Improved electrical, structure, and mechanical properties of poly (o-toluidine) polymer by multiwalled carbon nanotubes

TARIQ J. ALWAN*
Al-Mustansiriyah University, College of Education, Physics Department, Baghdad, Iraq

Poly(o-Toluidine) (POT) and POT-doped multiwalled carbon nanotubes (MWCNTs) were successfully prepared by in situ chemical oxidative polymerization in an acidic medium with ammonium persulfate $(NH_4)_2S_2O_8$ as oxidant. MWCNTs were used at different weight ratios as reinforcement to improve the mechanical and electrical properties of POT. Scanning electron microscopy, X-ray diffraction, and Fourier transform infrared spectroscopy analyses were conducted to characterize the morphology, structure properties and functional groups of the prepared samples. The electrical conductivity of POT and POT–MWCNTs was measured by two-probe method at room temperature. The electrical conductivity increased with increasing weight ratio of MWCNTs, that is, from 3.93×10^{-6} S/cm in the nanocomposite with 0 wt% MWCNTs to 2.36×10^{-5} S/cm in the nanocomposite with 0.3 wt% MWCNTs. The tensile strength and hardness of the POT and POT–MWCNTs nanocomposite samples were also measured.

(Received December 28, 2018; accepted August 20, 2019)

Keywords: POT, POT-MWCNTs, Conductive polymer

1. Introduction

Conductive polymers are characterized by unique properties, mix between metals and conventional polymers properties [1]. Poly(o-Toluidine) (POT) is one of the most famous conductive polymers and has been widely investigated. However, POT has few applications due to their poor processability and mechanical properties [2,3]. In this regard, POT is mixed with one or more other materials to create a POT composite with different physical properties and improved mechanical properties [4][5].

Many researchers have successfully prepared POT composites with improved mechanical properties [6]. However, mixing POT with conventional polymers negatively affects the electrical properties of conductive polymers. To improve the mechanical and electrical properties of POT composites, scholars have used multiwalled carbon nanotubes (MWCNTs) as reinforcement in POT [7][8][9].

A POT–MWCNTs nanocomposite comprises POT matrix and MWCNTs that possess unique properties, as instance, electrical percolation behavior [10], electrical conductivities [11] [12], Field Emission and mechanical properties [13][14], which cannot be obtained when using each material alone. Polymerization in the presence of MWCNTs leads to a planar conformation of POT along the tubes. As such, POT–MWCNTs with unique electrical, thermal, and mechanical properties have become a potential candidate for a wide range of organic electronic applications [10][11].

In this study, we prepared POT and POT–MWCNTs nanocomposites by site polymerization methods with different weight ratios. Electrical conductivity, structure, and mechanical properties of the samples were evaluated to determine the effect of MWCNTs on the fabricating of POT–MWCNTs nanocomposites.

