

# **Development of Carbon Nanotubes and Polymer Composites Therefrom**

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#### **Abstract**

Multiwall carbon nanotubes (MWNT) were produced using the arc-discharge graphite evaporation technique. Composite films were developed using MWNT dispersed in polystirol polymer. In the present work, various properties of the polymeric thin film containing carbon nanotubes were investigated by optical absorption, electrical resistivity and the same have been discussed.

Keywords: carbon nanotube, arc-discharge evaporation, polymer composite

## 1. Introduction

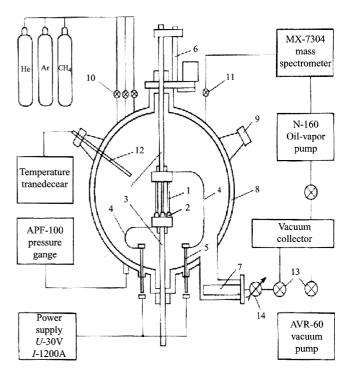
The discovery of the carbon nanotubes has created enormous interest in the recent years due to their unique structures and properties [1]. This led to much speculation about their unexplored properties and potential applications [1-3]. It has been established that depending upon the structure, they are either metallic or semiconducting and also have exceptional mechanical properties [4-5]. However, the actual applications of the carbon nanotubes are still to be explored in commercial terms. Since the size of the particles are in the in order of nano-dimensions, new technology become apparent but control and manipulation become difficult. An attempt has been made to develop the carbon nanotubes composite films with polymer (Polystrol) and evaluates its various properties like electrical resistivity, optical properties etc..

# 2. Experimental

#### 2.1. Development of multiwall Carbon Nanotubes

Multiwall carbon nanotubes (MWNT) were produced using the arc-discharge graphite evaporation technique. The apparatus for arc discharge graphite evaporation is described in the Figure 1 [6, 7]. A vacuum chamber of 50 cm in diameter and 150 litres in volume has double water-cooled walls. The electrodes were installed vertically in the centre of the chamber. Diameter of the lower graphite cathode was 60 mm. The upper movable anode was combined of seven 6 mm-diameter and 200 mm-length graphite rods (Spectroscopic Grade), which were spaced from each other by about

1 cm. The d.c. arc current was typically 800 Ampere at 35-40 Volts. The arc vaporisation was carried out in He gas of



**Fig. 1.** Experimental Set Up for the Synthesis of Multiwall Carbon Nanotubes 1) Graphite Electrodes, 2) Electric Arc, 3) Water cooled manipulators, 4) Flexible current leads, 5) Vacuum -tight current leads, 6) Manipulator drive, 7) Cloth filter, 8) Water cooled chamber shell, 9) Windows, 10, 11) Finely tuned gas valves, 12) Movable thermocouple, 13) Vacuum valves and 14) Pressure setting valves.

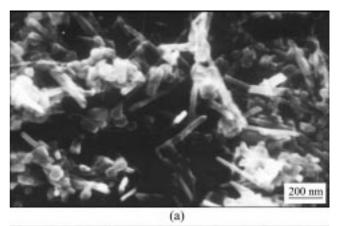
800 Torr. Simultaneous evaporation of seven rods during 15-20 minutes produces a carbon deposit at cathode up to 40 mm in diameter and about 30 mm height. The cathode deposit weight may achieve up to 50 wt% of the evaporated rods depending on their moving rate and the He gas pressure.

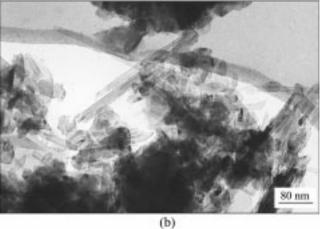
#### 2.2. Development of the composite films

Composite films from Multiwall carbon nanotubes (MWCNT) dispersed in Polystrol polymer is developed. The ratio of the MWCNT and the polymer was kept about 50% by weight and the thickness of the film was around 150-200 microns. Electrical resistivity of the composite films were measured from 4 K to 300 K by four point contact method. Optical absorption of the composite film was measured on Photometer KFK-3 Russian Model in the wavelength range of 300-1000 nm. Transmission Electron micro-graphs were taken on JEM-2010.

