of CNTs, such as electric conductivity and mechanical strength, are still far below the expectation. For example, the strength of CNT fibres are inferior even compared to conventional carbon fibres; the strength of CNT fibres are around 1GPa without polymer binders, while the strengths of carbon fibres are ranged from 1 to 4GPa.[15]

These inferior mechanical properties of macroscopic assembly of CNTs are induced from the weak interaction between CNTs. The supporting forces for these materials are van der Waals force, entanglement of CNTs or intercalation by anionic ions.[3-12] The weak inter-CNT force also affects the electric conductivity. The electric conductivity of CNT thin films are ranged from 10 to 1000 S/cm according to film thickness and CNT preparation process, which is lower than that of a single CNT showing 10,000–30,000S/cm.[16] Different from that of a single CNT, the electric conduction of macroscopic assembly of CNTs depends on the conduction between CNTs, i.e. inter-CNT conduction, rather than conduction through each CNT. [11, 12, 16] Therefore, the introduction of cross-linking between CNTs is expected to enhance the mechanical properties and to characterize the electric conduction behaviour compared to those assembled only by weak-interactions.

Controlled chemical treatments of CNTs, such as acid treatment, oxidation and plasma etching, produce functional groups on their surface.[3] When the functional groups on CNTs can be activated, these functionalized CNTs can be interconnected as shown in the ring closure of
CNTs[17] or in the formation of junction between CNTs by amide groups[18] by reactions between the surface functional groups. Therefore, it can be expected that a solid bulk form of CL-CNT can be fabricated When all the CNTs are cross-linked together, i.e., the CNTs are sintered together.

In this study, a solid form of cross-linked CNTs (CL-CNTs), in which the CNTs are cross-linked each other by chemical bonds, was fabricated by spark plasma sintering of the functionalized CNTs. The carboxyl and hydroxyl groups, which are the most common functional groups on CNTs, are used for the cross-linking of CNTs. The effect of cross-linking between CNTs on their mechanical and electrical properties are investigated by comparing the CL-CNT with the functionalized CNT pellet, which is fabricated by the same process except cross-linking process by spark plasma sintering.

2. Experimental Procedures

Multi-walled CNTs (MWNTs) prepared by the arc discharge process were supplied by Iljin Nanotech (Seoul, Korea). The CNTs (100 mg) were purified by sonication in 100 ml of HCl for 5 hours. The purified CNTs were acid treated in 100 mL of a 3:1 mixture of H₂SO₄ and HNO₃ with sonication for 6 or 10 hours. The acid-treated CNTs were separated from the acid by centrifugation and dispersed in water. The CNTs were washed with water several times and filtered to a slurry using vacuum suction filtration. A graphite mould 15 mm in diameter was filled with the CNT slurry and pressed in a vacuum while drying at room temperature. The dried CNTs in the graphite mould were spark plasma sintered (Dr. Sinter Lab. 1505; Sumitomo Coal Mining, Tokyo, Japan) at 400ºC for 1 hour at a 20ºC min⁻¹ heating rate under 30 MPa pressure in a vacuum pressure of 1.5Pa.

The DSC analysis (DSC 204F1; Netzsch, Selb, Germany) of a CNT pellet was performed just before spark plasma sintering and before pressing, i.e. CNT bucky paper forms. The XPS analysis was performed using ESCA2000 (VG Microtech). The specific heat was measured in the DSC analysis and the thermal diffusivity was measure using a laser flash method (LFA 447; Netzsch).
The compression test was performed using a sample, with thickness of 1.5 mm and with diameter of 1 mm, by an Instron 8848 microforce testing system (Instron, Norwood, MA, USA). The electrical conductivity was measured using a four-point probing method.

3. Results and Discussion

The concept of new fabrication process for CL-CNTs is outlined in Fig. 1(a). MWCNTs prepared by the arc discharge process are purified by HCl to remove the metallic catalyst. The purified CNTs are treated with a mixture of H$_2$SO$_4$ and HNO$_3$ to attach functional groups, such as carboxyl and hydroxyl groups, on both the surfaces and the ends of CNTs. The functionalized CNTs are dispersed in water and filtered to obtain a slurry form. The functionalized CNT pellet is fabricated through pouring the functionalized CNT slurry into a graphite mould and drying in vacuum at room temperature. During the drying process, the functionalized CNT slurry is pressed under 30 MPa in order to enhance the contact between CNTs in the graphite mould. The possible chemical modification of functionalized CNT pellets is estimated by DSC analysis as shown in Fig. 1(b), in which endothermic reactions are observed at 250 and 265ºC.

