Applied Nanomaterials and smart Polymers,
Online ISSN: 2981-0434
Vol. 1, No. 3

ANSP

Enhannced Electrical Conductivity of Polythiophene and Polypyrrole Multi-layer Coatings on PMMA Substrate with Carbon Nanotubes

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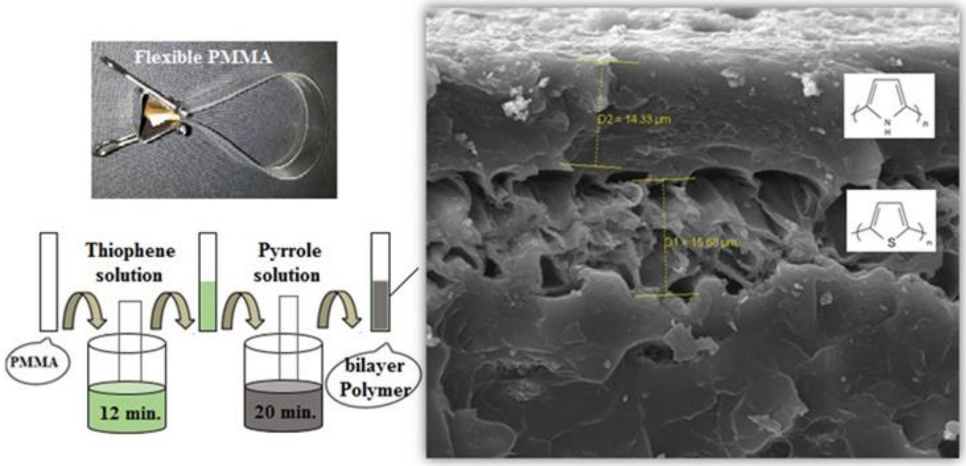
ABSTRACT

In this study, we aimed to enhance the electrical conductivity of polymeric layers for potential applications in organic electronics such as sensors and capacitors. Electrically conductive polythiophene (PTh) and polypyrrole (PPy) layers were deposited on a poly methyl methacrylate (PMMA) substrate using an in-situ chemical oxidative deposition method with $FeCl_3$ as a catalyst and acetonitrile and deionized water as solvents. To further improve conductivity, multi-layer PTh and PPy, in the presence of carbon nanotubes (CNT), were applied on the PMMA substrate. The reaction times for synthesizing PTh and PPy were optimized to be 12 and 20 minutes, respectively, based on electrical properties. Fourier-transform infrared spectroscopy (FTIR) was used to identify the different components of the conductive polymers on the PMMA substrate. The morphology and thickness of the layers were investigated using scanning electron microscopy (SEM). The electrical conductivity of the layers was measured using a four-point probe device. The highest electrical conductivity of 100.93 S/cm was achieved for the two-layer poly pyrrole-polythiophene/CNT coating on the PMMA substrate. These findings demonstrate the potential of this multi-layer conductive coating for various organic electronic applications.

Keywords

Fluorocarbons, Gentamicin, Antimicrobial, Waterproof, Blood-resistance.



