



Microwave Plasma Polymerization of Polyaniline/MWCNT Composite Thin Films for Optoelectronic Applications

Ahmed S.Wasfi* and Hadeel A.Ismail

Physics Dep., College of Science, University of Baghdad/Iraq.

Abstract : The nanocomposite films of polyaniline (PANI) and multi-walled carbon nanotubes (MWCNTs) were synthesized by in situ microwave plasma polymerization with a novel method that having coupled an atomizer head (automotive fuel injector) to inject the monomer and MWCNTs simultaneously in to the plasma reactor. The pristine MWCNTs were functionalized during its path to the substrate through plasma environment to obtain uniform dispersion within the PANI matrix. Scanning electron microscopy SEM, X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) are employed to distinguish the pure PANI and the PANI-CNT nanocomposite. XRD and SEM reveal the homogeneous coating of PANI onto the CNT demonstrating that carbon nanotubes were well dispersed in polymer matrix. The overgrowth of CNTs particles by PANI governs all process and can easily be observed through the increasing films thicknesses with CNTs concentration. The interaction between the quinoid ring of PANI and the MWCNT causes PANI chains to be adsorbed at the surface of MWCNT, thus forming a hollow core surrounding the MWCNT was confirmed from FT-IR.

Nanocomposite film shows high electrical conductivity of 29.17 S/cm for film of 1.5 wt% MWCNTs compared to pure PANI film (10^{-8}) S/cm. The Incorporation of plasma functionalized CNTs into PANI matrix improved the transport properties of the nanocomposite.

Key words : Polyaniline composite, Carbon nanotubes, in situ plasma polymerization, Electrical conductivity.

Introduction

The fast development in solid-state electronic devices would not have been possible without the improvement of new thin film deposition processes and superior thin film qualities. Among the wide variety of available options, plasma organic polymer film has been one of the most extensively studied materials due to its exceptional and talented mechanical and physicochemical properties [1, 2].

Plasma polymers are unique and different from traditional polymers in that they lack the repeat structure that usually defines a polymer chain. Moreover, the chains are branched and randomly ended with a high degree of crosslinking which increases with the intensity and energy of bombarding plasma ions. One of the advantages of plasma polymers is the fact that they tend to deposit as high quality thin, pin hole free films in a simple one step process and have a propensity to be very adherent to the substrates being coated which are hardly possible to obtain by the conventional methods [3, 4]. These properties are essential in the application of plasma polymers as typical coatings for optoelectronic applications [5].

The mechanism of plasma polymerization is very complex. The ionization which takes place in the plasma system breaks the precursor gas into ions, free electrons, radicals and neutral fragments. The recombination of these radicals form high molecular weight compounds called polymers. The free radicals are trapped in these films which continue to react and change the polymer network over time. Since radicals are formed by fragmentation of monomer, some elements and groups may be absent in resulting polymer chain. The degree of fragmentation depends on electron density or plasma input power and monomer flow rate [6, 7].

It has been reported that conductive polymer thin films have great potential for use in optoelectronic devices. Since the conductive polymers with delocalized π electrons offer unique physical properties which are inaccessible in conventional polymers, so development of new π conjugated polymers films with high conjugation lengths and degree of inter chain order are likely to achieve better materials for the use of conducting and semiconducting material [8, 9].

Polyaniline (PANI) is one of the favorable conducting polymers due to its high conductivity, easiness of preparation, and good environmental stability, which makes it appropriate as a matrix for preparation of conducting polymer nanocomposites. It can be synthesized by chemical, electrochemical, or plasma methods, and in each case, the composition, morphology, and physical properties of the resulting polymer are strongly dependent on the detailed reaction conditions [9, 10].

Polymers are usually polyconjugated structures which are insulators in their pure state; but when treated with oxidizing or reducing agents they can be converted into compounds having reasonable electrical conductivity, also the insertion of conducting nano scale fillers (like carbon nanotubes CNTs) may improve their electrical conductivity [11]. The carbon nanotubes can be considered as natural partners for intrinsically conducting polymers. Their dimensions and electronic structure combine well with the polymer chain structure and the delocalized electron system of these electro-active polymers. Their mutual interactions may lead to greatly favorable effects between both constituents, which might contribute to further enhancements in organic polymer optoelectronic devices [12]. In order to improve the adhesion of the interface between the polymer and the nanotubes, it is possible to introduce functional groups into the surface of nanotubes or using the plasma treatment.