The spark plasma sintering process has paid attention by its characteristic heating method and its ability to sinter the powders, which have not been sintered by other sintering processes. During the spark plasma sintering process, the specimens in the graphite mould were heated by an applied pulsed electric current over 1000A. (See Supporting Informations, Fig. S1. for schematics of spark plasma sintering equipment) The exact sintering mechanism during the spark plasma sintering is not yet understood clearly. However, it is suggested that the spark plasma can be generated by the highly pulsed current, which activates the surfaces of the specimens. In addition, owing to the pulsed current, the high voltage and current is applied between particles by its large impedance. The functionalized CNT pellet is spark plasma sintered at 400ºC for 1 hour under a pressure of 30 MPa. An outward form of CL-CNT, fabricated by spark plasma sintered from functionalized CNT pellet, is black and rigid, which resembles the bulk graphite. It should be noted that gas ejection occurs
during the spark plasma sintering, as shown in Fig. 1(c), at the temperature ranged from \(220^\circ C\) to \(300^\circ C\), which is close to the temperature of endothermic reactions in DSC analysis.

Fig. 1. (a) Schematic of the process used to fabricate CL-CNT. The functionalized CNTs are compressed to keep them in close contact with each other, and this is cross-linked using spark plasma sintering to form chemical bonds between the functionalized CNTs. (b) DSC analysis of an as-pressed CNT pellet before spark plasma sintering and (c) the changes in the vacuum pressure during spark plasma sintering of a pressed CNT pellet. The arrows indicate the peaks from ejection of gas in cross-linking during spark plasma sintering.
A bulk piece of CL-CNT, with a diameter of 15 mm and a thickness of 1.5 mm, was fabricated using the above process, as shown Fig. 2(a). The CL-CNT is stiff enough to be polished into a mirror surface and can be machined by wire cutting method. As the CNTs in CL-CNT are not re-dispersed in water by sonication, the CNTs are confirmed to be cross-linked together as a result of the spark plasma sintering process. The surface morphology before and after spark plasma sintering is compared in Fig. 2(b) and (c), but little changes are observed on the surface morphology by spark plasma sintering process. However, the CL-CNTs exposed on a fracture surface are observed as shown in Fig. 2(d) and (e). This morphology further supports the postulate that the CNTs are cross-linked together as a result of the reactions between the functional groups on the surface of CNTs during the spark plasma sintering under an applied pressure of 30MPa.

![Figure 2](image)

**Fig. 2.** (a) Micrographs of fabricated CL-CNT and wire-cut CL-CNT sample. (b) the SEM micrographs of surface of functionalized CNT pellet before spark plasma sintering and (c) CL-CNT after spark plasma sintering.

The chemical status of CNTs at each process step is characterized by FT-IR spectroscopy as shown in Fig. 3. The pristine CNTs as received shows small bands around 3000–3500 cm\(^{-1}\), which is supposed as O-H bonding in hydroxyl and carboxyl groups. This fact means that the pristine CNTs are partially oxidized before acid treatments. In the functionalized CNT pellet, after the acid
treatments, the band around 3000~3500 cm\(^{-1}\) becomes enlarge. At the same time, peaks at 1050 cm\(^{-1}\) and 1200 cm\(^{-1}\) are appeared, which are supposed to the C-O bonding in alcohol and phenols, respectively. In the CL-CNTs, after spark plasma sintering of functionalized CNT pellet, the peaks at 1050 cm\(^{-1}\) and 1200 cm\(^{-1}\) disappears. (See Supporting Informations, Figure S2 for more detail FT-IR analysis in the range of 500~2000 cm\(^{-1}\)) Instead, a broad peak near 1100 cm\(^{-1}\) formed, which is supposed as ester group formation. In addition, band around 3000~3500 cm\(^{-1}\) become small. In these phenomena, it can be thought that the condensation of hydroxyl group and carboxyl groups into ester group is happened during the spark plasma sintering of functionalized CNT pellets, which induces cross-linking of CNTs. It is also supported by the X-ray photoelectron spectroscopy (XPS) analysis of the carbon and oxygen as shown in Fig. 4, which is a useful tool to analyze the surface chemistry of CNTs.[19] In XPS analysis of carbon in functionalized CNT pellet, a peak caused by carboxyl groups is shown at a binding energy of 288.8 eV as shown in Fig. 4(a). After spark plasma sintering, the intensity of this peak decreases, while another peak at a binding energy of 291.1 eV caused by ester groups increased, as shown in Fig. 4 and Table 1. From FT-IR and XPS analysis of
functionalized CNT pellets and CL-CNTs, it can be suggest that the functionalized CNT are cross-linked during the spark plasma sintering of functionalized CNT pellets by a dehydration reaction between carboxyl groups or between carboxyl and hydroxyl groups. Consequently, the gas ejected during the spark plasma sintering process is considered as H$_2$O. These reactions are also supported by the XPS analysis of oxygen before and after spark plasma sintering. The peak due to oxygen in C–O single bonds decreases, while the peak due to oxygen in C=O double bonds remains constant by the spark plasma sintering, indicating that the relative amount of C-O single bonds decreases by the dehydration reaction during the cross-linking process.