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1. Introduction

With the increasing demand for portable and flexible devices, soft electronics have gained significant attention in various applications including flexible photovoltaics, optics, sensors, batteries, and supercapacitors. One of the key challenges in developing these devices is achieving stretchable and flexible conductive electrodes, which serve as the fundamental core unit. Conductive polymers, such as polyaniline, polypyrrole, and polythiophene, have emerged as a class of organic materials with unique electrical and optical properties comparable to those of inorganic semiconductors and metals [1]. These polymers have attracted considerable interest in various scientific fields due to their technological applications in solar cells [2], sensors [3], supercapacitors [4], rechargeable batteries [5], and more. Among them, polythiophene (PTh) and polypyrrole (PPy) stand out due to their environmental stability, high electrical conductivity, and ease of synthesis using chemical methods [6]. However, PTh exhibits relatively low electrical conductivity due to the lack of electrons in its anti-bonding orbit and wide energy gap. PPy, on the other hand, suffers from limited electrochemical stability and low permeability. To expand the application scope of PTh and PPy, extensive research has focused on doping them with other nanoparticles [7-9]. For instance, PPy-coated cotton fabric electrodes were prepared by Xu et al. through in-situ chemical polymerization on various templates [10]. Zhang et al. coated conductive polymers on the surface of reduced graphene oxide (RGO) sheets via an in-situ polymerization process to fabricate CP/RGO electrodes for supercapacitors [11]. Tong et al. coated polypyrrole on carbon nanotube (CNT) paper to create electrodes for all-solid-state supercapacitors [12]. Thakur et al. synthesized composites of PTh and CNTs using an easy in-situ polymerization method and observed improved electrochemical performance compared to pure PTh [13]. Zhang et al. reported the galvanostatic polymerization of PTh onto MWCNT-modified carbon paper, resulting in a PTh/MWCNT composite with an interlaced framework morphology and excellent supercapacitor performance [14]. In addition to producing conductive electrodes with conductive polymer films, these materials have also been used to coat polymeric substrates such as transparent flexible films of polyethylene terephthalate (PET) [15-17] and piezoelectric, semi-transparent, and flexible PVDF nanocomposite films [18]. Among these polymers, Poly(methyl methacrylate) (PMMA) is a clear, colorless polymer widely utilized as a gate dielectric in organic thin films. PMMA boasts thermal and mechanical stability, as well as high electrical resistivity (>2×1015 Ω/cm), making it an ideal dielectric layer for organic electronics [19]. Yousefi coated PTh on PMMA as an alternative to ITO glass for use as an electrode in solar cells. Under optimized reaction conditions, the highest electrical conductivity reported was 0.74 S/m with a conductive layer thickness of 37 micrometers [20].

In this study, we present a facile approach to assemble thin and uniform PPy/MWCNT and PTh/MWCNT layers on a flexible PMMA sheet, forming a one-dimensional nanostructure by improving the in-situ chemical oxidation polymerization method. The addition of deionized water and acetonitrile in the aqueous reaction system plays a crucial role in tuning the morphology and thickness of PTh and PPy by controlling the polymerization rate. This approach overcomes the challenge of enhancing the interfacial bonding between the polymer and carbon nanotubes. The resulting PTh/MWCNT and PPy/MWCNT composites exhibit a uniform structure without agglomeration or irregular nanoparticles on the composite surface. Furthermore, the synthesis process does not require surfactant assistance, and the nanocomposite thickness can be precisely controlled by adjusting the solvent and $FeCl_3$ content and altering the PTh/MWCNT and PPy/MWCNT mass ratio.

2. Experimental

2.1. Materials

The 1 mm thick transparent PMMA sheet used in this study was produced by Year Long Company in Taiwan using the solution casting technique. Figure 1 demonstrates the flexibility and transparency of the PMMA sheet. The Multi-Walled Carbon nanotubes were purchased from Nanostartech Co in Tehran, Iran, while Pyrrole and thiophene were purchased from Merck Company. Anhydrous Iron (III) chloride (FeCl3, Merck) and acetonitrile (CH3CN, DaeJung Korea) were used as the oxidant.

2.2. Instruments and procedures

The electrical conductivity was measured using the FPP-SN-554 model from Sanat Nama Javan Co in Iran, employing the four-point microprobe method. Scanning electron microscopy (VEGA/TESCAN, Czech Republic) was used to observe the morphology, EDX pattern, and thickness of the layers. Prior to testing, the SEM samples were coated with a thin layer of gold. Fourier transform infrared (FTIR) spectra in the spectral range of 400 to 4000 cm-1 were obtained using a Bruker Equinox 55 spectrometer in ATR mode.

2.2.1. Synthesis of conducting polythiophene

A conducting polythiophene was synthesized through the following experimental procedure. Firstly, a monomer solution was prepared by mixing 0.5 mL of thiophene with 10 mL of acetonitrile. Separately, an oxidant solution was prepared by dissolving 1.8 grams of anhydrous $FeCl_3$ in 20 mL of acetonitrile. Both solutions were stirred individually for 20 minutes. Next, PMMA substrates were cut into 1*5cm2 pieces and thoroughly washed with deionized water, followed by cleaning with ethanol. The prepared PMMA film was then immersed in the oxidant solution, and the monomer solution was added dropwise while continuously stirring at room temperature. As a result, the initially colorless thiophene solution transformed into a dark-colored solution.The polymerization process was allowed to proceed for only 12 minutes under stirring conditions. This led to the deposition of a polythiophene layer on the surface of the PMMA substrate.

