



ISSN NO. 2320-5407

Journal homepage: <http://www.journalijar.com>

INTERNATIONAL JOURNAL  
OF ADVANCED RESEARCH

## RESEARCH ARTICLE

## Synthesis, Characterization and Electrical Properties of poly(*m*-toluidine)/modified MWCNT Conducting Polymer Composites

Biswa Ranjan Sarangi, Matru Prasad Dash  
Synergy Institute of Technology, Bhubaneswar

### Manuscript Info

#### Manuscript History:

Received: 08 May 2013  
Final Accepted: 18 May 2013  
Published Online: June 2013

#### Key words:

Multiwalled Carbonnanotube (MWCNT), poly(*m*-toluidine); polymerization; conducting polymer

### Abstract

We describe here the synthesis of hydrochloric acid (HCl) doped poly(*m*-toluidine) (PMT) with carboxylic groups containing multi-walled carbon nanotubes (c-MWCNTs) via in situ polymerization. *m*-Toluidine monomers were absorbed on the surface of MWCNTs and polymerized to form PMT/c-MWCNT composites. The composites were characterized by using FTIR, SEM, TEM and XRD analysis. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images showed that both the thinner fibrous phase and the larger block phase could be observed. The individual fibrous phases had diameters about 100 nm, and therefore must be the carbon nanotubes (diameter 20–30 nm) coated by a PMT layer. The electrical conductivities of PMT/c-MWCNT composites were improved relative to those of PMT without c-MWCNTs.

Copy Right, IJAR, 2013;. All rights reserved.

## 1. Introduction

Carbon nanotubes (CNTs) including multi-walled and single-walled carbon nanotubes (MWCNTs and SWCNTs, respectively) with exceptional structural, mechanical and electronic properties [1, 2] have received considerable interest in fabricating advanced functional materials [3, 4]. Currently, much attention is paid to the formation of CNTs/conducting polymer composites which are considered as a promising approach to exploit synergetic effects arising from the components and show potential for many electronic devices such as PEDOT/CNTs in organic light emitting diodes, PPV/CNTs in photovoltaic cells, PPy/ CNTs in battery and PANI/CNTs in supercapacitors [5–7]. Among various conducting polymers, PANI is a promising candidate for practical applications due to its good processibility, environmental stability and reversible control of electrical properties by both charge-transfer doping and protonation [8]. The combination of CNTs and PANI into composite materials by

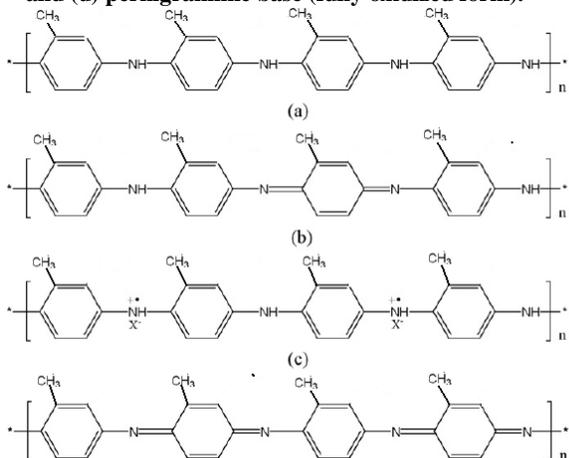
tailoring their properties has stimulated researchers interest in this unexploited field of research. Extensive efforts have been made to fabricate PANI/CNTs composites based on physical adsorption of PANI onto the surface of CNTs and grafting of PANI onto CNTs by functionalization of nanotubes [9]. Non-covalent methods show the advantage of leaving electronic structure of CNTs intact, but it is a more effective way to disperse SWCNTs than MWCNTs since polymer chain length and surface coverage necessary for inducing steric repulsion in MWCNTs dispersions are much higher than those required for dispersion of SWCNTs [10]. Also, insolubility of pristine CNTs in solvents and lack of compatibility with polymers cause bad dispersion of CNTs and block the application of such composites [11–13]. Therefore, it is necessary to introduce the strength of binding between MWCNTs and conjugated polymers to increase interaction between components in the composites [14]. The best way to solve the problem is to create functional groups on the back bone of MWCNT. Attachment of functional groups to MWCNTs can increase the solubility of nanotubes in solvents for better processing. Modified MWCNTs

