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Electrical Conductivity of Polyaniline Fiber Synthesized by Interfacial Polymerization and Electrospinning

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Abstract

Polyaniline fiber is a promising biosensor material due to the capability of this material as an effective mediator for electron transfer. The polyaniline in fibre has wider surface to increase the electron transfer. In this work, polyaniline structure synthesized by interfacial polymerization was compared to polyaniline structure obtained from electrospinning to get a better fibre structure. Interfacial polymerization was carried out to form a polymerization between the water phase and the organic phase. The water phase was prepared from dopants, initiator and aquadestilata and the organic phase was was made from toluene as an organic solvent and aniline monomer. Electrospinning was conducted by using a dc high voltage 15 kV and 0.5 mm syringe needle to produce fibers from a melt polymer solution taken from interfacial polymerization. The scanning electro microscope results confimed the formation of polyaniline in structure of fiber. Resistance measurement by using LCR meter showed that polyaniline fiber resulted from electrospinning is more conductive than polyaniline fiber formed by interfacial polymerization method.

Keywords*: polyaniline, fiber, conductivity*

1. Introduction

Among several types of conductive polymers, polyaniline (pani) is one of the conductive polymers with a range of very varied structure [1, 2]. Pani has a high stability in the environment, reversible electrical and optical properties through redox reactions and doping-dedoping or protonation-deprotonation and it is easily synthesized. The electrical properties of polyaniline can be modified via the redox doping by making the amount variations of electrons or variations in the number of protons in acid doping proton. Polyaniline in the state emeraldine protonated has semiconducting properties with conductivity of 100 S / cm. Polyaniline will also become a polymer if conductivity is less than 10^{-9} S / cm and it approaches the metal if the conductivity greater than 10^{4} S / cm [3]. The use of differences acid in protonic of dopants and dopant humidity affects the preparation of the polymer chain and inter-chain interactions. These attributes support the existence of polyaniline as sensors.

Along with the development of nanotechnology, polyaniline in the form of fiber structure particularly has become a major focus in recent years. Polyaniline fiber displays its own advantages in fibre size. The size of the fiber in the materials generates more surface area than the other materials. Polyaniline morphology is influenced by the size of the formed fiber. The fiber size effects the electrical and optical properties of polyaniline fiber and it plays significantly to sensitivity of detection in sensor applications [4]. Various methods have been developed to synthesize fiber polyaniline, such polymerization methods interfacial [5], electrospinning [6], chemical oxidative polymerization [7] and bulk polymerization [8]. Polyaniline material is easily synthesized through a chemical or electrochemical process, but polyaniline in the fiber structure was successfully shaped by using interfacial or electrospinning. However, most the methods were carried out individually and there is no record for the result of combination among two methods. In this works, polyaniline resulting from the interfacial polymerization with dopants HCl was proposed to be applied as material to form polyaniline fiber with electrospinning.

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2. Methodology of Research

In this work, polyaniline was proposed to be a product of two methods i.e. interfacial and electro spinning method. It was proposed to use interfacial method to compose polyaniline material at the first process. At the second process, polyaniline produced from the interfacial polymerization was used to produce polyaniline fiber from electrospinning.

2.1. Interfacial Method

One of the methods used to obtain polyaniline is the interfacial polymerization method. Interfacial polymerization is a polymerization stage that occurs at the interface between the aqueous solution containing in the first monomer and an organic solvent containing in a second monomer.

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In this work, synthesis of polyaniline was initially prepared by using interfacial polymerization method with the dopant concentration variation HCl in a two-phase system solution. These two phase solutions were an organic phase and aqueous or water phase. Polymerization was completed by comparing the number of moles of the aniline monomer with initiator ammonium peroxy disulphate (APS) in ratio 4:1. Aniline was added to the toluene in order that the organic phase volume reached 50 ml. The APS, HCl and solvent aquadestilata mixed with a certain ratio so that the volume of the aqueous phase reached 50 ml. Before the organic phase and the aqueous phase were mixed, they were placed on a magnetic stirrer for 5 minutes. These two solutions then were mixed into a clear glass bottle without stirring. Shortly after mixing, polyaniline was initially formed at the boundary of the two phases (Figure1). This process allowed throughout the night in order to complete the polymerization occurs.