In the present work, nanocomposite thin films of polyaniline and multi wall carbon nanotubes MWCNTs of different concentrations were deposited by microwave plasma polymerization of aniline; the morphological and structural properties of PANI in the composites were investigated using SEM, AFM, and FT-IR. The electrical conductivity of PANI and PANI/MWCNT composite films of different CNTs concentrations were inspected by Hall Effect.

Experimental

The plasma polymerization system used in this work and the procedure of film deposition has been reported in an earlier publication [13]. The precursor's aniline (Merck supplier) and carbon nanotubes (CNTs) with different concentrations, after being dispersed ultrasonically in aniline for 30 min, were injected simultaneously into the plasma reactor through atomizer (automotive fuel injector) operates in a pulsed manner, as it can maintain a good vacuum isolation between the pressurized aniline reservoir and the plasma reactor. The rate for monomer injection was set at 0.0333 ml per min for 30 min in total. The thickness of the deposited films depends on the quantity of the injected monomer in the Ar plasma as a spray pulse of controlled duration. This control of the spray pulse duration and their repetition with time were essential to keep the pressure in the chamber within the plasma working pressure range of 0.5-1.0 mbar. When a pulse of the monomer entered the evacuated reactor, most of the liquid directly vaporized by flash boiling in the plasma stream and when the residence time is properly chosen, it is expected to have high radical concentration close to the substrate. In fact, plasma induced polymerization of aniline molecules with MWCNTs was composed of two successive processes, namely, the surface activation (functionalization) of MWCNTs and polymerization of aniline. The aniline monomer is adsorbed on the surface of CNTs due to their high surface area and their reactivity, moved in the plasma stream the polymerization reaction starts on the CNTs particles and continues in the direction of the substrate. Consequently, the deposit is expected to contain plasma functionalized CNTs particles with PANI, chemically bonded, embedded in PANI matrix.

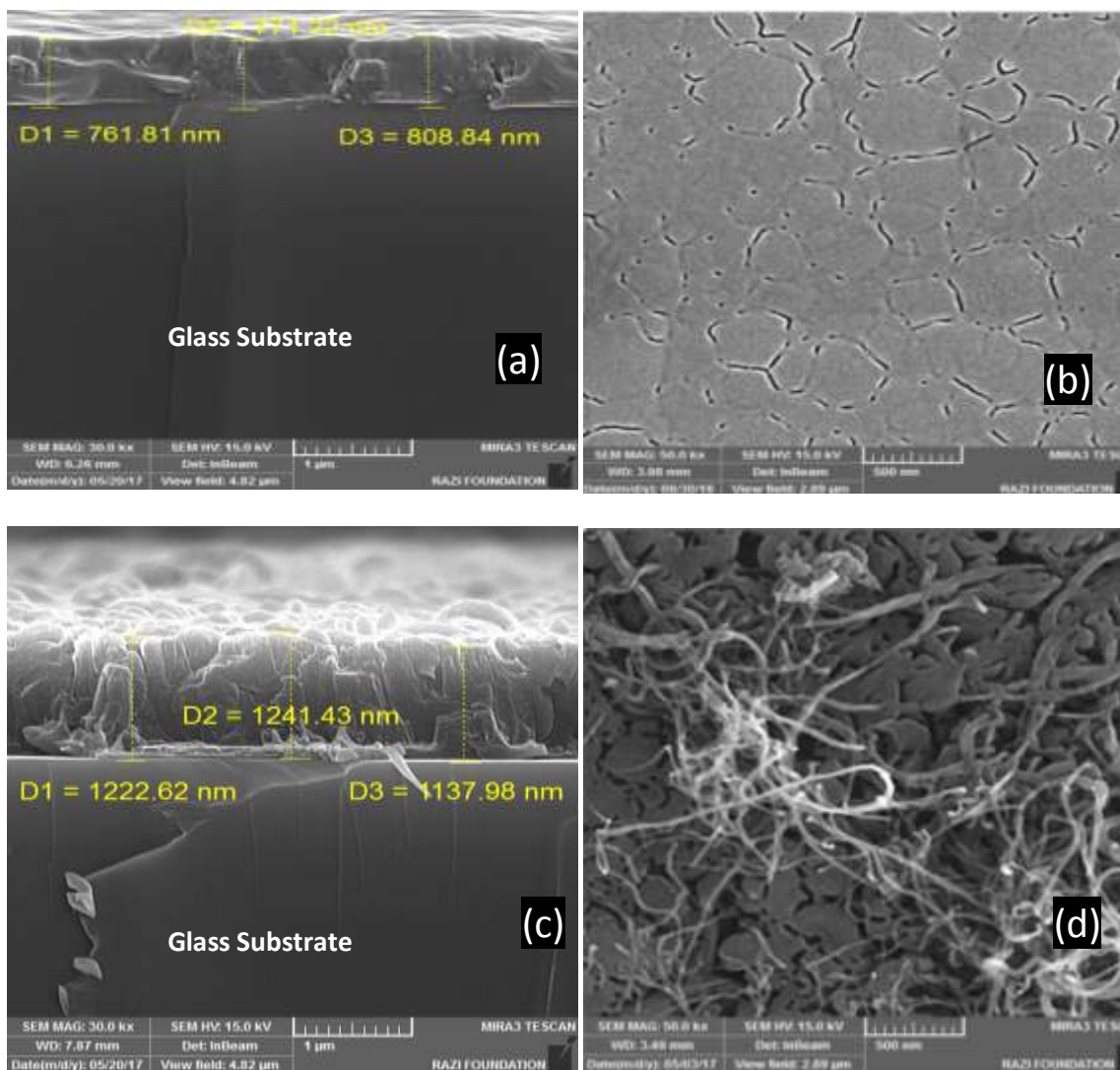
After a proper cleaning procedure, the glass substrate was fixed inside the plasma reactor. Different concentrations of CNTs mixed with aniline were used to deposit PANI/MWCNT nanocomposite thin films on the glass substrates.