\*Corresponding author: Dr Matru Prasad Dash  
Asst Professor in Physics, Synergy Institute of Technology, Bhubaneswar

can be easily fixed on the interface via chemical bonds [15] or doping effect such as PANI nanostructures doped with sulfonated MWCNTs via a self-assembled process [16]. However, the major disadvantage of PANI/CNT is its insolubility in common organic solvents and its infusibility. Preparation of alkyl group substituted PANI/CNT is a method to obtain soluble PANI/CNT composites. Soluble methyl-substituted PANI called poly (m-toluidine) (PMT) have been synthesized by electrochemical and chemical method. Recently, PMT was also found to have additional advantage with respect to PANI due to its faster switching time between the oxidized and the reduced states .Fig. 1 outlines the four different oxidation states of PMT.

In the present communication, we wish to describe the synthesis and characterization of PMT with MWCNT fabricated by in situ polymerization .The nanocomposites were characterized by a number of techniques including Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and electrical conductivity.

**Fig. 1. Four different redox forms of PMT: (a) leucoemeraldine base (fully reduced form), (b) emeraldine base (halfoxidized form), (c) conducting emeraldine salt (half-oxidized and protonated form), and (d) pernigraniline base (fully oxidized form).**



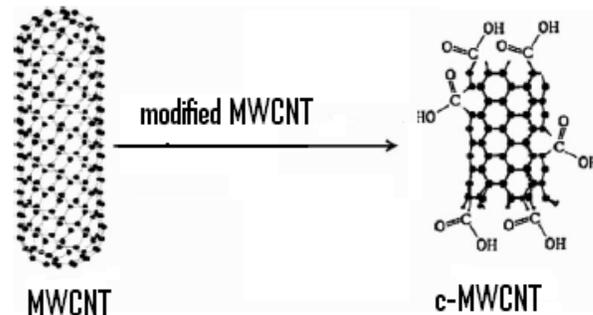
## 2. Work-up procedure.

### 2.1 Materials.

m-Toulidine was purchased from Aldrich, Multi-walled CNT (<90% purification) used in this study was purchased from Cheap Tubes (USA, 10– 20 nm diameter). Other reagents like ammonium persulfate (APS), hydrochloric, sulfuric, and nitric acid (Sigma Chemicals) were of analytical grade.

## 2.2Oxidation of MWCNT:

**Fig2.Modification of MWCNT**



MWCNTs were suspended in a 3:1 mixture of concentrated H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> and refluxed for 30 min in an ultrasonic bath. The solution was magnetically stirred and heated at 60 °C for 24 h. This treatment provides carboxylic acid groups at defects in the surface of tubes and exfoliates graphite. The obtained c-MWCNTs were filtered through 0.2- $\mu$ m polytetrafluoroethylene (PTFE) membrane filter, washed with plenty of deionized water until the pH value was around 7, and then dried at 70 °C for 24 h. The expected modified structure of c-MWCNT is shown in the fig-2

## 2.3 Synthesis of PMT/c-MWCNT polymer composites.

PMT/c-MWCNT composites were synthesized by in situ chemical oxidative polymerization. In a typical composite synthesis experiment, various weight ratio of c-MWCNTs were dissolved in 80mL 1M hydrochloric acid solutions and ultrasonicated over 2 h, then transferred into a 250mL beaker. 0.428 g m-toluidine monomer was added to the above c-MWCNTs suspension. Then a 20ml 1M hydrochloric acid solution containing 0.912 g ammonium persulfate (APS) was added into the suspension with constant mechanical stirring at room temperature. The reaction mixture was stirred for a further 12 h, and then filtered. The remaining filter cake was rinsed several times with distilled water and ethanol. The powder thus obtained was dried under vacuum at 60 °C for 24 h. The % of c-MWCNT were used 0, 2, 5%.

## 3. Measurements.

### 3.1 FTIR spectra.

The Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 8700 spectrometer, in the range 400–4,000 cm<sup>-1</sup>

### 3.2Morphology

Morphology of the PMT/c-MWCNT composite was investigated using a Philip XL 30 SEM at an accelerating voltage of 25 kV. The sample was

fractured at liquid nitrogen temperature and then was coated with a thin layer of gold before observation.

