



CHAPTER IV
MANUSCRIPT

*Electrospun Polydiphenylamine-Polyethylene oxide
as a Methanol Sensor Material*

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Abstract

This work aims to investigate the electrical sensitivity of PDPA pellets, films and fibers, when they are exposed to methanol vapor. The de-doped-PDPA (De-PDPA) pellets were doped with HCl acid at various doping ratios: 1:1, 10:1, 100:1, and 200:1. PDPA and its blends with PEO at various ratios were also fabricated into fibers by electrospinning. The De-PDPA pellets doped at the doping ratio of 100 show the highest electrical sensitivity toward methanol vapor. The electrical sensitivity of the PDPA electrospun fibers is relatively lower, relative to De-PDPA cast films, with increasing amount of PEO when exposed to methanol vapor.

Keywords: Conductive polymer, Gas sensor, Polydiphenylamine, electrospinning process

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1. Introduction

Recently, several countries adopt rigorous environmental standards and regulation on volatile organic compounds (VOCs). In particular, the VOCs consist of the primary alcohols such as methanol, n-propanol, ethanol, butanol, pentanol, and heptanol. The primary alcohols are widely used in the chemical, industrial, and production technology processes [1]. But the toxicity of these primary alcohols is harmful towards human beings with very serious irreversible effects through breathing and in contact with skin [2].

Therefore, highly effective sensors are required to identify and to measure various kinds and quantities of VOCs. Conductive polymers, CPs have been utilized as effective gas sensors owing to many advantages over metal oxide materials. CPs have light weight, less expensive, high sensitive and short response time at room temperature, ease to synthesize and their molecular chain structure can be modified conveniently by copolymerization and structure derivations [3]. Polyaniline and their derivatives have been reported to exhibit good responses towards alcohol vapors, especially methanol, ethanol, and propanol [4]. Polyaniline has many outstanding properties; inexpensive monomer, ease of synthesis, and good environmental stability [5]. However it has problems in its solubility and the processibility. This problem can be overcome by using N-aryl substituted derivatives of polyaniline; polydiphenylamine (PDPA). PDPA can be prepared by the chemical or electrochemical oxidative polymerization of diphenylamine which occurs through the 4, 4' C-C phenyl-phenyl coupling mechanism instead of the head-to-tail polymerization of polyaniline [6]. Thus, PDPA combines the chemical structure of polyaniline and poly (p-phenylene) which can improve its solubility and processibility [7]. Furthermore, PDPA can be doped with sulfonic acid or methane sulfonic acid, grafted with hydrophilic side chain, hyperbranched, and made to be composites with other polymers to improve its solubility [6, 7, 8, 9].

The sensitivity of chemical gas sensors can be strongly affected by the specific surface area of sensing materials [10, 11]. Hence a higher specific surface area of a sensing material leads to higher sensor sensitivity. Electrospun nanofibers have a larger surface area and can be modified as a sensor having augmented sensor characteristics [12].

In this work, we synthesized PDPA via the oxidative polymerization and doped it with 5M HCl at various doping levels. PDPA and its blends with PEO at various ratios were also fabricated into fibers through an electrospinning process. Then we investigated the effects of doping level and the amount of PEO on the electrical conductivity and sensitivity of de-doped PDPA pellets, doped-PDPA pellets, fibers, and electrospun fibers towards methanol vapor.

2. Experimental

2.1 Materials

Diphenylamine (ACS reagent, Sigma Aldrich) was used as the monomer. Ammonium persulfate (AR grade, Riedel-de Haën) and 36.5-38% Hydrochloric acid (ACS reagent, J.T. Baker) were used as the oxidant and the catalyst, respectively. Polyethylene oxide (AR grade, ACROS organics), with the molecular weight 600,000, was used to improve the processibility in the electrospinning method. Ammonium hydroxide solution (AR grade, Panreac), toluene (AR grade, Panreac), isopropyl alcohol (AR grade, Burdick & Jackson), ethanol (AR grade, Lab Scan), methanol (AR grade, Lab Scan), and dichloromethane (AR grade, Lab Scan) were used without further purification.

2.2 Synthesis of Polydiphenylamine (PDPA)

PDPA was synthesized via the interfacial polymerization [13]. A 0.2 M solution of diphenylamine in toluene, and a 0.25 M solution of ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) in distilled water, and 1 M solution of hydrochloric acid (HCl) were prepared in distilled water. The solutions of the monomer and the oxidizer were first cooled to temperature between -2 and 0°C and then mixed momentarily. The reaction was carried out under a continuous intense stirring for 4 h where the temperature of the reaction mixture was maintained at the between -2 and 0°C . At a certain time interval, the reaction mixture was precipitated into a 5-fold excess of isopropyl alcohol having a green color, filtered, and the mixture was washed many times with distilled water until the reaction was neutral (colorless).

2.3 Neutralization of Polydiphenylamine (PDPA)

HCl-doped PDPA (1.8 g), 5 mL of ethanol, and 20 mL of 1 N NH_4OH solution were mixed with intensive stirring. The neutralization was taken place at room temperature, 27°C , for 24 h. The neutralized PDPA was washed a few times with ethanol/water mixtures (3/1, v/v) until no colored supernatant was observed. The dark purple PDPA particles were dried under vacuum at room temperature for at least 24 h [8].

2.4 Doping Process

The PDPA was doped with HCl solutions at room temperature, 27°C , by precisely controlling the mole ratio between PDPA and 5M HCl solution [6].

2.5 Preparation of PDPA Electrospun Fibers

First, PDPA was dissolved in dichloromethane (DCM). The PDPA solutions were blended with polyethylene oxide (PEO) at various concentrations; 95:5, 97:3, 98:2 %w/w. The PDPA contents in the solutions were 30% and 50%. Then solutions were stirred and processed in an ultrasonic bath to ensure homogeneous PDPA solutions. Electrospinning of the PDPA solution was performed at a flow rate of 10 mL/h with a potential difference of 10 kV. A distance between the syringe tip and the collector is 15 cm. Membranes were accumulated on the collector (drum) covered with an aluminium foil on the collecting surface [10].

2.6 Characterizations

The polymers were first characterized for the functional groups by a FT-IR spectrometer (Thermo Nicolet, Nexus 670) in absorption mode with 32 scans and a resolution of $\pm 2 \text{ cm}^{-1}$, wavenumbers range of $4000\text{-}400 \text{ cm}^{-1}$, and using a deuterated triglycine sulfate as a detector. Optical grade KBr (Carlo Erba Reagent) was used as the background material. De-PDPA and D-PDPA were intimately mixed with dried KBr at a weight ratio of PDPA: KBr = 1:20.

A thermogravimetric analyzer (Perkin Elmer, TGA7) was used to determine the thermal behavior of the polymer. The experiment was carried out by weighting a

powder sample of 5-10 mg and placed it in a platinum pan, and then heated it under nitrogen flow with the heating rate 10 °C/min from 30-800°C.

The particle sizes of De-PDPA were determined by using a particle size analyzer (Malvern, Masterizer X).

