

SYNTHESIS, CHARACTERIZATION AND ELECTRICAL PROPERTIES OF POLY 2-AMINOBENZOTHAZOLE DOPED BY MWCNTS

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Abstract

Poly(2-aminobenzothiazole) (PAT) is a relatively new heterocyclic conducting polymer having a sulfur and nitrogen-rich chemical structure. During the past decade or so, there have been notable advances on the development of PAT. Especially, PAT and PAT-based composites have shown great potential for their applications in photovoltaic cells, solar cells and anti-corrosion organic coatings. In this study, 2-aminobenzothiazole was successfully prepared as pure polymer and as composite materials with multi-wall carbon nanotubes (MWCNTs). FTIR, X-ray diffraction and SEM images were investigated, showing that the composite of poly 2-aminobenzothiazole: MWCNTs was successfully synthesized. The electrical features of the pure polymer and the composite thin films were examined. The findings show that the conductivity of the pure polymer and composite thin films are about 1.67×10^{-6} (S/cm) and 4.1×10^{-2} (S/cm), respectively, exhibiting a significant enhancement by a factor of 2.5×10^4 times as a results of doping the pure polymer by 1% wt MWCNTs.

Keywords: poly 2-aminobenzothiazole, poly 2-aminobenzothiazole:MWCNTs composite, nanocomposite, surface morphology, electrical conductivity.

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Introduction

Organic conducting materials are referred to as 'synthetic metals' [1] and are considered intrinsic and naturally conducting[2]. These materials are composed of π conjugated molecules which show enhancement in electro-optical properties when they are doped or substituted by other chemical groups[3]. These conductive polymers have huge applications in many area such as rechargeable batteries,[4] modified electrodes,[5] photovoltaic and solar cells,[6] sensors,[7, 8] electrochromic display devices, light-emitting diodes [9] bioelectronics[10] and bioimaging[11] [12]. Major of conjugated polymers have been improved to utilize in new generation polymeric

1 devices. Among electroactive polymers poly-2- aminobenzothiazole is considered one of
2 promising materials which have many applicable features like antitumor , anti-corrosive ,
3 antimicrobial , and electro activities[13,14]. Several interesting studies have pointed out that
4 chemically and electrochemically polymerized derivatives of thiazole have conducting and
5 electrochromic properties [15,16]. Several studies mentioned that conductivities of aminothiazole
6 polymers can be improved by doping reaction[17]. Copolymers of thiazole with other conducting
7 monomers have also been prepared and examined in photovoltaic applications area[18].

8 Carbon nanotubes and other types of nanomaterials have wide range of interest over recent years
9 due to their inherent remarkable mechanical and electrical properties. Growing attention has been
10 focused on the CNT surface modification, namely the interface between the CNT and surrounding
11 polymer matrix. Several ways of functionalization are applied such as chemical electrochemical ,
12 and plasma.[19] This functionalization is used to functionalize their nano surfaces and side
13 chains. Potential and promising applications of nanotube compounds can be improved by making
14 some modifications in the structural composition. This modification can be led to enhancement
15 the reactivity and improve the functional performance of the nano-network. Typically, oxidation
16 of nanotubes, mainly insert carboxyl and hydroxyl, have been found to promotion the carbonic
17 surface. The existence of oxygen-containing groups leads to increases the solubility in polar
18 media and improve the possibility for further groups functionalization [20]. The aim of this study
19 is to prepare a poly(2-aminobenzothiazole) (PABT)/ (MWCNT) nanocomposite via chemical
20 polymerization, characterize its chemical structure and morphology by using spectral techniques,
21 and evaluate and enhance its thermal and electrical properties of nanocomposite. The
22 nanocomposite has been prepared by modification of (MWCNT) with carboxylic groups via
23 treatment with suitable acidic medium and then has interaction with electroactive
24 polyamionbenzothiazole to creation nano-composite.

26 **Experimental**

27 **Materials**

28 Multi-walled Carbon Nanotubes (MWCNTs) with outer diameter of 10- 30 nm and a purity of
29 approximately 90% are used in this study. 37% hydrochloric acid (HCl), 65% nitric acid (HNO₃)
30 and 95% sulfuric acid (H₂SO₄) are purchased from Sigma-Aldrich. 2-aminobenzothiozol(Sigma
31 Aldrich), deionized water, , Dimethylformamide(DMF) , ammonium persulfate(NH₄)₂S₂O₈ , pre-
32 patterned ITO substrates consist of interdigitated ITO fingers are purchased from Ossila
33 compony

35 **Instruments and measurement systems**

Nicolet FT-IR Spectrometer, X-ray Diffraction Measurements, Thermo gravimetric analysis TG, Scanning Electron Microscopy SEM, Energy Dispersive X-Ray(EDX) ,Centrifuge , Keithley 2400 source meter was used to measure I-V characteristics.

Samples preparation

Modification of Multi-walled Carbon Nanotube

One of the most common MWCNT functionalization techniques is oxidation by adding hydroxyl -OH, carboxyl -COOH, and carbonyl -CHO groups, which provide hydrophobicity and improve the surface accessibility for further chemical modifications, using oxidizing acid solutions such as HNO_3 , $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$, or $\text{H}_2\text{SO}_4\text{:HNO}_3$ that can be used to oxidize MWCNTs.

Chemical oxidation was carried out using a mixture of sulfuric acid and nitric acid 90 mL, 30 mL respectively in a ratio of 3:1 in solutions to reduce the destruction of the nanotubes for half an hour, after which 0.3 g of multi-walled Nano carbon was added. [21] The mixture was stirred magnetically for six hours at a temperature of 50 °C. It was washed with water several times using a centrifuge. Then it was dried at room temperature at 30 °C for 12 hours as shown in Fig. 1.