### 3.3 TEM

TEM experiments were performed on a Hitachi H-8100 electron microscope with an acceleration voltage of 200 kV.

### 3.4 XRD.

X-ray diffraction (Rigaku, D/Max, 2,500 V, Cu-K $\alpha$  radiation: 1.54056 Å) experiments were carried out on both the plain PMT and the composite samples. Wide-angle X-ray diffractograms were recorded at temperature of 30 °C after isothermal crystallization at this temperature for 1 h in the range of 0–70 (2 $\theta$ ).

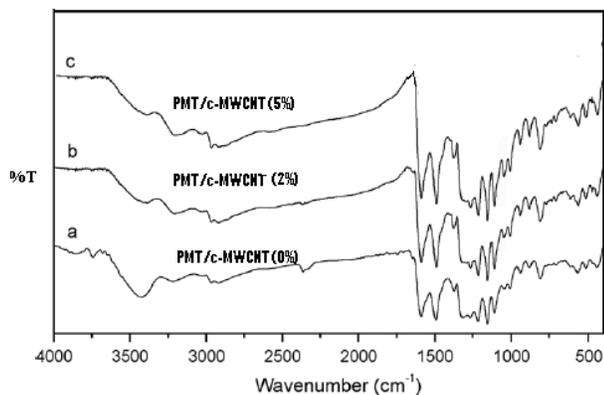
### 3.5 Conductivity.

The standard Van Der Pauw DC four-probe method was used to measure the electron transport behaviors of PMT and PMT/c-MWCNT composites. The samples of PMT and PMT/c-MWCNTs were pressed into pellet. The pellet was cut into a square. The square was placed on the four probe apparatus, providing a voltage for the corresponding electrical current could be obtained. The electrical conductivity of samples was calculated by the following formula:  $\sigma$  (S/cm) =  $(2.44 \times 10^4 / S) \times (I/E)$ , where  $\sigma$  is the conductivity, S the sample side area, I the current passed through outer probes, and E the voltage drop across inner probes.

## 4. Results and discussion.

### 4.1.FTIR.

Fig3. FTIR of PMT/c-MWCNT

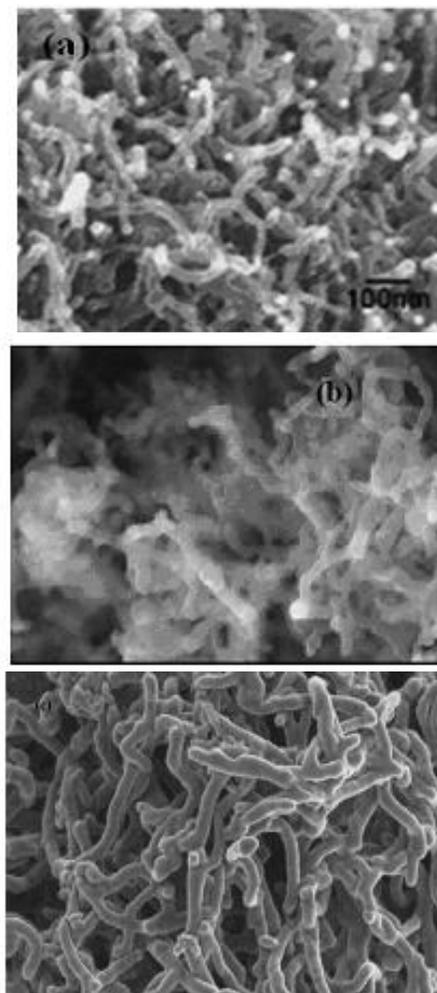


The FTIR spectra of PMT and PMT/c-MWCNT composites are presented in Fig.3. For PMT, the absorption band at around 3220 cm<sup>-1</sup> corresponds to N–H stretching mode of secondary amine. The two bands at around 1490 and 1592 cm<sup>-1</sup> are assigned to the stretching vibration of the benzoid and