2.2.2. Synthesis of conducting polypyrrole

The monomer solution was prepared by adding 0.5 mL of distilled pyrrole to 10 mL of acetonitrile. The oxidant solution was prepared by adding 2 grams of anhydrous FeCl3 to 20 mL of distilled water. Both solutions were stirred separately for 20 minutes. Then, similar to the previous sample, the PMMA film was immersed in the oxidant solution, and the monomer solution was added dropwise. The initially colorless pyrrole solution turned into a dark-colored solution. The polymerization was allowed to proceed for just 30 minutes under stirring, resulting in the deposition of a polypyrrole layer on the PMMA surface.

2.2.3. Functionalization of MWCNTs

To functionalize the MWCNTs, 0.2 grams of purified MWCNTs were sonicated at 50°C for 2 hours in a 20 ml mixture of sulfuric and nitric acid. The ratio of sulfuric acid to nitric acid was 3 parts sulfuric acid to 1 part nitric acid. Afterwards, deionized water was added to the mixture, and it was filtered using a poly carbonate membrane filter paper with a pore size of 0.4 µm. The filtered material was then washed multiple times with deionized water until a pH value of 7 was achieved.

Finally, the material was dried completely in an oven at 80°C for 24 hours.

2.2.4. Synthesis of CNT/Polymer nanocomposite

To synthesize nanocomposites, carbon nanotubes were dispersed in the solvent at a weight ratio of 1%. Subsequently, the monomer solution and CNTs solution were added dropwise simultaneously while continuously stirring at room temperature to the oxidant solution. After a duration of 15 minutes, a layer of polymer and carbon nanotube (nanocomposite) was synthesized on the PMMA substrate.

2.2.5. Synthesis of bilayer conductive polymer

The first layer is coated on the PMMA substrate using the synthesis method mentioned in the previous sections. After drying the first layer, the second layer is polymerized using the same synthesis method, ensuring good adhesion to the first layer. Figure 1 illustrates a schematic of the polymer synthesis on the PMMA film.

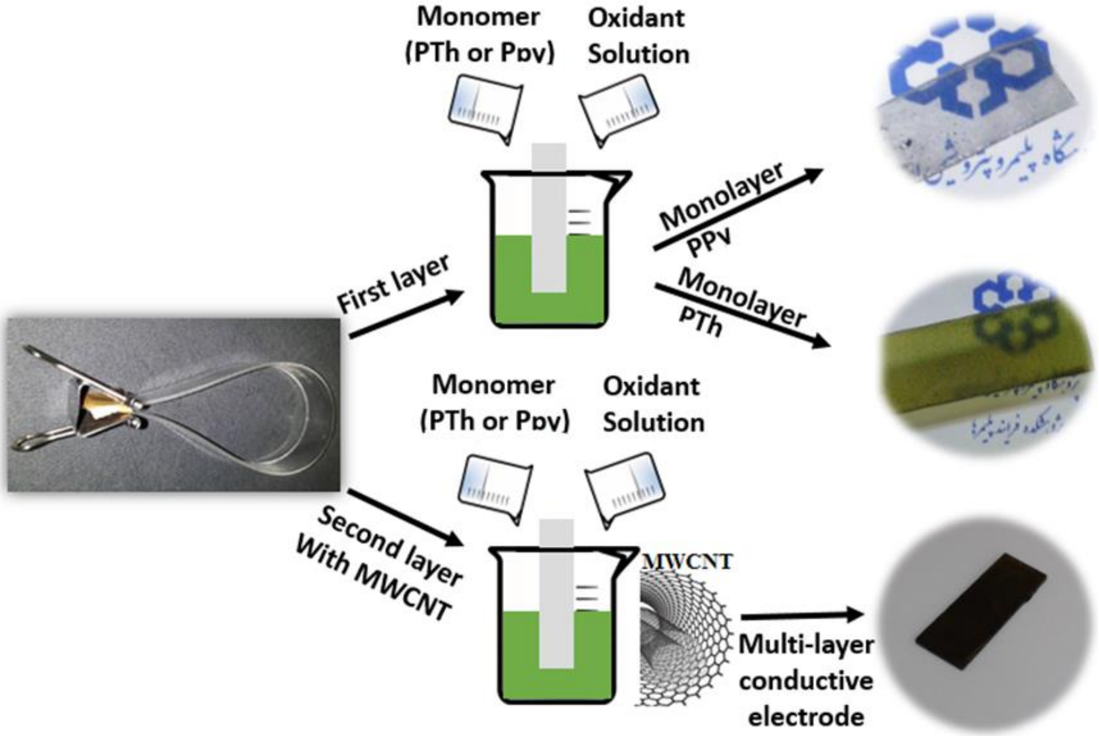

Fig1. Schematic of polymer synthesis on PMMA film.