The XRD pattern of De-PDPA, D-PDPA at various doping mole ratios (1:1, 10:1, 100:1, 200:1) and electrospun PDPA were recorded on a X-ray diffractometer (Rigaku, D/MAX 2200). It was operated at a scan range 5-90 degree, a scan step of 0.05 degree, a scan speed 5 degree/min, and with 30mA and 40 KVP [8].

The morphology and diameter of PDPA electrospun fibers were determined by using a scanning electron microscope (JEOL, JSM-5410LV). A small section of the PDPA electrospun fibers were placed on the SEM sample holder and sputter-coated with gold [14].

2.7 Conductivity Measurement

Electrical conductivity was measured by using a custom-built two-point probe. To determine the electrical conductivity, doped-PDPA was compressed into 2.5 cm diameter circular pellets and PDPA electrospun fibers with different amount s of PEO were cut into a circular shape. The specific conductivity, σ (S/cm) was calculated using the following relation

$$\sigma = I/KVt, \quad (1)$$

where, I is the measured current (A), V is the applied voltage (V), t is the film thickness, and K is the geometric correction factor. A geometric correlation factor was calibrated by using standard silicon wafer sheets with known specific resistivity values. The measurements were performed in the linear Ohmic regime, i.e. the specific conductivity values are independent from the applied DC current. The measurements were carried out at 25°C and repeated at least three times.

Measurements of conductivity responses of doped PDPA and PDPA electrospun fibers were recorded using a specially constructed gas cell. It consisted of two chambers connected in series. The chambers were made from stainless steel.

The second chamber contained the two point probe meters for the conductivity measurement. The temperature controllers, connecting to both chambers, were used to monitor and control the temperature within the gas chambers.

The differences in the change of electrical conductivity ($\Delta\sigma$) at various doping ratios were calculated by following equation;

$$\Delta\sigma = \sigma_{\text{MeOH}} - \sigma_{\text{N}_2\text{initial}}, \quad (2)$$

The sensitivity is defined as the electrical conductivity response divided by the conductivity at the initial N_2 .

$$\text{sensitivity} = \Delta\sigma / \sigma_{\text{N}_2\text{initial}}, \quad (3)$$

where, $\Delta\sigma$ is the difference in the specific electrical conductivity (S/cm), $\sigma_{\text{N}_2\text{initial}}$ is the specific electrical conductivity in N_2 before exposure (S/cm), and σ_{MeOH} is the specific electrical conductivity under methanol exposure (S/cm).

3 Results and Discussion

3.1 Characterization of Polydiphenylamine and Doping Process

The FT-IR spectra are shown in Fig. 1(a). The absorption band at 3388 cm^{-1} and 3053 cm^{-1} can be assigned to the N-H stretching and the C-H in aromatic rings, respectively [15]. The absorption bands at 1594 , 1503 , 1318 and 1173 cm^{-1} are due to the quinoid ring stretching, the phenyl hydrogen, the benzenoid ring stretching, and the vibration band of N_2 in quinine, respectively [4, 8, 16].

The dedoped-PDPA (De-PDPA) was doped with HCl at various doping mole ratios ($\text{N}_{\text{HCl}}/\text{N}_{\text{monomer}}$). The mole ratios chosen were 1:1, 10:1, 100:1, and 200:1. The FT-IR spectra of the polymer are compared to each others as shown in Fig. 1(b). The spectra show the N-H stretching peaks at 3400 cm^{-1} [17]; the peak intensity significantly decreases as the doping mole ratio is increased.

The thermal behavior of the De-PDPA and D-PDPAs was investigated by using the TGA technique. The thermogram of De-PDPA shows two-stage weight losses between 300 and 450°C. The first one is due to decomposition of De-PDPA main chain. The second refers to the complete degradation of De-PDPA [7]. The doped PDPA with hydrochloric acid has higher thermal stability as shown by two degradation steps at 410 and 570°C, due to the chemical absorption between hydrochloric acid and the PDPA main chain as shown in Fig. 2(a).

From XRD, the interplanar spacing between aromatic groups can be identified with the peaks at 18.6 and 21.2 Å for De-PDPA [8]. After chemically oxidized with HCl, D-PDPA spectrum shows two peaks at 18.52 Å and 21.1 Å which is nearly identical to De-PDPA. The doping process does not disrupt the original orientation of the PDPA crystallites, and the crystalline phase is retained under the doping. The particle size analysis gives the particle diameter of De-PDPA about 125.96 µm, with the standard deviation of 5.51 µm.

3.2 Characterization of Polydiphenylamine Electrospun Fibers

The FT-IR spectra of PDPA electrospun fibers are shown in Fig. 1(a). The spectra show the same absorption bands as De-PDPA. This indicates that the chemical structure is the same as those of the electrospinning method.

The thermal behavior of the PDPA electrospun fibers were investigated by using the TGA technique. The thermograms of De-PDPA electrospun fiber and D-PDPA_100:1 show two transition temperatures at 330, 295°C and 410, 342°C (fig. 2(b)). It is unambiguously observed that the De-PDPA electrospun fibers are highly stable than the D-PDPA electrospunfibers.

The XRD pattern of the De-PDPA electrospun fibers shows two peaks at 18.6 and 21.2 Å for De-PDPA fiber. The D-PDPA electrospun fiber has the same peaks as those of the De-PDPA fiber. This can be attributed to the fact that the electrospinning process does not interrupt the orientation of PDPA molecules.

The morphology and diameter of PDPA electrospun fibers were investigated by using a scanning electron microscope. SEM micrographs, (Fig. 3(f)), show that the pure PDPA cannot be processed into ultrafine fibers. To improve the processability of PDPA, solutions of PDPA with poly(ethylene oxide) (PEO) added

were electrospun into ultrafine fibers. The average diameter of the PDPA electrospun fibers is in the range of about 2-3 μm and increases with increasing PDPA concentration. It is also evident that increasing the PEO content also increases the diameter of the fibers [18]. A critical concentration of 2 wt% PEO in solution was required in order to achieve PDPA/PEO electrospun fibers (Fig. 4). With more PEO content, the solution had a higher surface tension, so larger drops occurred at the end of the tips, the diameters of fiber were increased [18]. The size of the electrospun fiber was affected by the ratio of the PDPA/PEO content [14].

3.3 *Electrical Conductivity of Polydiphenylamine*

The electrical conductivity of dedoped-PDPA (De-PDPA), doped-PDPAs (D-PDPA), PDPA film, and PDPA electrospun fibers was measured by a custom-built two point probe (Keithley, Model 6517A). Table 1 lists the average electrical conductivity values of De-PDPA, D-PDPA, and all samples. The average electrical conductivity value, taken from two samples of each, of D-PDPAs is higher than those of De-PDPA. The conductivity increases by two orders of magnitude from the lowest doping mole ratio to the doping mole ratio of 100 of 5M hydrochloric acid solution and varies from 1.52×10^{-6} to 1.79×10^{-4} S/cm. Extended chains D-PDPAs are obtained by the repulsion force between the positive charges of the counter anions (Cl^-) along back bone. So the specific conductivity of D-PDPAs is higher than that De-PDPA because electrons can move more easily along the polymer chain. At higher doping mole ratios, the polymer shows the higher specific conductivity than lower doping mole ratios, since it has higher repulsion force with increasing doping mole ratios. In addition, When the doping ratio is higher than 100, the electrical conductivity decreases, because the agglomeration of PDPA particle and the excessive unreacted dopant.