Results and Discussion

Characterization of PANI/ MWCNT Nanocomposite

The Scanning electron microscopy (SEM) showed that PANI films have a continuous, smooth and tidy surface as in fig. 1-a and b (figure1-a,c,e film cross-sectional image technique), whereas, PANI/MWCNT films show high roughness which rises with the CNT concentration. The example presented in Fig.1-c, and 1- d, for 0.5 wt % of MWCNTs and fig.1-e, and 1-ffor 1 wt % of MWCNTs showed a high density of MWCNTs was embedded and well dispersed in the polymer matrix and all CNT particles are covered by PANI developing a continuous matrix. The overgrowth of CNTs particles by PANI, which governs all process, is easily observed through the increasing films thicknesses with CNTs concentration.

The MWCNTs themselves are smooth and with diameters of 20–30 nm [see Fig. 1-d]. When they are introduced into in-situ aniline plasma polymerization system, CNTs' smooth surfaces change into rough structure, as presented in Fig. 1-d. In the mean time, their diameters are enhanced to 50 –100nm. These figures show that CNTs is homogenously coated by PANI and dispersed very well through PANI matrix, they may assist as conducting bridges connecting the isolated PANI islands.



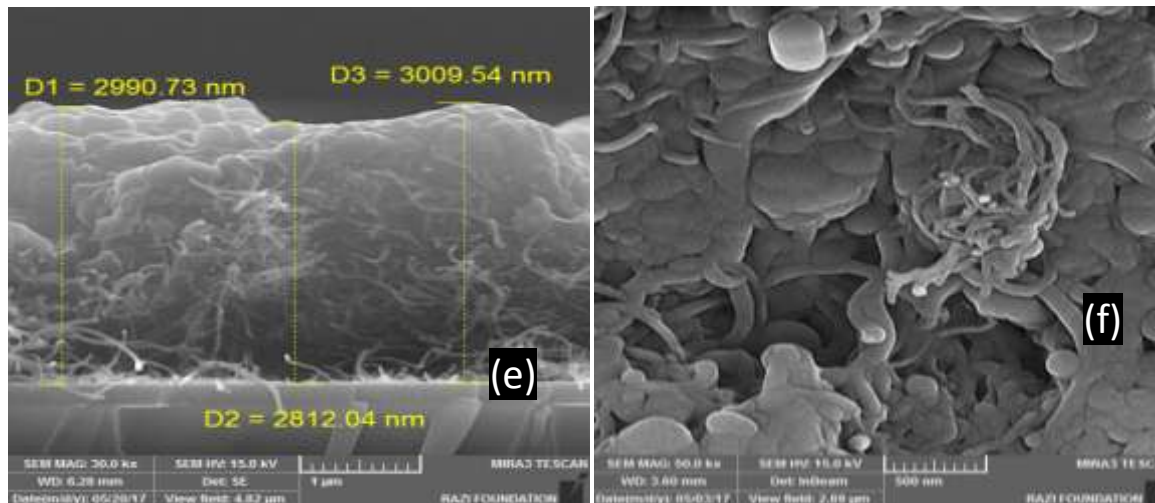


Fig. 1 SEM images of films deposited under the same conditions, a and b: PANI film, c and d: PANI/MWCNT composite of 0.5 wt% MWCNTs concentration, e and f: PANI/MWCNT composite of 1 wt% MWCNTs concentration.

