JOURNAL OF MATERIALS SCIENCE LETTERS **21**, 2002, 565 – 568

Preparation of carbon nanotubes composite sheet using electrophoretic deposition process

CHUNSHENG DU, D. HELDEBRANT, NING PAN*
Division of Textiles and Clothing, University of California at Davis, CA 95616, USA
E-mail: npan@ucdavis.edu

Since the discovery by Ijima [1] in 1991, carbon nanotubes have attracted tremendous attention. Interest in such a material arise from the fact that the mechanical, chemical, electrical, optical, magnetic, and electro- and magneto-optical properties of these nanotubes are different from their bulk properties, attributed largely to the quantum confinement effects [2–11]. For instance, theoretical predictions have suggested that the Young's modulus of carbon nanotubes could be as high as 1–5 TPa [12, 13] and the theoretical tensile strength as high as 200 GPa [14]. Various experimental techniques [15–19] conducted on the mechanical properties of carbon nanotubes also showed very promising results, albeit still much smaller than theoretical prediction. Furthermore, it is widely accepted that the issue of heat dissipation in miniature devices becomes increasingly important as the size of the device reduces. Therefore, carbon nanotubes may play an important role in improving the performance and stability of nanosized devices because of their high thermal conductivity.

In spite of the vast potential of nanoscale materials, some inherent problems have hindered significantly, in some case prohibitively, further progress. First, it is extremely difficult to manipulate the sample for any tests due to its sheer size. To conduct a measurement on an individual nanotube, researchers have to select a suitable tube, which is extremely difficult and may result in the situation that the selected tube is very likely not a typical one, and this may be one of the reasons why similar researches usually lead to different results. Next, although many theoretical predictions have indicated unique properties of the nano materials, the traditional test methods and equipment are not designed for them so that it is extremely difficult to say the least to get direct experimental evidence and reliable data to validate the predictions. As a result, we are still largely in a primary stage to probe and investigate the properties, and have proceeded even more slowly for practical applications.

Obviously, by assembling the nanotubes into a macroscale object, we can then conduct all the conventional tests at samples of manageable dimensions to examine the material properties, which in turn will lay a solid foundation of experimental evidence to facilitate further studies of all related issues. More importantly, a new bulk material made of nanotubes may offer many attractive applications of its own at the conventional scale. Even though the properties of this new assembly of nanotubes may not be as distinct as those of individual nanotubes, they should be significantly different from those of the conventional bulk. So it is conceivable that the macro-size materials assembled from carbon nanotubes will have potential applications to macro-level uses. The burgeoning research and application of nano composites is just such an attempt. The major problem in nano composites, however, is the low volume fraction of the nano reinforcement, due to the extreme difficulty of dispersing the nano material uniformly into the matrix. This becomes a hurdle for the further improvement of the properties of nano composites.

Electrophoretic deposition (EPD) may provide an alternative in which charged particles dispersed in a stable suspension are driven by a DC electric field to move towards an oppositely charged electrode and build up a closely packed/bonded layer. EPD has the advantages of short formation time, little restriction in the shape of substrates, simple deposition apparatus and suitable for mass production. Most importantly, it is much easier to

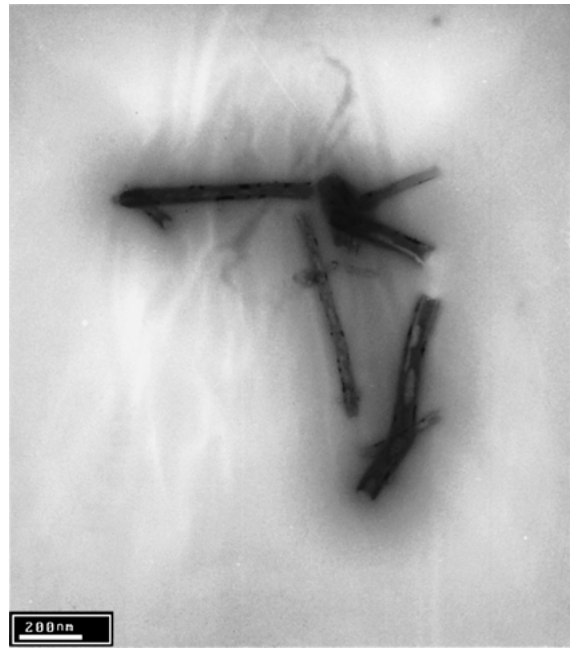

Figure 1 Transmission electronic microscope image of multi-walled carbon nanotubes.

*Author to whom all correspondence should be addressed.