The average electrical conductivity value of D-PDPA film is much higher than that D-PDPA electrospun fiber which varies from 8.14×10^{-5} to 2.05×10^{-6} S/cm. Furthermore, Chronakis [14] showed that the lower the PEO content of the PDPA/PEO electrospun fibers, the higher the electrical conductivity becomes, because of PEO act as insulating molecules. But in our case the electrical conductivity of D-PDPA film and fiber which has 3%w/w PEO content shows high

electrical conductivity and sensitivity, as 3%w/w PEO is the optimum PEO content yielding a lower diameter and a smoother surface than 2 and 5%w/w PEO contents. In addition, D-PDPA_100:1 were electrospun into fiber with the 3%wt PEO content of 30 and 50%wt PDPA in a DCM solution. This yields the electrical conductivity values between 1.06×10^{-4} and 6.37×10^{-5} S/cm, respectively. The electrical conductivity of 30%wt PDPA in a DCM solution is higher than that of 50%wt PDPA in a DCM solution. As can be seen in the SEM micrographs (fig. 4(d), 4(h)), the 50%wt PDPA content has a rough surface and a larger fiber diameter of , therefore a lower specific surface area and a lower electrical conductivity. Comparing with the D-PDPA_100:1 film and fiber with 3%w/w PEO content, the electrical conductivity of D-PDPA film is higher than that of the D-PDPA fibers because of the D-PDPA fibers are highly porous (fig. 3, 4), thus making the 'fill factor' of the PDPA fibers less than that of a film [18]. Another reason is that methanol molecule may have interact with immine N_2 , So it interrupts the electron transfer on PDPA backbone.

3.4 Electrical Conductivity of Polydiphenylamine when Exposed to Methanol

The selectivity of the D-PDPA_100:1 pellet, film and electrospun fiber towards methanol vapors was investigated by exposing the sensor materials to methanol at 10%v/v. The electrical conductivity response ($\Delta\sigma = \sigma_{\text{gas}} - \Delta N_{2\text{initial}}$) is defined as the difference in the steady state electrical conductivity values when exposed to target gas and the steady state conductivity when exposed to N_2 at 1 atm and at $25 \pm 1^\circ\text{C}$. Due to the differences in initial electrical conductivity of various samples, the sensitivity ($\Delta\sigma / \sigma_{N_{2\text{initial}}}$), defined as the ratio between the electrical conductivity response and the electrical conductivity when exposed to N_2 is used for a comparison purpose.

The electrical conductivity response and sensitivity of all samples are listed in Table 1. The patterns of electrical conductivity when samples were exposed and by MetOH and N_2 is also shown in Figs. 5(a), 5(b), and 5(c). The sensitivity of D-PDPA pellet, 30% wt D-PDPA film with 3%w/w PEO content, and 30% wt D-PDPA electrospun fiber with 3%w/w PEO content are $0.0045 \pm 0.012\%$, $1.25 \pm 0.13\%$, and $0.0362 \pm 0.016\%$, respectively. D-PDPA film shows higher sensitivity than other D-PDPA electrospun fibers, Similar finding was found in the study of polypyyrole and

its composites with 3A zeolite and polyamide toward four chemicals in a lacquer thinner [19]. PA20_PPy13_3A50 film and PPy_3A50 pellet showed positive responses toward methanol vapor. The sensitivity of PA20_PPy13_3A50 film had the highest sensitivity: it was 25 times higher than that of PPy_3A50 pellet. PA20_PPy13_3A50 fiber bundle had no response towards the methanol vapor. The sensitivity of 30% wt D-PDPA electrospun fiber showed higher sensitivity than 50% wt D-PDPA electrospun fiber since the 50%wt D-PDPA has a rough surface and a larger diameter of fiber than those of 30%wt D-PDPA, as can be seen in SEM micrographs in Figs. 4(d) to 4(h). The positive electrical conductivity response and sensitivity can be identified by the interaction between MetOH and D-PDPA. The representative MetOH can interact at the positive charge on the imine nitrogen, or the polaron and the bipolaron species, via the induction bonding electron density of MetOH. Upon interaction with MetOH vapor, the protons in the $-N^+H-$ sites in the conjugated PDPA are withdrawn by adsorbed MetOH molecules. So, the hole density in the PDPA main chain becomes lowered, resulting in a decrease in electrical conductivity when compare with the values in air. Replacing MetOH with N_2 , the process is reversed and the conductivity returns to the original value.

3.5. FTIR Investigations of Reactions of Adsorbed MetOH Vapor

FTIR spectra of D-PDPA_100:1 sample was taken and is shown in Fig. 7. The spectra of sample were collected before, during at 50 minutes interval, and after the MetOH exposure, in order to study the interaction between the samples and MetOH. The FTIR spectra of MetOH show the absorption bands at 1012 and 1056 cm^{-1} which can be assigned to the C-OH stretching in alcohol. Bands at 2868 and 2972 cm^{-1} are assigned to the CH_3 stretching, and the band at 3705 cm^{-1} is assigned to the OH stretching. The IR spectrum shows a peak at 1317 cm^{-1} which can be assigned to the benzenoid structure, a peak at 1500 cm^{-1} is assigned to the phenyl H_2 , a peak at 1595 cm^{-1} is assigned to the quinoid structure, a peak at 3385 cm^{-1} is assigned to the N-H stretching; all are PDPA characteristics [4, 8,16]. The FT-IR spectra after the exposure also shows a peak of the MetOH region. During the MetOH exposure, the IR spectrum shows a peak of MetOH and one new peak at 1401 cm^{-1} which can be assigned to the vibration of an oxygen atom of MetOH

interacting with imine N_2 , and it remains observable after MetOH is removed and replaced with N_2 . This indicates that the interaction between MetOH and D-PDPA_100:1 is irreversible. The proposed mechanism of D-PDPA when exposed to MetOH is shown in Fig. 8.

4 Conclusions

In the present study, polydiphenylamine (PDPA) was synthesized via the oxidative polymerization by using ammonium persulfate as the oxidant and doped with hydrochloric acid. PDPA and its blends with PEO at various ratios were also fabricated into fibers by an electrospinning process. The PDPA pellet, film, and fiber were investigated for their interaction with MetOH vapor towards sensor applications. The effects of doping level and the amount of polyethylene oxide on the electrical conductivity and sensitivity of de-doped PDPA pellets, doped-PDPA pellets, PDPA film and PDPA fibers towards MetOH vapor were investigated.

For the effect of doping level, the D-PDPA_100:1 pellet has the highest electrical conductivity sensitivity due to the highest repulsion force with increasing doping mole ratios. At 3% w/w of PEO, the D-PDPA film has higher electrical conductivity and sensitivity than those of the D-PDPA fiber. Furthermore the D-PDPA_100:1 shows the positive electrical conductivity response when exposed to MetOH. The positive electrical conductivity response and sensitivity can be identified by the interaction between MetOH and D-PDPA. From FTIR investigation, the MetOH-D-PDPA interaction is irreversible.