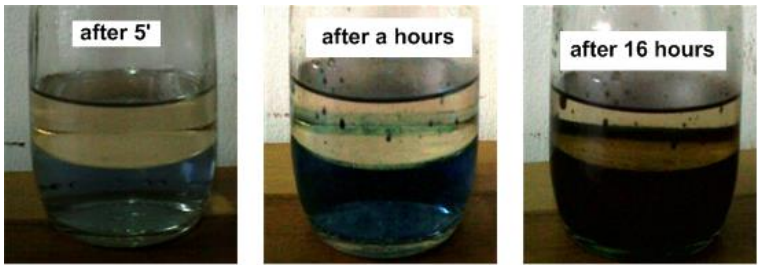


Figure 1. Polymerization Interfacial Process. The condition of solution after mixed the organic phase and the aqueous phase

2.2. Electrospinning Methods

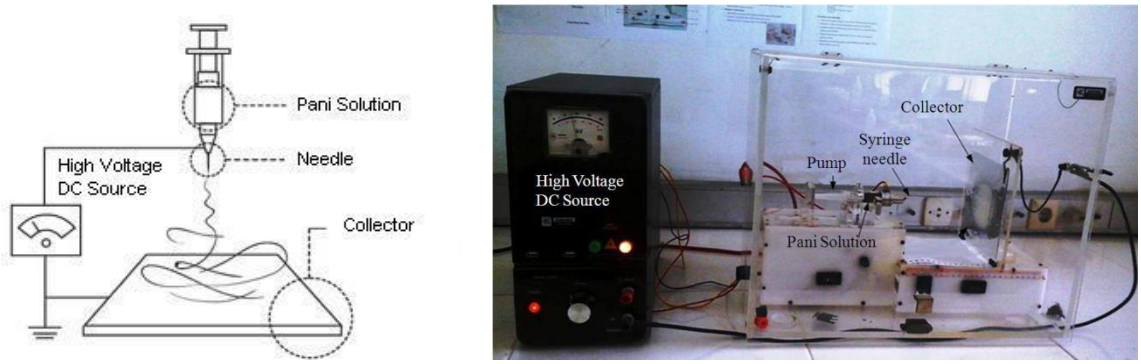
Electrospinning is a process where fiber of the material was formed by using an electric field and syringe needle. The result of this method was a fiber with diameter in order of acquisition around the micro to nanometer. In this electrospinning experiment, there were three stages had to be completed in a polyaniline fiber fabrication. Those are (i) transformation of a polyaniline doped into polyaniline dedoped, (ii) composing the feed solution for electrospinning and (iii) electrospinning process.

Polyaniline resulting from the interfacial polymerization with dopants HCl doped polyaniline was formed and prepared for solution material in electrospinning process. To eliminate the influence of HCl or to avoid the change of the doped polyaniline into undoped, then it was important to do a washing with NH_3. In this washing process, the applied molar NH3 was proportional to the dopant molar of HCl.

Electrospinning feed solution was made by mixing a solution of polyaniline - dimethyl sulphoxide (DMSO) with a solution of polyvinyl alcohol (PVA). Polyaniline solution in the DMSO was created in concentration of 5 wt% and PVA solution was made in a concentration of 15% wt. After mixing step by using stirring machine for 1 hour, the feed solution was allowed to

remain stand for 10 hours before it was used in the process electrospinning. The last step was intended to eliminate any bubbles remained during the mixing process.

Electrospinning process was conducted by using a dc high voltage 15 kV and 0.5 mm syringe needle. The distance between the tip of the needle with the collector was 11 cm long and 1 cm needle was applied. The process was done in duration of 15-30 minutes. Figure 2 (a) gives illustration of electrospinning mechanism. Figure 2 (b) shows the detail equipments used in the process of electrospinning.



(a) (b)

Figure 2. (a) Electrospinning Mechanism (b) Laboratory set up for electrospinning

2.3. Resistance Measurement

It is important to get electrical characteristics of polyaniline as the results of combining process namely interfacial and electrospinning. To get this information of electrical characteristics, this work used LCR meter EDC 1630 as measurement device to measure resistance (R) of polyaniline. The output of this tool was fairly accurate because the capacitor or inductor device under test did not has a significant resistive component of impedance. The testing voltage was kept constant at 1 volt and the testing frequency was varied in the range of 0-20 kHz. As the frequency was set to be 0 kHz, then testing voltage was a direct current voltage. This tool gave the resistance value by assuming that the sample has an internal series resistance (R_s).

To find the conductivity of tested polyaniline, the analysis is carried out by using the relationship defining that the conductivity (σ) in Siemens is inverse of the resistivity (ρ) and it is formulated as [9]:

$$\sigma = \frac{1}{\rho} \tag{1}$$

while resistance value (R) is proportional to resistivity (ρ) of material and it is formulated as

$$R = \rho \frac{l}{A} \tag{2}$$

for given length and the longitudinal plane of material
Based on equation (1) and (2), conductivity can formulated as :

$$\sigma = \frac{A}{l}\left(\frac{1}{R}\right) \cong \frac{1}{R} \tag{3}$$

then the trend of conductivity is obtained by inversing the value of R.

3. Results and Analysis

In this section, the results of interfacial polymerization and electrospinning to produce polyaniline are presented. The conductivity characteristic is presented as the result of resistance measurement by using LCR meter. The resulting composite morphology was observed by using scanning electro microscope (SEM).