0261–8028

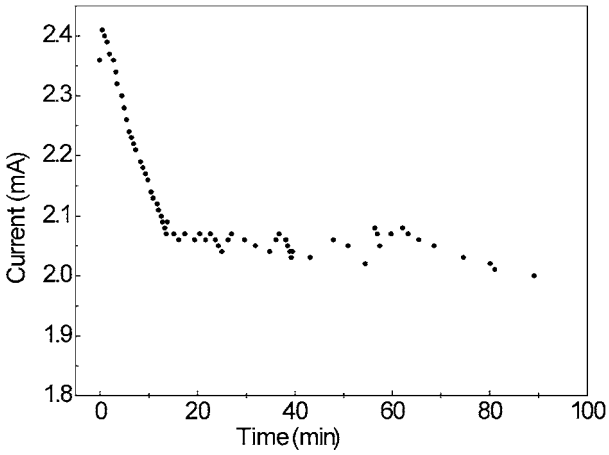

Figure 2 Diagram of deposition current as a function of deposition time.

increase the volume fraction of the nano reinforcement, and the microstructure of the layer formed can be well controlled by preparing stable suspension.

In this communication, we report such a method to prepare carbon nanotubes sheet using EPD. Multi-walled carbon nanotubes with a diameter range of 70 to 140 nm prepared by chemical vapor deposited method were used (Fig. 1). EPI-Rez resin and EPI-CURE curing agent (aliphatic amine) were employed as the matrix. Carbon nanotubes were dispersed in ethanol in which the mixture of resin and the curing agent was already dissolved. The mixed solution was then ultrasonicated for 30 min to form a stable suspension. Two aluminum electrodes were kept parallel at 50 mm apart in the suspension; a constant deposition voltage of 45 V was used for EPD. The deposition current was measured using Hewlett-Packard Multimeter.

The pH value of the suspension is 9, indicating that there is base dominance in the mixture of resin and curing agent. This resulted in the formation of $R_3N^+OH^-$, and the absorption of the positive charges on the suspended carbon nanotubes, making themselves positively charged. Meanwhile the applied DC field forced the positively charged nanotubes to move towards and deposit on the cathode. A sheet of a carbon nanotube composite thus formed on the cathode at the end of the process, which was then dried and cured in air over night. The surface morphology of the carbon nanotube

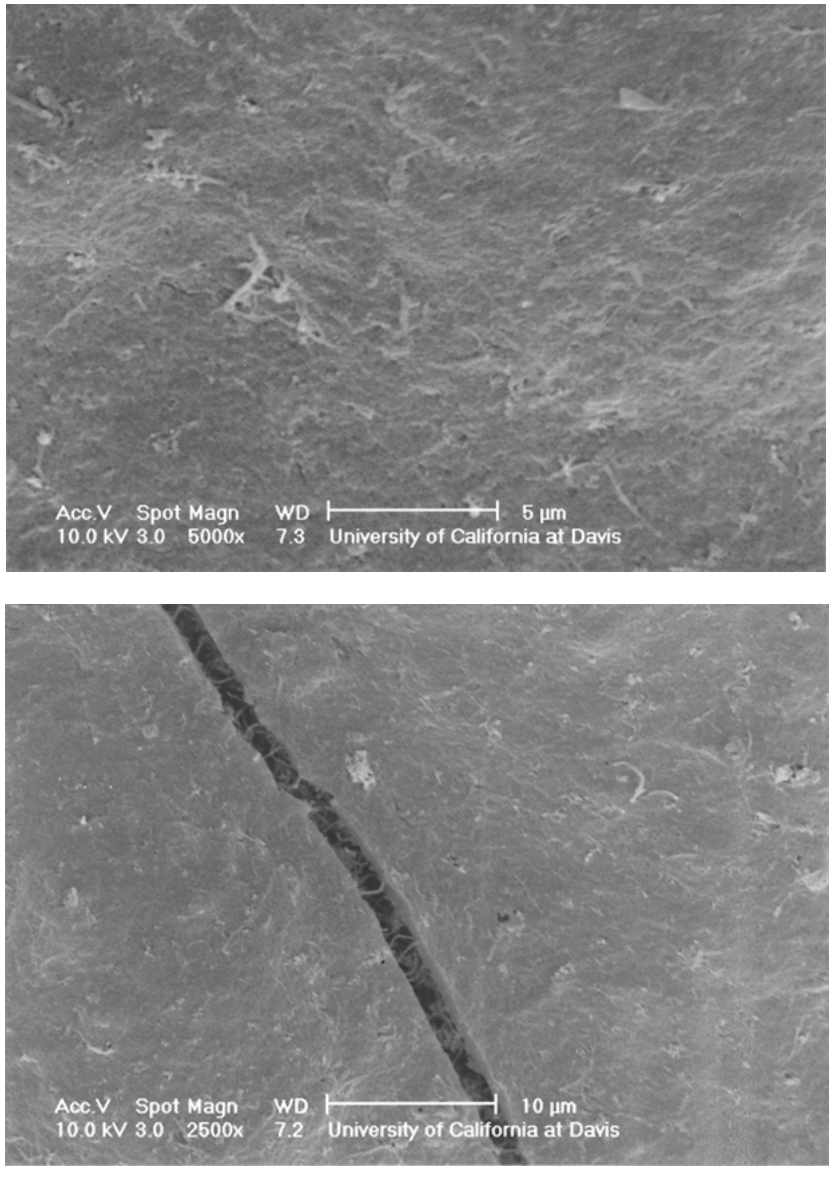

Figure 3 SEM images of the carbon nanotubes composite sheet with higher resin concentration.