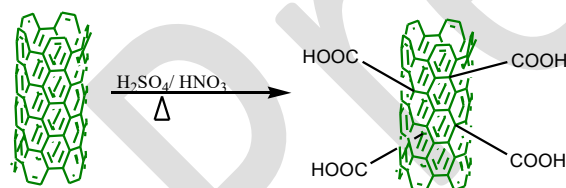


Fig. 1. Modification of multi-walled carbon nanotube.

Syntheses of polymer 2-Aminobenzothiazol

The oxidative condensation (OP) reactions of 2-aminobenzothiazole were carried out in an aqueous acidic medium as suggested for other aromatic amines [22] An aqueous solution of ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was chosen as a common oxidant for the oxidative condensation reactions of phenolic compounds. Ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ has a high oxidation potential as well as being inexpensive, and therefore, is preferred for oxidative condensation reactions. The synthesis methods are summarized in Fig. 2. The synthesis procedures were as follows: 1 g (7 mmol) of 2-aminobenzothiazole monomer was dissolved separately in 50 mL aqueous solutions containing 1 mL of concentrated hydrochloric acid. The solutions were placed in 250 cm³ three-necked round-bottom flasks equipped with a condenser, a thermometer, and a magnetic stirrer. The reaction mixtures were heated to 70 °C and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution (prepared by dissolving (1.5974 g (7 mmol) ammonium persulfate) in 8 mL deionized water) was added to the reaction medium dropwise. The reactions were kept for 6 h under the influence of the reflux and the solution colors turned dark brown. Then the heat was turned off

and stirring was continued for 72 h to complete the polymerization. Dark brown solids were obtained and were filtered and dried at 38 °C. The equation for the preparation of 2-aminobenzothiazole polymer is shown in Fig. 2.

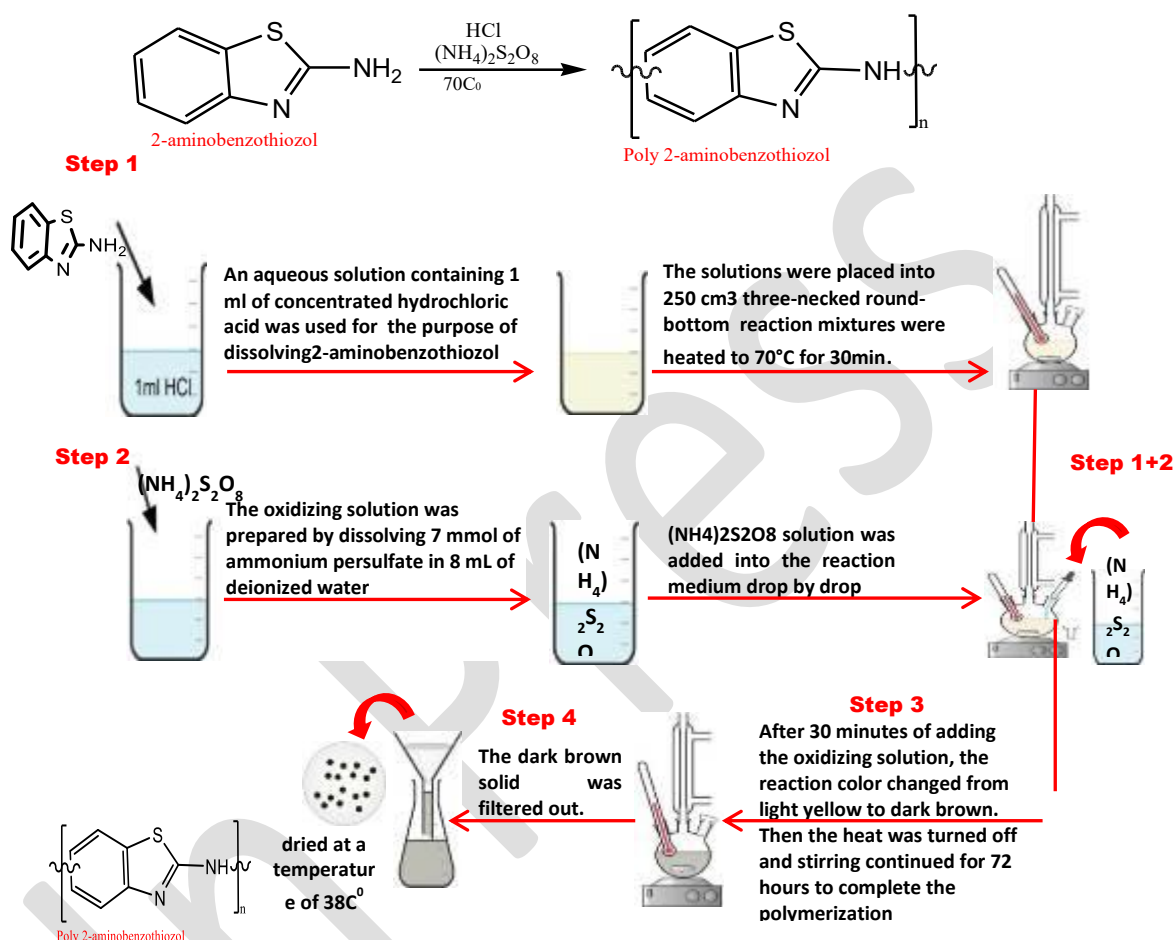


Fig. 2. Schematic diagram of polymer 2-Aminobenzothiazole preparation steps.

