CHAPTER III

EXPERIMENTAL

3.1 Materials

In preparation of PAni-PVA blended film, aniline hydrochloride (Aldrich), ammonium peroxodisulfate, $(NH_4)_2S_2O_8$ (Fluka), concentrated ammonium hydroxide, 30% (Merck), methanol (Merck) and concentrated hydrochloric acid, 38% (Merck), all in analytical grade, were used to synthesize the polyaniline (PAni). Polyvinyl alcohol (Fluka), citric acid (Aldrich), and N-methylpyrolidinone (NMP) (Aldrich) of analytical grade were used to prepare blended films. For ammonia sensing of films, ammonium hydroxide (Merck) was used as the source of ammonia gas.

3.2 Methodology

3.2.1 Synthesis of Polyaniline-Polyvinyl Alcohol Blended Film (PAni-PVA blended film)

3.2.1.1 Preparation of Polyaniline Emeraldine Base (PAni-EB)

PAni-EB was prepared by the method described by Stejskal [63] with a slight modification. Aniline hydrochloride (purum; 2.59 g, 20 mmol) was dissolved in distilled water to 50 ml of solution. Ammonium peroxodisulfate (purum; 5.71 g, 25 mmol) was dissolved in water also to 50 ml of solution. Both solutions were kept for 1 hour at room temperature. Then, both solutions were mixed and left for polymerization at room temperature for 24 hours. The green precipitate of polyemeraldine salt (PAni-ES) was collected and washed with 600 ml of 0.1 M HCl, 600 ml of water and 750 ml of 0.1 M NH_4OH, respectively. Then it was converted to polyemeraldine base (PAni-EB) form by stirring the PAni-ES with 500 ml of 0.1 M NH_4OH for 5 hours. The dark blue powder of PAni-EB was filtered and washed with

750 ml of 0.1 M NH_4OH, 100 mL of methanol and water until the filtrate was neutral. The dark blue powder of PAni-EB was dried in oven at 60 °C for 12 hours.

3.2.1.2 Preparation of Polymer Films

The PVA solutions were prepared by dissolved 3 g of PVA in 30 ml of water and stirred the solution for 1 hour at 120 °C. The PVA solutions were prepared in 6 batches. Then, different amounts of citric acid were added into the PVA solution as described in Table 3.1 and stirred at 120 °C for 15 minutes.

Table 3.1 Percent of citric acid in PVA solution

PVA solution	PVA (g)	PVA (% w/v)	Citric acid (g)	Citric acid (% w/v)
Batch 1	3.0	10	-	-
Batch 2	3.0	10	0.6	2
Batch 3	3.0	10	1.2	4
Batch 4	3.0	10	1.8	6
Batch 5	3.0	10	2.4	8
Batch 6	3.0	10	3.0	10

PAni-EB solution was prepared by dissolved 0.2 g of PAni-EB in 10 ml of N-methyl-2-pyrrolidone (NMP). The solution was sonicated for 30 minutes and then filtered with 0.5 μm filter paper (Whitman).

To prepare PAni-PVA blended films, each batch of PVA solutions was mixed with 1 ml of PAni-EB, stirred for 10 minutes and left a rest for a night. Then, the solution was cast on a glass substrate and left to dry at room temperature for a night. Finally, the PAni-PVA blended film was heated in the oven at 100 °C for 1 hour.

For PVA and PVA-citric acid films, 10% w/v PVA solution and 10% w/v PVA with 4% citric acid solution were prepared and followed the same casting process as PAni-PVA blended film preparation.

3.2.2 Characterization of PAni-PVA Blended Film

3.2.2.1 Fourier-Transform Infrared Spectrometer (FT-IR)

FT-IR was used to identify the characteristic functional groups of the synthesized PAni-EB, PAni doped hydrochloric and PAni-doped citric acid. 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 and the resolution of $\pm$ 4 cm^{-1}.

3.2.2.2 Scanning Electron Microscope (SEM)

Morphological studies of the films (PVA, PVA-citric acid, PAni-EB-PVA and PAni-PVA blended film) were carried out by JSM-6400 scanning electron microscope (JEOL).

3.2.2.3 Conductivity of Polymer Films

The electrochemical behavior of PVA, PVA-citric acid, PAni-EB-PVA and PAni-PVA blended film was investigated by measurement of conductivity responses. The 2×2 cm of each polymer film was exposed to 90 ppm of ammonia gas and the changes of conductance were monitored using a Protek 608 digital multimeter (Protek).