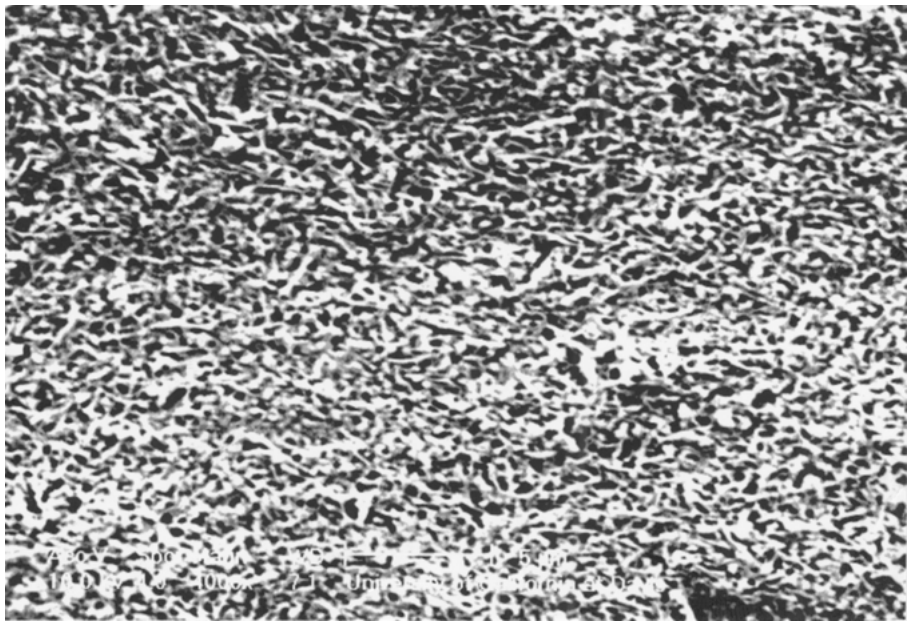

Figure 4 SEM images of the carbon nanotubes composite sheet with lower resin concentration.

composite sheet was later characterized using a scanning electron microscope (Philips XL30).

Fig. 2 is the diagram of deposition current as a function of deposition time. It shows that initially deposition current decreased drastically in a short time after the voltage was applied, and then reached a steady level as the deposition progressed. The fast current drop is due to the sudden increase of the charged nanotube concentration near the cathode when the DC electric field formed. Under this circumstance, concentration potential [13] whose direction was opposite to the applied voltage would appear, resulting in the slowdown of nanotube movement, and the drop of the deposition current. After the initial surge of nanotubes deposited on the cathode, the concentration near the cathode became stable, and the deposition current maintained virtually constant.

Fig. 3 shows the SEM of the carbon nanotube sheet. It can be seen that the surface is very smooth and nanotubes are not easily detected even under a high magnification (Fig. 3a). To make nanotubes detection possible, the sheet sample was put into a fume hood where the remaining ethanol evaporated at such a fast rate that microcracks were introduced on the sample surface. By carefully analyzing the microcracks, nanotubes can be found in between the cracks (Fig. 3b). It is demonstrated that the carbon nanotubes in the suspension where indeed deposited on the electrode, but could not be detected directly because of a continuous resin layer formed on the surface of the sample.

The nanotubes can be easily detected when the concentration of resin in the suspension was lowered and less continuous resin layer was formed. Fig. 4 shows the SEM image of the composite sheet prepared from a suspension with low concentration of resin, namely 5 kg/m^3. It can be seen that the carbon nanotubes formed the backbone of the composite and resin bonded them together, and the nanotubes were uniformly dispersed in the sheet.

Thermo-gravimetric analysis (TGA) was performed on the EPD sheet under nitrogen atmosphere, which minimized the mass loss of carbon nanotubes due to oxidation, while allowing the resin to decompose almost completely. Fig. 5 shows the TGA curves of the pure carbon nanotubes, pure resin and EPD sheet with low resin concentration. It can be calculated from TGA curves that the nanotube loading in the EPD sheet is about 55 wt%, which is relatively large comparing to similar reported values [20–23]. The nanotubes loading in another sample can be calculated in the same way, at about 43 wt%.

