

2001

Conducting polymer-carbon nanotubes composites

May Tahhan

University of Wollongong, uow_tahhanm@uow.edu.au

N. Barisci

University of Wollongong

Gordon G. Wallace

University of Wollongong, gwallace@uow.edu.au

Follow this and additional works at: <https://ro.uow.edu.au/scipapers>



Part of the [Life Sciences Commons](#), [Physical Sciences and Mathematics Commons](#), and the [Social and Behavioral Sciences Commons](#)

Recommended Citation

Tahhan, May; Barisci, N.; and Wallace, Gordon G.: Conducting polymer-carbon nanotubes composites
2001.

<https://ro.uow.edu.au/scipapers/1>

Conducting polymer-carbon nanotubes composites

Abstract

During the course of this work, three different approaches to the formation of conducting polymer/carbon nanotube (CP/CNT) composites were investigated. The first approach involved the preparation of CNT dispersions using Poly methoxy aniline-5-sulfonic acid (PMAS) as a stabilizer. The second approach investigated involved the use of CNT as the dopant in the electropolymerization of CPs. The third approach involved the electrochemical deposition of a thin polymer film onto the surface of CNT paper. These CNT/CP composites were characterized to determine capacitance, conductivity and mechanical strength.

Keywords

capacitance, carbon nanotubes, composite materials, conducting polymers, electrical conductivity, mechanical strength

Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

Publication Details

This paper was originally published as: Tahhan, M, Barisci N and Wallace, GG, Conducting polymer-carbon nanotubes composites, Proceedings of the 2001 1st IEEE Conference on Nanotechnology, 28-30 October 2001, 229-232. Copyright IEEE 2001.

Conducting Polymer – Carbon Nanotubes Composites

Tahhan, M., Barisci, N., Wallace, G.G.

Intelligent Polymer Research Institute, University of Wollongong,
Northfields Avenue, Wollongong, NSW 2522, Australia.

Introduction

The discovery of nanotubes (1) has created a great deal of interest due to the exceptional properties they exhibit. For example, a high electrical conductivity of 5000 S/cm (2) and elastic modulus of > 640 GPa for a single nanotubes "rope" (3), as well as a very high toughness and buckling resistance (4) have been reported.

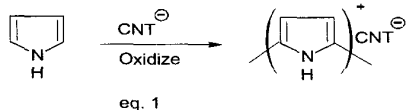
Our Recent work on nanotubes actuators (5) suggests that these materials will exceed all other actuator materials in terms of stress generation, switching speed and operating lifetime. Others have shown that carbon nanotubes (CNT) will be useful as sensing material (6), hydrogen storage (7) and as the active component in supercapacitors (8).

Electrofunctional materials, such as conducting polymers (CPs), are also intriguing molecular structures because of their ability to dramatically change properties when simulated by an electrical signal (9). These materials offer exciting prospects for a wide range of new devices such as smart windows, artificial muscles, membranes, solar cells, batteries, capacitors, and even corrosion protection coatings. The electrofunctional ability can also be used for sensor applications, where an electrical signal is generated by a change in environment. Often practical applications of CPs are hindered by the limited mechanical strength or the low conductivity of the material.

By combining CNT and CPs we aim to significantly improve the performance of CPs devices such as sensors and actuators (10). Literature and recent experimental evidence support the viability of our proposed approach. CPs have already been deposited on CNT by ourselves as well as Ajayan et al (11). Work by Coleman and co-workers (12) showed that the luminescent performance of poly (p-phenylene vinylene) polymers was enhanced by incorporating CNT into the polymer matrix. Others have coated CNT dispersions using chemical oxidation approach and shown that CNT do, indeed, affect the electrochemical properties of CPs. (13).