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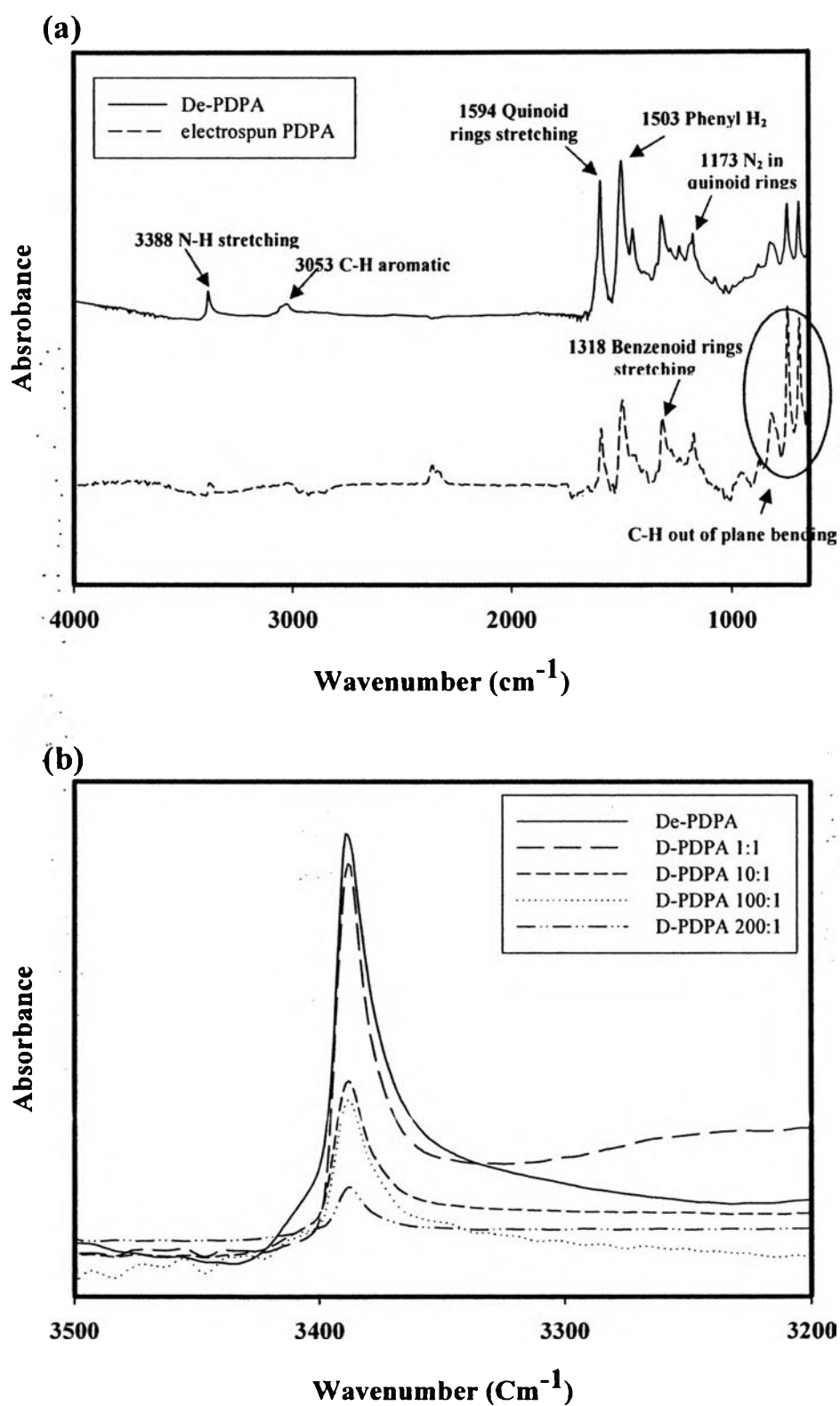


Fig. 1- FT-IR spectra of (a) D-PDPA and PDPA electrospun fiber. (b) D-PDPA of various doping levels 1:1, 10:1, 100:1, 200:1.