quinonoid ring. The characteristic band at 2918 cm<sup>-1</sup> can be assigned to the stretching vibration of the methyl (–CH<sub>3</sub>) group. The band at 1375 cm<sup>-1</sup> is due to the symmetric deformation of methyl group. The bands at 1316 and 1210 cm<sup>-1</sup> can be assigned to the C–N vibration. The three bands appearing at 807, 877 and 936 cm<sup>-1</sup> are attributed to an out-of-plane C–H vibration, 1,2,4-substitution in the benzenoid rings, and an in-plane C–H vibration of quinoid rings. All of these data are similar to the spectra of PMT salts, which confirm that the obtained sample is in its doped phase[17]. Clearly, the FTIR spectra of PMT/c-MWCNT composites are almost identical to that of PMT, indicating that m-toluidine was polymerized on the surface of c-MWCNTs to form PMT/c-MWCNT composites.

### 4.2 SEM.

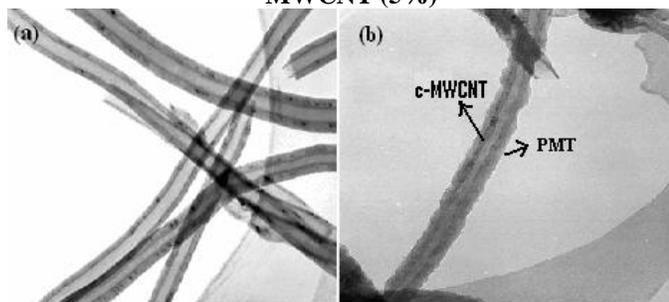
Fig4. SEM images of; a. c-MWCNT; b.PMT/c-MWCNT (2%); c.PMT/c-MWCNT (5%)



The SEM pictures of the pristine c-MWCNTs, and nanocomposite with 2, and 5, % of c-MWCNTs are presented in Fig.4. Figure 4a shows the disentanglement of the c-MWCNTs, and the slight reduction in the length of the nanotube is observed after oxidation with 3:1 concentrated H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> mixture. In the case of nanocomposites (Fig. 4b,4c), a tubular layer of coated copolymer film is clearly present on the surface of c-MWCNTs, and the diameter of the nanocomposite is increased substantially as compared to that of the c-MWCNTs, depending on the copolymer content. From these observation, it can be attributed that the coating of copolymer takes place only at the outer surface of the c-MWCNTs. The formation of the copolymer-coated tubular nanocomposite is believed to arise from the strong interaction between the co-monomer and c-MWCNTs. This interaction is thought to be made up of two components: one is the  $\pi$ - $\pi$  electron interaction between the MWCNTs and the comonomer [18] and the other is the hydrogen bond interaction between the carboxyl group of the c-MWCNTs and amino group of the co-monomers. Such a strong interaction ensures that the comonomer molecules are adsorbed on the surface of the c-MWCNTs. The polymerization of co-monomer inside the c-MWCNTs is hindered by the restricted access of the reactants to the interior of the c-MWCNTs because of the presence of the carboxyl group at the meta position of the co-monomer. This is in agreement with the findings reported in the literature [19].

#### 4.3 TEM:

**Fig5. TEM image of a.MWCNT.b.PMT/c-MWCNT (5%)**

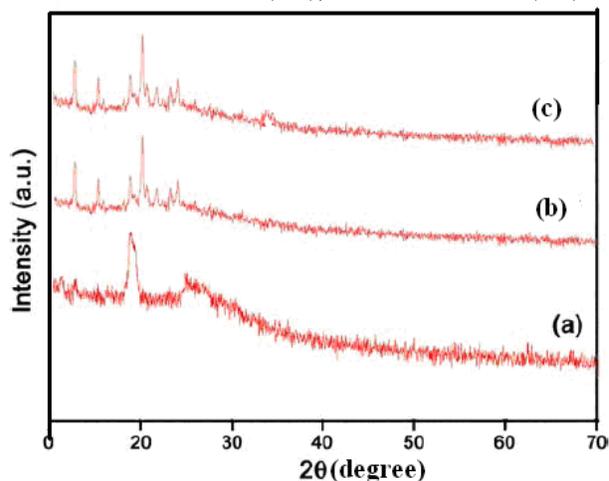


The TEM spectra of the c-MWCNT and PMT with 5% c-MWCNT are presented in Figure5. The uniform deposition of PMT on the c-MWCNT is similarly demonstrated by transmission electron microscopy (TEM), which shows the bilayered structure of coated C-MWCNT. As the internal cavity is well discernible, we conclude that the coating with PMT takes place only at the outer surface of the