During the course of this work, three different approaches to the formation of CP/CNT composites were investigated. The first approach involved the preparation of CNT dispersions using Poly methoxy aniline-5-sulfonic acid (PMAS) as a stabilizer. These dispersions were characterized using UV-Vis, particle size and zeta potential and then filtered to produce CNT paper. The properties of the dispersions as well as the mats formed from these dispersions have been investigated and compared to material produced using a smaller molecular dispersant (SDS – sodium dodecyl sulfate) as well as a non-conducting polymeric dispersant (PVA – poly vinyl alcohol).

The second approach investigated involved the use of CNT as the dopant in the electropolymerization of CPs, equation (1).



The third approach involved the electrochemical deposition of a thin polymer film onto the surface of CNT paper. These CNT/CP composites were characterized to determine capacitance, conductivity and mechanical strength.

Experimental

1- TritonX 100 (TX100) standard dispersion preparation.

1g of CNTs (grown catalytically and supplied by Rice company), and 0.1g of TritonX 100 were added to 100ml Milli-Q water, and then sonicated for 30min.

2- Preparation of Poly(vinyl diene fluoride) (PVDF) filter paper.

PVDF filter paper with pore size of 0.22µm were cut to size to fit the microfiltration cell, the filters were wet in 50:50 v/v Milli-Q water to ethanol for 1 hour.

3- Preparation of surfactant solutions.

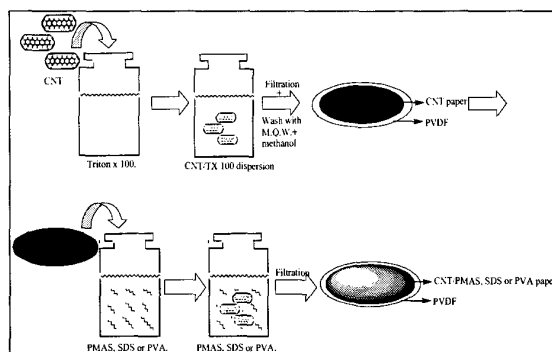
A 0.2% w/w surfactant to water solution of Poly(vinyl alcohol) (PVA) anionic, Poly(methoxy aniline 5-sulfonic acid) (PMAS) inherently conducting polymer, and 0.1M of Sodium dodecyl sulfate (SDS) anionic, were prepared.

4- Preparation of dispersions.

50ml of TX100 standard dispersion were filtered using the previously wet PVDF membrane in a stirred filtration cell (model 8050 purchased from Amicon/Millipore) under nitrogen pressure of 400KPa. The resultant CNTs mat was washed with 150ml of Milli-Q water then 150ml methanol; methanol is used to remove any remaining TX100. The CNTs mats were peeled of the PVDF membrane, each mat was placed in 20ml of each of the surfactant solutions, which were then sonicated for 4-hours, an additional 20ml of each of the surfactant solutions were added to the different dispersions and then sonicated for further 4-hours.

5- CNTs mats from the different dispersions.

50ml of each of the different dispersions prepared previously were filtered through PVDF membranes, under nitrogen pressure of 400Kpa, and CNT/surfactant mats were obtained Scheme (1).



Scheme (1). Preparation CNT/surfactant papers.

Results and discussion

1. Characterization of CNT/surfactant dispersions

1.1 Electrochemical characterization

Cyclic voltammograms for each of the different surfactant solutions were recorded, Pt, Au, and glassy carbon electrodes were used as the working electrode. The potential window varied depending on the electrode. In general, for Pt-electrode $E = -0.8, +1.2V$, for Au-electrode and glassy carbon electrode $E = -0.4, +1.2V$.