## 3. Results and Discussions

Electrode (cathode) deposits of graphite which is mainly carbon nanotubes (about 70-80%) rest is polyhedral graphitic phase. The arc discharge process is characterised by extremely high temperature, presence of electromagnetic fields, significant pressure and temperature gradients. These extreme conditions make it possible to produce metastable nanometer-scale carbon structures. Carbon soot condensed on the water-cooled reactor walls contains cage molecules fullerenes C<sub>60</sub>, C<sub>70</sub>, or, when catalytic metal particles are coevaporated, single-wall nanotubes (SWCNT) can be produced. A carbon deposit filled by multiwall nanotubes, polyhedral and quasi-spherical particles, and amorphous carbon growths onto the cathode. The cathode deposit growth rate, its size and morphology depend on several conditions: type and pressure of buffer gas; arc current characteristics; size, configuration and moving rate of electrodes, and the addition of another elements to the anode material. Usually, the deposit is defined roughly in two regions, namely, outer 3-5 mm thick part looking as petal-like material from graphite sheets and inner part consisting of nanoparticles. Figure 2a shows the scanning electron photograph of the inner part of the deposit of the pristine material of the carbon nanotubes that is as deposited on the cathode. Figure clearly shows that many tubular structures are present along with other graphiteic phase. Figure 2b shows the Transmission Electron Micrographs of the carbon nanotubes. Micrographs clearly shows that deposit electrode is enrich in the carbon nanotubes. However, other graphitic phase is also present which clearly brings out that separation or purification of the carbon nanotube without damaging the end caps is quite diffcult. From the TEM photograph it has been observed that most of the carbon nanotubes are with closed endings.

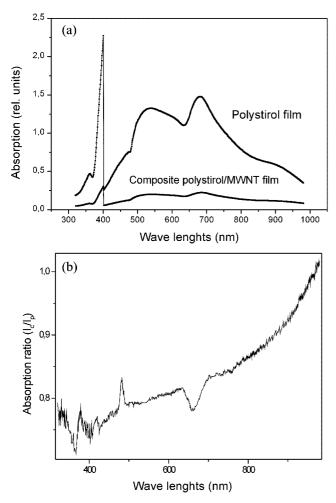




**Fig. 2.** Micrographs of the Carbon Nanotubes. (a) Scanning Electron Micrograph (SEM), (b) Transmission Electron Micrograph (TEM).

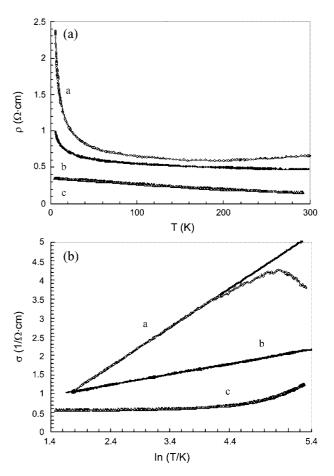
Optical absorption spectra of composite film presented on Figure 3. In the figure, the curves are shown for only Polystrol resin film and of the polymeric composite film containing the carbon nanotubes. From the figure it is clear that the curve of composites film has about five to six times less absorption which may be attributed due the presence of the carbon nanotubes, which are showing absorption. When these two curves are normalised that is from the curve of polystrol resin curve of composite film is divided so that the contribution of the carbon nanotubes alone can be obtained and the same is plotted in the Figure 3(b). From this curve there are some additional peaks have observed at about 500 nm, which may be attributed due to the interactions of the polymer resin and the carbonaceous materials.