Preparation of 2-aminobenzothiazole with MWCNTs composites

Poly 2-Aminobenzothiazole composites were prepared from Multi-walled Carbon Nanotubes (MWCNTs) using weight percentage (1%) composite material. In general, the reaction conditions for preparing 1% Multi-walled Carbon Nanotubes (MWCNTs) polymer composite were given as follows:

1g (7 mmol) of 2-aminobenzothiazole monomer was dissolved separately in 50 mL of aqueous solutions containing 1mL of concentrated hydrochloric acid. The solutions were placed in 250 cm³ three-neck round-bottom flasks equipped with a condenser, a thermometer, and a magnetic

stirrer. The reaction mixtures were heated to 70 °C, and 0.01g of multi-walled carbon nanotubes (MWCNTs) were added to the mixture and ultra-sonicated at 25 °C for 3 h in an ultrasonic bath (7 mmol). The oxidizing solution was added. (prepared by dissolving (1.5974 g (7 mmol) ammonium sulfate in 8 mL of deionized water) was added to the reaction medium drop-wise. The reactions continued for 6 h under the influence of the reversal and the solution turned dark brown. Then the heat was turned off and stirring continued for 72 h to complete the polymerization. The solid fraction was collected using centrifugation, washed with deionized water and dried at 38°C. The preparation steps of 2-aminobenzothiazol:MWCNTs composite were illustrated in Fig.3 and the hydrogen bonding of 2-aminobenzothiazol polymer with multi-walled Nano carbon tube (MWCNTs) was shown in Fig.4.

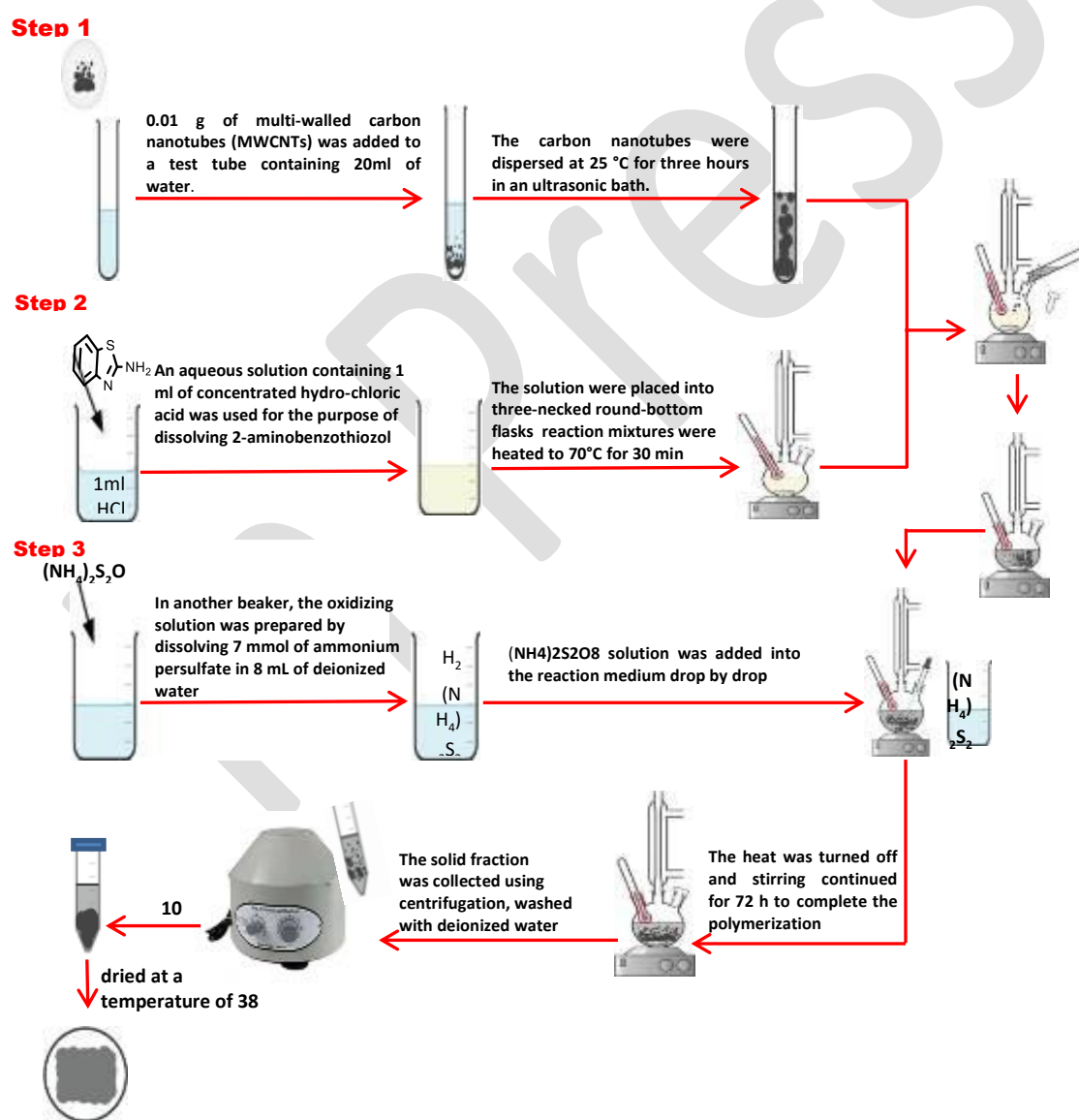


Fig. 3. Schematic diagram of 2-Aminobenzothiazol:MWCNTs composite preparation steps.