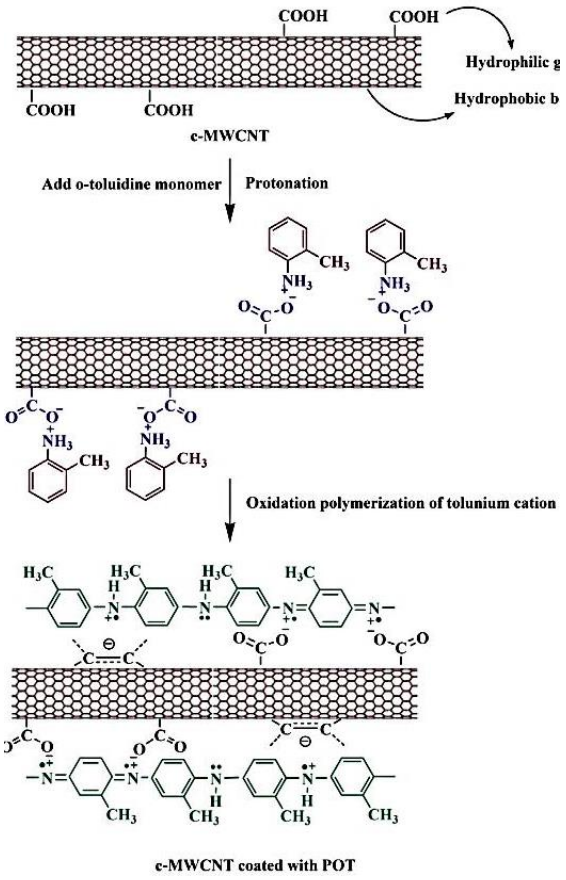
2. Experimental

The MWCNTs (diameter 10-30 nm, crystallite size 4.82 A^o and electrical conductivity 10^6 S/cm) was used, the as received MWCNTs were functionalized following the route reported by Kulkarni et al. [16].

POT was prepared through the following methods. In brief, 2.5 g of o-toluidine was added to 100 ml of 1 M HCl, placed in a three necked flask, and subjected to in situ oxidative polymerization at 273 K by use ice. Subsequently, 15 g of ammonium persulfate was dissolved in 50 ml of 1 M HCl in a separatory funnel and carefully added dropwise to the o-toluidine/HCl solution under constant stirring at 273 K for 30–40 min. The temperature of the solution during the interaction was maintained at 273 K. The combined solution in a three-necked flask constantly stirred at room temperature for 24 h. A dark green solution was obtained as precipitate and washed with distilled water and methanol three times. The precipitate was then dried in oven at 353 K to obtain dark green POT.

POT–MWCNTs nanocomposite was prepared using the same steps but the o-toluidine/HCl solution was added with MWCNTs at different weight ratios (0.1, 0.2, and 0.3

wt%). The interaction between POT and MWCNT during in situ polymerisation process is presented in Scheme 1. [9]. The site-selective interaction between the quinoid rings of POT and the MWCNT leads to POT deposit onto the surface of MWCNT.



Scheme 1. In situ polymerisation of POT–MWCNT nanocomposite [9]

POT and POT–MWCNTs nanocomposite powders were pressed into disc-shaped pellets with 1.3 cm diameter and 0.3–0.35 cm thickness by using a hydraulic press type (Specac) under a pressure of 5 ton/cm^2. The morphology of the samples was investigated by scanning electron microscopy (SEM, Hitachi S-4160 SEM). Infrared analysis was conducted using SIDCO England series FT-IR spectrometer at 400–4000 cm^{-1}. The structures of the prepared samples were characterized using Philips X-ray diffractometer. Hardness test was carried out using Hardness model TH200. Tensile strength was calculated using the following equation [16]:

$$\sigma_T = \frac{0.4\,F}{\pi\,R^2} \qquad (1)$$

where F is the crushing force, and R is the pellet radius.

3. Results and discussion

The morphology images of the POT and POT–MWCNTs samples are shown in Fig. 1. The SEM image of POT reveals conventional granular POT particles, and the morphological study indicates irregularly shaped POT aggregates. MWCNTs exert a strong effect on the morphology of the polymer in the nanocomposites. The SEM image of the nanocomposite with 0.1 wt% MWCNTs shows POT conglomeration and well-dispersed MWCNTs. The SEM images of the nanocomposites with 0.2 and 0.3 wt% MWCNTs show homogeneous coating of conductive polymer onto the nanotubes. MWCNTs are well dispersed in the conducting polymer, leading to their increased diameters. The SEM image of POT–MWCNTs nanocomposites shows the formation of interwoven fibrous structure and that enhanced conductivity. We can assume that some monomers may have polymerized on the surface of MWCNTs and the remaining amount of aniline monomer may have polymerized into the granular structures. This hypothesis is confirmed by S. G. Bachhav et al. [10], S. B. Kondawar et al. [11] and S. Husain et. al. [13].