Fig. 4. The XPS analysis from carbon in (a) functionalized CNT pellet before spark plasma sintering and (b) CL-CNT after spark plasma sintering, and from oxygen (c) in functionalized CNT pellet before spark plasma sintering and (d) in CL-CNT after spark plasma sintering.
Table 1. Relative XPS peak intensity of functional groups in CL-CNTs and CNT pellet.

<table>
<thead>
<tr>
<th>Materials</th>
<th>C-C, C=C (%)</th>
<th>C-O- (%)</th>
<th>C=O (%)</th>
<th>CO-O- (%)</th>
<th>C-O-CO- (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functionalized CNT pellet</td>
<td>65.3</td>
<td>12.6</td>
<td>7.1</td>
<td>7.2</td>
<td>7.8</td>
</tr>
<tr>
<td>CL-CNT</td>
<td>64.0</td>
<td>11.4</td>
<td>5.6</td>
<td>8.0</td>
<td>10.9</td>
</tr>
</tbody>
</table>

The compressive strengths of the CL-CNT are measured as 65–110 MPa according to the acid treatment time before sintering as shown in Fig. 5(a), which is slightly stronger than graphite and similar to those of pure noble metals, such as silver and gold. However, the functionalized CNT pellets cannot be machined into specimen for compressive test, because it was easily destroyed during the machining. Comparing to the strength of functionalized CNT films in the literatures, which is reported as about 7MPa,[20] the strength of CL-CNTs are several times higher. The elastic moduli of the CL-CNT are measured as 0.75–1 GPa. (See Supplementary Information, Figure S4 for nanoindentation results of CL-CNT) It has been reported that the elastic modulus and deformation behavior of CNT bundles are dependent on the characteristics of the bonds between CNTs[21] and the covalent bonding between CNTs effectively resists the shearing between CNTs. Therefore, the reasonably high compressive strength of CL-CNT is resulted from the cross-linking of the CNTs. The higher strength and modulus are measured in longer CNTs because the resistance to shearing between CNTs is increased when the CNTs are cross-linked together on a wider interfacial area. In addition, it should be noticed that the carbon fibers consist of networks of graphene layers. Therefore, it can be expected that, when the CL-CNTs are fabricated into fibrous form, the strength of CL-CNT fiber can be comparable to those of carbon fibres.

The electrical conductivity at room temperature increases by cross-linking of CNTs during spark plasma sintering, as shown in Fig. 5(b). The electrical conductivity of the CL-CNTs, prepared by spark plasma sintering of CNTs acid-treated for 10 hours was measured as 24 S/cm, while that of functionalized CNT pellet, which is fabricated by same process as CL-CNT except spark plasma sintering, was measured as 2 S/cm. One remarkable thing is that the scattering of electric conductivity in functionalized CNT pellets is larger than those of CL-CNTs, which varies from 0.8
S/cm to 8 S/cm. It has been reported that the electrical conductivity of a CNT thin films is dependent on CNT fabricating process, thin film thickness, doped chemicals and the functional groups on CNTs.[11,12,15,21] In this case, however, the characteristics of the functional groups or doped chemicals on the CNTs are not expected to affect the change of electrical conductivity during the spark plasma sintering process, because both functionalized CNT pellets and the CL-CNTs undergo same acid-treatment process. (See Supporting Information Figure S4, for XPS results of wide binding energy ranges obtained from the CL-CNTs) In addition, the effect of thickness can be excluded for considering the difference of electric conductivity. Instead, it is considered that inter-CNT conduction determines the electric conductivities.[12,16]

