

Dispersion of single wall carbon nanotubes by in situ polymerization under sonication

Cheol Park ^{a,*}, Zoubeida Ounaies ^a, Kent A. Watson ^a, Roy E. Crooks ^b,
Joseph Smith Jr. ^c, Sharon E. Lowther ^c, John W. Connell ^c,
Emilie J. Siochi ^c, Joycelyn S. Harrison ^c, Terry L. St. Clair ^c

^a ICASE, Advanced Materials & Processing Branch, NASA Langley Research Center, Mail Stop 226,
6 West Taylor Street, Hampton, VA 23681-2199, USA

^b Lockheed Martin, Advanced Materials & Processing Branch, NASA Langley Research Center, Mail Stop 226,
6 West Taylor Street, Hampton, VA 23681-2199, USA

^c Advanced Materials & Processing Branch, NASA Langley Research Center, Mail Stop 226,
Hampton, VA 23681-2199, USA

Received 10 March 2002; in final form 1 August 2002

Abstract

Single wall nanotube reinforced polyimide nanocomposites were synthesized by in situ polymerization of monomers of interest in the presence of sonication. This process enabled uniform dispersion of single wall carbon nanotube (SWNT) bundles in the polymer matrix. The resultant SWNT–polyimide nanocomposite films were electrically conductive (antistatic) and optically transparent with significant conductivity enhancement (10 orders of magnitude) at a very low loading (0.1 vol%). Mechanical properties as well as thermal stability were also improved with the incorporation of the SWNT.

© 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Single wall carbon nanotubes (SWNT) have generated tremendous interest because of their unique combination of electronic, mechanical, chemical, and thermal properties. Potential applications reported have included chemical probes, sensors, hydrogen storage, nanoprobes, and

memory storage [1–4]. SWNTs, however, have rarely been used as electrical or mechanical inclusions in a polymer matrix because of the difficulty in achieving efficient dispersion. This difficulty is primarily due to the non-reactive surface of SWNT. Intrinsic van der Waals attraction among tubes, in combination with their high surface area and high aspect ratio, often leads to significant agglomeration, thus preventing efficient transfer of their superior properties to the matrix. Although a number of studies have focused on dispersion of SWNT, complete dispersion of SWNT in a poly-

* Corresponding author. Fax: +757-864-8312.

E-mail address: c.park@larc.nasa.gov (C. Park).

mer matrix has rarely been achieved. Most dispersion studies have been directed toward chemical modification of the nanotube surface [5–7]. Although many researchers have tried to solubilize nanotube ends and exterior walls through various functionalization routes, dispersion via functionalization has found limited success. Furthermore, covalent functionalization disturbs the extended π -electron systems (sp^2 orbitals) of the nanotube surface, responsible for the many attractive attributes of SWNTs.

In the present Letter, a process to effectively disperse SWNT bundles in an aromatic polymer is reported. This process involves in situ polymerization of the monomers of interest in the presence of sonication during the polymerization process. Although a similar process has been reported for coating multi-wall carbon nanotube (MWNT) with a conductive polymer, dispersion of the nanotubes in a continuous polymer matrix has not been addressed [8]. In this study, aromatic polyimides were used as a continuous medium to prepare SWNT reinforced polyimide nanocomposites. The goal of this study was to develop a method to efficiently disperse SWNT bundles into a given polymer matrix on a nanoscale level to produce an electrically conductive (antistatic) and optically transparent nanocomposite film.

2. Experimental

A batch of purified laser ablated single wall carbon nanotubes (SWNT) was obtained from Rice University. The concentration of the catalysts (Ni and Co) in the purified SWNT was less than 3 wt% based on elemental analysis (Desert Analytics, ICP-MS). Transmission electron microscopy (TEM) and atomic force microscopy (AFM) images along with Raman spectroscopy have shown that these SWNTs were about 1.2–1.6 nm in diameter and 3 μm long. The as-received purified SWNTs are agglomerated into bundles. Cross-sectional dimensions were not determined, but focusing experiments with TEM indicate that they are closer to rounded bundles than to flat ribbons with the diameter near 40 nm [9]. These SWNT bundles often formed micrometer scale agglomer-

ates observed in optical microscopy. The density of the SWNT was estimated theoretically to be about 1.4 g/cm^3 [10]. The polymer used as a matrix was a colorless polyimide (CP2) [11]. The diamine and dianhydride used to synthesize the CP2 were 1,3-bis(3-aminophenoxy) benzene (APB) and 2,2-bis(3,4-anhydrodicarboxyphenyl) hexafluoropropane (6FDA), respectively. The diamine (APB) was purchased from Mitsui-Toatsu and used as-received. The dianhydride (6FDA) was purchased from Imitec and used after sublimation. As-received anhydrous dimethyl formamide (DMF, Fisher Scientific) was used as a solvent.

