

CHAPTER III

EXPERIMENTAL

This work can be divided into two main parts. The first is to investigate the effect of electrospinning process such as, electric potential, the distance between the needle and collection screen, the diameter of needle and the flow rate of polymer solution on morphological appearance of electrospun citric acid doped polyaniline-polyvinylalcohol mats. The second part is to evaluate the NH₃ sensing of electrospun mats achieving from optimum conditions.

3.1 Electrospinning of citric acid doped Polyaniline-polyvinylalcohol

3.1.1 Materials

Aniline hydrochloride was purchased from Aldrich, ammonium peroxydisulfate, (NH₄)₂S₂O₈, was purchased from Fluka, concentrated ammonium hydroxide, 30%; methanol and hydrochloric acid, 38%; all in analytical grade were purchased from Merck and used to synthesize the polyaniline (PANi). Polyvinyl alcohol was purchased from Fluka. Citric acid and N-methyl-2-pyrrolidone (NMP) of analytical grade were purchased from Aldrich.

3.1.2 Methodology

3.1.2.1 Preparation of Emeraldine Base Polyaniline (PANi-EB)

Emeraldine base polyaniline (PANi-EB) was synthesized by the oxidative polymerization of aniline in acidic media, which followed the method described by Chatuporn [14]. Aniline hydrochloride (2.59 g, 20 mmol) was dissolved in distilled water to 50 mL of solution and kept for 1 hour at room temperature, ammonium peroxydisulfate (5.71 g, 25 mmol) was dissolved in water to 50 mL of

solution also kept for 1 hour at room temperature and added to the above solution under constant stirring in ice bath at 0-5°C. The resulting dark green solution was stirred continuously and left at rest to polymerize for 24 hour at 0-5°C. The polyemeraldine salt (PANi-ES) was precipitate. The precipitate was washed with HCl, water and NH₄OH, respectively. Then it was converted to polyemeraldine base (PANi-EB) form by treating the PANi-ES with 0.1 M NH₄OH for 5 hours. The dark blue powder of PANi-EB was filtered and washed with NH₄OH, methanol and water until the filtrate was neutral and subsequently was dried in oven at 60°C for 12 hours.

3.1.2.2 Preparation of citric acid doped PANi-PVA solution

The citric acid doped PANi solution was prepared by slowly dissolved 0.02 g of PANi-EB in 1 mL of N-methyl-2-pyrrolidone (NMP). The solution was vigorous stirred for 1 hour at room temperature and then filtered using 0.45 µm PTFE filter to remove any particulate matter. Then, 1.2 g of citric acid was added and stirred for 1 hour.

PVA was used to assist fiber formation because it good chemical stability, film forming ability and high hydrophilicity, except for its poor stability in aqueous solution. Therefore, PVA must be insolubility by crosslinking to create a stable membrane with good chemical properties and less swelling in water. The PVA solution was prepared by mixing of 3 g of PVA and 30 mL water and then heat the solution for 1 hour at 120 °C. The citric acid doped PANi solution was mixed with PVA solution and stirred for 1 hour to obtain homogeneous solutions of citric acid doped PANi-PVA.

3.1.2.3 Electrospinning Process

The electrospinning apparatus as shown in Figure 3.1, consists of a high voltage power supply (230 series, Bertan High Voltage Research) was used to charge the as-prepared polymer solutions between the needle and the collection screen, a syringe pump (NE-1000, Prosense) to control the flow rate of the polymer

solution, a 3-mL disposable syringe with hypodermic needle and the gold electrode attached to aluminium foil as collection screen. To investigate the effects of some of the key process parameters, we conducted electrospinning at different conditions. The parameters studied were diameter of needle of 0.55 and 0.80 mm, flow rate of 10 and 15 $\mu\text{l}/\text{min}$, distance between needle and collection screen of 10 to 25 cm and electric potential of 10 to 30 kV. Polymer solution was pumped to needle by a syringe pump. A positive potential was applied to the polymer blend solution, by attaching the lead to the high voltage power supply directly to the outside of the needle. The collector plate was made of copper and covered with gold electrode attached to an aluminum foil and that placed horizontally from the hypodermic needle as the grounded counter electrode. When the electric field reaches a critical value, the charged polymer solution overcomes the surface tension and a jet is formed. As the jet travels toward the collection screen the solvent evaporates and the fibers are collected on the collection screen. Subsequently, the aluminum foil was removed from the collection screen, and dried in an oven at 100 $^{\circ}\text{C}$ for 1 hour.