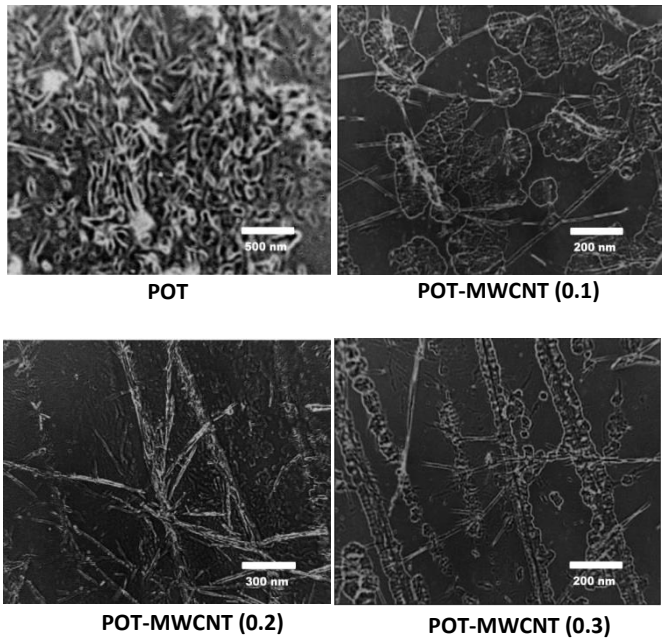


Fig. 1. SEM images of POT and POT-MWCNTs with different MWCNTs weight ratios

Fig. 2 shows the X-ray diffraction (XRD) patterns of POT and POT–MWCNTs nanocomposites. Fig. 2.a shows the XRD pattern of POT. No characteristic peaks were detected, indicating that POT has an amorphous structure, similar to the report of K. Kumari et al. [3] Fig. 2.b, c, and d shows the XRD patterns of the nanocomposites. The characteristic peaks of polycrystalline POT–MWCNTs nanocomposite were found at 2θ=11.58°, and 26.84°.

The 2θ= 26.84° corresponds to the (020) reflections of POT polycrystalline state. The XRD pattern of the POT–MWCNTs nanocomposite shows a crystalline peak at 11.58°, this peak assigned to the MWCNTS and has intensity increases with increasing MWCNTs weight ratio. This peak has high intensity and sharpness, indicating the presence of long-range conjugation. Moreover, this peak is sharper in the POT–MWCNTs nanocomposite because of enhanced conjugation in MWNCTs [17].