A dilute SWNT solution, typically around 0.05 wt% in dimethylformamide (DMF), was prepared by homogenizing for 10 min (750 rpm with a 6 mm diameter rotor) and sonicating for one and a half hours in an ultrasonic bath (40 kHz). The sonicated SWNT solution was transferred into a three neck round bottom flask equipped with a mechanical stirrer, nitrogen gas inlet, and drying tube outlet filled with calcium sulfate. After stirring the SWNT solution for 10 min, the diamine (APB) was added into the SWNT solution. The SWNT and diamine mixture continued to be stirred for 30 min before adding the dianhydride (6FDA). The entire reaction was carried out in the flask immersed in an ultrasonic bath (40 kHz) until the solution viscosity increased and stabilized. Additional stirring was continued overnight to form the SWNT–poly(amic acid) solution without sonication. Solid content for SWNT–poly(amic acid) was 15% (w/w) in DMF. Acetic anhydride and pyridine were used as catalysts to imidize the SWNT–poly(amic acid) chemically.

A series of SWNT–CP2 nanocomposite films were prepared using the in situ polymerization under sonication with SWNT concentrations ranging from 0.01 to 1.0 vol%. The density of pure CP2 was about 1.4 g/cm^3 , which is very close to that of the SWNT. As a control sample, a nanocomposite film (1.0 vol%) was prepared by direct mixing the pre-dispersed SWNT solution with a pure CP2 polyimide solution by stirring. The SWNT–CP2 solutions prepared were cast onto a glass plate and dried in a dry air-flowing chamber. Subsequently, the dried tack-free films were cured at 110, 170, 210, and 250 $^\circ\text{C}$ for 1 h each in an

air-circulating oven to obtain solvent-free free-standing films. Dispersion of the SWNT into the polymer matrix was assessed via optical and transmission electron microscopy. Glass transition temperatures of the films were determined by differential scanning calorimetry (DSC). Conductivity of these films was evaluated according to ASTM D257 with a Keithley 8009 Resistivity Test Fixture and a Keithley 6517 Electrometer. Optical properties of these films were evaluated with a Perkin–Elmer Lambda 900 UV/Vis/NIR spectrophotometer. Mechanical properties of the films were evaluated by a dynamic mechanical thermal analyzer (DMA, Rheometrics). Thermal stability was investigated by dynamic thermogravimetric analysis (TGA, Seiko) at a heating rate of 2.5 °C/min in air.

3. Results and discussion

The polymerization reaction between the diamine and dianhydride was slightly retarded by the presence of the SWNT, and the viscosity of the solution increased more slowly compared to the reaction without SWNT. This retardation was possibly due to decreased mobility of the aromatic diamine, resulting from π – π overlap interactions with the SWNT surface [12,13]. The glass transition temperature (T_g) of the nanocomposites, however, remained unchanged at around 199 °C over the whole range of SWNT loadings. Excessive cavitation force by a low-frequency sonic horn (20 kHz) released a tremendous pressure as a shock wave through the surrounding medium, degrading the molecular weight of the polymer as evidenced by a decrease in solution viscosity. To prevent degradation, a high frequency, low power sonic bath (>40 kHz) was used for the in situ polymerization with SWNT under sonication.

The SWNT–CP2 nanocomposite films examined with an optical microscope showed that dispersion of the SWNT was homogeneous in the polyimide matrix (not shown). Dispersion was significantly improved compared to the control sample prepared by direct mixing, although a few large agglomerates of bundles (about a few μm) were still visible. Since the resolution of optical

microscopy is limited to a micrometer, only qualitative assessment was allowed. To investigate the dispersion in a nanometer scale, transmission electron microscopy was employed. Transmission electron microscopy with a thin section of 1.0 vol% SWNT–CP2 nanocomposite microtomed to 90 nm thick revealed that thin SWNT bundles were dispersed uniformly throughout the whole polymer matrix (Fig. 1). The inset of Fig. 1 shows fine features of SWNT bundles at high magnification. These were observed throughout the area shown in Fig. 1. Intact SWNT bundles in the matrix are visible as darker features. The fine features, evident as a 0.34 nm spacing, were observed in the bundle contrast regions, parallel to the length of the tube bundles. This is thinner than the average diameter of individual nanotubes (1.4 nm), which is possibly due to focused overlapped nanotubes although the main reason is not obvious at the present moment. This feature was not found in samples of the pristine polyimide and is thus an indication of the presence of the nanotubes within the composite. Similar features were found in a different SWNT–polyimide system in our lab and in as-grown bare SWNT bundles in literature [14]. Although the SWNT tend to remain as bundles, their thickness was reduced in the polymer matrix versus pristine SWNT. TEM study of the nanocomposite, such as in Fig. 1, showed a bundle diameter range of 2–20 nm. Magnetic force micrographs visualized cross-sections of the dispersed nanotube bundles ranging from 2 to 12 nm in diameter after correction from the magnetic probe tip dimension [15], which is consistent with the TEM results.