3. Results and Discussion

3.1. ATR-FTIR spectroscopy

To examine the mixing-induced interaction between MWCNTs and PTh, as well as MWCNT and PPy, and provide evidence for their formation on PMMA substrate, FTIR spectroscopic analyses were carried out in ATR mode. The broad peak ranging from 1260-1000 cm-1 can be explained by the C-O (ester bond) stretching vibration. A peak at 1195 cm-1 is assigned to –O-CH3 stretching vibrations [21]. These peaks are sharper in the sample containing thiophene and carbon nanotube due to the presence of carbon. The FTIR spectra of pure PMMA and PMMA coated by MWNT-PTh and PTh composite are shown in Figure 2. There are several low-intensity peaks in the range of 2800-3100 cm-1 that can be attributed to the aromatic C-H stretching vibrations and C=C characteristic band (1637 cm-1)[22]. The absorption peaks related to the C-Cl bond are in the range of 550-780 cm-1 by doping of polythiophene with FeCl3. The absorption bands observed at 1320 and 1192 cm-1 indicate the C-H bond band and C=S stretching[23]. The peaks at 1110 cm-1 and 787 cm-1 respectively indicate the C-H aromatic bond on the surface and outside the surface changed in the vibrations of the thiophene ring. The peak at 831 cm-1 shows C-S stretching that can be seen in spectra blue and green[24]. The peak at 628 cm-1 indicates the changed C-S-C ring in polythiophene [25].

ATR spectra of pyrrole and pyrrole/CNT samples coated on PMMA were analyzed to identify the presence of various functional groups. The obtained spectra showed distinct peaks corresponding to different bonds and vibrations.The bands at around 3400 cm−1 and 1640 cm−1 are responsible for physisorbed moisture(blue curve). Distinct absorption bands for C–O–C are seen in the regions 1250–1050 cm−1 (stretching) and 960–880 cm−1 (deformation)[26].

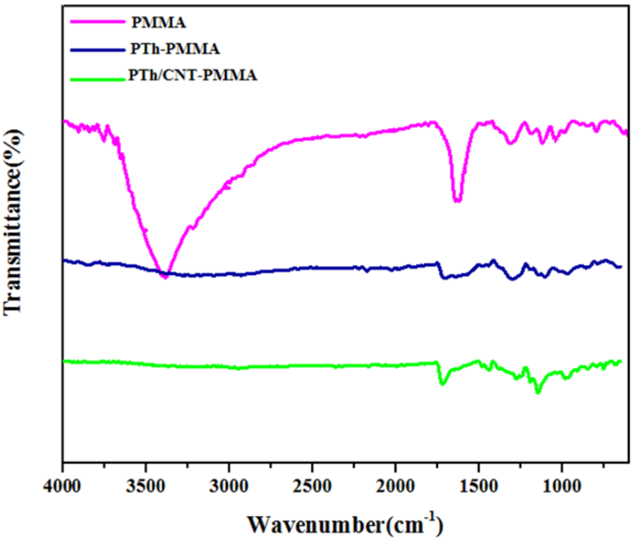

Fig2. FTIR Spectra of PMAA(purple) PMMA coated by PTh,(blue) PMMA coated by PTh/CNT composite samples(green).

This is consistent with the chemical structure of pyrrole, which contains a nitrogen atom. The peaks near 1615 cm-1 and 1547 cm-1 can be attributed to the asymmetric and symmetric ring stretching vibrations of the C-N bond and C-C bond, respectively[27]. These peaks confirm the presence of the pyrrole ring in the sample (orange and green curve). The peak near 1168 cm-1 suggests the doping of polypyrrole. Doping refers to the introduction of dopant molecules or ions into the polymer matrix, which can alter its electrical properties. The presence of this peak indicates that the pyrrole sample has been doped with certain substances, potentially enhancing its conductivity. The peak at 1039 cm-1 indicates surface modification of the C-H bond and N-H stretching vibration. This suggests that the pyrrole sample has undergone some form of surface treatment or modification, possibly to improve its compatibility with other materials or to enhance its performance in specific applications. Peaks at 1704 cm-1 and 1726 cm-1 correspond to the stretching vibrations of the C=O bond, indicating the presence of carbonyl groups in the pyrrole sample. These carbonyl groups could be a result of oxidation or other chemical reactions involving the pyrrole molecule. The peak at 1134 cm-1 corresponds to the C-O bond, suggesting the presence of oxygen-containing functional groups in the pyrrole sample. These groups could be the result of oxidation or other chemical modifications. The peak at 820 cm-1 is related to the C-H aromatic bond, further confirming the presence of aromatic rings in the pyrrole sample. Absorption peaks related to the C-Cl bond are observed in the range of 550-780 cm-1[28]. This suggests the presence of chlorine-containing compounds in the pyrrole sample, potentially as impurities or residues from the synthesis process[29].