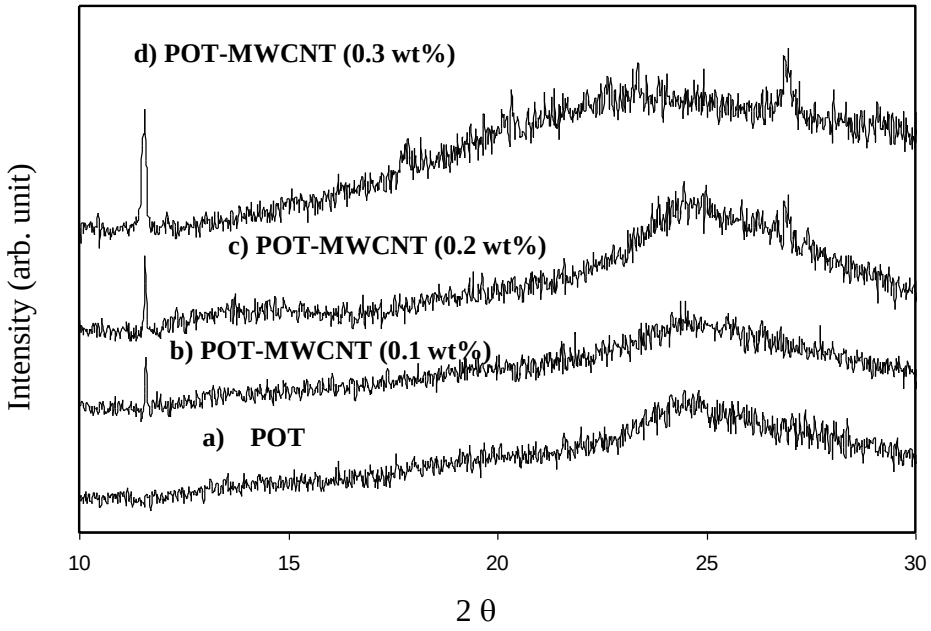


Fig. 2. XRD spectra of POT and POT-MWCNTs with different MWCNTs weight ratios

The average crystallite size (CS) of the samples can be calculated from the X-ray spectrum by using full-width at half maximum (FWHM) method (Scherrer relation) [18].

$$C.S. = \frac{D\,\lambda}{\Delta\beta\,\cos\theta} \qquad (2)$$

where $\Delta\beta$ is the FWHM of the XRD peak at diffraction angle θ, D is the Scherrer's constant (D = 1), and λ is the X-ray wavelength. Table 1 shows the average CS of the samples. The CS of nanocomposite with 0.1 wt% MWCNTs is about 13.96 A^o, which increases to 28.32 A^o when the weight ratio of MWCNTs is increased to 0.3 wt%. Hence, the crystallization state of POT–MWCNTs nanocomposites is enhanced with increasing weight ratio of MWCNTs.

Table 1. Some physical parameters of POT and POT–MWCNTs samples

Samples	crystallite size A	σ S.cm^{-1}	Hardness	Tensile MPa
POT	Amorphous	3.93×10^{-6}	481	2.45
POT-MWCNT (0.1 wt%)	13.96	7.85×10^{-6}	508	2.58
POT-MWCNT (0.2 wt%)	17.44	1.57×10^{-5}	555	2.82
POT-MWCNT (0.3 wt%)	28.32	2.36×10^{-5}	573	2.91

The samples were also characterized by FTIR spectroscopy. FTIR spectra were recorded, and the characteristic bands for the functional groups are shown in Fig. 3. The FTIR spectra of POT show the presence of the expected functional groups; for example, the band at 1506 cm^{-1} is related to benzenoid C–N bond, the band at 1380 cm^{-1} is due to the symmetric deformation of the methyl group, the band at 1300 cm^{-1} refers to C–N bonds, and the bands at 1107 and 1172 cm^{-1} are assigned to the C–H bond [19].

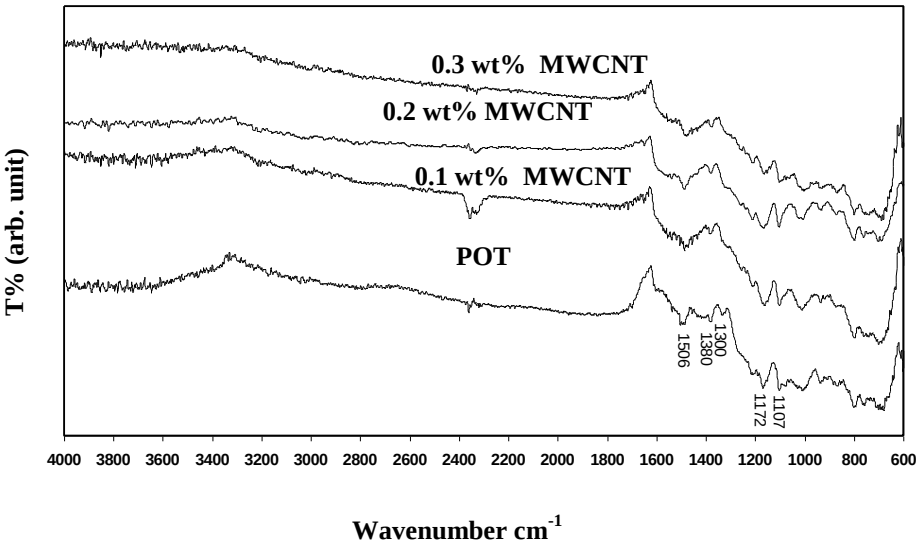


Fig. 3. FTIR spectra of POT and POT-MWCNTs with different MWCNTs weight ratios

The FTIR spectra of the nanocomposites with different MWCNT weight ratios present similar features to those of the POT spectrum; meanwhile, the intensity of the bands in the nanocomposite spectra shows minimal changes. No additional vibrational bands were detected in comparison to the spectrum of the POT sample because carbon bonds are already present in the POT functional groups. This finding is in agreement with the report of S. B. Kondawar et al. [11].