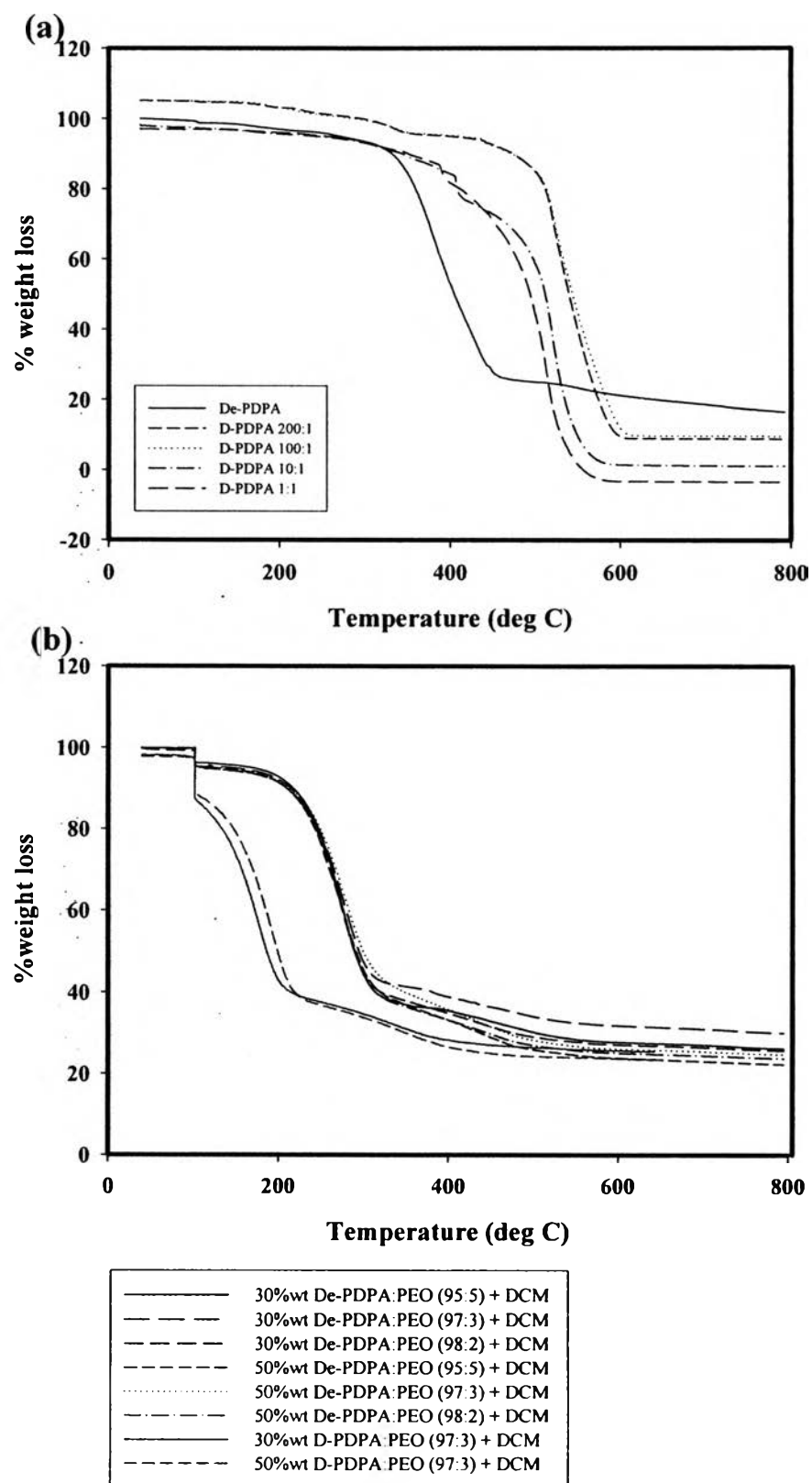


Fig. 2- Thermogravimetric analysis (TGA) of (a) De-PDPA, D-PDPA 200:1, 100:1, 10:1, 1:1. (b) PDPA electrospun fibers at various PDPA:PEO contents.

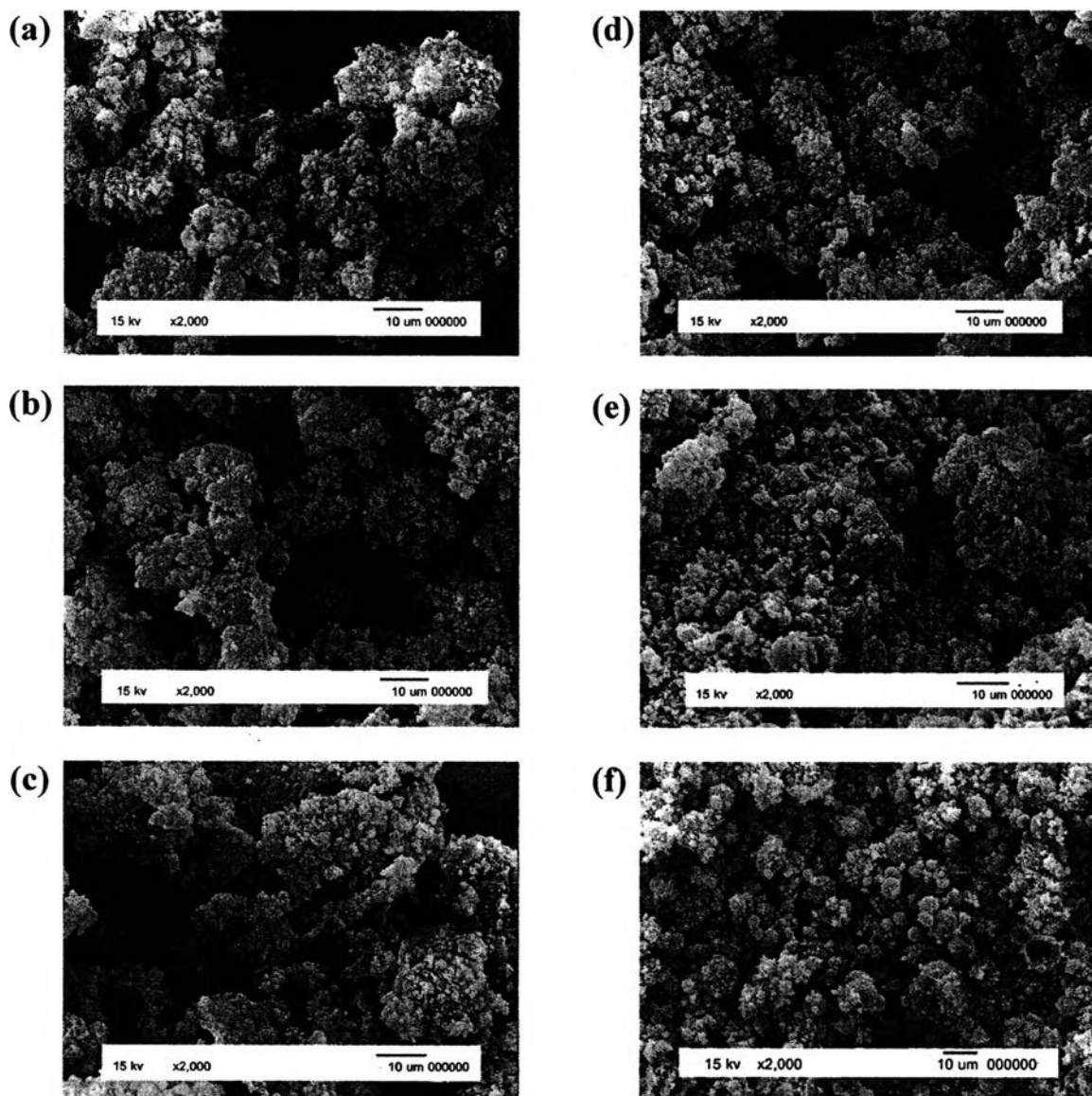


Fig.- 3- The morphology of (a) De-PDPA pellet, (b) D-PDPA_1:1 pellet, (c) D-PDPA_10:1 pellet, (d) D-PDPA_100:1, (e) D-PDPA_200:1, (f) pure D-PDPA electrospun fiber at magnification 2000.

