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Preparation of Alignment Nanofibersfrom Polyaniline/polystyrene Blend by Electrospinning Technique

Dalal M. Alhilfi Kareema M. Ziadan Alaa S. Alkabbi*
Physics Department, College of Science, Basrah University, Basra, Iraq

Abstract
Electrospinning method is important technique to prepare aligned nanofiber Materials . Oriented nanofibers of solution PS mixed with PANI-DBSA conducting polymers solution were prepared by electrospinning process. PANI-DBSA/PS nano composite are characterized by X-ray diffraction (XRD), Scanning electron microscope (SEM) and Fourier transform infrared spectroscopy (FTIR). X-ray diffraction showed semi-crystalline peaks and the grain size about 40 nm. SEM measurements reveal that the prepared samples are fibers in shape and uniformly aligned over the surface of the substrates. The average diameter of nanfibers is about 70 nm. The composite nanofibers shows good conductivity but use of PS as polymeric plasticizer in lowers the electrical conductivity as compare to pure PANI.DBSA.
Keywords: Electrospinning, Conducting Polymer, PANI-DBSA/PS, Nanofiber

1.Introduction

Conducting polymers are of considerable interest for their excellent electrical and optical properties at room temperature**.** The synthesis of nanostructure conducting polymers has been getting more attention. The increasing interest is due to many useful properties which are characterized of these materials over conventional, bulk structure. The properties of nonmaterial's, such as nanowires, nanotubes and nanofibers (NFs), are highly dependent on their size, shape, and high surface area per unit volume. So, controlling these factors for nanoscale conducting polymers are of great importance to use these types of materials in a solar cells, photodetectors, light emitting diodes and other optoelectronic devices (Huang J. 2006, Tariq J. A et.al 2013). Many methods have been used to prepared nanofibers from conducting polymers such as template synthesis (Huang Z.M. et.al 2003), melt blowing (Ondarcuhu T. et.al 1998), phase separation (Ma P.X. et.al 1999), self-assembly (Whitesides G.M et.al 1996) and electrospinning (Grzybowski B.J. et.al 2002). Electrospinning is a method where nanofibres are prepared from an electro statically driven jet of polymer solution, the fibers are collected as a randomly align on a metal electrode (Li D., Xia Y. et.al 2004, Veluru J. B. et.al 2007, Deitzel J.M. et.al 2001). This method has importance feature simple, versatile technique for generating nanofibers from a rich variety of materials including polymers, semiconductors, composites, and ceramics (Rani R. et al. 2016, Zhang F. et al. 2016, Mudra E. et al. 2016, Huang S. et al. 2016). Also, it offers many possibilities to control the diameter, length, pore network and alignment over a macroscopic area which gives them a palatable for many applications (Mirjalili M. et al. 2016, Watanabe T. et al. 2016).

Polyaniline (PAni) which can be prepared by chemical or electrochemical methods is an important member of conducting polymers due to tunable of its electrical and optical properties, easy synthesis and good thermal stability which broaden the application to various fields (Amado F.D.R et al. 2016, Kaitsuka Y. et al. 2016). Various authors have reported studies on polyanilin composite material. These studies show that the properties of polymer composite have been improved and increase the potential applications in photovoltaics and some other fields of electronics (Abbas S.J. et al. 2014, Liu D. et al. 2015).

In present work, PANI.DBSA is prepared by chemical oxidation, then this polymer blend with polystyrene polymer to prepared PANI.DBSA/PS nanofibers by using electrospinning technique. We have studied the structure and physical properties of prepared PANI.DBSA/PS nanofibers thin film as compared to PS in PANI.DBSA thin films.

2. Experimental

2.1. Materials

Polystyrene polymer of molecular weight (Mw=88,500) used in current study has purchased from Aldrich. Aniline (99.0%) is purchased from fisher scientific. Ammonium Per sulfate (NH4)2S2O8 (98.0%), Dodecyl Benzene Sulfonic Acid (DBSA) and HCl are purchased from Fuka. All the chemicals used are of AR grade and are used as purchased without further purification.

2.2. Preparation of PANI-DBSA / PS thin Films

polyaniline PANI doped with DBSA was synthesized by the oxidative polymerization of anilin in acidic media. The polymerization method has been reported by our group (Kareema M.Z. et al. 2016).