The surface topography evidenced by AFM, for PANI and PANI/MWCNT composite (Fig. 2) show distinguishing features. PANI films have a continuous and smooth surface with roughness average of 0.38 nm, while, PANI/MWCNT films show high roughness with roughness average of 25 nm which increases with the CNT concentration. The example presented in Fig. 2 for 1 wt% CNTs shows a high density of nanoparticles. All CNT particles are covered by PANI forming a continuous matrix which encloses nanocarbon particles in small cages.

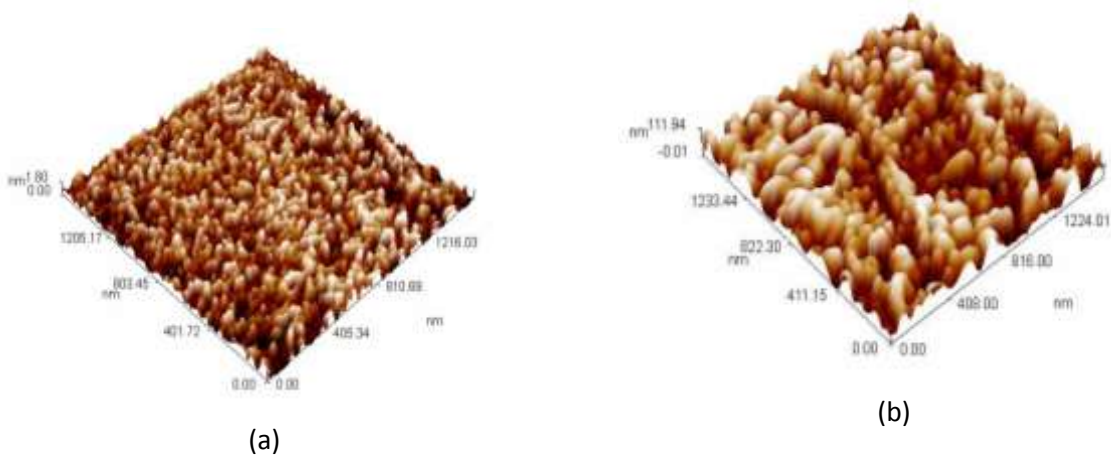


Fig. 2 AFM topography for PANI film (a), and PANI/MWCNT composite film of 1.5 wt% concentration of MWCNTs (b).

The X-ray diffraction patterns of pure PANI and PANI/MWCNT composite are shown in figure 3. The diffraction peaks at 26.5° and 43° correspond to graphite-like structure derived from CNTs, as it can be seen in Fig. 3(a) and (b), while PANI's crystalline peaks appear at 12° , 16° and 26° , which can be assigned to the (011), (020) and (200) reflections from crystal planes of PANI, respectively [14]. Comparing the XRD pattern of PANI/MWCNT with that of PANI, similar diffraction peaks can be observed.

The peak around 26° is the typical of π conjugation in PANI. PANI is only partially crystalline with conducting domains separated by large amorphous regions as obvious from the XRD spectrum. Conductivity is limited by strong disorder. PANI/MWCNT composite shows the crystalline peaks at 26° with higher intensity and sharpness. The presence of diffraction peak at 26° which is common in both PANI and PANI/MWNT; specify the presence of long range conjugation, in both samples. This peak is much sharper in PANI/MWCNT composite because of the enhanced conjugation in MWCNTs [15].

