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A STUDY OF THE POSSIBILITY OF MANUFACTURING ELECTRICALLY CONDUCTIVE WEBS OF POLYANILINE AND POLYLACTIC ACID USING ELECTROSPINNING TECHNIQUE

Annotation: *Polyaniline (PANI) is one of the most electrically conductive polymers that have been investigated and studied because of its unique advantages such as its ease of preparation or synthesis and ease of doping (and redoping) and good stability in the surrounding conditions in addition to the low price of monomer. In this research, poly-lactic acid (PLA) and poly-aniline (PANI) mats were manufactured using electrospinning technique by two ways. A solution of PLA/PANI was prepared and spun on electrospinning device. PLA mats were manufactured and aniline was polymerized on the resulting mats. The morphology and diameters of prepared nanofiber mats were scanned* *by scanning electron microscope. The diameters were determined by image j program and the values ranged between (84.028- 119.978) nm. The electrical conductivity of the resulting mats was studied using the four-point technique. The electrical conductivity values were ranged between (1.6 -3.2)* 10^{-6} *s/cm.*

Keywords: *Conductive Polymers, Poly Aniline, Poly Lactic Acid, Electrical conductivity*

ИЗУЧЕНИЕ ВОЗМОЖНОСТИ ПРОИЗВОДСТВА ЭЛЕКТРОПРОВОДЯЩИХ СЕТЕЙ ПОЛИАНИЛИНА И ПОЛИЛАКТИЧЕСКОЙ КИСЛОТЫ С ПОМОЩЬЮ ТЕХНИКИ ЭЛЕКТРОВРАЩЕНИЯ

Аннотация: *Полианилин (PANI) является одним из наиболее электропроводящих полимеров, которые были исследованы и изучены благодаря своим уникальным преимуществам, таким как легкость получения или синтеза и легкость легирования (и повторного легирования) и хорошая стабильность в окружающих условиях в дополнение к низкая цена мономера. В этом исследовании маты из полимолочной кислоты (PLA) и полианилина (PANI) были изготовлены методом электроформования двумя способами. Раствор PLA / PANI готовили и центрифугировали на устройстве для прядения. Были изготовлены маты PLA и на полученных матах полимеризовался анилин. Морфологию и диаметры полученных матов из нановолокон сканировали с помощью сканирующего электронного микроскопа. Диаметры были определены программой изображения j, и значения находились в диапазоне (84,028-119,978) нм. Электропроводность полученных матов изучалась с использованием четырехточечной методики. Значения электропроводности находились в диапазоне (1.6 -3.2)* 10^{-6} *s/cm..*

Ключевые слова: *Проводящие полимеры, Поли анилин, Поли молочная кислота, Электропроводность*

Introduction:

Electrically conductive polymers are organic materials with a main chain comprising π-electron conjugated electrons and are responsible for their important and distinctive properties such as: 1- Electric conductivity, 2- Low energy needed for optical transmission, 3- Low ionization potential, 4- High electronic familiarity. The extended π conjugate structure in conducting polymers has alternating single and two bonds along the polymeric chain. The relatively high value of the electrical conductivity shown by these polymers was called synthetic metals due to their properties similar to the properties of minerals [1, c. 20], For these conductive polymers there is many applications such as electrolysis [7, c. 440], separation and filtration films [5, c. 873], chemical separation (chromatography), live tissue engineering [4, c. 365], and chemical and biological sensors [6, c. 290].

Polyaniline (PANI) is one of the most important organic conducting polymers due to its simple oxidative polymerization and excellent electrical conductivity combined with relatively high levels of chemical stability [1, c. 23]. PANI has attracted considerable attention for its potential applications in various fields, such as electromagnetic interference (EMI) shielding [2, c. 23], microwave absorption [3, c. 880], chemical sensors [4, c. 67], corrosion protection coatings [5, c. 73] rechargeable batteries [6, c. 299], and hydrogen storage [7, c. 447].

The PANI doped with strong protonic acids is difficult. PANI doped with organic acids containing long alkyl chains.