c-MWCNT. The polymerization of PMT inside the c-MWCNT is hindered by the restricted access of reactants to the interior of the c-MWCNT. The comonomer molecules are uniformly polymerized on the surface of c-MWCNTs and form a tubular nanocomposite. The diameter of the nanocomposite becomes larger than that of the c-MWCNTs after polymerization.[20,21]

#### 4.4 XRD:

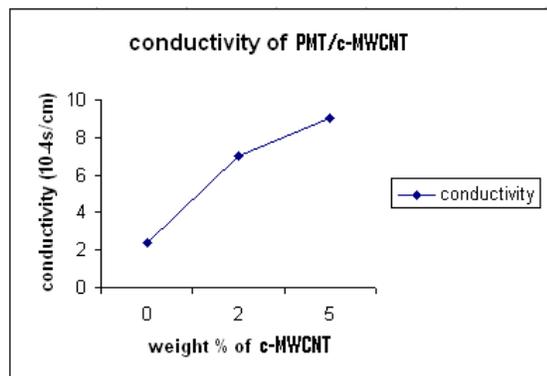
**Fig6. X-ray diffraction data of a PMT/c-MWCNT (0%); b PMT/c-MWCNT (2%); c PMT/c-MWCNT (5%)**



The X-ray diffraction data for PMT and PMT/c-MWCNT composites of 2 and 5% are shown in Fig. 6. The spectrum of bare copolymer depicts two peaks at the region of  $2\theta=18.1^\circ$  and  $25.2^\circ$  shown in Fig.6a which arise from the momentum transfer perpendicular to the chain direction [22, 23]. XRD pattern of nanocomposite (Fig. 6b and 6c) shows that there are two obvious phases: the copolymer phase and the c-MWCNTs phase which has several sharp peaks at  $2\theta=6.2^\circ$ ,  $11.8^\circ$ ,  $19.4^\circ$ ,  $20.9^\circ$ ,  $23.8^\circ$ , and  $26.3^\circ$ . It implies that the nanocomposites possess a more crystalline nature than the bare copolymer. This can be attributed to the fact that the crystalline phase of the copolymer is most probably developed in the nanocomposite matrix. The appearance of a small peak at  $2\theta$  value of  $26.3^\circ$  suggests the existence of c-MWCNTs in the nanocomposite [24].

#### 4.5 Conductivity:

**Fig. 7. Conductivity versus the weight percent of c-MWCNT/PMT composites**



The electrical conductivities of PMT and PMT/c-MWCNT composites are measured using the standard Van Der Pauw DC four-probe method and shown in Figure 7. The conductivity of MWCNT is about 0.2 S/cm. The conductivities of PMT synthesized in the presence of hydrochloric acid shows a room temperature conductivity of  $2.4 \times 10^{-4}$  S/cm. The lower room temperature conductivity of PMT than PANI probably has something to do with its substituted group and low protonic acid doping degree. Meanwhile, the addition of 2 wt.% c-MWCNT into PMT, the conductivity at room temperature increases from 2.4 to  $7 \times 10^{-4}$  S/cm. With the continuous increase in the content of c-MWCNT, the conductivity at room temperature gradually increases from  $7 \times 10^{-4}$  S/cm for 2 wt.% MWCNT-containing PMT/c-MWCNT composites to  $9 \times 10^{-4}$  S/cm for 5 wt.% MWCNT-containing PMT/c-MWCNT composites. The conductivities of PMT/c-MWCNT composites with 5 wt.% c-MWCNTs content at room temperature are much more higher than those of PMT without c-MWCNTs. The reason is probably that c-MWCNTs serve as a “conducting bridge” between the PMT conducting domains, which increases the effective percolation.