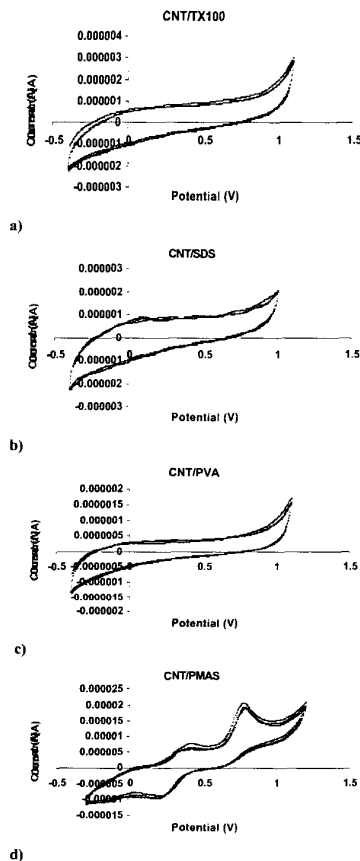


Fig.1. Cyclic Voltammetry of CNT paper, a)CNT/TX100, b)CNT/SDS, c)CNT/PVA and d)CNT/PMAS in 0.1M $NaNO_3$. The following electrodes were used Ag/AgCl reference electrode, Pt-mesh auxiliary electrode and glassy carbon working electrode. The potential window was $E = -0.4, +1.2V$, and the scan rate was 50mV/s.

As we can see from the cyclic voltammograms (CV's) for the different surfactant, the CV's for CNT, CNT/SDS, and CNT/PVA do not exhibit reduction/oxidation peaks. However, the CV for the CNT/PMAS does exhibit redox peaks, which is the expected electrochemical behavior of a conducting polymer.

1.2 UV-Vis spectra of CNT/surfactant dispersion

A UV-1601, UV-Visible spectrophotometer (Shimadzu), was used to recorded the UV-Vis spectra of the different dispersions.

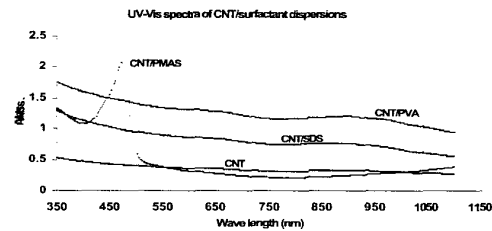


Fig 2. UV-Vis spectra of CNT/surfactant dispersion.

As expected the only dispersion that showed a response was the CNT/PMAS dispersion around 400nm. This is due the yellow color of PMAS.

2. Characterization of CNT/surfactant mats

2.1 Conductivity

A digital micrometer was used to measure the thickness of the CNT mats. The CNT/surfactant mats were cut into 2.5cm X 0.3cm pieces, and four point probe resistance measurements were recorded, Table 2. A constant current of 1mA was passed through the outer two electrodes and the voltage difference between the inner two electrode was measured after 10sec. This measurement was repeated four times for each sample.

Table 2.

Mat	Thickness (μm)	σ (S/cm)
CNT (TX)	41	160
CNT (DS)	33	175
CNT (PVA)	22	1×10^{-5}
CNT (PMAS)	20	307

The results in Table 2, provide further evidence of the polymer being retained in the matrix of the CNT mat. Where a much more insulating composite was obtained with PVA as dispersant and the most highly conducting sample was that containing the electronically conducting PMAS.

2.2 Capacitance

The electrochemical cell consisted of a Pt-mesh electrode as the auxiliary electrode an Ag/AgCl as the reference electrode, a 2.5 X 0.5 cm pieces of the different mats was used as the working electrode. The electrolyte used was 1M $NaNO_3$.

The Scan rates used were 50, 25, 10, 5 mV/s, the potential window was $E = -0.1, +0.3 V$. Measurements were taken at $E = 0.1V$. The difference between the oxidation and reduction current was plotted as a function of the scan rate. The best straight line was plotted, and the capacitance measured from its slope.

In all cases a response indicative of the capacitive nature of the CNT electrodes was observed. Values were significantly low when the insulating polymer PVA was used as dispersant, Table 3

Table 3.