Electrospinning concept:

In a typical electrospinning process a high voltage is used to create an electrically charged jet of polymer solution or melt, which dries or solidifies on extrusion to leave a polymer fiber [6, c. 301]. Three major components are needed to complete the process (Fig. 1): a high voltage power supply, a capillary tube with a spinneret and a collector which is normally grounded [8, c. 350]. Most often the spinneret is connected to a syringe which supplies the polymer solution and the solution can be fed through the spinneret at a constant rate using a syringe pump[9, c. 1065]. When a high voltage is applied, the pendant drop of polymer solution at the nozzle of the spinneret becomes statically charged and the induced charges are evenly distributed over the surface[10, c. 150]. The surface tension of the droplet would normally result in a sphere at equilibrium [11, c. 200]. but it is distorted in the electric field, because charges within the droplet migrate to the surface that faces the collector The accumulation of charge causes a protrusion to appear on the end of the droplet, distorting the droplet into a conical shape known as the Taylor cone [14, c. 1566]. With increasing field strength, the repulsive electrostatic force overcomes the surface tension and a charged jet of fluid is ejected from the tip of the Taylor cone when a critical value is attained[14, c. 505]. The polymer solution is discharged as a jet which then undergoes a stretching and whipping process (a series of connected loops) [13, c. 2908], leading to the formation of a long thin thread. As the solvent evaporates, solid polymer fibers with diameters ranging from micrometres to nanometres are formed and lay on a grounded collecting metal sheet or drum.

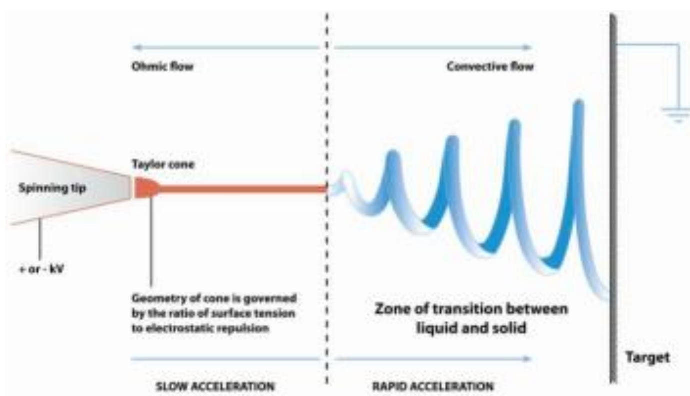

Fig 1. Schematic illustration of the setup used for electrospinning ultrafine fibers.

Electrospinning device components:

Electrospinning device components can be divided to three mean equipment:

1. Extrusion equipment: a pump and the syringe and needle.
2. The collector
3. High voltage power supply: gives a very high voltage up to 50 Kv.

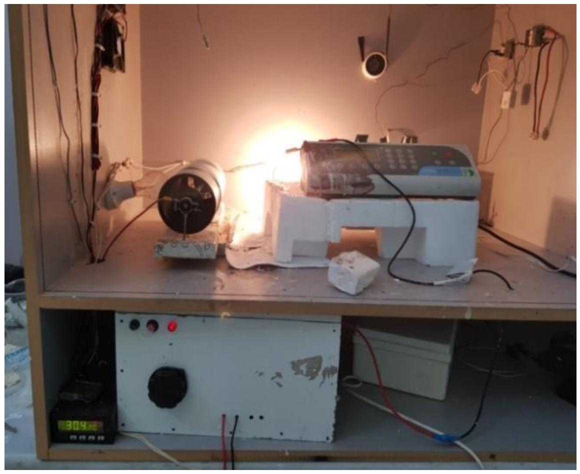

Fig 2. Illustrate Electrospinning device

Processing conditions:

Process control in electrospinning process is typically limited to identifying the operating conditions that produce fibers with acceptable properties. However, within a laboratory setting, even with these conditions identified, it is reported that there still remains significant variation in the quality of the produced materials. These variations are a result of an incomplete understanding or consideration of all the process variables. There are many factors influencing the morphology of the fibers or fibrous constructs produced and these can be divided into solution parameters, process parameters and ambient parameters which are listed in Table 1.