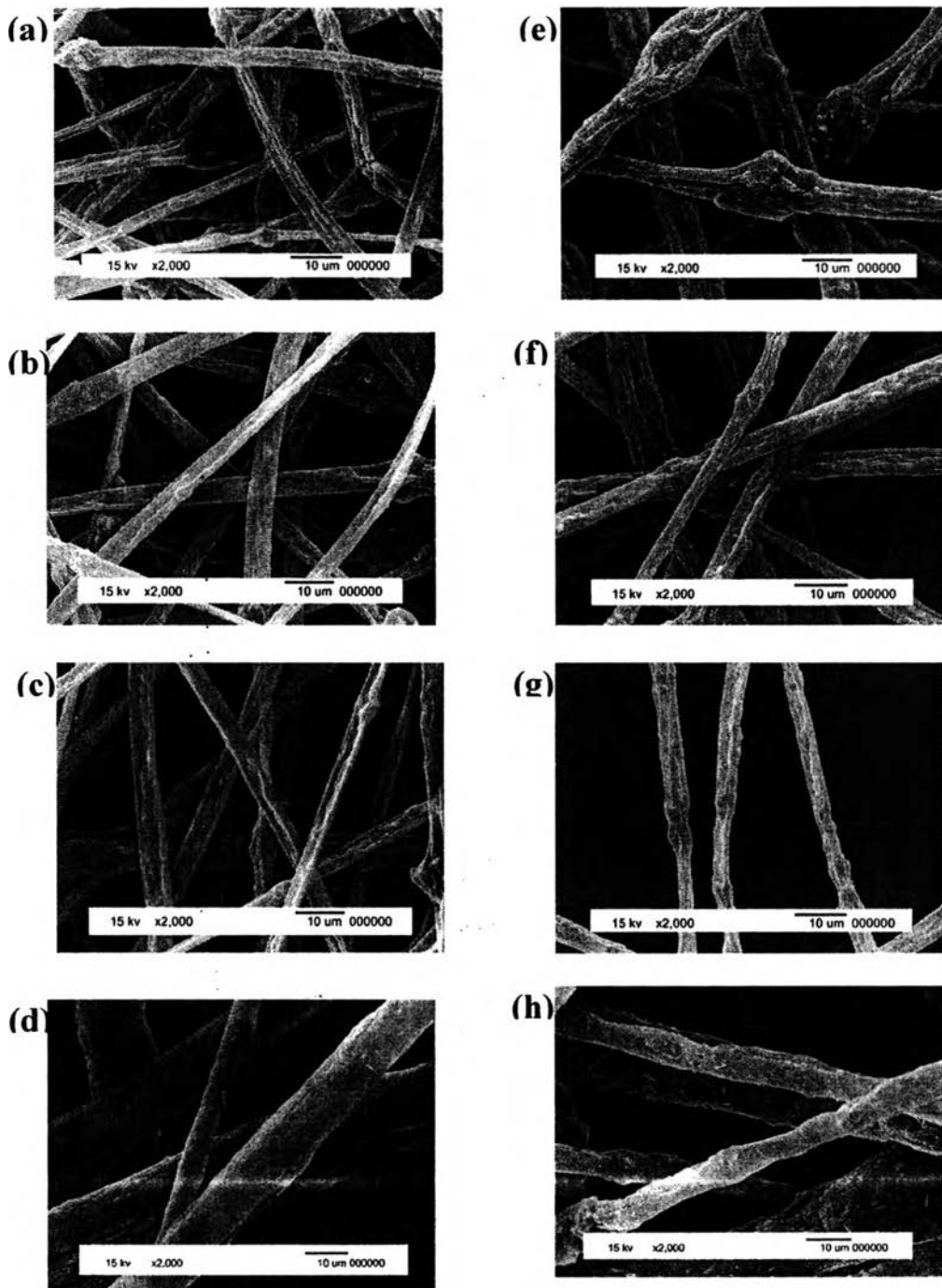


Fig. 4- SEM micrographs of PDPA electrospun fibers from the solutions of 30 and 50 %wt PDPA with various PEO concentrations. The PEO contents of the fibers are (a) 30 %wt PDPA, 5 %wt PEO , (b) 30 %wt PDPA, 3 %wt PEO, (c) 30 %wt PDPA, 2 %wt PEO, (d) 30 %wt D-PDPA, 3 %wt PEO, (e) 50 %wt PDPA, 5 %wt PEO, and (f) 50 %wt PDPA, 3 %wt PEO, (f) 50 %wt PDPA, 2 %wt PEO, (f) 50 %wt D-PDPA, 3 %wt PEO The scale bar is 10 μm .

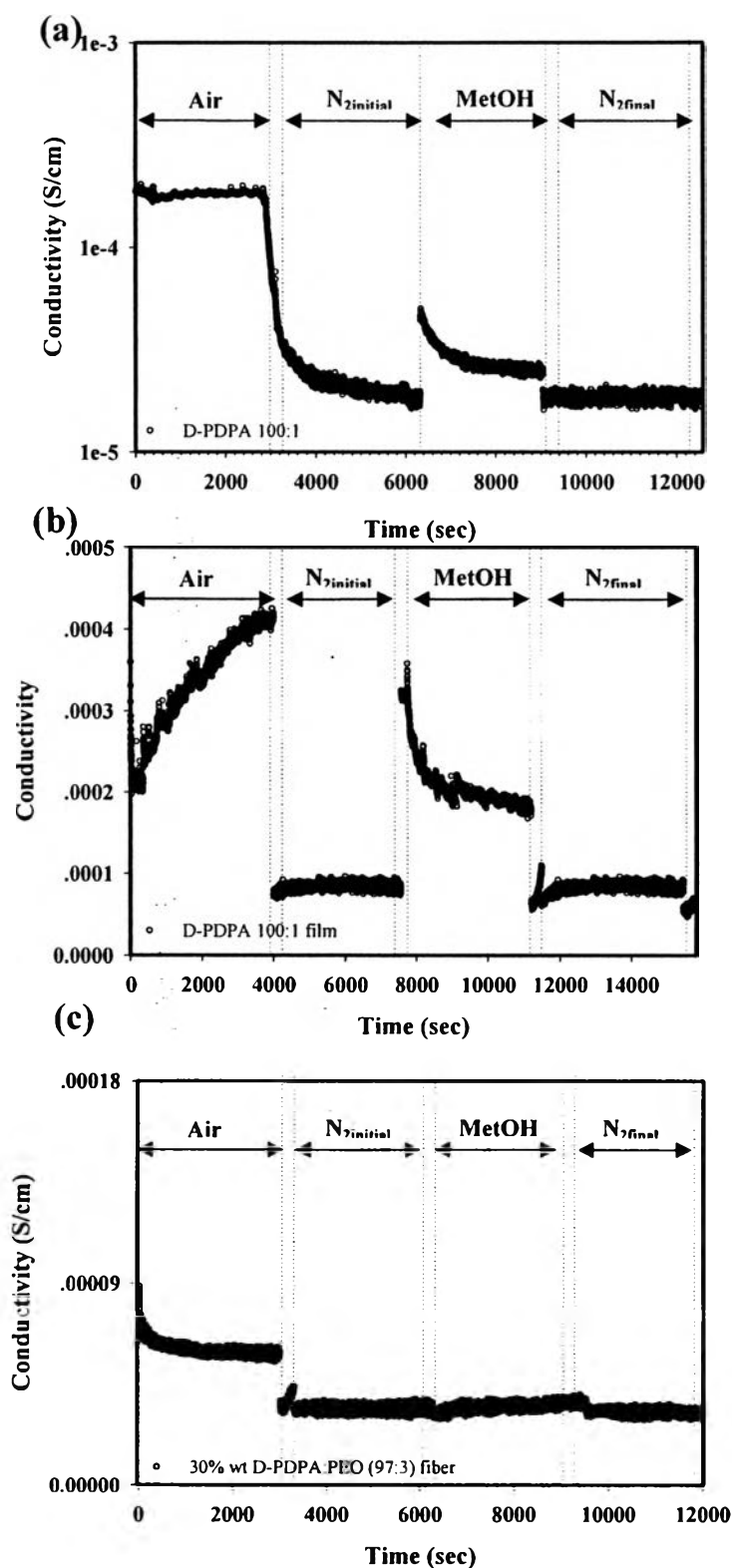


Fig. 5- Specific conductivity values of (a) D-PDPA_100:1, (b) 30%wt D-PDPA:PEO (97:3) film, (c) 30%wt D-PDPA:PEO (97:3) electrospun fiber when exposed in Air, N_2 , and MetOH at $25 \pm 1^\circ\text{C}$, 70%RH.