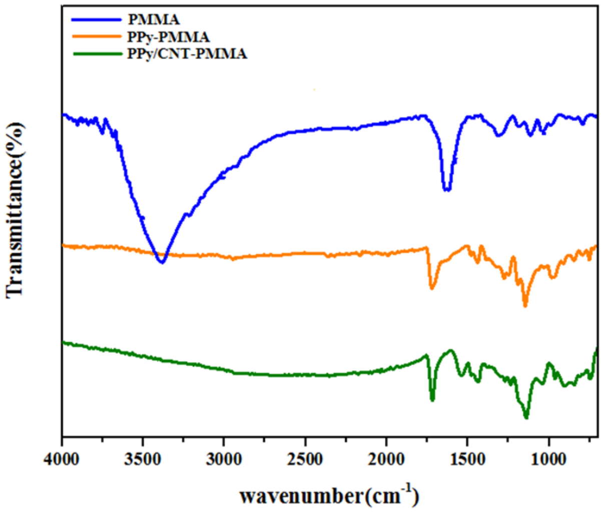

Fig3. FTIR spectrum of PMMA(blue), polypyrrole coated on PMMA(orange), polypyrrole/CNT coated on PMMA(green).

3.2. Morphology

For the morphological analysis, two different samples were prepared: one for surface morphology and the other for bulk and thickness observations. Figure 4(b) shows the image of polythiophene synthesized with 1% weight of carbon nanotubes on a PMMA substrate at a magnification of 1 µm. In this image, it can be observed that the spherical particles of polythiophene are uniformly dispersed in a chain-like manner on the surface of the nanotubes. The presence of the polymer has led to an increase in the diameter of the carbon nanotubes, as shown in Figure 4(a).

Furthermore, Figure 4(c) illustrates the SEM image of polypyrrole synthesized with 1% weight of carbon nanotubes on a PMMA substrate. Similar to the previous case, polypyrrole is uniformly dispersed on the surface of the carbon nanotubes. This morphology suggests a strong interaction between the polypyrrole and the carbon nanotubes, leading to a well-dispersed and interconnected structure. These observations indicate the successful synthesis and uniform dispersion of both polypyrrole and polythiophene on the carbon nanotubes, which can have significant implications for various applications in the field of nanocomposites and nanoelectronics. By adding carbon nanotubes, the conducting polymer particles are more uniformly and orderly distributed within the polymer network structure. This can indicate an improvement in the morphology and arrangement of the polymer particles[30]. Additionally, carbon nanotubes can act as a conducting bridge, enhancing the surface conductivity of the polythiophene. Therefore, adding carbon nanotubes to polythiophene can lead to improvements in the electrical and mechanical properties of the structure[31].

By adding nanotubes to conducting polymers, the particle size becomes larger. This increase in size may occur due to the physical combination between nanotubes and polymers or the absorption of nanotubes into polymer chains[32]. Adding nanotubes leads to an improvement in the distribution of particles in the polymer structure.
This improvement can lead to better ordering and regulation of particles in the polymer matrix, as well as reducing the formation of masses and particle aggregations.