Table.1 Variables of the electrospinning process divided into classifications:

Solution parameters	Process parameters	Ambient parameters
Material selection	Electromagnetic fields	Humidity
Solvent selection	(strength and orientation)	Temperature
Concentration Viscosity	Spinning distance	Atmosphere Air movement

	Solution flow rate	
Dielectric constant	Spinneret morphology	
Conductivity	Collector morphology	
Surface tension		
Elasticity		

Experiments:

Device equipment and Materials:

Chemical Materials:

Aniline (C_6H_7N) (molar mass (93,13) gr / mol, Density (1.02 Kg / L))

Poly Lactic Acid (PLA) (Strip (D =1.75 mm), Density (1.25 g / cm3))

Dimethylformamide (DMF), Acetone, and Ammonium persulfate ($(NH4)_2\ S_2O_3$). all of analytical reagent grade, were purchased from Merck. Chemicals were used as received without further purifications.

Electrospinning Device:

We worked on a device have been designed in Albaath university- Chemical and Petroleum Engineering Faculty- Textile and Spinning Department as shown in fig(2).

Electrospinning device consists of:

1. **Extrusion equipment:** A pump and the syringe and needle.

   The syringe pump of this device has been designed in order to use of a variety of syringes. The system is able to inject the certain volume of solution with different rates
2. **The collector:** Rotating chrome cylinder covered with aluminum sheet was used.
3. **High voltage power supply:** The volt was about (5 – 250) Kv.

Scanning Electron Microscopy (SEM): Fiber morphology and fiber diameter were determined using scanning electron microscope, which have magnification ability up to (5000) times.

Fig 3. Scanning Electron Microscopy (SEM)

DC-Electrical Conductivity: The electrical properties of the electrospun nanofibers were measured by four-point probe technique. Before measuring the conductivity, the nanofiber samples (dimensions 2 × 2 cm2) were conditioned for (24 h) in (25 ± 1°C) and (35 ± 5%) relative humidity. The electrical current (I) was measured with KEITHELY-220 programmable Current Source and KEITHELY-617 programmable electrometer. The electrical conductivity σ was calculated using Van der Pauw relation by using Eq (1).

$$\sigma = \frac{d}{t \times w}\frac{I}{V} \qquad (1)$$

where d is the distance between the electrodes (cm), (t) and (w) are the sample's thickness and width respectively (cm).

fig 4. four-probe homemade device

Preparation of electrospinning solutions:

The solutions were prepared in three steps:

1. **Preparation of PANI:**

(50 ml) of aniline was dissolved in (25 ml) of Hydrochloric acid (HCL). The solution was cooled to (-2 °C) by using an ice bath. (3.8 g) of Ammonium persulfate ($(NH4)_2 S_2O_3$) was dissolved in (25 ml) of HCL. Tow solutions were mixed were mixed gradually for two hours to form Poly aniline. The mixture was stirred on the magnetic stirrer for (24 hours). A small amount of sodium hydroxide (NaOH) was added to the mixture to deposit polyaniline. The deposit was filtered and washed with distilled water and ethanol then the result was dried for a day by using woven drier.

2. **Preparation of PLA:**

A solution of poly lactic acid was prepared with a concentration of (5% wt) where (5g of PLA) was dissolved in (100 ml) mixture of Acetone and Dimethylformamide (DMF) with a ratio of (60:40 / DMF: Acetone). The mixture was heated to (70 °C) with magnetic stirring for (5) hours.

3. **Preparation of electrospinning solution:**

Two types of solutions were spin:

1. PLA solution
2. PLA + PANI: Which prepared by adding PANi powder to PLA solution with different weight concertation (Pani(g)/PLA(g)).