Mat	Capacitance F/g
CNT (TX)	39
CNT (DS)	35
CNT (PVA)	0.02
CNT (PMAS)	29

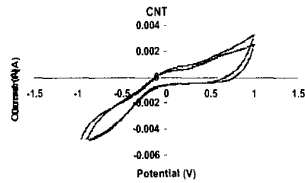


Fig.4 Cyclic Voltammety of CNT paper, CNT/TX100 in 1M NaMO₃. The potential window was E = -1, +1V. The scan rate was 50mV/s.

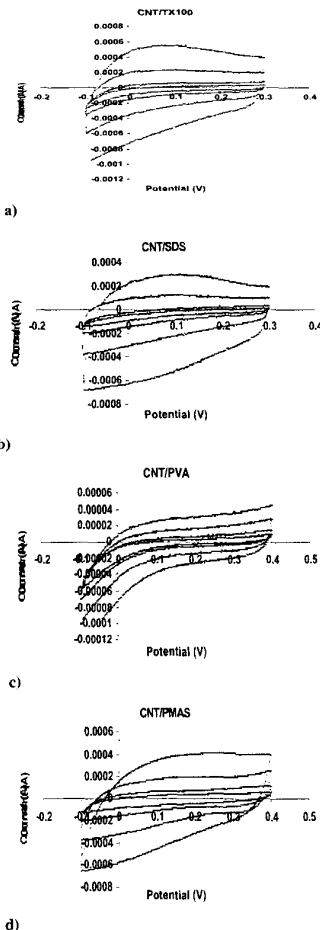


Fig.5 Cyclic Voltammety of CNT paper, a)CNT/TX100, b)CNT/SDS, c)CNT/PVA and d)CNT/PMAS in 1M NaMO₃. The potential window was E = -0.1, +0.3V. Different scan rates were applied 50mV/s, 25mV/s.

2.3 Mechanical Properties

The mechanical properties were measured using Instron 4302. 10N were applied as force, and the speed used was 1mm/s. From the recorded measurements Force (N) was plotted against Extension (mm). Also, Stress σ (MPa) = F(N) / W(mm) X T (mm), was plotted against strain, where strain = Extension(mm)/Gage length(mm). From the plot of Stress vs. Strain we can obtain σ_{Break} (MPa), and ϵ_{Break} %. Also, from the slop of the curve we can calculate E (young modulus) GPa.

The values obtained for Young's modulus (Y) Table 4, were low compared to the values reported by other groups (14). However, there are many factors to consider. First, the CNT mat that was used in these measurements was not annealed. Secondly the Y value when considering single walled CNT depends on the diameter of the CNT. The Y value for a single CNT have been reported to be about 1 TPa, while for a rope of CNT (15-20nm in diameter) the Y values drops to about 100 GPa. (15). This is reflected in our study where the paper used consists of bundles of combined ropes, which means that the Y value will be much smaller as seen in Table 4. In addition, the value for the cross sectional area used when calculating the stress values is not the real area, since we are using a mesh of ropes and not a single rope. This also means that there are pockets of air within the mesh. Finally, the stress values obtained are more probably due to shear stress than to tension stress.

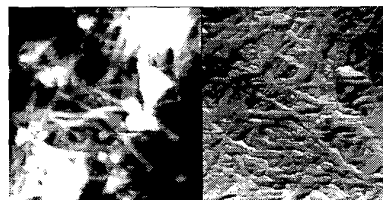
Table 4.

Mat	σ_{Break} (MPa)	ϵ_{Break} %	Y (GPa)
CNT (TX)	3	3	0.15
CNT (DS)	Weak	Weak	Weak
CNT (PVA)	Weak	Weak	Weak
CNT (PMAS)	47	1	6.40

The sample that combines CNT and the conducting polymer has the highest Young's modulus value 6.4 GPa. This indicates that these composites do actually have improved mechanical properties.

3.4 AFM

The morphology of the mats formed from each dispersant was examined using AFM Fig 6, and was found to be similar in each case. However, the CNT ropes are more entangled, bulkier and longer in some papers than others. This means that different surfactants affect the packing order of the CNT ropes with in the matrix of the papers, which in turn will affect the mechanical properties of these papers.