3.1. Conductivity Characteristics

Figure 3 shows DC conductivity of polyaniline from interfacial polymerization and electrospinning in room temperatures. It was found that the conductivity values were changed with type of fabrication of polyaniline. The interfacial polymerization polyaniline (IP Pani) had smaller conductivity than electrospinning polyaniline (ES Pani). The conductivity was increased increased along with an increase in the molarity of dopant for both results of interfacial polymerization and electrospinning. The conductivity of polyaniline from interfacial polymerization was higher than electrospinning.

The increment of dopant molarity increased caused the content of H^+ in the formation of also increassed. The presences of these cations lead to the distance between the conduction band and valence band wider. The presence of these dopants also affected the increase in the degree of oxidation, the percentage of protonation and crystallinity. The increase in the degree of oxidation lead to the change of the formation of polaron, so that the increment of dopants molarity in polymerization resulted in increasing the value of the conductivity of polyaniline [12,13].

The presence of PVA in the feed solution of electrospinning lead to reduce the conductivity properties of materials. Reduction of conductivity properties was also influenced by the initial conditions of polyaniline with DMSO solution preparation. To facilitate the solubility of polyaniline in DMSO, the polyaniline was washed with HNO_3 firstly to reduce the effects of dopants. This will naturally lead polyaniline into to be undoped.

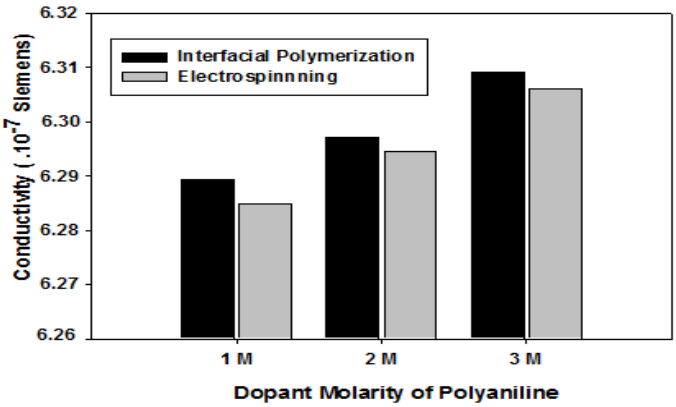
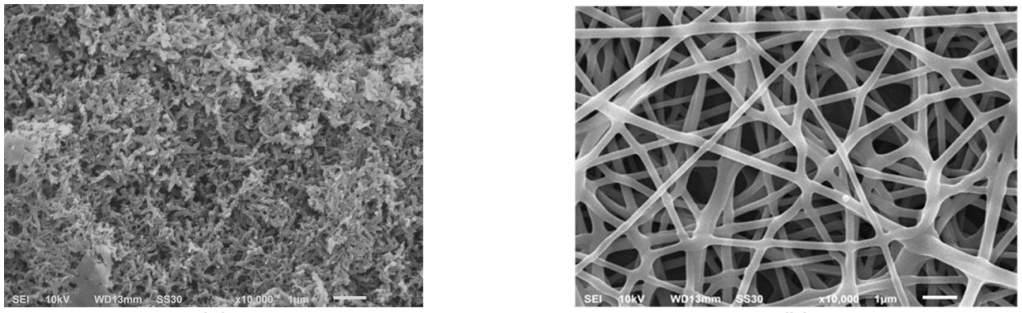


Figure 3. DC Electrical Conductivity of Polyaniline

3.2. Microstructute of Polyaniline Fiber

The results of fabrication for polyaniline fiber from polymerization interfacial and electrospinning has presented in the image of the scanning electron microscope (SEM) in Figure 4. This figure shows the image of polyaniline fiber with dopants 1 M HCl. It was found that the result of fiber diameter polymerization interfacial was 58.1 ± 0.2 nm and the result of electrospinning was 202.6 ± 2.5 nm. Polyaniline fiber diameter resulting from interfacial polymerization was smaller than the product obtained from electrospinning, because the effect of addiotinal PVA in the feed solution electrospinning polyaniline. The morphology of polyaniline resulting from the elektrospininng was more organized than the fiber product from interfacial polymerization, because of the electrostatic force of charged molecules that existed in the feed solution polyaniline under influence of high voltage between the needle tip and electrode. Polyaniline obtained from interfacial polymerization showed the form of the nanofiber. The addition of PVA caused the fiber diameter to be wider and clean.



(a) (b)

Figure 4. Structure of Polyaniline Fiber: (a) Result of interfacial polymerization, (b) Result of Electrospinning

4. Conclusion

The works to produce polyaniline in the fiber structure by using combination of polymerization interfacial and electrospinning method have been carried out successfully. This combined method gave significant effect on the size of diameter and conductivity of polyaniline fiber. The diameter of polyaniline fiber resulted from interfacial polymerization was smaller than the product from electrospinning. However, electrospinning made the appearance of fiber clearer than the fiber obtained from electrospinning. Investigation showed that polyaniline fiber resulted from electrospinning proces was more conductive than polyaniline fiber formed by interfacial polymerization.

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