The degree of dispersion of the SWNT in the polymer matrix was largely influenced by their state of dispersion in the solvent. The pre-dispersed SWNT remained dispersed in the low viscosity diamine and dianhydride monomer solution during sonication. This was presumably due to implosion of the cavitation bubbles and microstreaming of a jet of the solvent from the implosion onto the SWNT surface, which prevented the dispersed nanotubes from re-aggregating [16]. At the completion of the in situ polymerization, it appears that the highly viscous solution restricts Brownian motion and sedimentation, thus stabi-

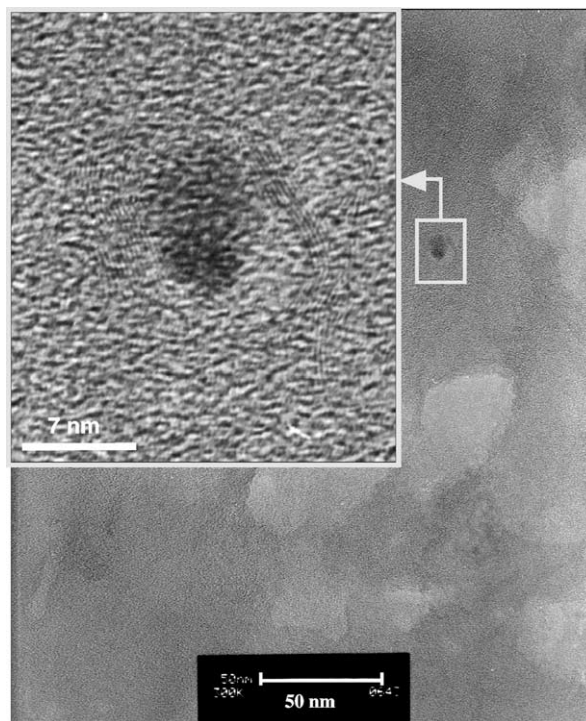


Fig. 1. TEM micrograph of 1.0 vol% SWNT-CP2 nanocomposite. The inset shows SWNT bundles dispersed in the polymer matrix at higher magnification.

lizing the nanotube dispersion from re-aggregation. In addition, the mechanical action of the ultrasound may aid in the removal of amorphous carbon, thus making more of the SWNT surface available for interaction with the aromatic monomers. The highly aromatic diamine and dianhydride can favorably interact with the graphene surface of the nanotubes via π - π overlap interaction [13,14], further stabilizing of the solution.

In situ polymerization under sonication kept the SWNT dispersed throughout the reaction, producing reasonably transparent, antistatic SWNT-CP2 nanocomposites at very low SWNT loading (≤ 1.0 vol%). Volume conductivity of the SWNT-CP2 nanocomposite films was measured, and is shown in Fig. 2. The conductivity of the pristine CP2 polyimide was 6.3×10^{-18} S/cm. A sharp increase of the conductivity was observed between 0.02 and 0.1 vol%, and then it increased moderately at loading levels in excess of 0.1 vol%. This behavior indicates that the percolation threshold of the nanocomposite resides between

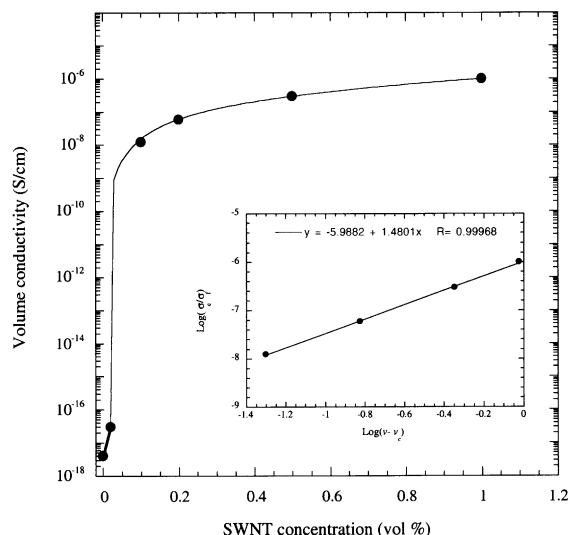


Fig. 2. Volume conductivity of SWNT-CP2 nanocomposites. The inset is a power law plot of the conductivity of the nanocomposite with $(v - v_c)$ on a logarithmic scale.