Solution has been obtained from dissolving of 5 mg of prepared PANI-DBSA polymer in 10ml of chloroform ($CHCl_3$) with stirring for 8-9 hours. Polystyrene (PS) dissolved in chloroform followed by stirring at

room temperature till the PS is completely dissolved. The PS solution was added to PANI-DBSA solution and put under stirring for 12 h. The PANI-DBSA/PS solution was used to prepare thin films samples by electrospinning method. The electrospinning setup, shown in Fig.1, was built in our lab.

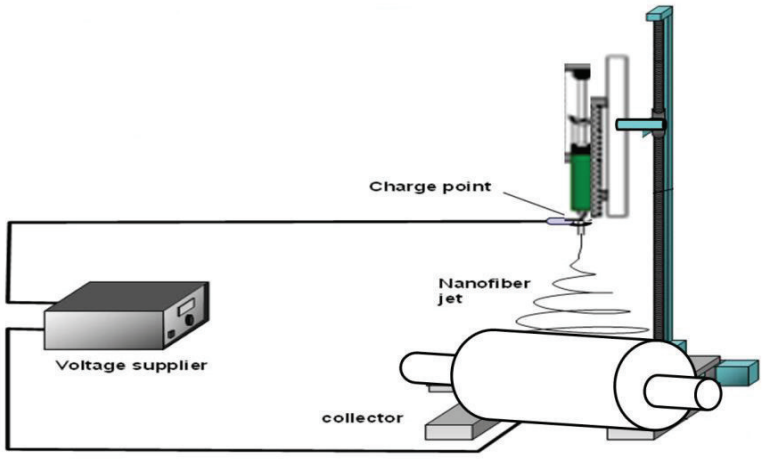

Figure1. The electrospinning setup

1 ml of the solution PANI.DBSA/ PS was placed in hypodermic syringe, the syringe was connected to a metal needle, and in vertically state for rotating collecting aluminum drum connected to a different speed Ac motor. The tip of the needle and moving collector was connected to high voltage DC power supply. The anode of the DC high voltage power supply was clamped to a syringe needle tip and the cathode was connected to a metal Collector. During electrospinning, the applied voltage was 15 kV, the distance between the tip and collector was 19 cm, and the flow rate of the spinning solution was 0.1 ml/h.

2.3. Characterization

The diameter and morphology of the electro spun PANI-DBSA/PS composite fibers were determined by SUBARA 55VP-48-06 scanning electron microscope(SEM, Germany).Wide angle X-ray diffraction was carried out using a(X ' Pert Pro MPD- Philips) X-ray diffract meter and filtered CuKα radiation(λ = 1.5405 A°). The functional group of preparation composite fibers of the PANI-DBSA and PS were obtained by scanning the samples in collected from a FTIR spectrometer (FTIR_8400S) in the wavenumber range of 4000–200 cm^{-1}. Absorption spectra of the thin films on the glass substrate have been measured by a UV/VIS/NIR computer controlled spectrophotometer Perkin Elmer LAMBDA 750 in the range 300–900 nm at room temperature. The electrical measurements of thin films are done using electric contacts in a coplanar configuration. Aluminum electrodes used for electrical contacts are deposited by thermal evaporation at room temperature on planar geometry of the thin films (electrode gap ∼1 cm. The current is monitored using a Fluke 8845A Digit precision multimeter.

3. Result and Discussion

3.1. FT-IR Spectroscopy

The composition of the of PANI-DBSA /PS nanofibers thin film have been investigated using FTIR spectra, Fig.2c. For comparison, FT-IR spectra of pure PANI and PS are presented in Figure (2a, 2b), respectively. In the FT-IR spectra of PANI-DBSA/PS nanofibers, the Peaks at wavelengths (3000-3080) cm^{-1} attributed to (C-H aromatic stretching vibration). The absorption bands at 2852-2924, 1734-1600, 1452-1492 and 752-788 cm^{-1} are corresponding to the C-H stretching vibration, C = C bond, stretching vibration of benzene ring and C-H out of plane bending vibration of benzene ring, respectively. The C-O stretch has been apperaid in the absorption peak at 1219 cm^{-1}. The Peaks at 1178 and 1180 cm^{-1} are back to CH in-plane deformation. Peak at 1035 cm^{-1} is attribute to C-N stretch. It is appeared that the FTIR spectra of the PANI-DBSA/PS composite nanofibers contain the characteristic peak of pure (PANI-DBSA) and (PS) with slight deviation (Kareema M.Z. et al. 2015, Kumar A. et al. 2015, Taghipour Z. et al. 2014). J. J. Espinoza et al. attributed this deviation to the different type of noncovalent interaction between the conductive Polymer and PS matrix. (Espinoza J.J et al. 2015).