In this section, the electrical properties of POT and POT–MWCNTs nanocomposites were evaluated. The effects of MWCNT weight ratio on the electrical conductivity of POT were investigated. The mechanism of electrical conductivity in the polymers was determined based on voltage–current characteristics [20].

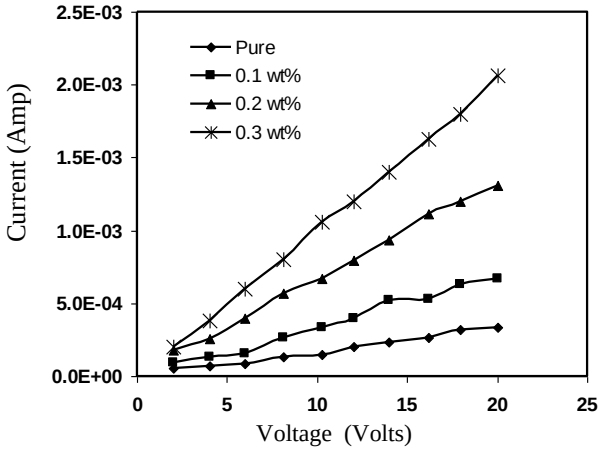


Fig. 4. The I-V curves for POT and POT-MWCNTs with different MWCNTs weight ratios

The current–voltage characteristics of prepared samples with different MWCNT weight ratios are shown in Fig. 4. The electrical conductivity values are presented in Table 1. The electrical conductivity increases with increasing MWCNT weight ratio, that is, from 3.93×10^{-6} $S.cm^{-1}$ in POT only to 2.36×10^{-5} $S.cm^{-1}$ in the nanocomposites with 0.3 wt% MWCNT. Doping with MWCNTs improves the structures and properties of POT, leading to increased conductivity of the nanocomposite compared with pure POT. The increased conductivity could also be attributed to the good interaction between POT and MWCNTs [9][12][21]. May be noted that conductivity is generally low, this is due to used the POT as it prepared without oxidizing by acids after prepared.

The mechanical properties of the samples were investigated to determine the effect of MWCNT weight ratio on the tensile strength and hardness of the fabricated nanocomposites.

The hardness values of POT–MWCNTs nanocomposites are shown in Table 1. The POT–MWCNTs sample with 0.3 wt% MWCNTs possesses higher hardness (about 573 MPa) than the two other samples. The high hardness value could be due to overlap and stacking, which reduce the movement of polymer molecules and increase the resistance of the material to scratching and cutting; hence, the nanocomposites are more resistant to plastic deformation than POT alone [22][223].

The interaction between conducting polymer POT molecules and MWCNTs changes the tensile properties of the nanocomposites. The tensile strength values of the nanocomposites with different weight ratios of MWCNTs are shown in Table 1. The highest tensile was found in POT–MWCNTs nanocomposites with 0.3 wt% MWCNTs. This finding could be due to the high degree of miscibility between POT and MWCNTs. Moreover, MWCNTs are well dispersed in POT, settle down at the voids and interface positions, and act as cross-linking centers among the POT molecules [24].