0.02 and 0.1 vol%, where the nanocomposite converts from a capacitor to a conductor. Incorporation of 0.1 vol% SWNT increased the conductivity 10 orders of magnitude, which surpassed the antistatic criterion of thin films for space applications (1×10^{-8} S/cm).

The measured conductivity can be described by a percolation-like power law equation [17],

$$\sigma_c = \sigma_0(v - v_c)^t,$$

where, σ_c is the conductivity of the nanocomposite (S/cm), σ_0 is the conductivity of the conductive reinforcement, v is the volume fraction of the reinforcement, v_c is the percolation threshold, and t is the conductivity critical exponent. As shown in the inset of Fig. 2, this equation is valid at concentrations above the percolation threshold ($v > v_c$) and only in the vicinity of v_c . The measured conductivity of the nanocomposite exhibited a linear relationship with respect to $(v - v_c)$ in a logarithmic plot with a correlation factor of 0.999. This high correlation suggests that the power law relationship was appropriately applied for this system and yields values of the v_c and t of approximately 0.05 vol% and 1.5, respectively. These percolation threshold and critical exponent values were lower than the calculated values for three-dimensional systems reinforced by a filler with a high aspect ratio [18]. The voltage–current measurement results exhibited a non-linear behavior (non-ohmic), indicating that the conduction among the nanotubes possibly resulted from a quantum tunneling effect.

Table 1
Optical and thermal properties of SWNT–CP2 nanocomposite films

SWNT concentration in CP2 (vol%)	Transmission at 500 nm (%)	Temperature at 5 wt% loss (°C) ^a
0	85	444
0.1	68	461
0.2	62	474
0.5	54	481
1.0	32	479
1.0 ^b	<1	N/A

^a TGA: Dynamic heating at the rate of 2.5 °C/min in air after holding 30 min at 100 °C.

^b This film was prepared by direct mixing.

The optical properties were studied with UV/Vis spectrophotometry and the results normalized at 34 μm thick are listed in Table 1. In general, transmission at 500 nm decreased with increasing the SWNT concentration, and the films prepared by the in situ polymerization under sonication transmitted more light than that prepared by direct mixing. With 0.2 vol% of SWNT in CP2, the film exhibited 1×10^{-7} S/cm with 62% transmission of visible light at 500 nm. The CP2 film containing 1.0 vol% SWNT incorporated via the in situ polymerization under sonication still transmitted 32% of visible light at 500 nm while that prepared by the direct mixing transmitted less than 1%. The absorption at 500 nm increased linearly with the nanocomposite film thickness obeying Beer's law. This behavior indicates that the dispersion of SWNTs in the polymer matrix was homogeneous.

Dynamic mechanical data shown in Fig. 3 show that modulus increased with increasing the nanotube concentration, with up to a 60% improvement at 1.0 vol% SWNT loading level. The dotted line predicted by Cox model is in good agreement with the experimental results (solid line), assuming the

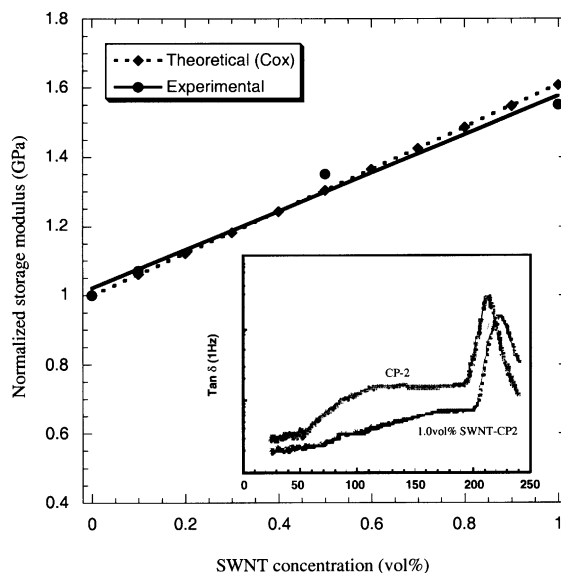


Fig. 3. Storage modulus of SWNT–CP2 nanocomposite films versus SWNT concentration. The inset shown $\tan \delta$ curve as a function of temperature.

modulus of the SWNT is 1 TPa and the aspect ratio is 1000. The $\tan \delta$ peak decreased and shifted up 10 °C with SWNT incorporation at 1.0 vol% as seen in the inset of Fig. 3. The thermal stability of CP2 was enhanced by the addition of SWNT as demonstrated by an increase in the temperature at which 5 wt% weight loss occurred (Table 1). This improvement leveled off at SWNT concentration of 0.5 vol%. The uniformly dispersed nanotubes presumably provided thermo-oxidative stability to the polymers in the vicinity of the tube surfaces.