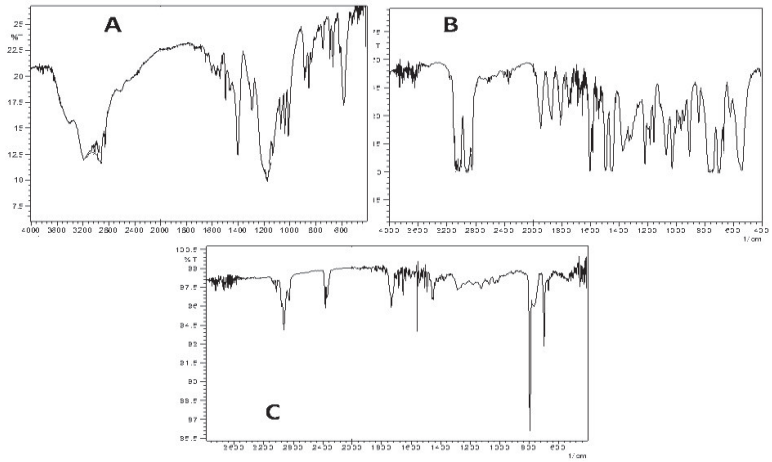

Figure2. FT-IR spectra of (a)PANI pure (b)PS and (c) NF PANI-DBSA/PS.

3.2. Structure and properties of thin films

Fig.3 shows the X-ray diffraction pattern (XRD) of PANI-DBSA/PS nanofibers, PANI-DBSA and PS thin films. The diffractogram of PANI-DBSA exhibited peaks around 2θ =17.76°, 18.53°, 19.62°, 20°, 20.77°, 23° and wide peak at 24.19° which refers to crystalline structure of PANI-DBSA, these produced from doping with DBSA which induce the crystalline nature of PANI (Basavaraja C. et al. 2009). The XRD pattern of PS, exhibited a wide peak around 2θ = (15-25)° indicates that the PS is amorphous material [Sudha J.D. et al. 2009). The XRD pattern of PANI-DBSA/PS nanofibers films shows the two low intensity peaks at 2θ= 23° and 24.19°, these two peaks match well with the peaks in the PANI-DBSA diffractogram. So, we can presume that the appearance of these two low peaks in PANI-DBSA/PS may be due to the presence of polystyrene which increase the amorphous nature of composite material.

The crystallite size (G) of PANI-DBSA/PS nanofibers thin film at highest intense crystalline peak (2θ= 24.19°) was determined from the Scherer relation (Cullit B.D. et al. 1978).

$$G = \frac{K\lambda}{\beta \cos\theta} \qquad (1)$$

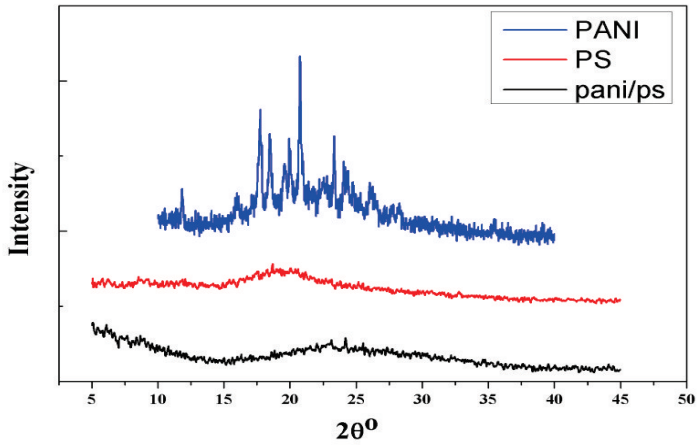

Fig.3. X-ray diffraction patterns of NF PANI-DBSA/PS, PANI-DBSA and PS thin films.

where, K is the shape factor for the average crystallite (0.999), β is the full width at half maxima of the crystalline peak in radians and λ is the wavelength of the x-ray. The crystallite size is equal to 40 nm .these result (less than 100nm) confirms that the prepared fibers thin films are in the nano scale.