The property of these two samples is significantly different. The electrical resistance was measured using a Multimeter using a separation between contacts of 10 mm. The resistance of the sample with higher nanotubes fraction was about 7 kilo-ohm, while the low fraction one was nonconductive due to the continuous resin layer formed on nanotubes' surface.

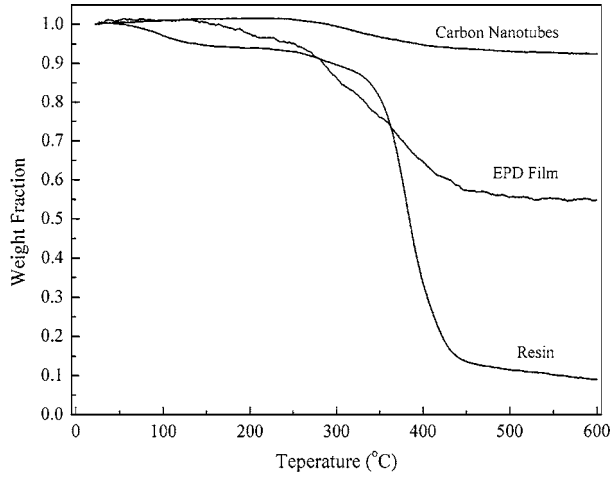

Figure 5 TGA curves of the pure carbon nanotubes, pure resin and composite sheet with lower resin concentration.

In conclusion, EPD using the ethanol/resin/curing agent/nanotubes suspension system is a simple and practical process to prepare carbon nanotubes composite sheets with relative ease of uniform dispersion of nanotubes into the matrix and increase of the volume fraction of the nano reinforcement. Most importantly, our preliminary results also showed that the electrical properties could be controlled by modifying the resin concentration in the suspension.

Acknowledgment

The authors wish to gratefully acknowledge Jeff Yeh for supplying the carbon nanotubes. Special thanks are given to Kameron Chun for experiments assistance, Michael Dunlep for TEM assistance, Grete Adamson for SEM assistance and Lei Li for helpful discussion.

References

1. S. IIJIMA, *Nature* **354** (1991) 55.
2. L. E. BRUS, *Appl. Phys.* A **53** (1991) 465.
3. *Idem., J. Chem. Phys.* **80** (1984) 4403.
4. Y. WANG, *Acc. Chem. Res.* **24** (1991) 133.
5. A. HENGLEIN, *Topics Curr. Chem.* **143** (1988) 113.
6. H. WELLER, *Angew. Chem., Intl. Ed. Engl.* **32** (1993) 41.
7. A. HENGLEIN, *Chem. Rev.* **89** (1989) 1861.
8. T. W. EBBESEN, H. J. LEZEC, H. HIURA, J. W. BENNETT, H. F. GHAEMI and T. THIO, *Nature* **382** (1996) 54.
9. T. PICHLER, M. KNUPFER and M. S. GOLDEN, *Phys. Rev. Lett.* **80** (1998) 4729.
10. L. CHICO, V. H. CRESPI and L. X. BENEDICT, *ibid.* **76** (1996) 971.
11. L. LANGER, V. BAYOT and E. GRIVER, *ibid.* **76** (1996) 479.
12. G. OVERNEY, W. ZHONG and D. TOMANEK, *Z. Phys. D—Atoms Molecules Clusters* **27** (1993) 93.
13. M. M. J. TREACY, T. W. EBBESEN and J. M. GIBSON, *Nature* **381** (1996) 678.
14. M. MEYYAPPAN and J. HAN, *Prototype Tech. Int.* **6** (1998) 14.
15. J. P. LU, *Phys. Rev. Lett.* **79** (1997) 1297.
16. E. W. WONG, P. E. SHECHAN and C. M. LIEBER, *Science* **277** (1997) 1971.
17. H. D. WAGNER, O. LOURIE, Y. FELDMAN and R. TENNE, *Appl. Phys. Lett.* **72** (1998) 188.
18. B. I. YAKOBSON, C. J. BRABEC and J. BERHNOLC, *Phys. Rev. Lett.* **76** (1996) 2511.
19. X. TAN and S. HUANG, *Ch. J. Chem. Phys.* **11** (1998) 416.
20. D. QIAN, E. C. DICKEY, R. ANDREWS and T. RANTELL, *Appl. Phys. Lett.* **76** (2000) 286.
21. M. S. P. SHAFFER and A. H. WINDLE, *Advanced Materials* **11** (1999) 937.
22. Z. JIA, Z. WANG, C. XU, J. LIANG, B. WEI, D. WU and S. ZHU, *Materials Science and Engineering* A **271** (1999) 395.
23. X. GONG, J. LIU, S. BASKARAN, R. D. VOISE and J. S. YOUNG, *Chemistry of Materials* **12** (2000) 1049.

Received 19 July 2001
and accepted 14 January 2002