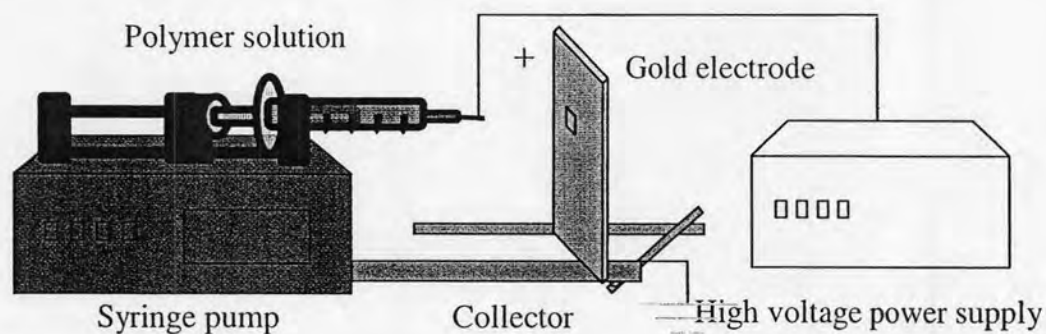


Figure 3.1 Schematic of the electrospinning process.

3.1.2.4 Characterization of electrospun citric acid doped PANi-PVA mats

3.1.2.4.1 Fourier-Transform Infrared Spectrometer (FT-IR)

FT-IR was used to identify the characteristic functional groups of the synthesized PANi-EB. Infrared spectra were recorded by KBr technique using a FT-IR spectrometer (Impact 410: Nicolet) in the wavenumber range of 400 - 4000 cm^{-1} using the absorbance mode with 32 scans with the wavenumber resolution of $\pm 4 \text{ cm}^{-1}$. This PANi-EB was the starting material for the preparation of conducting polyaniline solution.

3.1.2.4.2 Scanning Electron Microscope (SEM)

The morphology of the electrospun citric acid doped PANi-PVA mats was determined using JSM-6400 Scanning Microscope. The diameter of fibers was reported as the average values with standard deviation ($n=30$) by SemAfore program.

3.2 Ammonia Sensing

3.2.1 Electrical Resistance of electrospun citric acid doped PANi-PVA mats

Electrical resistance measurements were made using Agilent 34405A Multimeter. The electrochemical behavior of electrospun citric acid doped PANi-PVA mats on gold electrode of each piece was exposed to 90 ppm of ammonia gas and the changes of resistance were monitored.

3.2.2 Experimental set-up for ammonia sensing

Ammonia sensing of electrospun citric acid doped PANi-PVA mats were observed by the measurement change of resistance. The resistance of electrospun mats was recorded by a digital multimeter (Agilent 34405A). The ammonia gas used in the system was generated from ammonium hydroxide. The concentration of ammonia gas in system was determined by OLDHAM Mx2100 ammonia sensor.

The experimental apparatus for ammonia sensing, shown in the Figure 3.2, was set up to monitor the sensing of electrospun mats. The chamber was made from acrylic resin. A glass watch was performed in the chamber 1 in front of the fan which was installed on the wall. Ammonia gas was generated by a fan until ensure that ammonia gas in chamber 1 was a uniform distributed. The gas was then pumped and guided through a pipe to the chamber 2. Electrospun fiber on gold electrode was connected to the two probes of digital multimeter at fixed position in chamber 2. The resistance of electrospun mats was measured and recorded every 10 seconds by digital multimeter. The air was then purged using pump 2 into chamber 2 instead of ammonia gas and the chamber 1 was opened to let ammonia outside.