Preparation of 2-aminobenzothiazol and 2-aminobenzothiazol:MWCNTs thin films

The pure polymer and composite thin films were fabricated as follows: dissolved 0.02 g of 2-Aminobenzothiazol and 0.02 g of 2-Aminobenzothiazol:MWCNTs composite in 2 mL of DMF solvent separately. The both solution were dispersed at 40 °C for 10 min in an ultrasonic bath. Then each solution was casted on interdigitated ITO substrates at 40 °C for 3 hours. [22]

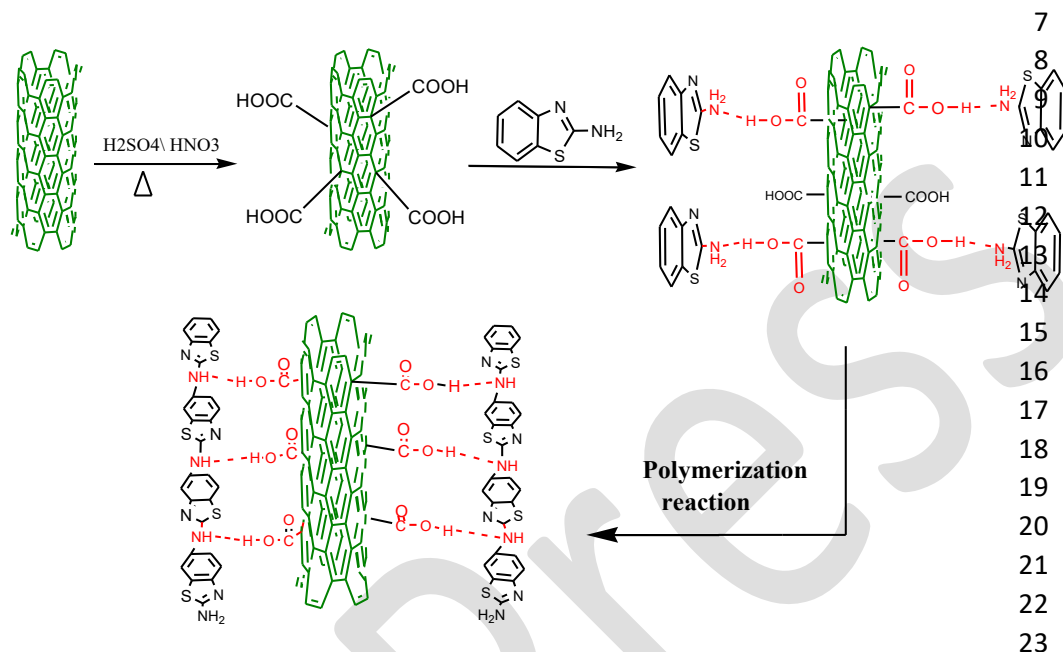


Fig. 4. the hydrogen bonding of 2-aminobenzothiazol polymer with multi-walled Nano carbon tube (MWCNTs).

Results and discussion

Structural analysis

FTIR Spectroscopy

It is essential to understand our synthesized compounds. In this study, FT-IR was applied to examine the various structures of compounds. Fig. 5(a) shows the FTIR spectra of monomer compound obtained from fluka. We will list assign some main peaks. A medium absorption band show at 3338 cm^{-1} and a at 3273 cm^{-1} in case of monomer, which could be due to NH_2 stretching vibration of primary amine. A medium absorption band appearing at 3055 cm^{-1} in case of monomer attributed to C-H stretching vibration of benzene ring. The peak at 1643 cm^{-1} relates to the C=C stretch of benzene. The C=N stretch has a peak at 1589 cm^{-1} . The peaks at about 1120 to 1107 cm^{-1} corresponded to the C-H out-of-plane bending vibration. The medium absorption band appears at 626.8 cm^{-1} which could be attributed to C-S symmetric stretching vibration. Fig. 5(b) appears the FTIR spectra for CNTs-COOH. The IR spectrum for the CNTs-COOH shows new adsorption band with characteristic -COOH peak at 3358 cm^{-1} . Another peak appears an absorption at 2924 cm^{-1} which is attributed to symmetric and asymmetric CH_2 stretching, while

1695 cm^{-1} is assigned to carboxylic C = O stretching for acidic group. Moreover, sharp carboxylic peak of C=O stretch attributed to $-\text{COOH}$ group was also observed at 1745 cm^{-1} . [24]

Fig. 6(a) shows the FTIR spectra of prepared polymer compound. We will list assign some main peaks. A broad absorption peak is observed from 3600 to 2000 cm^{-1} in the spectrum of polymer attributed to electronic transitions from valence band to conduction band in the polymer film. This peak is usually broad and can obscure other peaks in the entire region of 3400 to 2000 cm^{-1} peak at 3402 cm^{-1} appears as a broad absorption in polymer may be due to OH strong hydrogen bonded group in H_2O molecules of hydration in polymer. It is noted that NH_2 band was disappeared in spectrum.[16] This indicates the polymerization is formed via NH_2 Further. Medium absorption band which appears at 3325 cm^{-1} could be due to NH stretching vibration of amine. A medium absorption band appearing at 3055 cm^{-1} in case of monomer attributed to C-H stretching vibration of benzene ring. The peak at 1622 cm^{-1} relates to the C=C stretch of benzene. The C=N stretch has a peak at 1589 cm^{-1} . The peaks at about 1120 to 1107 cm^{-1} corresponded to the C-H out-of-plane bending vibration. The medium absorption band appears at 626.8 cm^{-1} which could be attributed to C-S symmetric stretching vibration.