Electrospinning Parameters:

The electrospinning process was performed according to the following Parameters:

Table 2. Electrospinning Parameters

Exp. No	PLA concentration %	PANI concentration g/g %	Flow rate ml/h	Distance between syringe needle and collector cm	Voltage supply Kv
1	5	0	5	10	20
2	5	1.5	5	10	20

Polymerization of aniline hydrochloride onto electrospun nanofibers mats of polylactic acid:

Another way to prepare samples was prepared by bulk oxidative solution polymerization of PANI onto electrospun non-woven fibers mats of PLA. The PANI ratio in the composite is about (50 % w/w).

RESULTS AND DISCUSSION

Morphology of the Nanofiber Mats:

All samples of nonwoven nanofibers mats were prepared then scanned under scanning electron microscope (SEM) and analyzed using Imagej program to get the average nano-fibers diameter for each sample.

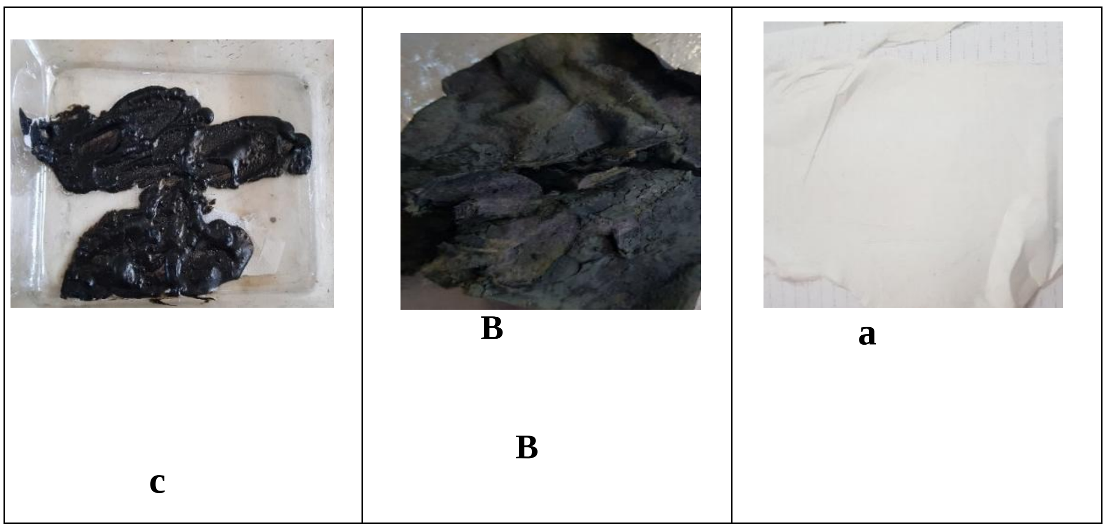

Fig 5. (a) PLA nanofiber non-woven mat, (b) PLA/PANI nanofiber non-woven mat, (c) Polymerization of PANI onto PLA mats