The electric conductivity of CNT bucky paper or CNT thin films are much smaller than that of single carbon nanotubes.[16] This indicates that the electric conductivities of macroscopic assemblies of CNTs, such as bucky paper, pellet, thin films and fibers, are dependent on inter-CNT transport of charge carriers because it is not expected that the charge carriers, for example electrons or doped ions, move through the contacts between CNTs with same as they moves within single CNT.[12,16] It resembles grain boundary of polycrystalline materials, which act as major scattering cites for electron movement. The mechanism for inter-CNT conduction is not fully understood yet. However, the thermally activated tunnelling at inter-CNT contacts is considered as one of possible explanation.[16, 24]

Fig. 5. (a) Stress-strain relationship obtained in the compressive test and (b) electric conductivity at room temperature of CL-CNT spark plasma sintered and functionalized CNTs pellets acid treated
for 10 hours.

The measured electric conductivity of CNT pellets and CL-CNTs according to temperatures, normalized by those at room temperature, are shown in Fig. 6. In case of CNT pellet, the electric conductivity increases with increasing the temperature until 300K similar to semiconductors. In case of CL-CNTs, there are scattering at the temperature ranged 110K and 250K, while whole trends are similar to those of semiconductor. The activation energies can be calculated from Fig. 6(b) for CNT pellets to analyze the mechanism for thermally activated process. Two activation energies can be deduced by considering the conduction through semiconductor-semiconductor or metal-metal contacts, which transport the charge carrier easily, and semiconductor-metal contacts, which requires relatively larger activation energy to transport the charge carrier. It should be noticed that the activation energy of CL-CNTs are slightly smaller than that of functionalized CNT pellets, which is supposed as the role of cross-linking between CNTs in the enhancement of electric conductivity. Similar results are reported in molecularly linked Au particles, where alkanedithiol linker molecules, containing less than 5 carbons, between Au particles make metallic electric path.

![Fig. 6. (a) The normalized electric conductivity according to temperature and (b) the ln( ) vs 1/T plot Stress-strain relationship of CL-CNTs and CNT pellets. The CNTs in both CL-CNT and CNT](image)
pellet are acid-treated for 10 hours. The arrows in plot (a) indicate the semiconductor-metal transition.

4. Summary

In summary, a solid form of CNTs, named as CL-CNT, in which the CNTs are cross-linked together, was fabricated by spark plasma sintering of functionalized CNTs. The compressive strength of CL-CNT is measured as about 110 MPa and the cross-linking between CNTs increased the strength as a consequence of the chemical bonding between CNTs. The electrical conductivity of CL-CNT was increased by the cross-linking between CNTs, which promotes inter-CNT electric conduction path. These phenomena can enlarge the potential of macroscopic assemblies of CNTs, including CNT thin films, bucky papers and fibers for various application fields.

Acknowledgements

The authors really appreciate to Dr. C. J. Kim and Dr. B. H. Jun in Superconductor Laboratory, Korea Atomic Energy Research Institute for their help on measuring the electric conductivity of samples under cryogenic condition. This work is supported by a grant code no. 06K1501-00510 from the Center for Nanostructured Materials Technology, under the 21st Century Frontier R&D Programs of the Ministry of Science and Technology and by the Korea Research Foundation Grant (MOEHRD) (KRF-2005-005-J09701)

References


[7] Li YL, Kinloch IA, Windle AH, Direct Spinning of Carbon Nanotube Fibers from Chemical Vapor Deposition Synthesis, Science 2004; 304; 276-278


[19] Okpalugo TIT, Papakonstantinou P, Murphy H, McLaughlin J, Brown NMD, High resolution XPS characterization of chemical functionalised MWCNTs and SWCNTs, Carbon, 2005; 43; 153-161


Table Caption

Table 1. Relative XPS peak intensity of functional groups in CL-CNTs and CNT pellet.