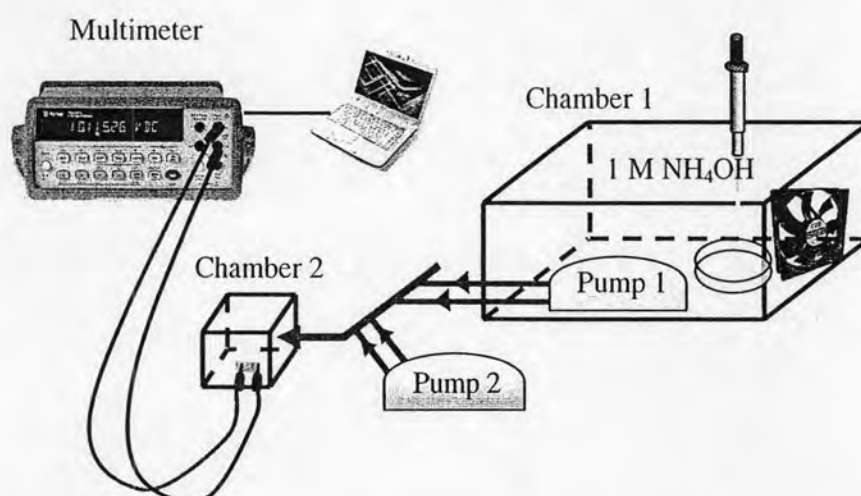


Figure 3.2 Schematic view of the experimental set-up used for ammonia sensing.

3.2.3 Effect of PANi concentration

The viscosity affects much on the diameter of electrospun fibers. The viscosity increased, the spinning drop changed from approximately hemispherical to conical, the length of the jet increased as well. Fiber diameter also increased with solution viscosity and was approximately proportional to jet length. Moreover, PANi concentration can improve the resistance response of electrospun citric acid doped PANi-PVA mats. The change of resistance of electrospun mat is increased as the percent of PANi increased. Various polymer blend solutions were prepared with the concentration of PANi ranging from 2 to 6 %wt/v and the concentration of PVA was 10 %wt/v as described in Table 3.1. In each percent of PANi was doped with 1.2 g of citric acid. The resistance of electrospun mats at various percent of PANi was measured at 90 ppm exposed ammonia gas.

Table 3.1 Percent of PVA: PANi

Polymer solution	PVA		PANi		PVA : PANi
	% wt/v	mL	% wt/v	mL	% wt/wt
PVA-PANi	10	30	2	1	99.3 : 0.7
PVA-PANi	10	30	3	1	99.0: 1.0
PVA-PANi	10	30	4	1	98.7 : 1.3
PVA-PANi	10	30	5	1	98.4 : 1.6
PVA-PANi	10	30	6	1	98.0 : 2.0

3.2.4 Effect of citric acid

Citric acid was a dopant can improve the resistance response of electrospun citric acid doped PANi-PVA mats. The change of resistance of electrospun mat is increased with the increasing of citric acid. Therefore, citric acid concentrations were varied to study the resistance trend. The different amounts of citric were varied at 0.6, 1.2, 1.8, 2.4 and 3.0 g and then added into 2% PANi. The concentration of PVA was 10 %wt/v. The resistance of electrospun mat at varies amount of citric acid was measured at 90 ppm exposed ammonia gas.

3.2.5 Effect of solvent

In the electrospinning process of a polymer solution, solvent is one of the main contributors influence the morphological appearance and electrical resistance. The obtaining morphology of electrospun fibers was depended on solvent evaporation during spinning and also impacted on the electrical resistance. In this work, 97:3 %wt/wt of PVA: PANi was dissolved in different solvent, i.e., N-methyl-2-pyrrolidone (NMP), chloroform, acetone as described in Table 3.2. The change of resistance was measured at 90 ppm exposed ammonia gas.