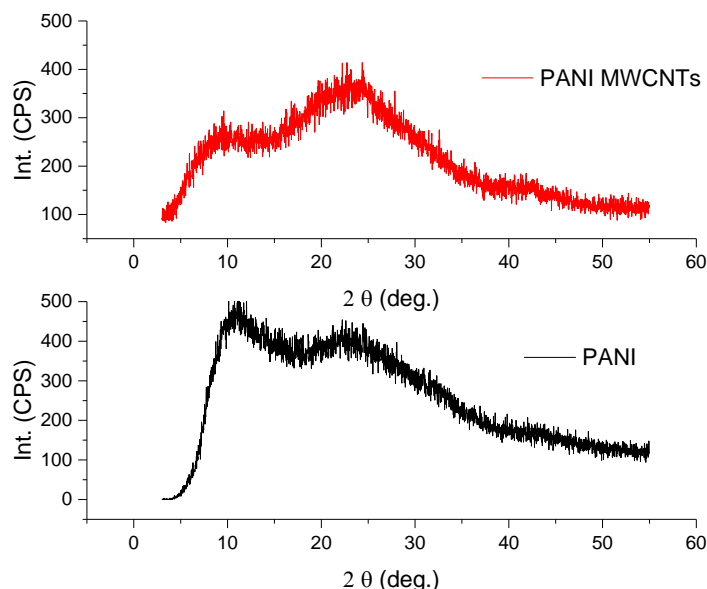


Fig. 3 XRD for PANI film and PANI/MWCNT composite film of 1.5 wt% concentration of MWCNTs.

The FT-IR spectra recorded for PANI, MWCNTs and its nanocomposite in the $400\text{-}4000\text{ cm}^{-1}$ range is shown in Figure 4. It shows complex features of both PANI and CNTs and superimposed effects due to the chemical bonding between the dangling bonds on the nanocarbon surface and polyaniline.

For pure PANI, the characteristic peaks at ~ 1651 and $\sim 1454\text{ cm}^{-1}$ are assigned to the C=C symmetric and symmetric stretching of quinoid and benzenoid rings, respectively. The peak at 2934 cm^{-1} corresponds to C-H stretching of aromatic ring, while the characteristic peaks at 1292 and 1107 cm^{-1} are attributed to the C-N stretching vibration of the secondary aromatic amine group and aromatic C-H in plane bending vibration respectively [16, 21]. The peak at 760 cm^{-1} represents C-H out of plane bending vibration and the small peak at 896 cm^{-1} represents para-distributed aromatic rings indicating polymer formation [17]. The band at $\sim 3400\text{ cm}^{-1}$ indicates the stretching of N-H band of aromatic ring in PANI and composite [16]. In the FT-IR spectrum of plasma functionalized MWCNTs, the peaks at 1458 and 1512 cm^{-1} attributed to bending vibration of O-H group and carbonyl, respectively. The intense peak at $\sim 1720\text{ cm}^{-1}$ corresponded to the C=O stretching vibration mode, representing the formation of the carboxylic groups at both ends and on the sidewalls of the CNT's, responsible for mixing CNT's with PANI [16]. The peak at 3460 cm^{-1} characteristic of an O-H stretch was observed due to carboxylic groups. These results specified that the CNTs had been effectively oxidized into carboxylated carbon nanotubes [19]. In PANI/MWCNT composite additional bands at 1107 , 1134 , 1180 cm^{-1} are observed which are specific for CC, -C-NH aromatic rings. That is the main feature, which confirms that PANI-chains are bonded to CNT's surface. The band at $\sim 1134\text{ cm}^{-1}$ is considered to be a measure of the degree of electron delocalization and consequently it is the characteristic peak of PANI conductivity [20]. The intensity of this peak increases with addition of CNTs, which agrees well with our increased conductivity measurement. This may propose that strong interaction between CNTs and PANI enables effective degree of electron delocalization, and thus improves the conductivity of polymer chains.