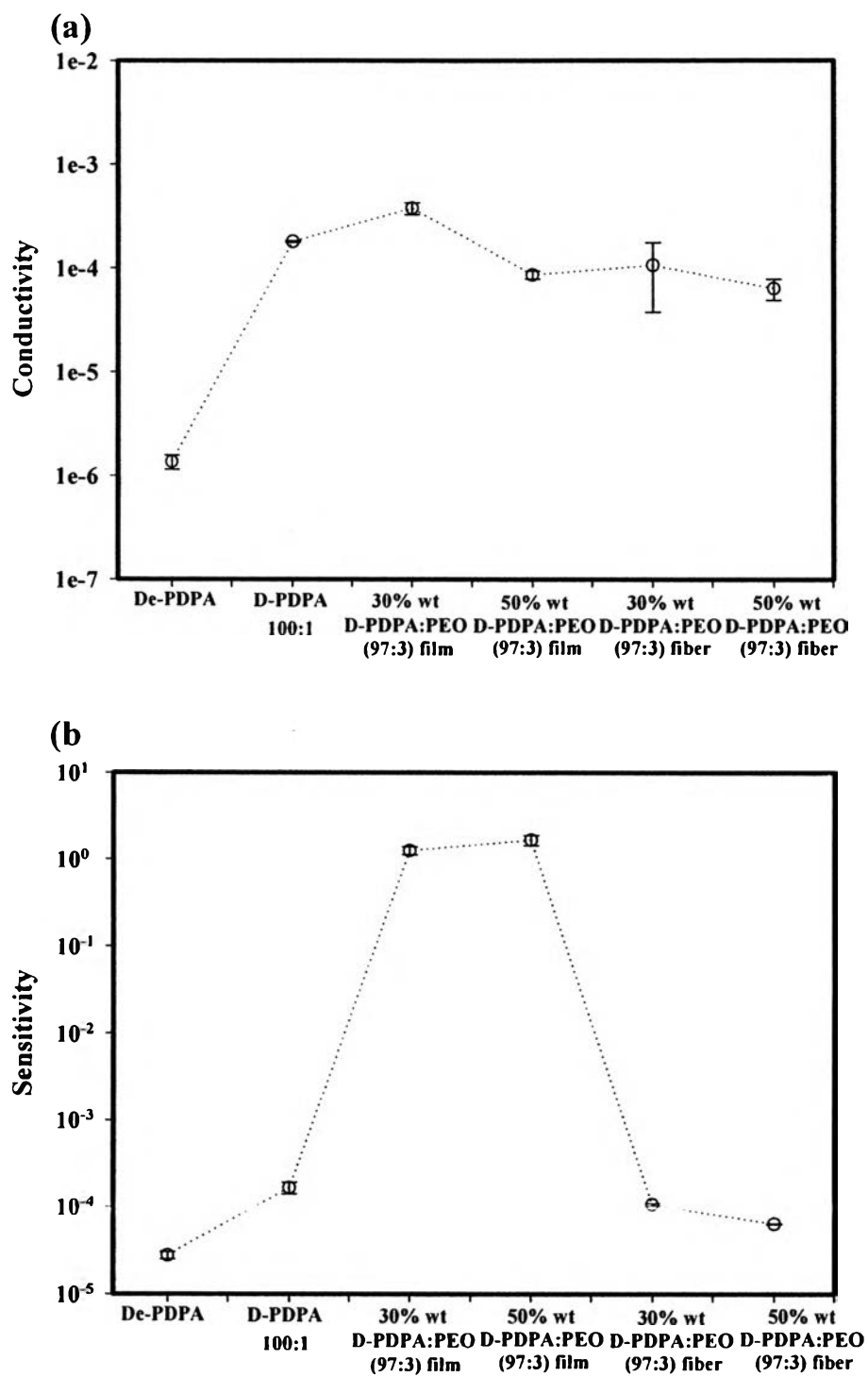


Fig. 6- (a) The electrical conductivity and (b) The sensitivity of De-PDPA, D PDPA_100:1, 30% wt PDPA:PEO (97:3) film, 50% wt PDPA:PEO (97:3) film, 30% wt PDPA:PEO (97:3) fiber, and 50% wt PDPA:PEO (97:3) fiber when exposed to MetOH.

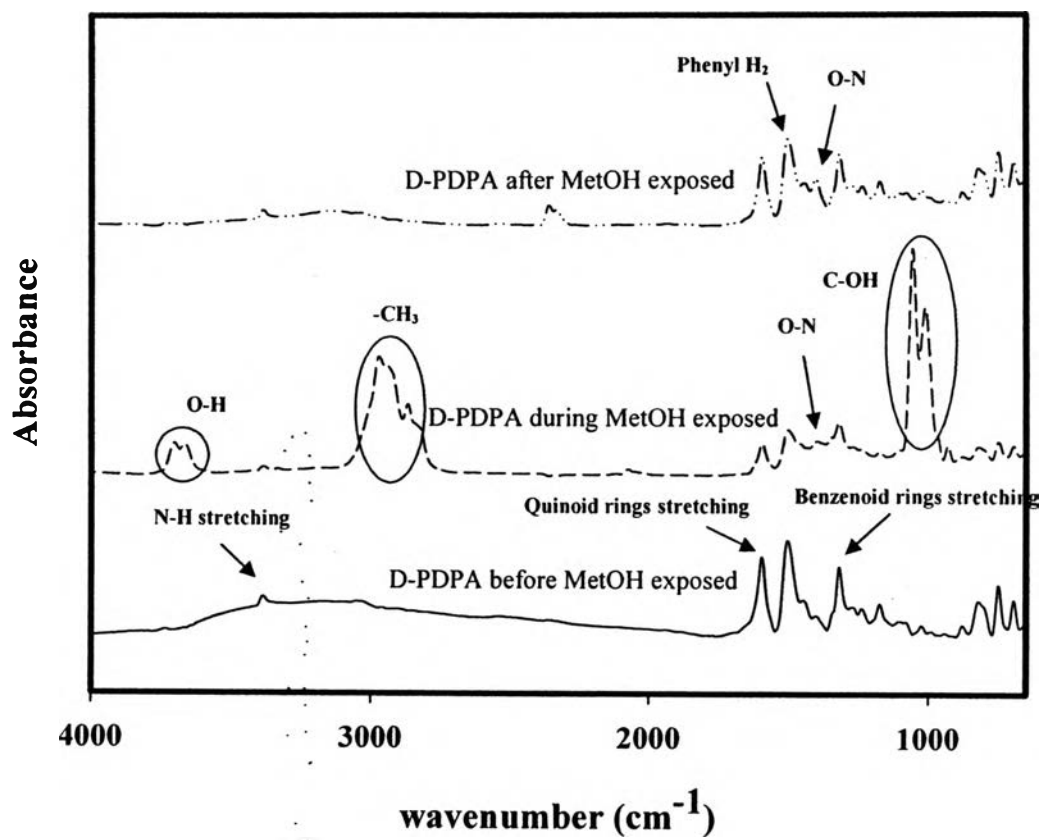


Fig. 7- IR spectra of D-PDPA exposed to MetOH (MetOH=10% v/v, pressure at 1 atm and T at 25°C).