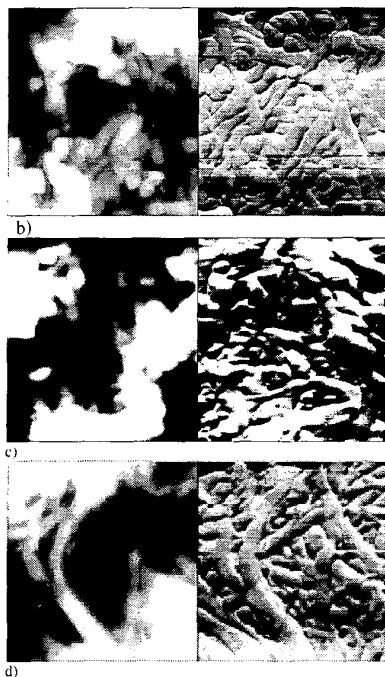


Fig 6 AFM pictures of the different CNT papers, a)CNT/TX100, b)CNT/SDS, c)CNT/PVA and d)CNT/PMAS at 1 μ m.

12. J. N. Coleman, A.B. Dalton, *et al*, *Proc. - Electrochem. Soc.*, **98-25**: 147-153, 1998.
13. J. Fan, M. Wan, D. Zhu, B. Chang, Z. Pan, and S. Xie, *J. Appl. Polym. Sci.*, **74**(11): 2605-2610, 1999.
14. Y. Min-feng, S. B. Files, S. Arcipalli, and R.S. Ruoff, *Phys. Rev. Lett.*, **84**(24): 5552-5555, 2000.
15. L. Yulin, and P. K. Liaw, *JOM*, **53**(3): 31-41, 2001.

Conclusion

It is envisaged that more highly conducting (with higher capacitance) papers with better mechanical properties can be produced using customized stabilizers that are electronically conductive and that can be later crosslinked to bind the paper together.

References

1. S. Iijima, *Nature*, **354**: 56, 1991.
2. R. S. Lee, H.J. Kim, J.E. Fischer, A. Thess, and R.E. Smalley, *Nature*, **388**(6639): 255-257, 1997.
3. D. A. Walters, L.M. Ericson, *et al*, *Appl. Phys. Lett.*, **74**(25): 3803-3805, 1999.
4. M. R. Falvo, G.J. Clary, *et al*, *Nature*, **389**(6651): 581-584, 1997.
5. R. H. Baughman, C. Cui, A.A. Zakhidov, Z. Iqbal, J.N. Barisci, G.M. Spinks, G.G. Wallace, A. Mazzoldi, d. De Rossi, A.G. Rinzler, *et al.*, *Science*, **284**(5418): 1340-1344, 1999.
6. A. Fisher, R. Hoch, D. Moy, C. Niu, N. Ogata, and H. Tennent, in *PCT Int. Appl.*, Wo. p. 77 pp, 1996.
7. M. Bockrath, D.H. Cobden, *et al*, *Science*, **275**(5308): 922-1925, 1997.
8. C. Niu, E.K. Sichel, R. Hoch, D. Moy, and H. Tennent, *Appl. Phys. Lett.*, **70**(11): 1480-1482, 1997.
9. G. G. Wallace, G.M. Spinks, and P.R. Teasdale, *Conductive Electroactive Polymers: Intelligent Materials Systems*, Lancaster, PA: Technomic, 169 pp, 1996.
10. G. M. Spinks, S. Moulton, T.W. Lewis, and G.G. Wallace, *Synthetic Metals*, 2000. **In Press**.
11. C. Downs, J. Nugent, P.M. Ajayan, D.J. Duquette, and S.V. Santhanam, *Adv. Materials*, **11**(12): 1028-1031, 1999.