Figure Captions

Fig. 1. (a) Schematic of the process used to fabricate CL-CNT. The functionalized CNTs are compressed to keep them in close contact with each other, and this is cross-linked using spark plasma sintering to form chemical bonds between the functionalized CNTs. (b) DSC analysis of an as-pressed CNT pellet before spark plasma sintering and (c) the changes in the vacuum pressure during spark plasma sintering of a pressed CNT pellet. The arrows indicate the peaks from ejection of gas in cross-linking during spark plasma sintering.

Fig. 2. (a) Micrographs of fabricated CL-CNT and wire-cut CL-CNT sample. (b) the SEM micrographs of surface of functionalized CNT pellet before spark plasma sintering and (c) CL-CNT after spark plasma sintering. (d) and (e) Interconnected CNTs observed at the fractured surface of CL-CNT. The arrows indicate the cross-linked parts of CNTs.

Fig. 3. The FT-IR spectroscopy of pristine MWNT, functional CNT pellet acid treated for 10 hours and CL-CNT after spark plasma sintering.

Fig. 4. The XPS analysis from carbon in (a) functionalized CNT pellet before spark plasma sintering and (b) CL-CNT after spark plasma sintering, and from oxygen (c) in functionalized CNT pellet before spark plasma sintering and (d) in CL-CNT after spark plasma sintering.
Fig. 5. (a) Stress-strain relationship obtained in the compressive test and (b) electric conductivity at room temperature of CL-CNT spark plasma sintered and functionalized CNTs pellets acid treated for 10 hours.

Fig. 6. (a) The normalized electric conductivity according to temperature and (b) the ln( ) vs 1/T plot Stress-strain relationship of CL-CNTs and CNT pellets. The CNTs in both CL-CNT and CNT pellet are acid-treated for 10 hours. The arrows in plot (a) indicate the semiconductor-metal transition.
Mechanical and electrical properties of cross-linked carbon nanotubes**

Seung I. Cha*, Kyung T. Kim**, Kyong H. Lee, Chan B. Mo, Yong J. Jeong, and Soon H. Hong

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology
373-1 Kusung-Dong Yusung-Gu, Daejoen 305-701, Korea
*Current affiliation: International Center for Young Scientist, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, JAPAN
**Current affiliation: LCD R&D Center, SAMSUNG ELECTRONICS Cp., LTD. San #24 Nongseodong, Giheung-Gu, Yongin, Gyeonggido 446-771, Korea

Supporting Information

Fig. S1. Schematics of spark plasma sintering system.
Figure S2. The FT-IR analysis of carbon nanotubes in each process step at detail scale.
The cross-linking between CNTs does not involve enhancement of thermal conduction as shown in Table S1. It means the charge carrier does not transport the thermal energy between CNTs. When the CNTs are acid-treated with sonication in a mixture of H$_2$SO$_4$ and HNO$_3$ at a 3:1 ratio, the CNTs are functionalized with both carboxyl and hydroxyl groups and they become shorter simultaneously. Therefore, longer acid-treatment before sintering induces shorter CNTs and it provides higher resistance for thermal conduction between CNTs.

### Table S1. Measured physical properties of CL-CNT.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (g cc$^{-1}$)</th>
<th>Specific Heat (J g$^{-1}$ K$^{-1}$)</th>
<th>Thermal Diffusivity (mm$^2$ s$^{-1}$)</th>
<th>Thermal Conductivity (W mK$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL-CNTs from acid-treated for 6 hours</td>
<td>1.907</td>
<td>0.845</td>
<td>0.78</td>
<td>1.258</td>
</tr>
<tr>
<td>CL-CNT from acid-treated for 10 hours</td>
<td>2.029</td>
<td>0.837</td>
<td>0.72</td>
<td>1.221</td>
</tr>
</tbody>
</table>

Fig. S3. The nanoindentation results of CL-CNT prepared from CNTs acid-treated for 10 hours. (a) The load-indentation depth curves and (b) hardness and Young’s modulus.
Fig. S4. The XPS spectroscopy of CL-CNTs, with whole binding energy range.
Fig. S5. The normalized XPS spectra for the raw multi-walled CNTs, functionalized CNTs and cross-linked (CL)-CNTs.