Table 3.2 Type of solvent

Solvent	PVA		PANi		PVA : PANi
	% wt/v	mL	% wt/v	mL	% wt/wt
N-methyl-2-pyrrolidone	10	30	2	5	97 : 3
Chloroform	10	30	2	5	97 : 3
Acetone	10	30	2	5	97 : 3

3.2.6 Response time and Recovery time

The advantage of electrospun citric acid doped PANi-PVA mats is its reversibility. The resistance of electrospun mat changed on the exposure of ammonia gas and come back to the initial resistance when turn off the gas. The response time of electrospun citric acid doped PANi-PVA mats was the time period that the resistance of the electrospun mat stopped changing on the exposure of ammonia gas. The recovery time was the time period that allowed the resistance of the electrospun mat returning to an initial value after turn off the ammonia gas. The determination of response time and recovery time was illustrated in Figure 3.3.

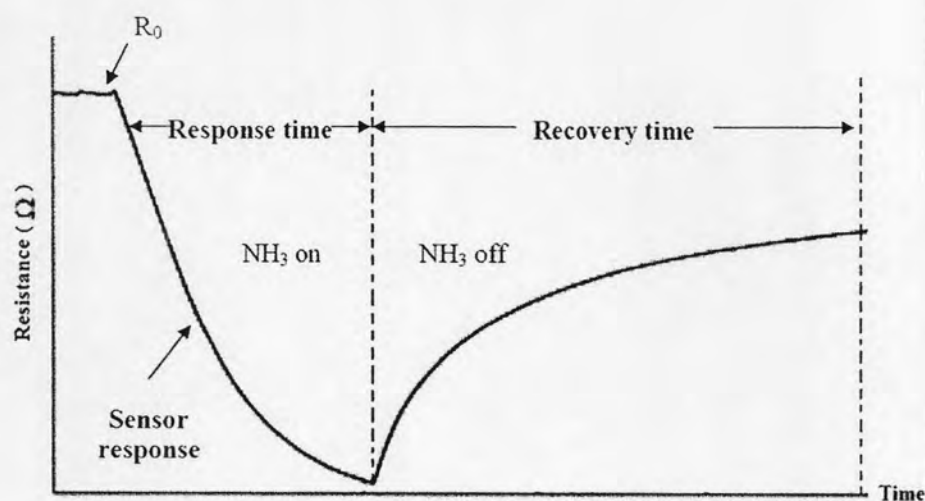


Figure 3.3 Response time and recovery time.

3.2.7 Repeatability

The repeatability of electrospun mat was studied for continuous exposure to ammonia gas. Adsorption and desorption time were fixed at optimum response time and recovery time as obtained from section 3.2.6. The exposure to 90 ppm of ammonia gas was repeated until the resistance response was not constant.

3.2.8 Linearity

To determine the method useful range, linearity was studied. The linearity of electrospun PANi-PVA mats was constructed by ammonia concentrations variation in the range of 1-100 ppm. The linearity plotted by the ammonia concentration and the resistance signals.

3.2.9 Comparison of sensing capability between electrospun mats and cast film

The results of sensing performance of electrospun mats were compared to those of the casting PANi-PVA blend film by measuring the change of resistance under NH_3 gas 90 ppm.

3.2.10 Application in real sample

The citric acid doped PANi-PVA mat was applied to determine the concentration of ammonia gas in real sample to show the capability of the developed material for ammonia sensing. The content of ammonia gas inside the pig house of animal farm at Department of Animal Husbandry, Faculty of Veterinary Science, Chulalongkorn University, Nakornpathom was examined. The calibration curve obtained from 3.2.8 was used to quantify the amount of ammonia gas using the electrospun mat. The concentration of ammonia gas from electrospun mat sensor was then compared with OLDHAM Mx2100 ammonia sensor.