Electrical resistivity of the composites films was measured using four point contact technique in the temperature interval of 4.2-300 K. The dependence of electrical conductivity with temperature is shown in Figure 4. Typical behaviour of the temperature dependence of the conductivity is presented for the composite film (Figure 4a). In the figure, curve 'a' and 'b' are of the polymer composite films and curve 'c' is of the



**Fig. 3.** Optical Spectra of Polymer and Composite Film. (a) Polymer and Composite Film, (b) Only Carbon Nanotubes.

as deposited cathode material (Pristine material). Figure 4 is having linear curve as well as the logarithim scale curve of the conductivities of the films. Since the resitivity of the polymer composite film is enormously high as compared to the pristine material, the curve of the pristine material (curve c) is normalised to the same scale by dividing it by a factor of 5000 The temperature dependencies are non-metallic from 300 K up to 4.2 K, in accordance to the measurements made for individual multiwall nanotubes and for multiwall nanotube bundles [8]. Curves in Figure 4 show the following to the logarithmic temperature dependence. Similar conductivity dependence, being characteristic of disordered twodimensional systems. Such proportion has been shown to be typical for the two-dimensional disordered conductors. Nonmetallic behavior of  $\sigma(T)$  may be caused by structural defects in nanotubes composing the carbonaceous sample. Actually, the measurements on the individual multiwall nanotube demonstrated that the resistivity of defective nanotubes is an order of magnitude larger that of straight



**Fig. 4.** Electrical Resistivity of the Composites Film (a) and (b) Polymer Composite Film (c) Pristine Material (Carbon nanotubes as deposited). [In Graph 'a' values of Curve c is multiply by 5000 and in Graph 'b' curve c is divided by 5000 to make in same scale'.

nanotubes [9]. From the electrical resitivity test measured from 4 K to 300 K, it is evident that the resistivity of the polymer film is high as compared to the pristine material (Carbon nanotubes). However it is possible to develop conducting polymer film containing carbon nanotubes.

#### 4. Conclusions

Developed the Multiwall Carbon Nanotubes (MWCNT) using the arc-discharge graphite evaporation technique. Developed the polymeric films containing carbon nanotubes. It is found that from the optical absorption of the composite film that the some of the carbon nanotubes have shown the absorption capabilities. Even though the electrical conductivity of the polymeric composite film is far less as compared to the pristine material but conducting polymer films can be developed by dispersing carbon nanotubes which may find some good applications in near future.

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#### References

- [1] Iijima, S. Nature 1991, 354, 56.
- [2] Heer, W. A. de.; Chatelain, A.; Ugarte, D. Science 1995,

- 270, 1179
- [3] Tans, S. J.; Devoret, M. H.; Dai, M.; Thess, A.; Smalley, R. E.; Geerligs, L. J.; Dekker, C. *Nature* **1997**, *386*, 474.
- [4] Mintmire, J. W.; Robertson, D. H.; White, C. T. J. Phys. Chem. Solids. 1993, 54, 1835.
- [5] Chico, L.; Benedict, L. X.; Louie, L. G.; Cohen, M. L. Phys. Rev. 1996, B54, 2600.
- [6] Okotrub, A. V.; Shevtsov, Yu. V.; Nasonova, L. I.; Sinyakov, D. E.; Novoseltsev, O. A.; Trubin, S. V.; Kravchenko, V. S.; Mazalov, L. N. *Pribory and Tekhnika Experim.* 1995, 1, 193.
- [7] Okotrub, A. V.; Shevtsov, Yu. V.; Nasonova, L. I.; Sinyakov, D. I.; Chuvilin, A. L.; Gutakovskii, A. K.; Mazalov, L. N. Neorgan. Mater. 1996, 32, 974.
- [8] Kaiser, A. B.; Dusberg, G.; Roth, S. Phys. Rev. 1998, B 57, 1418
- [9] Dai, H.; Wong, E. W.; Lieber, C. M. Science 1996, 272, 523.