3.2.3 Ammonia Sensing by PAni-PVA Blended Film

3.2.3.1 Experimental Set-up For Ammonia Sensing

Ammonia sensing characteristics of PAni-PVA blended films were observed by the measurement of conductivity changes of PAni-PVA blended films. The conductivity was recorded by a Protek 608 digital multimeter (Protek). The ammonia gas used in the system was generated from ammonium hydroxide. OLDHAM Mx2100 ammonia sensor (Oldham) was used to determine the concentration of ammonia gas in the system.

A simple apparatus as shown in Figure 3.1 was set up to monitor the sensing of polymer films to ammonia gas. The chamber was made from acrylic resin with a fan on the right wall to circulate the inside air. Ammonium hydroxide which is a source of ammonia gas was located in front of the fan to ensure a uniform distribution of ammonia gas in the chamber. A 2×2 cm polymer film was placed on a glass substrate and connected to the probes of the digital multimeter at fixed position. The conductivity of polymer film was measured and recorded every 5 seconds by the digital multimeter.

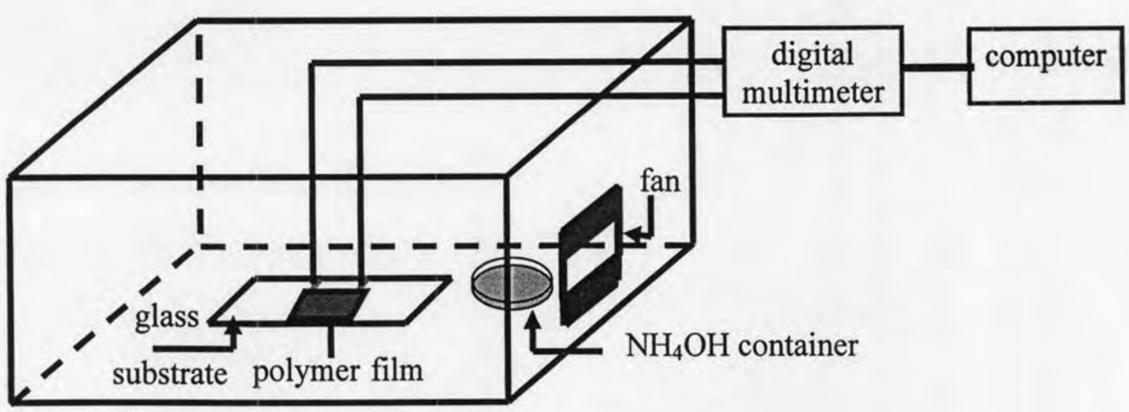

Figure 3.1 Schematic view of the experimental set-up for ammonia sensing.

3.2.3.2 Effect of Citric Acid

Citric acid was a dopant that can improve the conductivity response of PAni-PVA blended film. Therefore, citric acid concentrations were varied to study the conductivity trend. The different amounts of citric acid as described in Table 3.1 were added in PAni-PVA blended film. The conductivity response of polymer films at various amount of citric acid was recorded on the expose of 90 ppm of ammonia gas until reaching the equilibrium.

3.2.3.3 Effect of Film Thickness

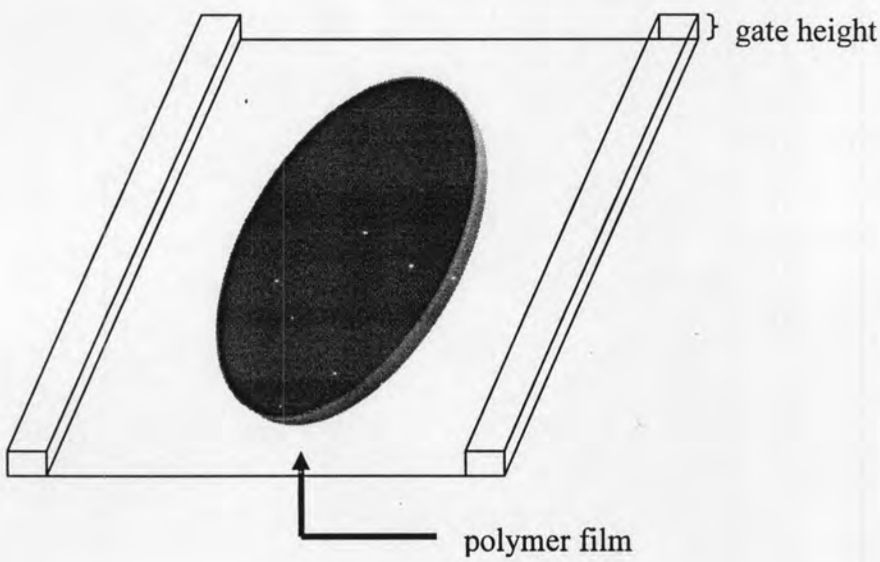

Figure 3.2 Casting unit

The thickness of the film was adjusted by the change of gate height in the casting unit. The height of the gate can be changed in the increment of 1 mm. The level 1 of gate height referred to the thickness of casting layer of 1 mm.