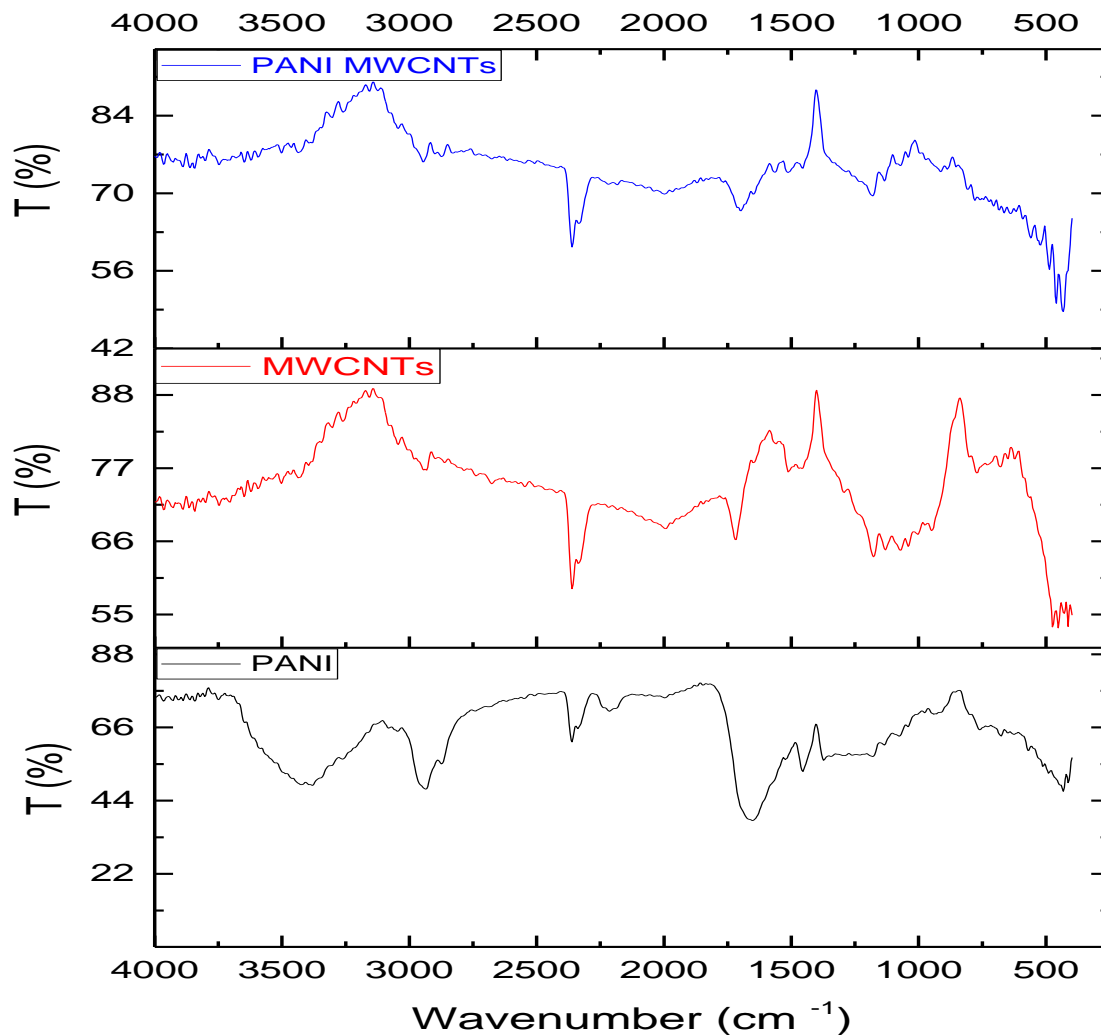


Fig.4 FT-IR spectra for PANI, MWCNT and PANI/MWCNT composite films of 1.5 wt% concentration of MWCNT.

The electrical conductivity of PANI and PANI/MWCNT composite films of different CNTs concentrations were examined by Hall Effect, the results are shown in table 1 and figure 5. It is obvious from the results that the conductivity increased with the concentration of the CNTs. PANI/MWNT composite film of 1.5 wt% concentration of MWCNTs showed a conductivity of (29.17) S/cm which is almost eight orders of magnitude greater than that observed for pure PANI (10^{-8}) S/cm used in the present work. Owing to the large aspect ratio (length is very large related to diameter) and surface area of MWCNTs, they may serve as conducting bridges between dispersed PANI connecting domain, improving charge delocalization[20]. The enhanced crystallinity of PANI with the addition of MWNTs as obvious from the XRD examinations is an additional reason for the high increase in conductivity.