Fig. 6(b) shows the FTIR spectra of prepared polymer composite. A broad absorption peak is observed from 3600 to 2100 cm^{-1} in the spectrum of composite attributed to electronic transitions from valence band to conduction band in the polymer film and hydrogen bonds between NH in polymer and COOH group in nanotube. This peak is broad and can vague other peaks in 3400 to 2000 cm^{-1} region. A medium absorption band shows at 3325 cm^{-1} which could be due to NH stretching vibration of amine, which may be overlap with the broad peak of hydrogen bonds. The peak at 1622 cm^{-1} relates to the C=C stretch of aromatic ring. The C=N stretch has a peak at 1589 cm^{-1} . The peaks at about 1120 to 1107 cm^{-1} corresponded to the C-H out-of-plane bending vibration. The medium absorption band appears at 625 cm^{-1} which could be attributed to C-S symmetric stretching vibration.[24]

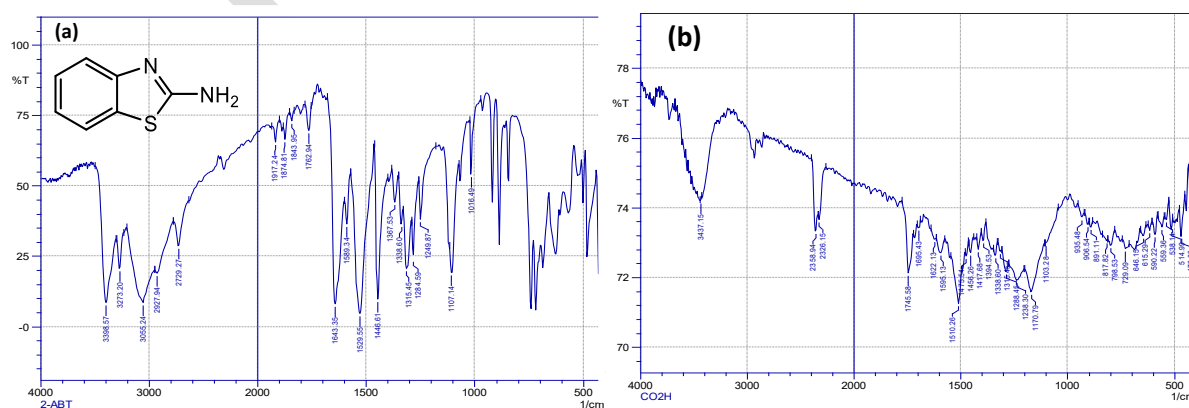


Fig. 5. FTIR spectra of (a) monomer compound, and (b) MWCNTs-COOH

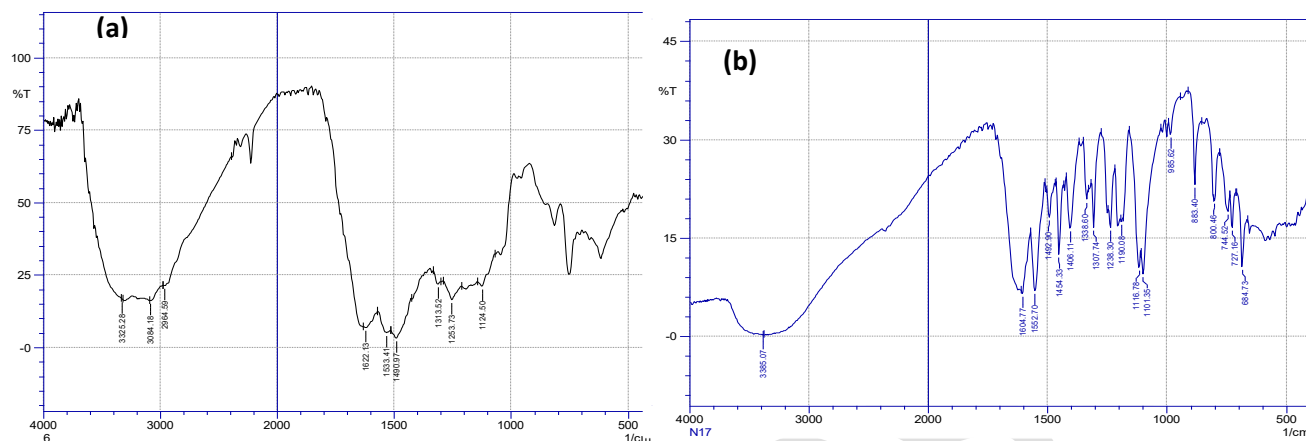


Fig. 6. FTIR spectra of (a) 2-Aminobenzothiazol, and (b) 2-aminobenzothiazol :MWCNTs composite.

Thermal characterization

TG–DTA curves are shown in Fig. 7. According to the obtained findings PAT and its composite thermally degrades in three particular steps. Materials start to decompose at 54°C and 63°C, respectively. As compared of the first degradation temperatures stabilities, the composite was more stable of polymer.

In general, aromatic thiazole- based polymers have high stabilities against thermal degradation attitude to their stable resonance structures. 5–11% weight losses between 20 and 140°C are due to losses of moisture, adsorbed solvent or monomer. The first steps could be indicated the degradation of the polymer chains from their bonds to form small sub-units and the others thermal are due to the degradation of those small units.[25] According to thermal curve, the polymer and its composite have finally converted to different subunits including NH₃, HCN, CS₂ and carbon residue. The overall weight losses to the original weight of PAT polymer at the end of decomposition was found to be 64% at 600 °C for the pure PAT, whereas, the overall weight losses of nanocomposite was lower than pure polymer (30% at 600 °C). These findings indicated that the thermal stability of the nanocomposite has enhanced due to the interaction between nanotube with PAT compared to homo-polymer (PAT).