4. Conclusion

POT–MWCNTs nanocomposites were produced successfully through in situ chemical oxidative polymerization. The characterization results indicate the well dispersion of MWCNTs in POT. The XRD data indicate the polycrystalline structure of all samples. The FTIR spectra show many peaks in POT–MWCNTs nanocomposites, indicating the incorporation of MWCNTs into POT. Finally, the electrical and mechanical measurements show that the electrical conductivity, hardness, and tensile values increase with increasing MWCNTs weight ratio. The nanocomposite with 0.3 wt% MWCNTs exhibits the highest electrical conductivity, hardness, and tensile values among all the samples fabricated.

References

[1] M. S. Freund, B. A. Deore, Self-doped Conducting Polymers, John Wiley & Sons Ltd, 2007.
[2] J. Bhadra, N. J. Al-Thani, N. K. Madi, M. A. Al-Maadeed, Arabian Journal of Chemistry **10**(5), 664 (2017).
[3] Kiran Kumari, Vazid Ali, Gita Rani, Sushil Kumar, G. B. V. S. Lakshmi, M. Zulfequar, Materials Sciences and Application **2**, 1049 (2011).
[4] James F. Shackelford, Introduction to Materials Science for Engineers, 3rd edition (Prentice Hall, 1999).
[5] C. Üçhöyük, Meral Karakisla, Mehmet Saçak, Indian Journal of Fibre and Textile Research **37**(2), 120 (2012).
[6] Seema Joon, Rakesh Kumar, Avanish Pratap Singh, Rajni Shukla, S. K. Dhawa, RSC Adv. **5**, 55059 (2015).
[7] Suman Lal, S. K. Tripathi, Nitin Sood, Samriti Khosla, Journal of Information Display **15**(3), 111 (2014).
[8] K. M. Zaidan, R. A. Talib, M. A. Rahma, F. H. Khaleel, Pelagia Research Library, Der Chemica Sinica **3**(4), 841 (2012).
[9] Arup Choudhury, Materials Chemistry and Physics **130**, 231 (2011).
[10] S. G. Bachhav, D. R. Patil, American Journal of Materials Science **5**(4), 90 (2015).
[11] S. B. Kondawar, M. D. Deshpande, S. P. Agrawal, International Journal of Composite Materials **2**(3), 32 (2012).
[12] Shihai Ding, Xiaofeng Lu, Jiani Zheng, Wanjin Zhang, Materials Science and Engineering B **135**, 10 (2006).
[13] Samina Husain, Shumaila, Avshish Kumar, M. Husain, Polymer Composites **39**(S2), E955 (2018).
[14] Vahid Saadattalab, Alireza Shakeri, Hamid Gholami, Progress in Natural Science: Materials International **26**, 517 (2016).
[15] M. V. Kulkarni, N. A. Charhate, K. V. Bhavsar, M. A. Tathe, B. B. Kale, Materials Research Innovations **17**(4), 238 (2013).
[16] P. H. Shipway, I. M. Hutchings, Powder Technology **76**, 23 (1993).
[17] K. K. Nagaraja, S. Pramodini, P. Poornesh, M. P. Telenkov, I. V. Kityk, Physica B **512**, 45 (2017).
[18] B. D. Cullity, S. R. Stock, Elements of x – ray diffraction, 3th edition (Prentice Hall in the United States of America, (2001).
[19] Kareema M. Ziadan, Hussein. F. Hussein, K. I. Ajeel, Energy Procedia **18**, 157 (2012).
[20] Tariq J. Alwan, Fatima S. Jalli, Optoelectron. Adv. Mat. **12**(1-2), 100 (2018).
[21] Yilmaz Hasim, Halil Ibrahim Unal, Bekir Sari. Journal of Applied Polymer Science **103**(2),1058 (2007).
[22] H. Seenaaa, Baghdad Science Journal **9**(2), 330 (2012).
[23] Weiwei Lin, Xiangxing Kong, Cesar Levy, Sensors & Transducers **187**(4), 129 (2015).
[24] P. Kalakonda, S. Banne, Nanotechnology Science and Applications **10**, 45 (2017).

*Corresponding author: tariqjaffer2000@yahoo.com