The film thickness of polymer blended film was studied in two levels (level 1 and level 2). After heated in the oven, the polymer film was thinner than the casting layer in which level 1 of gate height gave the film thickness of 0.15-0.20 mm and level 2 gave the film thickness of 0.25-0.30 mm.

The conductivity responses of polymer films on the exposure of 90 ppm of ammonia gas were compared for the different level of film thickness. In addition, the conductivity responses of different film thickness at level 1 (0.15, 0.17 and 0.19 mm) were measured on the exposure of 10 ppm and 90 ppm of ammonia gas.

3.2.3.4 Effect of Temperature and Humidity

The effects of temperature and humidity were studied to duplicated system for real measurement. Temperature and humidity were controlled in the ranges of 25 °C ± 2 to 40 °C ± 2 and 40 %RH to 60 %RH, respectively. The conductivity of polymer film at various temperature and humidity was measured when exposed to 90 ppm of ammonia gas.

3.2.3.5 Response Time and Recovery Time

The advantage of PAni-PVA blended film is its reversibility. The conductivity of the film changed on the exposure of ammonia gas and came back to the initial conductance when turn off the gas. The determination of response time and recovery time was illustrated in Figure 3.3. The response time of the PAni-PVA blended film was the time period that the conductivity of the film stopped changing on the exposure of ammonia gas. The recovery time was the time period that allowed the conductance of the film returning to an initial value after turn off the ammonia gas.

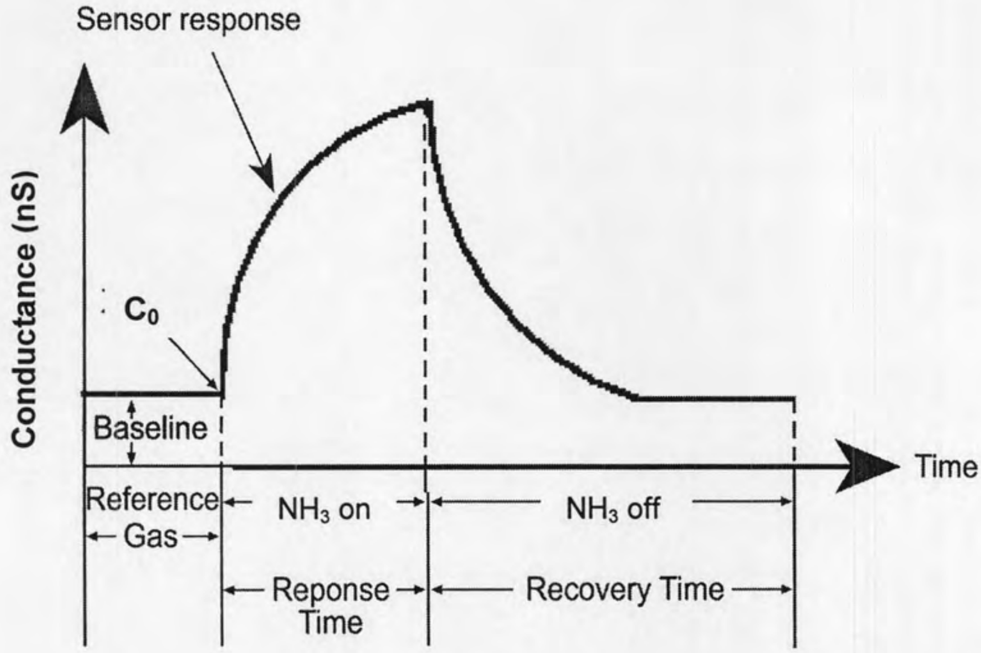

Figure 3.3 Response time and recovery time.

3.2.3.6 Repeatability

The repeatability of polymer film 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 3.2.3.5. The exposure to 90 ppm of ammonia gas was repeated until the conductivity response was not constant.

3.2.3.7 Linearity

The calibration curve of ammonia sensing by PAni-PVA blended film was constructed in the range of 10-100 ppm of ammonia gas. The calibration curve was plotted between the concentration of ammonia gas and the conductance change of the film. Linear regression method was used to determine the linearity of the response.