Table 1. Electrical conductivity of PANI and PANI/MWCNT composite films of different CNTs concentrations.

Sample PANI/MWCNT CNTs Concent. wt %	Carrier Concent. n_H (cm^{-3})	Resistivity ρ ($\Omega\cdot\text{cm}$)	Conductivity σ_{RT} (S/cm)
PANI only	$1.744 \times 10^{+9}$	$2.130 \times 10^{+7}$	4.695×10^{-8}
0.05%	$1.127 \times 10^{+13}$	$5.964 \times 10^{+3}$	1.677×10^{-4}
0.1%	$1.060 \times 10^{+17}$	$9.192 \times 10^{+0}$	1.088×10^{-1}
0.5%	$2.524 \times 10^{+19}$	3.179×10^{-1}	$3.146 \times 10^{+0}$
1%	$6.745 \times 10^{+20}$	4.175×10^{-2}	$2.395 \times 10^{+1}$
1.5%	$2.213 \times 10^{+21}$	3.428×10^{-2}	$2.917 \times 10^{+1}$

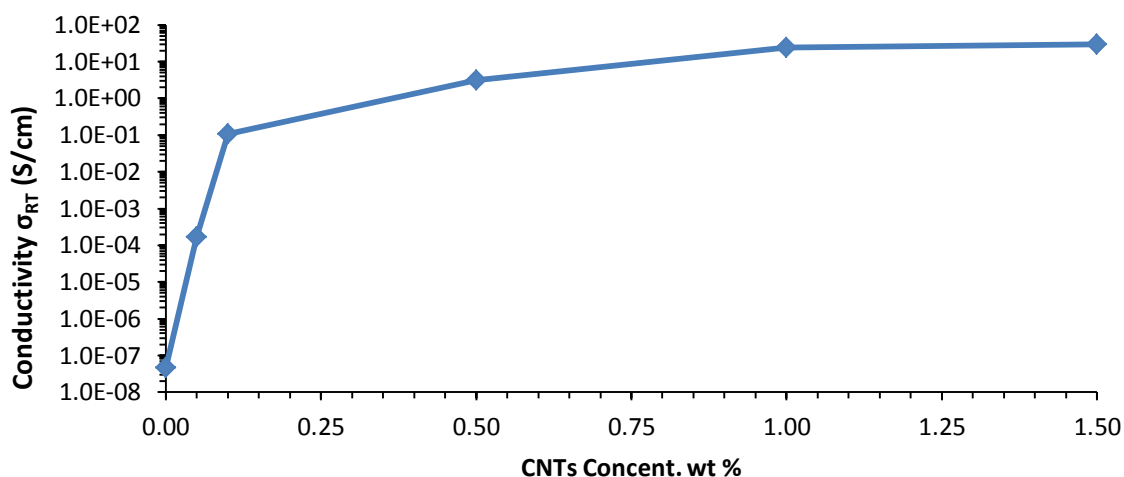


Fig.5 Room temperature electrical conductivity of PANI/MWCNTs composite versus the MWCNTs loading (wt%).

Conclusion

In situ plasma polymerization is considered as a very effective method to pointedly develop the nanotubes dispersion and the interaction between nanotubes and polymer matrix. It enables implanting of polymer macromolecules onto the convex walls of nanotubes. This then offers a better nanotubes dispersion and formation of a strong interface between the nanotube and the polymer matrix. PANI/MWCNT composite was successfully synthesized by microwave plasma polymerization. The XRD analysis showed that PANI is only partly crystalline with islands separated by large amorphous regions. SEM image shows that aniline is polymerized between the wedges of MWCNTs as well as on the tube surfaces, while FT-IR shows the effective structural modification and the formation of PANI/MWCNT composite. The incorporation of plasma functionalized CNTs into PANI matrix improved the transport properties of the nanocomposite.