4. Conclusions

An efficient dispersion of SWNT bundles in a polymer matrix was achieved. This method included in situ polymerization with SWNT and sonication during the reaction. The pre-dispersed SWNT dispersion remained stable throughout the reaction under sonication, producing a reasonably transparent, electrically conductive SWNT–CP2 nanocomposites at very low SWNT loading. The resultant SWNT–polymer nanocomposite exhibited significant conductivity enhancement (10 orders of magnitude) at a very low loading (0.1 vol%) without significantly sacrificing optical transmission. Mechanical properties as well as thermal stability were also improved by the incorporation of the SWNT. These SWNT–polymer nanocomposites are potentially useful in a variety of aerospace and terrestrial applications, due to their combination of electrical conductivity and high optical transmission.

Acknowledgements

We would like to thank Ms. Crystal Topping for experimental assistance and Dr. Youqi Wang

at Kansas State University for valuable discussion.

References

- [1] J. Kong, N.R. Franklin, C. Zhou, M.G. Chapline, S. Peng, K. Cho, H. Dai, *Science* 287 (2000) 622.
- [2] C. Liu, Y.Y. Fan, M. Liu, H.T. Cong, H.M. Cheng, M.S. Dresselhaus, *Science* 286 (1999) 1127.
- [3] S.S. Wong, E. Joselevich, A.T. Woolley, C.L. Cheung, C.M. Lieber, *Nature* 394 (1998) 52.
- [4] P.M. Ajayan, *Chem. Rev.* 99 (1999) 1787.
- [5] J. Chen, M.A. Hamon, H. Hu, Y. Chen, A.M. Rao, P.C. Eklund, R.C. Haddon, *Science* 282 (1998) 95.
- [6] E.T. Mickelson, C.B. Huffman, A.G. Rinzler, R.E. Smalley, R.H. Hauge, J.L. Margrave, *Chem. Phys. Lett.* 296 (1998) 188.
- [7] J.L. Bahr, J.M. Tour, *Chem. Mater.* ASAP (2001).
- [8] J. Fan, M. Wan, D. Zhu, B. Chang, Z. Pan, S. Xie, *J. Appl. Polym. Sci.* 74 (1999) 2605.
- [9] C. Park, R.E. Crooks, E.J. Siochi, N.D. Evans, E.A. Kenik, Adhesion of polyimide to single wall nanotube bundles revealed by energy filtered transmission electron microscopy (to be submitted).
- [10] D. Tomanek, Available from: <http://www.pa.msu.edu/cmp/csc/nanotube.html>.
- [11] A.K.St. Clair, T.L.St. Clair, W.S. Slemple, in: W. Weber, M. Gupta (Eds.), *Proceeding of the 2nd International Conference on Polyimides*, Society of Plastics Engineers, 1987, p. 16.
- [12] S. Curran, P.M. Ajayan, W. Blau, D.L. Carroll, J.N. Coleman, A.B. Dalton, A.P. Davey, A. Drury, B. McCarthy, S. Maier, A. Strevens, *Adv. Mat.* 10 (1998) 1091.
- [13] R.J. Chen, Y. Zhang, D. Wang, H. Dai, *J. Am. Chem. Soc.* 123 (2001) 3838.
- [14] P.C. Eklund, B.K. Pardhan, U.J. Kim, Q. Xiong, J.E. Fisher, A.D. Friedman, B.C. Holloway, K. Jordan, M.W. Smith, *Nano. Lett.* 2 (2002) 561.
- [15] P.T. Lillehei, C. Park, J.H. Rouse, E.J. Siochi, Imaging carbon nanotubes in high performance polymer composites via magnetic force microscopy, *Nano. Lett.* 2 (2002) 827.
- [16] T.J. Mason, *Sonochemistry: The Uses of Ultrasound in Chemistry*, The Royal Society of Chemistry, Cambridge, 1990 (Chapter 1).
- [17] S. Kirkpatrick, *Rev. Mod. Phys.* 45 (1973) 574.
- [18] M. Weber, M.R. Kamal, *Polym. Comp.* 18 (1997) 711.