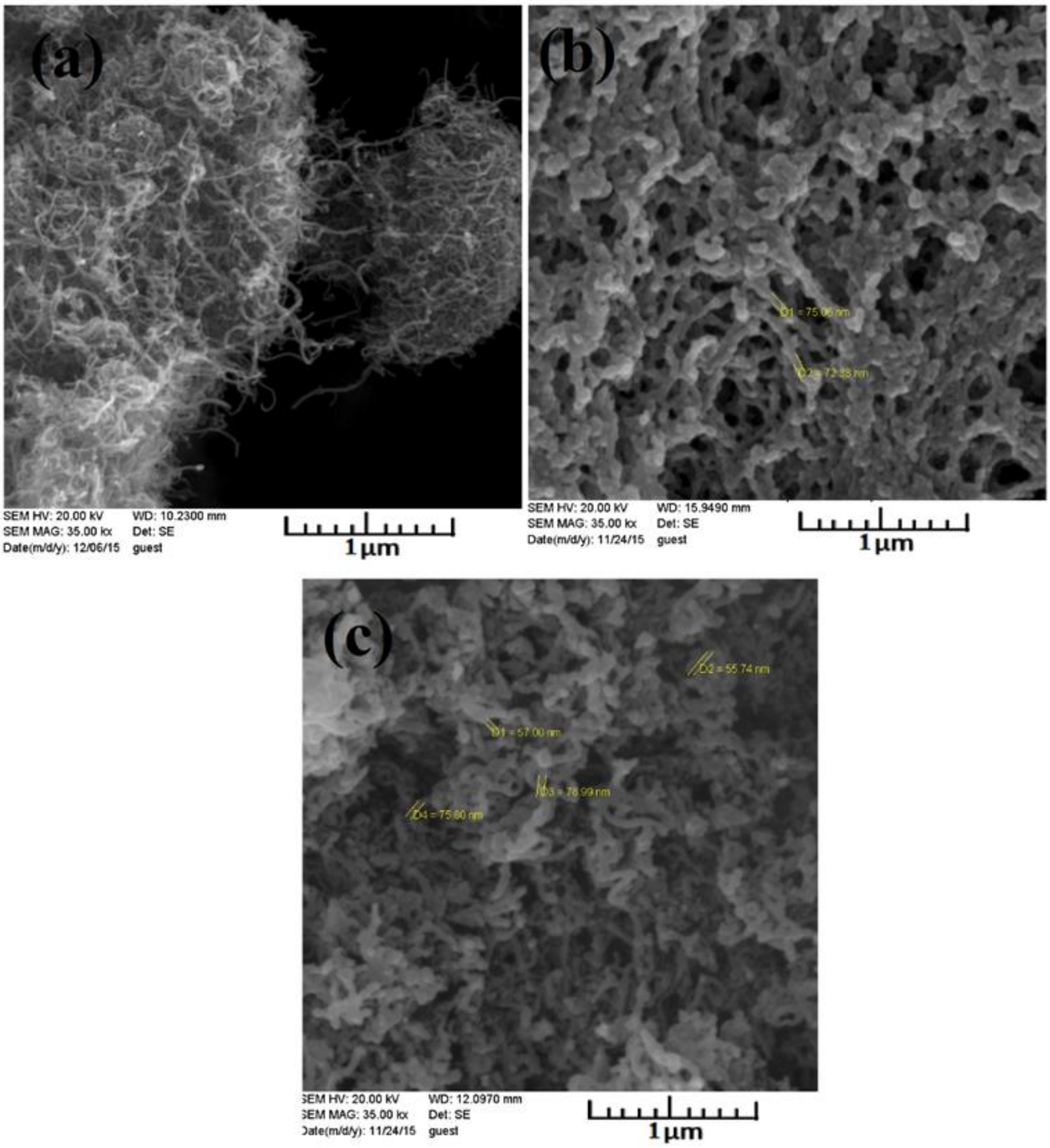

Fig4. SEM image of MWCNT(a), MWCNT-PTh(b) and MWCNT-PPy(c) surface.

It can also change the mechanical properties of conducting polymers. Nanotubes can act as mechanical reinforcements and increase the strength and hardness of the polymer[33]. The average diameter of the conducting polymer particles and the average diameter of the carbon nanotubes in the images obtained by scanning electron microscopy were calculated using Image J software, and the results are presented in Table 1. The diameter of the carbon nanotubes increased from 2.34 nm to 3.62 nm after synthesis with the pyrrole monomer. This diameter further increased to 8.61 nm in the synthesis with the thiophene monomer. As observed, in the monolayers, the diameter of the polymer particles increased with the addition of carbon nanotubes, which can be attributed to the penetration of carbon nanotubes into the polymer chain.

Table1. Particle size of composite layer components.