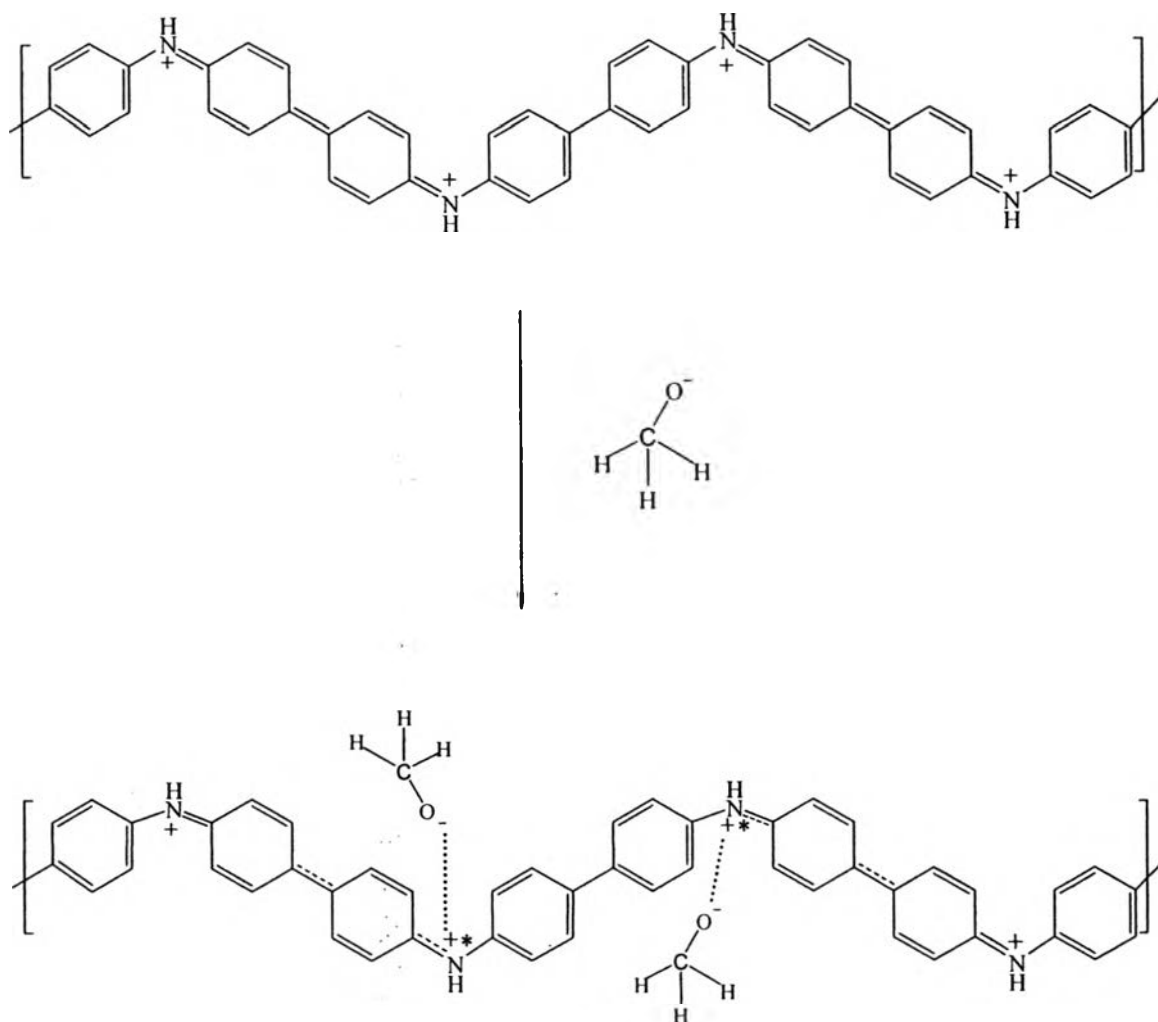


Fig. 8- Proposed mechanism of the MetOH-D-PDPA.

Table 1-: The electrical conductivity sensitivity and temporal response when MetOH are adsorbed on De-PDPA, D-PDPA samples, and PDPA electrospun fiber.

Sample	σ_{air} (S/cm)	$\sigma_{\text{N}_2 \text{ initial}}$ (S/cm)	$\Delta\sigma$ (S/cm)	Sensitivity ($\Delta\sigma/\sigma_{\text{N}_2}$)	Temporal response, t_i (min)	Recovery time, t_r (min)
De-PDPA	$(1.52 \pm 0.06) \times 10^{-6}$	$(2.77 \pm 0.02) \times 10^{-5}$	$(1.29 \pm 3.18) \times 10^{-7}$	0.0045 ± 0.012	-	-
D-PDPA 1:1	$(3.34 \pm 0.05) \times 10^{-5}$	$(2.26 \pm 0.02) \times 10^{-5}$	$(4.48 \pm 0.33) \times 10^{-6}$	0.198 ± 0.016	30	27
D-PDPA 10:1	$(1.57 \pm 0.01) \times 10^{-4}$	$(9.01 \pm 0.14) \times 10^{-5}$	$(1.80 \pm 0.18) \times 10^{-5}$	0.200 ± 0.023	20	67
D-PDPA 100:1	$(1.79 \pm 0.04) \times 10^{-4}$	$(1.94 \pm 0.002) \times 10^{-5}$	$(5.71 \pm 0.02) \times 10^{-6}$	0.295 ± 0.009	30	17
D-PDPA 200:1	$(5.43 \pm 0.02) \times 10^{-5}$	$(2.41 \pm 0.02) \times 10^{-5}$	$(1.43 \pm 0.11) \times 10^{-6}$	0.059 ± 0.005	29	34
30% wt D-PDPA(100:1):PEO (97:3) fiber	$(1.06 \pm 0.69) \times 10^{-4}$	$(5.62 \pm 3.08) \times 10^{-5}$	$(2.59 \pm 0.13) \times 10^{-6}$	0.0461 ± 0.032	25	20
50% wt D-PDPA(100:1):PEO (97:3) fiber	$(6.37 \pm 1.45) \times 10^{-5}$	$(4.45 \pm 0.45) \times 10^{-5}$	$(1.61 \pm 0.55) \times 10^{-6}$	0.0362 ± 0.016	26	28
30% wt D-PDPA(100:1):PEO (97:3) film	$(3.76 \pm 0.5) \times 10^{-4}$	$(8.52 \pm 0.14) \times 10^{-5}$	$(1.07 \pm 0.13) \times 10^{-4}$	1.25 ± 0.13	33	15
50% wt D-PDPA(100:1):PEO (97:3) film	$(8.59 \pm 0.74) \times 10^{-5}$	$(7.48 \pm 0.98) \times 10^{-5}$	$(7.88 \pm 9.69) \times 10^{-5}$	1.05 ± 1.169	30	20

σ = electrical conductivity values in air, N₂ and MetOH, $\Delta\sigma$ = the electrical response and $\Delta\sigma/\Delta\sigma_{\text{N}_2}$ = electrical conductivity sensitivity, at $T=25\pm 1$ °C, and at atmospheric pressure.

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