References:

1. Biederman H, Slavinska D," Plasma polymer films and their future prospects", Surf Coat Tech, 125,371-376, (2000).
2. P. J. F. Harris," Carbon nanotube composites", International Materials Reviews,49, 31-43, (2000).
3. Cho SJ, Bae IS, Jeong HD, Boo JH, "A study on electrical and mechanical properties of hybrid polymer thin films by a controlled TEOS bubbling ratio", Appl Surf Sci,254, 7817-7820, (2008)
4. Jiang H, Hong LG, Venkatasubramanian N, Grant JT, Eyink K, Wiacek K, Fries-Carr S, Enlow J, Bunning TJ," The relationship between chemical structure and dielectric properties of plasma enhanced chemical vapor deposited polymer thin films", Thin Solid Films, 515, 3513-3520, (2007).
5. Thomas Hanemann and DorotheeVingaSzabó, "Polymer-Nanoparticle Composites: From Synthesis to Modern Applications", Materials, 3, 3468-3517, (2010).
6. Yasuda, H. "Plasma Polymerization", Academic Press Inc.: Orlando, FL, (1985).
7. H. Biederman, "Plasma Polymer Films", Handbook, Imperial College Press, London,(2004).
8. C. Oueiny, S. Berlioz, Francois-Xavier Perrin, "Carbon nanotube–polyaniline composites", Progress in Polymer Science, Vol. 39, 627-816, (2014).
9. M. Totolin, M. Grigoras, D. Conduruta, "Plasma induced aniline polymerization", Journal of Optoelectronics and Advanced Materials, 9, p. 881 – 883, (2007).
10. S. B. Kondawar, M. D. Deshpande, S. P. Agrawal, "Transport Properties of Conductive Polyaniline Nanocomposites Based on Carbon Nanotubes", International Journal of Composite Materials 2(3): 32-36, (2012).

11. Wolfgang K. Maser, Raquel Sainz, M. Teresa Martinez and Ana M. Benito, " Electroactive polymer-carbon nanotube composites: smart organic materials for optoelectronic applications", *Contribution to Science* 4 (2): 187–192, (2008).
12. Peng-Cheng Ma, Naveed A. Siddiqui , Gad Marom , Jang-Kyo Kim, "Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: A review", *Composites: Part A* 41,1345–1367, (2010).
13. Ahmed S. Wasfi, Hammad R. Humud, Mohammed A. Abed, Mohammed E. Ismael, "Preparation of Polyaniline/Zinc Oxide Nanocomposite Thin Films by Microwave Plasma" *International Journal of Chem Tech Research*, 10, pp 886-892, (2017).
14. L. Ding, Q. Li, D. Zhou, H. Cui, H. An and J. Zhai, "Modification of glassy carbon electrode with polyaniline/multi-walled carbon nanotubes composite: Application of electro-reduction of bromate", *Journal of Electroanalytical Chemistry*, 668, pp. 44–50, (2012).
15. R. Menon, C. Yoon, D. Moses, A. Heeger and Y. Cao, "Transport in polyaniline near the critical regime of the metal-insulator transition", *Phy. Rev.*, 17685, (1993).
16. Y. Li, H. Peng, G. Li, and K. Chen, "Synthesis and electrochemical performance of sandwich-like polyaniline / graphene composite nanosheets," *European Polymer Journal*, 48, pp. 1406-1412, (2012).
17. M. V. Kulkarni and B. B. Kale, "Studies of conducting polyaniline (PANI) wrapped-multiwalled carbon nanotubes (MWCNTs) nanocomposite and its application for optical pH sensing," *Sensors and Actuators B: Chemical*, 187, pp. 407-412, (2013).
18. T. Wu, Y. Lin, "Doped polyaniline/multi-walled carbon nanotube composites: Preparation, characterization and properties", Elsevier publishing, *Polymer*, 47, pp. 3576–3582, (2006).
19. P. Liu, X. Wang, and H. Li, "Preparation of carboxylated carbon nanotubes/polypyrrole composite hollow microspheres via chemical oxidative interfacial polymerization and their electrochemical performance," *Synthetic Metals*, 181, pp. 72-78, (2013).
20. J.E. Huang, X.H. Li, J.C. Xu, H.L. Li, "well-dispersed single-walled carbon nanotube/polyaniline composite films", *Carbon*, 41, 2731–2736, (2003).
21. G. Socrates, "Infrared characteristic group frequencies, tables and charts", 2nd Ed. New York: Wiley; (1994).