Sample	Mean particle diameter of polymer (nm)	Mean particle diameter of CNT (nm)
PTh	120	
PTh-PPy	100	
PPy/CNT	92.3	62.3
PTh/CNT	150	61.8
PTh/CNT-PPy	100	67.1
CNT		34.2

3.3. EDX Analysis

To obtain more information about the structure of the samples, EDX analysis was performed. Figures 5 and 6 show the EDX images of the polythiophene/carbon nanotube nanocomposite. The scattering of sulfur in Figure 5 indicates the presence of polythiophene on the surface of poly(methyl methacrylate).

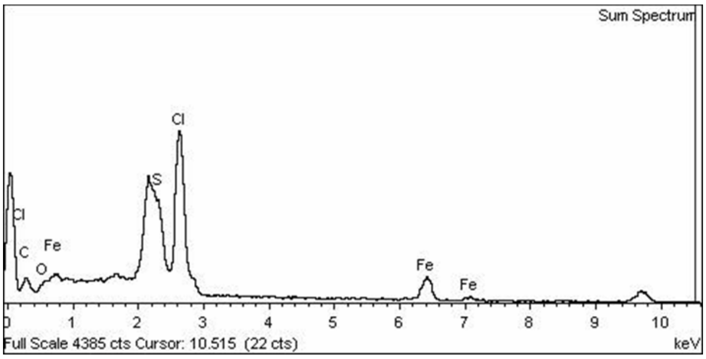

Fig6. The presence of Fe, S atoms in the PTh/CNT nanocomposite

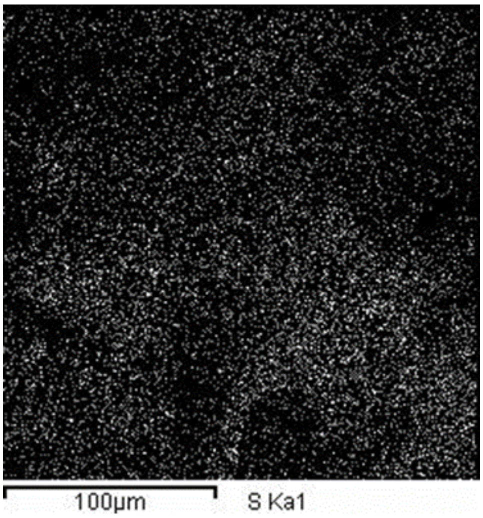

Fig5. Sulfur distribution in PTh/CNT layer.

Figures 7 and 8 show the EDX images of the poly(pyrrole)/carbon nanotube nanocomposite. The scattering of nitrogen in Figure 7 indicates the presence of poly(pyrrole) on the surface of poly(methyl methacrylate).

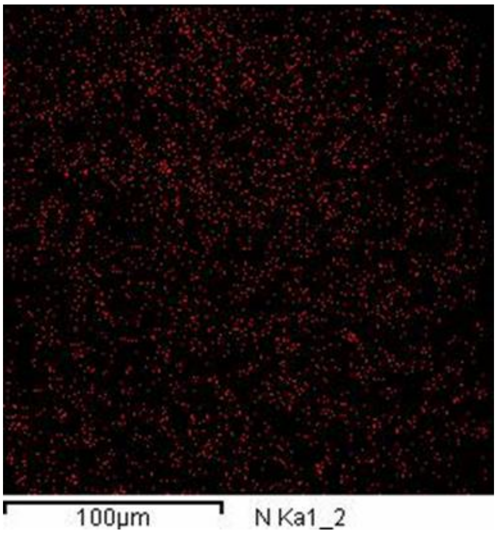

Fig7. Distribution of nitrogen atoms in PPy nanocomposite 1% by weight of CNT.

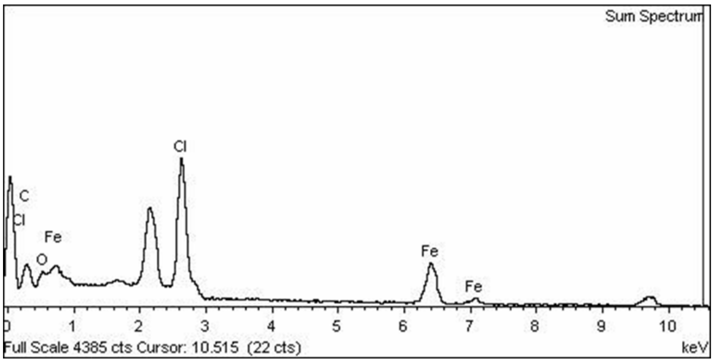

Fig8. Presence of C, Cl, Fe particles in PPy/CNT nanocomposite.