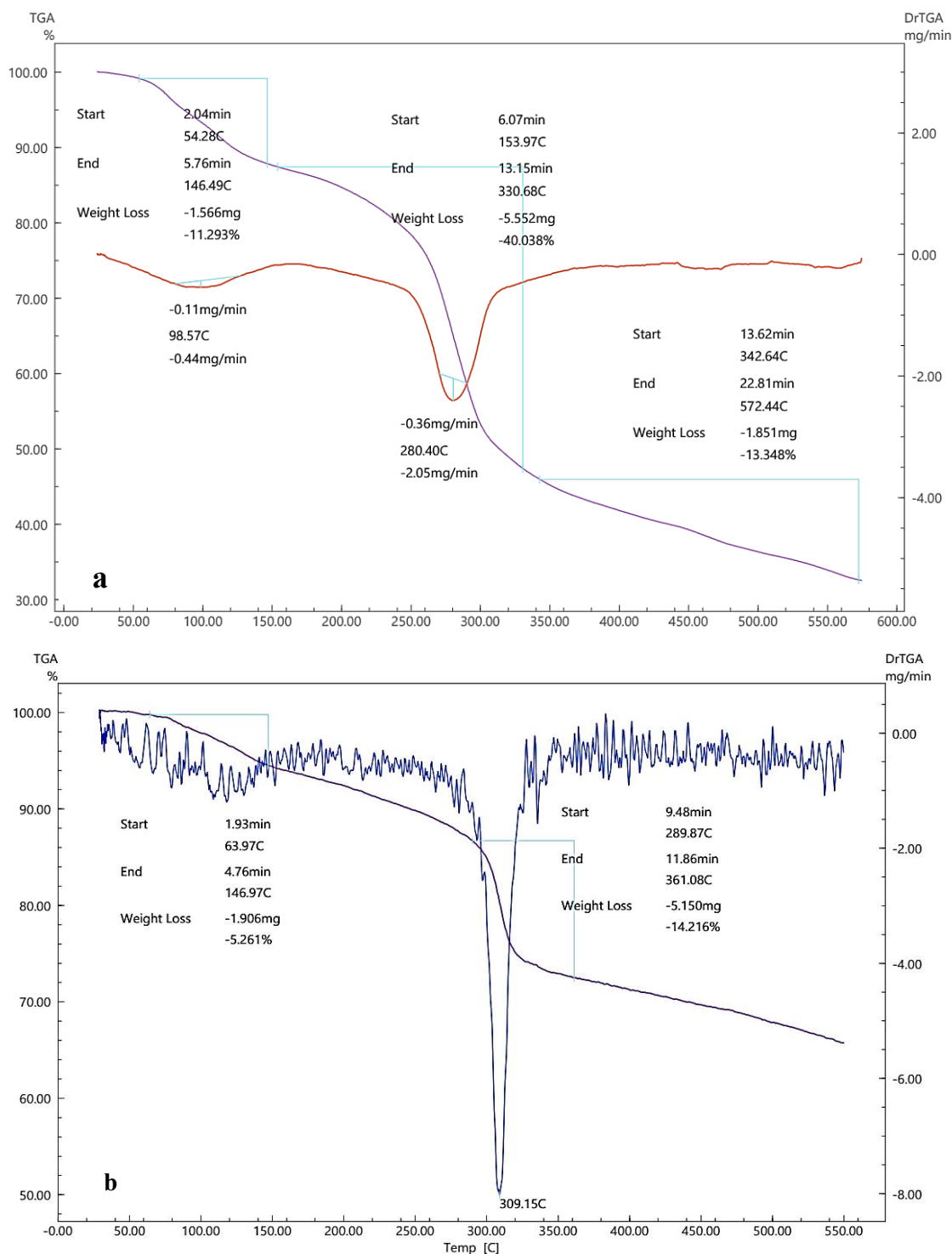


Fig. 7. TG curve of (a) poly 2-Aminobenzothiazol, and (b) poly 2-aminobenzothiazol:MWCNTs composite.

SEM measurements

Fig. 8 show the scan electron microscopy (SEM) images of the synthesized materials and fabricated thin films. From the SEM images in Figs. 8(b1) and 7(b2), it is clearly observed the MWCNTs located within the structure of the polymer, proving that the polymer:MWCNTs composite was successfully prepared. Further, the typical SEM images of prepared polymer exhibit that there are many pieces whose dimension are about some handers of nanometers.

Furthermore, as can be seen from the SEM images of the fabricated thin films, the surface morphology of the pure polymer thin film (see Fig. 8(c1) and 8(c2)) is smooth and uniform compared with that of the 2-aminobenzothiazol:MWCNTs films where a significant change in the surface topography was observed with high visibility of MWCNTs in the structure of the doped film as illustrated in Figs. 8(d1) and 8(d2). [26]