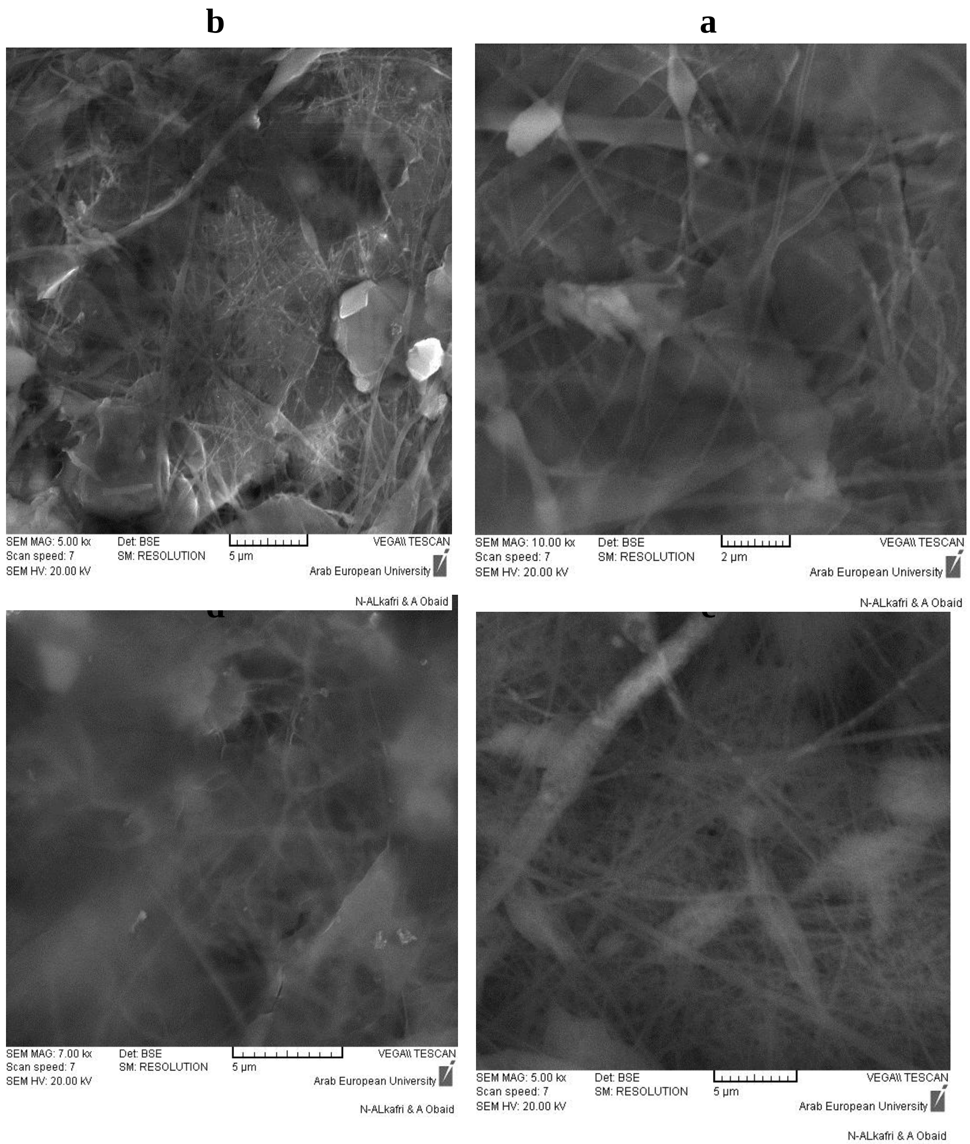

Fig 6. SEM micrographs of nanofiber mat: (a-b) PLA +PANI, (c-d) PLLA

The average diameter of each sample was measured and calculated, as listed in table (3).

Table (4) the values of average nano-fibers diameter

Sample	Diameter	Average	CV
PLA	75.143, 38.095 97.124, 60.234 102.575, 111.066, 121.96	84.028	31.8446
PLA/PANI	137.079, 200.537, ,131.635, 125.622, 124.719, 74.906, 112.36 52.967	119.978	44.0006

DC-Conductivity:

For DC conductivity (σ), 10 measurements were carried out for each of the 5 PLA/PANI and PLA nanofiber mats prepared as mentioned above with 5 measurements on each side .The average DC-conductivity of each sample was measured and calculated, as listed in table (4).

Table (4) illustrate Measured DC- Conductivity

Sample	**Thickness mm**	**Current mA**	**Electrical Conductivity s/cm**
PLA	0.02 mm	1×10^{-9}	1.6×10^{-6}
PLA/PANI (1.5 %)	0.02 mm	1×10^{-9}	2.8×10^{-6}
Polymerization of PANI onto PLA mats	0.02 mm	1×10^{-9}	3.2×10^{-6}

Results and Discussion:

- SEM micrographs show formation of nanofiber mats of PLA with randomly oriented fibers, beads free with average diameters about (84.028 nm). The average diameter of PLA/PANI nanofiber mat is about (119.978 nm)
- PANI nebulas are formed around PLA nanofibers, because of PANI placed on the surface of the fibers and distributed between the mat gaps.
- The DC conductivity (σ) measurements show (σ) values range of (1.6 – 3.2) 10^{-6} s/cm. We can attribute this difference to the high porosity of the nonwoven mats and to the random orientation of the fibers in the composite mat which implicates a random movement of the charge carrier between electrodes. The electrical conductivity could also be affected by the morphology of π-conjugation polymers from respect of density of electrons and arrangement of PANI molecular chains in the composite mat.