#### 5. Conclusion

PMT/c-MWCNTs nanocomposites were successfully synthesized via in situ polymerization method. SEM and TEM measurement ascertained that the c-MWCNTs were homogeneously dispersed in the copolymer matrix. The interaction between c-MWCNTs and copolymer chain was confirmed by FTIR. Room temperature conductivity of nanocomposite increased several times as increasing of percentage of c-MWCNT. The highly ordered structures of nanocomposites were confirmed by

XRD patterns. In addition, the versatility of this method could be extended to prepare other polymer/CNT nanocomposites by choosing appropriate experimental conditions.

#### Acknowledgments:

The authors are thankful to Mr. Binod Dash, Chairman, Synergy Group of Institutions for encouragement and suggestions.

#### References

- [1] S. Iijima, T. Ichihashi, 1993, 363, 603.
- [2] S. Iijima, Nature, 1991, 354, 56.
- [3] P.M. Ajayan, O. Stephan, C. Colliex, D. Trauth, Composite Science, 1994, 265, 1212.
- [4] E.W. Wong, P.E. Sheehan, C.M. Lieber, Science, 1997, 277, 1971.
- [5] H.S. Woo, R. Czerw, S. Webster, D.L. Carroll, Synth. Met, 2001, 116, 369.
- [6] H. Ago, K. Petritsch, M.S.P. Shaffer, A.H. Windle, R.H. Friend, Adv. Mater, 1999, 11, 1281.
- [7] S.R. Sivakkumar, W.J. Kima, J.A. Choi, D.R. MacFarlane, M. Forsyth, D.W. Kima, J. Power Sources, 2007, 171, 1062.
- [8] G. Premamoy, K.S. Samir, C. Amit, Eur. Polym. J, 1999, 35, 699.
- [9] B. Zhao, H. Hu, R.C. Haddon, Adv. Funct. Mater, 2004, 14, 1, 71.
- [10] R. Shvartzman-Cohen, E. Nativ-Roth, E. Baskaran, Y. Levi-Kalishman, I. Szleifer, R. Yerushalmi-Rozen, J. Am. Chem. Soc, 2004, 126, 14850.
- [11] V.G. Hadjiev, M.N. Iliev, S. Arepalli, P. Nikolaev, B.S. Files, Appl. Phys. Lett, 2001, 78, 3193.
- [12] A. Peigney, E. Flahaut, C. Laurent, F. Chastel, A. Rousset, Chem. Phys. Lett, 2002, 352, 20.
- [13] C. Bower, R. Rosen, O. Zhou, Appl. Phys. Lett, 1999, 74, 3317.
- [14] R. Haggemueller, H.H. Gommans, A.G. Rinzler, J.E. Fischer, K.I. Winey, Chem. Phys. Lett, 2000, 330, 219.

- [15] U.Dettlaff-Weglikowska, J.M.Benoit, P.W. Chiu, *Curr. Appl. Phys*, 2002,2 , 497.
- [16] Z.X. Wei, M.X.Wan, T.Lin, L.M Dai, *Adv. Mater*,2003,15, 2,136.
- [17] I.Fujita, M.Ishiguchi, H.Shiota, T.Danj, K.Kosai, *J. Appl. Polym. Sci*,1992,44 ,987.
- [18]A .tar, J.F .Stoddart, D. Steurman, M. Diehl, A. Bouaki, E.W Wong, X .Yang, S.W Chung, H. Choi, *J.R .Heath Angew Chem Int Ed* , 2001,40,1721.
- [19] M.Deng, B.Yang, Y. Hu , *J Mater Sci* , 2005,40,5021.
- [20] M.P.Dash, M.Tripathy, A.Sasmal, G. C.Mohanty, P. L. Nayak, *J Mater Sci* ,2010,45,3858–3865.
- [21] Y.Yu, B.Che, Z.Si, L.Li, W.Chen, G. Xue , *Synth Met* ,2005,150 ,271.
- [22] T.M.Wu, S.H. Lin, *J Polym Sci Part B Polym Phys* 2006,44 ,1413.
- [23] J .Zhang, D.Shan, S .Mu , *J Polym Sci Part A Polym Chem* ,2007,45,5573.
- [24] Jeevananda. T.,Siddaramaiah, N.H.Kim,S.B. Heo, J.H.Lee, *Polym Adv Technol*, 2008,19,1754.

\*\*\*\*\*