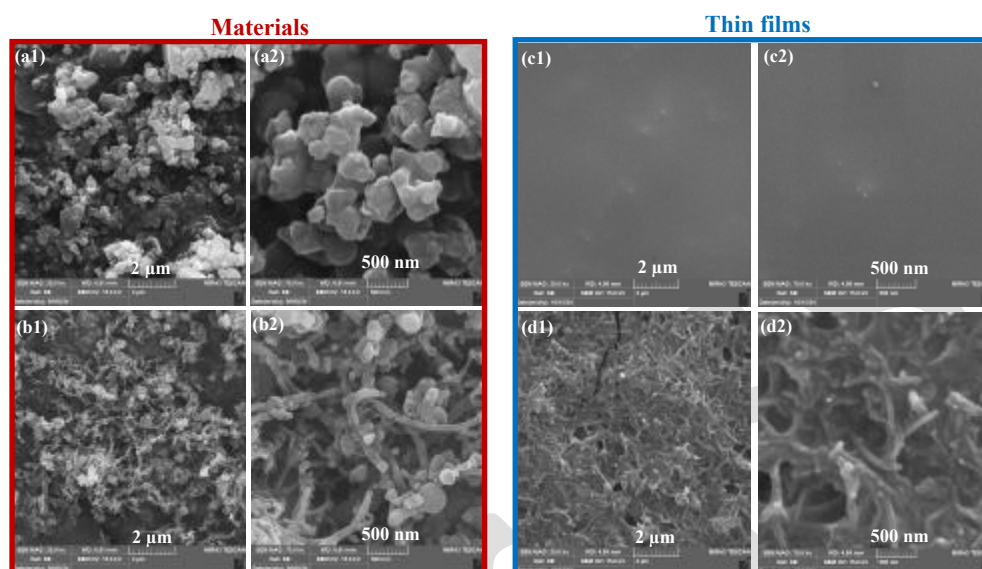


Fig.8. Scan electron microscopy (SEM) images of (a1) poly 2-Aminobenzothiazol, (b1) poly 2-aminobenzothiazol:MWCNTs composite, (c1) poly 2-Aminobenzothiazol thin film, and (d1) poly 2-aminobenzothiazol:MWCNTs composite thin film.

XRD measurements

XRD patterns of the poly 2-aminobenzothiazol and poly 2-aminobenzothiazol: MWCNTs composite were shown in Fig. 9. For the pure PAT, the broad reflection centered at a 2θ value around xx is merit of the amorphous polymer. Further, the poly 2-aminobenzothiazol: MWCNTs composite, additional two peaks appear at $2\theta = 23$ and 42 , which correspond to reflection of the MWCNT compound which was add to polymer matrix. The mass fraction of MWCNTs in poly 2-aminobenzothiazol: MWCNTs composite is sufficiently tiny that the MWCNTs diffraction peaks can hardly be noted for 1wt % MWCNTs -containing poly 2-aminobenzothiazol: MWCNTs composites. However, traces of diffraction peaks at $2\theta = 23$ and 42 were seen indicating that the MWCNTs had partly interacted with poly 2-aminobenzothiazol molecules.[27]

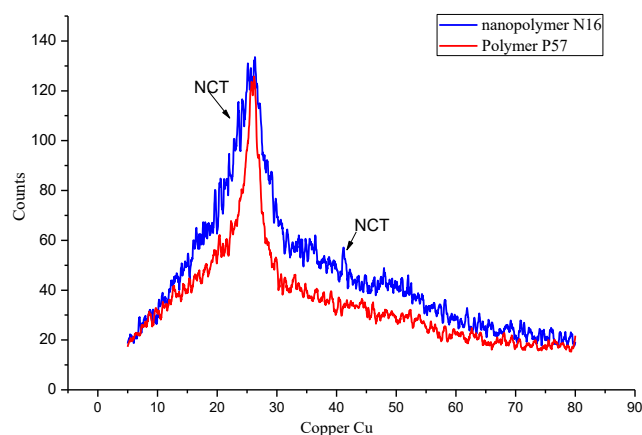


Fig. 9. X-ray diffraction (XRD) curve of poly 2-Aminobenzothiazol (red curve) , poly 2-aminobenzothiazol:MWCNTs composite

Electrical measurements

Current-voltage (I-V) characteristics of the pure polymer and 2-aminobenzothiazol:MWCNTs composite thin films under dark conditions. The measurements were carried out at room temperature over applied voltage range from 0.025 V to 10 V and the results plotted in Fig. 10. It was found that when the voltage increases, the current of the fabricated thin films increases gradually, showing a linear behavior (Ohmic low) for pure polymer thin film and nonlinear behavior for composite thin film. The conductivity σ of the two samples was determined from the following equation[28] :

$$\sigma = \frac{I \cdot d}{V \cdot L \cdot t \cdot N} \quad (1)$$

Where L is the length of fingers, d is the distance between the fingers electrodes, N is the number of fingers, t is the thickness of thin films. I and V are the electrical current and voltage, respectively. The resistivity was also calculated from the formula:

$$\rho = 1/\sigma \quad (2)$$

The values of the conductivity and resistivity of the fabricated thin films were evaluated and listed in Table 1.

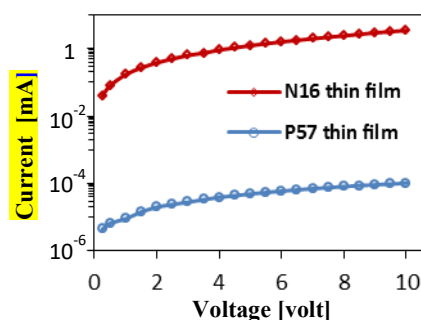


Fig.10. Current-Voltage (I-V) characteristics of the pure polymer (P57) and 2-aminobenzothiazol :MWCNTs composite (N16) thin films under dark conditions.

Table 1. The conductivity and resistivity values of the pure polymer and the composite thin films at room temperature.