One of a convenient technique has been used to study the microstructure of thin films is Scanning electron microscopy (SEM). So, the morphology of prepare sample have been examined using SEM as can be seen in Fig.4. As can be seen from the micrograph, the films are alignment nanofibers structure. The lengths of the nanofibers are uniform, smooth and very few beads and defect, while their widths have a relatively narrow size distribution with average diameters about 70 nm.

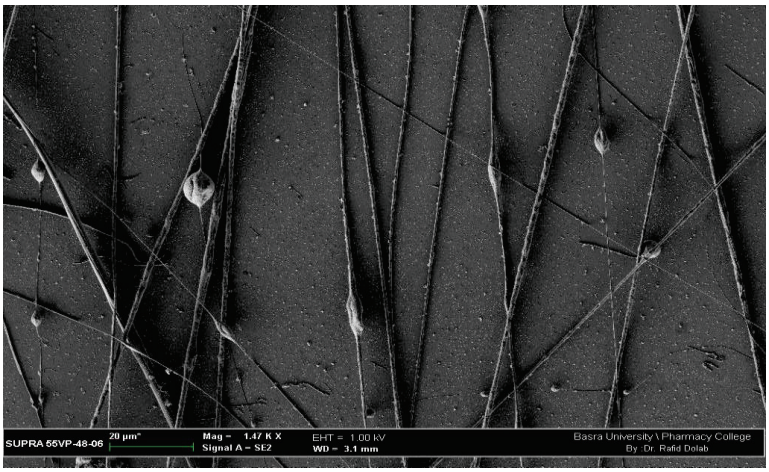

Figure 4. SEM images of nanofibers PANI-DBSA/PS nanocomposite.

Fig.5 shows the un-visible absorption spectra of PANI-DBSA/PS nanofibers, PANI-DBSA and PS thin films. The PS shows a shoulder in the UV region of range of spectra 290–310nm then the absorbance decreases in visible part of the spectra (Kumar A. et al. 2015, Kadhim R.G. 2016). Two absorption bands have been observed in the PANI-DBSA spectra, the first one at 350-450 nm which is attributed to the π-π^* transition and other at 650-780 nm which is corresponding to the polaron transition indicate that the polymer is in its emeraldine salt form (Dennany L. et al. 2011, Stejskal J. et al. 1993). Due to absorption of PANI-DBSA, the absorption of PANI-DBSA/PS nanocomposite fibers films shows a shoulder at 370, 630 nm and a broad absorption band in the region of 680-800 nm which due to the π-π^*, polaron and bipolaron transitions, respectively. The changes on its absorption band (a shift and a corresponding decrease in the intensity) though the PANI chains remain in their salt emeraldine form indicate that the interaction of PANI-DBSA/PS nanocomposite polymer exhibit a lower degree of electron delocalization along the polymer chains.

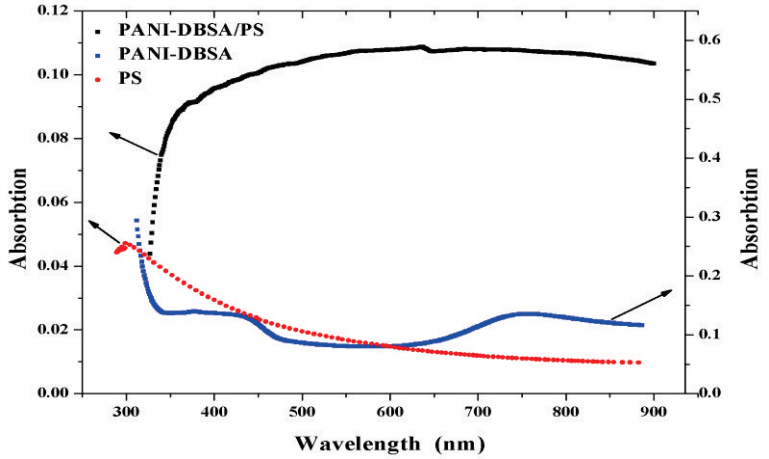

Figure 5. UV−vis absorption spectra of NF PANI-DBSA/PS, PANI-DBSA and PS thin films.