3.4. Measurement of Thickness

To measure the conductivity of the synthesized layers, the thickness of the layers was measured using a scanning electron microscope (SEM), and the surface resistivity of the sample was measured using a 4-point probe resistance meter. Figure 9 shows the SEM image of cross section of the bilayer polythiophene/carbon nanotube on PPy based on PMMA at a magnification of 20 μm. As can be seen, the thickness of the PTh/CNT layer is 5.76 μm and the thickness of the first layer (PPy) reported 30.88 μm. According to Figure 9, there is no gap between layers, which indicates good adhesion of the layers to each other. In the case of two layers, the thickness of PTh/CNT layer decreased compared to the case of single layer (103.31 μm) and this state increased the conductivity of the double layer sample. By adding CNT to PTh, the electrical resistance decreased and despite the increase in thickness, the conductivity increased up to two times (Table 2).

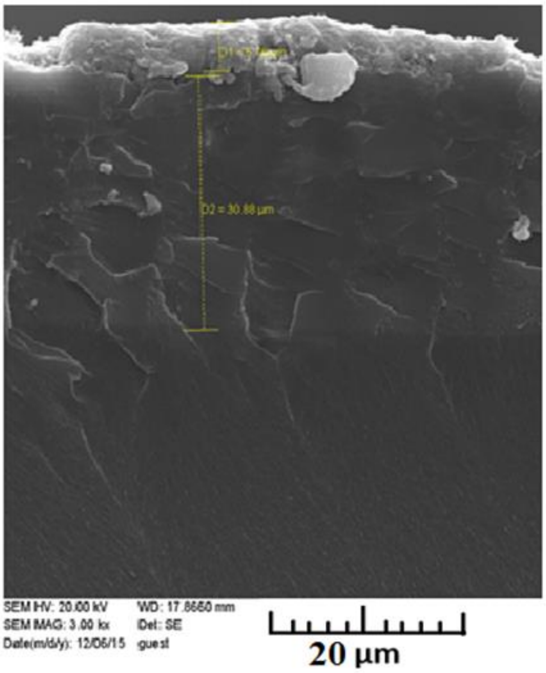

Fig9. SEM image of bilayer conductive polymer on PMMA substrate.

3.5. Electrical properties

As can be seen in Table 2, in single-layer samples, PPy with 1% carbon nanotube has the highest conductivity, which was reported as 10.09 S/cm. In the double layer samples, the highest conductivity was observed in the double layer of CNT/PTh on PPy based on PMMA substrate, which is 100.93 S/cm. It can be concluded that by adding layers the conductivity increases about 25 times. Adding CNT to PTh increases the conductivity, while adding this material to PPy does not have any effect on conductivity.

Table 2. Electrical properties of bilayers coated on PMMA substrate

First layer	Conductive layer thickness (µm)	Electrical resistivity (kΩ) (4-point)	Electrical conductivity (S/m) (4-point)	Second layer	Conductive layer thickness (µm)	Electrical resistivity (kΩ) (4-point)	Electrical conductivity (S/m) (4-point)
PTh	128.32	13	0.599	PPy/CNT	28.40	0.63	55.89
PPy	30.88	7.5	4.317	PTh/CNT	5.76	1.72	100.93
PPy	118.39	2.5	3.378	PTh	9.03	1.78	62.214
PTh	52.42	43.9	0.442				
PTh	34.63	53	0.544				
PTh/CNT	30.01	3.3	10.09				
PPy/CNT	103.31	4.3	2.251				

4. Conclusion

In this study, polythiophene (PTh), polypyrrole, polypyrrole/cnt, polythiophene/cnt successfully deposited on the PMMA substrate that coated by these polymer and nanocomposite as a first layer (two layers conductive polymer) and via a rapid chemical oxidative polymerization method using a binary organic solvent of CH3CN. Formation of polythiophene and polypyrrole were approved using FT-IR technique. The SEM images proved the formation of layer and its morphology. Increasing the number of conductive polymers, despite the increase in thickness, is reduced electrical resistance, so to be increased conductivity. By adding carbon nanotubes to thiophene, conductivity was increased But the addition of nanotubes to polypyrrole was not increased a lot because of the high conductivity of polypyrrole. Adding carbon nanotubes to polypyrrole was caused that the adhesion of the polymer had rised to PMMA substrate.

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