Conclusion:

PLA/PANI mats were manufactured using electrospinning technique. PLA mats were spun on electrospinning device, and Aniline was polymerized on the resulting mats. PLA/PANI mats were prepared on electrospinning device. PLLA nanofibers were beads free with good shielding of PLLA nanofibers by PANI and with a good electrical conductivity.

References:

1. [U. Lange, N.V. Roznyatovskaya, V.M. Mirsky, Conducting polymers in chemical sensors and arrays, Analytical chemical acts, 614 (2008) 1-26.
2. J. Janata, M. Josowicz, Conducting polymers in electronic chemical sensors, Nature materials, 2 (2003) 19-24.
3. N.K. Guimard, N. Gomez, C.E. Schmidt, Conducting polymers in biomedical engineering, Progress in Polymer Science, 32 (2007) 876-921.

4. G. Wegner, Polymers with Metal-Like Conductivity—A Review of their Synthesis, Structure and Properties, Angewandte Chemise International Edition in English, 20 (1981) 361.381
5. R.P. Kingsborough, T.M. Swager, Electrocatalytic conducting polymers: Oxygen reduction by a polythiophene-cobalt salen hybrid, Chemistry of materials, 12 (2000) 872-874.]
6. J. Pellegrino, The Use of Conducting Polymers in Membrane-Based Separations, Annals of the New York Academy of Sciences, 984 (2003) 289-305.
7. H. Bagheri, A. Mohammadi, A. Salemi, On-line trace enrichment of phenolic compounds from water using a pyrrole-based polymer as the solid-phase extraction sorbent coupled with high- performance liquid chromatography, Analytica chimica acta, 513 (2004) 445-449.
8. M. Gerard, A. Chaubey, B. Malhotra, Application of conducting polymers to biosensors, Biosensors 116 and Bioelectronics, 17 (2002) 345-359.
9. M. Mayukh, I.H. Jung, F. He, L. Yu, Incremental optimization in donor polymers for bulk heterojunction organic solar cells exhibiting high performance, Journal of Polymer Science Part B: Polymer Physics, 50 (2012) 1057-1070
10. Bini T B, Gao S, Tan T C, Wang S, Lim A, Hai L B and Ramakrishna S (2004).'Electrospun poly(l-lactide-co-glyoclide) biodegradable polymer nanofibre tubes for peripheral nerve regeneration', *Nanotechnology*, 15, 1459.
11. Peng, P. Zhu, Y. Wu, S.G. Mhaisalkar, S. Ramakrishna, Electrospun conductive polyaniline–polylactic acid composite nanofibers as counter electrodes for rigid and flexible dye-sensitized solar cells, Rsc Advances, 2 (2012)
12. K .McKeon, A. Lewis, J. Freeman, Electrospun poly (D, L-lactide) and polyaniline scaffold characterization, Journal of applied polymer science, 115 (2010) 1566-1572.
13. M. Gizdavic-Nikolaidis, S. Ray, J. Bennett, S. Swift, G. Bowmaker, A. Easteal, Electrospun poly (aniline-co-ethyl 3-aminobenzoate)/poly (lactic acid) nanofibers and

their potential in biomedical applications, Journal of Polymer Science Part A: Polymer Chemistry, 49 (2011) 4902-4910.
14. M.P. Prabhakaran, L. Ghasemi-Mobarakeh, G. Jin, S. Ramakrishna, Electrospun conducting polymer nanofibers and electrical stimulation of nerve stem cells, Journal of bioscience and bioengineering, 112 (2011) 501-507.