Sample	Conductivity	Resistivity	Enhancement
2-aminobenzothiozol	1.7×10^{-6} S/cm	0.68 MΩ.cm	-
2-aminobenzothiozol:MWCNTs N16	4.1×10^{-2} S/cm	24.5 Ω.cm	24000x

As can be seen from Fig.10 and Table 1, the conductivity of the pure polymer thin film increases from 1.7×10^{-6} S/cm to 4.1×10^{-2} S/cm as a results of doping by 1%wt of MWCNTs, showing a significant enhancement by a factor of 24000x. In contracts, the resistivity of the pure polymer reduce from 0.68 MΩ.cm to 24.5 Ω.cm. [29]

Temperature dependence of the current, conductivity and resistivity of the fabricated thin films were also investigated as illustrated in Fig.11. The measurements were carried out over temperature range from 20 °C to 110 °C at applied voltage of 5 V. The results revealed that the values of the electrical parameters, current and conductivity, increases gradually with increasing the temperature, while the resistivity reduces. It can be seen from Fig. 11, when the temperature increases from 20 °C to 110 °C, the conductivity of the pure polymer thin film increases from 1.6×10^{-6} S/cm to 2.8×10^{-6} S/cm, while the resistivity decreases from 0.625 MΩ to 0.356 MΩ, respectively. For composite thin film, the conductivity increase from 4.1×10^{-2} S/cm at 20 °C to 5.3×10^{-2} S/cm at 20 °C and the resistivity reduced from 25.35 Ω.cm at 20 °C to 18.85 Ω.cm at 110 °C. The optimization in the conductivity and resistivity is attributed to generate carriers as a result of the thermal-excitation process. It was also found that the temperature coefficients of the DC conductivity for the fabricated thin films are positive, indicating that the two samples are semiconductors.[30]

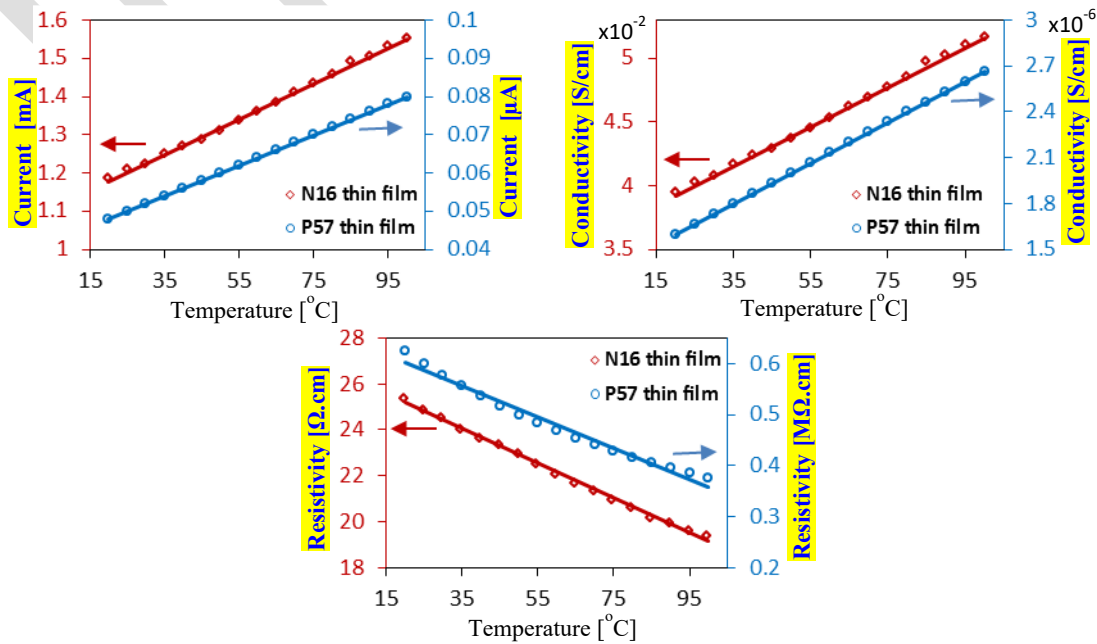


Fig.11. Temperature dependence of the current, conductivity and resistivity for the pure polymer (P57) and 2-aminobenzothiazole:MWCNTs composite (N16) thin films under dark conditions.

4. Conclusions

In this study, Poly(aminobenzothiazole) (PAT) was successfully synthesized by chemical-oxidative polymerization technique. Then composite material with modified carboxylic multi-wall carbon nanotubes (MWCNTs) was prepared. The structure of the polymer matrix and its composite were characterized by several techniques such as FT-IR, SEM, and TG techniques. The various peaks observed from the FTIR results confirm the functionalization of CNTs where new peak was shown in the spectrum due to oxidation process of CNTs. In addition, some other peaks were appeared at FTIR for the prepared polymer and interaction between CNTs and polymer chains. The TG findings pointed out that the thermal stability of the PAT polymer was improved as a result of doping by MWCNTs. The overall weight losses to the original weight of PAT polymer was found to be 64%, whereas, the weight losses of nanocomposite was 30%. These findings indicated that the thermal stability of the nanocomposite has improved due to the interaction between nanotube and polymer chains. The SEM images confirm that doping the pure polymer by MWCNTs was successfully prepared, where there are several MWCNTs overlap with the structure of the pure polymer. Thus, the carriers of the doped polymer could be increased due to increase the dopant energy levels. Consequently, The findings show that the conductivity of composite thin films reach to 4.1×10^{-2} (S/cm), exhibiting a significant enhancement by a factor of 24000 times as a results of doping polymer by 1% wt MWCNTs.

Acknowledgments

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