The electrical measurement of the PANI-DBSA/PS nanocomposite thin films has been carried out in coplanar configuration contacts. Up to the operating range, the variation of the current with voltage shows the ohmic behavior (graph not shown here). The conductivity value of PANI-DBSA/PS nanocomposite thin films in room temperature is equal to 2.86*10-6 $s^{-1}cm^{-1}$. This is larger to the conductivity of PS thin film $6.17*10^{-14}$ $s^{-1}cm^{-1}$ and smaller than those of PANI-DBSA conductive polymer $6.17*10^{-3}$ $s^{-1}cm^{-1}$. This due to that the charge transport in the nanofibers thin film has been hindered by the discontinuities on the PANI composite with the nonconducting PS polymer (Wei M. et al. 2005, Miyauchi M. et al. 2010).

The temperature dependence of the dark conductivity (σ_d) of Nanofibers thin films has been measured in the ohmic region. σ_d is measured by using the equation:

$$\sigma_d = \frac{lw}{vlt} \tag{2}$$

Where the photocurrent I is the dark current, v is the applied voltage between the electrodes, w is the width between the electrodes, t is the sample thickness and l is the length of electrodes.

Fig.6. shows the temperature dependence of the dark conductivity of nanofibers thin films. It is clear from the figure that the conductivities increase exponentially with temperature, increasing up to them maximum temperature.

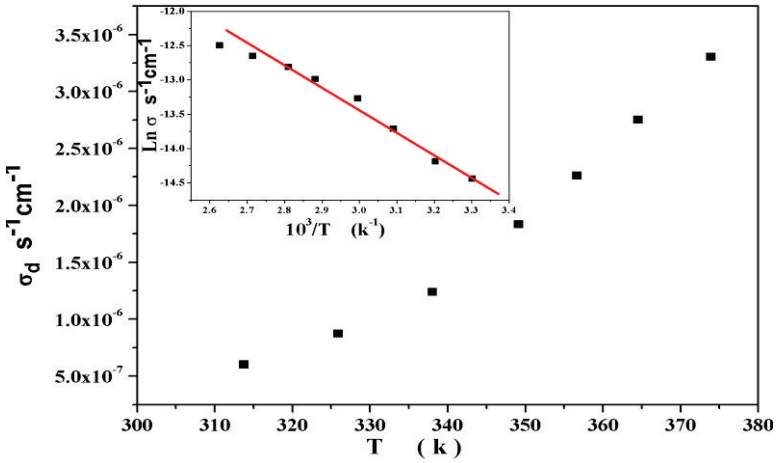

Figure 6. The temperature dependence of dark conductivity.

ln σ_d vs. 1000/T curve is plot is straight lines (inset of fig.6), indicating that the conduction is through an activated process which can be expressed as:

$$\sigma_d = \sigma_o exp\left(\frac{-E_a}{kT}\right) \quad (3)$$

Where E_a is the activation energy, ρ_o is the the pre-exponential factors, *T* is the temperature and *k* is the Boltzmann constant. The value of E_a is found from the slope of the straight lines which is equal to 0.27 eV.

4. Conclusion

Alignment nanofibers of PANI-DBSA/PS nanocomposite has been prepared using the electrospinning techniques. Results of SEM measurements confirm that the nanofibers illustrate a good alignment over the substrate surface in one direction with in naneo size diameters. X-ray diffraction measurement of these nanofibers thin film which shows semi- crystalline structure with average grain size is 41nm. A comparison of the optical and electrical measurements data indicates that the nanofibers thin film display the emeraldine salt structure properties of PANI thin film. the nanofibers thin films shows good conductivity even exist of PS which is insulating materials which may provide good mechanical properties to rise above the fragility of PANI. So, the nanofibers thin film takes advantage of the attractive mechanical properties of insulating polymers and the electrical properties of emeraldine salt PANI.

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