รายงานวิจัยฉบับสมบูรณ์

โครงการ
การพัฒนานาโนไฟเบอร์ของพอลิเมอร์นำไฟฟ้าเพื่องานตรวจวัดก๊าซพิษ

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กันยายน พ.ศ. 2549

สัญญาเลขที่ 4780087

รายงานวิจัยฉบับสมบูรณ์

โครงการ การพัฒนานาโนไฟเบอร์ของพอลิเมอร์นำไฟฟ้าเพื่องานตรวจวัดก๊าซพิษ

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สนับสนุนโดยสำนักงานคณะกรรมการอุดมศึกษา และสำนักงานกองทุนสนับสนุนการวิจัย

บทคัดย่อ

พอลิไพรอล (PPy) ที่ถูกสังเคราะห์ด้วยวิธีทางเคมี ในรูปของแผ่นที่อัดด้วยไฮโดรลิก และคอมพอสิตของ PPy กับ 3A ซีโอไลท์ (3A) และ ไนลอน 6 (Ny) อันได้แก่ แผ่นอัดของ PPy_3A50 ฟิล์มของ Ny20_PPy13 กลุ่มของเส้นใยนาโนของ Ny20_PPy13 ฟิล์มของ Ny20_PPy13_3A50 และกลุ่มของเส้นใยนาโนของ Ny20_PPy13_3A50 ได้ถูกเตรียมขึ้น ฟิล์มนั้นเตรียมจากการหล่อสารละลาย และเส้นใยนาโนนั้น เตรียมจากเทคนิคการปั่นเส้นใยด้วยไฟฟ้าสถิตย์ จากสารแขวนลอยของของผสม ในตัวทำละลายผสมระหว่างกรดฟอร์มิกและเอ็น-เมธิลไพรอลิโดน วัสดุเหล่านี้ ถูกนำมาวิเคราะห์ลักษณะต่างๆ และนำมาใช้เป็นวัสดุตรวจจับความชื้น วัสดุบางตัวที่ไม่ไวต่อความชื้นมากนัก จะถูกนำมาใช้เป็นวัสดุตรวจจับไอระเหยของสารเคมีที่มักใช้เป็นส่วนผสมในเลคเกอร์ คือ อะซิโตน เมธิลเอธิลคีโตน เมธานอล และโทลูอีน ในช่วงความเข้มข้นร้อยละ 0 – 20 โดยปริมาตรในไนโตรเจน ขึ้นกับอัตราการระเหยของสารเคมีแต่ละชนิด

3A ส่งผลต่อลักษณะและสมบัติของฟิล์มและเส้นใยของ Ny20_PPy13_3A50 พบว่า ฟิล์มมีความเป็นรูพรุนมากขึ้นเมื่อเทียบกับฟิล์มของ Ny20_PPy13 ส่วนเส้นใยของ Ny20_PPy13_3A50 มีขนาดใหญ่กว่า และมีค่าการนำไฟฟ้าจำเพาะน้อยกว่าเส้นใยของ Ny20_PPy13 ถึง 100 – 1000 เท่า กลุ่มของเส้นใยนาโนของ Ny20_PPy13 มีสภาพไวต่อไอระเหยของน้ำ มากกว่าแผ่นอัดของ PPy ถึง 1000 เท่า ในขณะที่กลุ่มของเส้นใยนาโนของ Ny20_PPy13_3A50 ซึ่งมี 3A ผสมอยู่นั้น มีค่ามากกว่าแผ่นอัดของ PPy เพียง 3 เท่า ฟิล์มของ Ny20_PPy13_3A50 และแผ่นอัดของ PPy_3A มีสภาพไวต่อไอระเหยของเมธานอลเข้มข้นร้อยละ 3 โดยปริมาตร สูงถึงร้อยละ 2422 (SD = 333) และ 107 (SD = 6) ตามลำดับ เมธานอลลดค่าการนำไฟฟ้าจำเพาะของแผ่นอัดของ PPy และกลุ่มของเส้นใยของ Ny20_PPy13_3A50 ลงร้อยละ 7.8 (SD = 0.3) และ 0 ตามลำดับ วัสดุตรวจวัดก๊าซพิษแต่ละตัวให้ลักษณะเฉพาะในการตอบสนองต่อไอของสารเคมีต่างกันออกไป งานวิจัยนี้ เป็นหนึ่งในความพยายามที่จะค้นคว้าวัสดุตรวจจับไอระเหยจากเลคเกอร์ที่เหมาะสม นอกจากนี้ ยังได้วิเคราะห์ถึงเหตุผลการเลือกตัวเติมแต่ง ส่วนผสม และสภาวะในการเตรียมวัสดุตรวจจับเหล่านี้ โดยเฉพาะเทคนิคการปั่นเส้นใยด้วยไฟฟ้าสถิตย์

Abstract

Chemically synthesized polypyrrole (PPy) in the form of hydraulic-pressed pellet, and PPy composites with 3A zeolite (3A) and nylon6 (Ny), i.e. PPy_3A50 pellet, Ny20_PPy13 film, Ny20_PPy13 fiber bundle, Ny20_PPy13_3A50 film, and Ny20_PPy13_3A50 fiber bundle have been prepared. The films and the fibers were fabricated by means of solution casting and electrospinning process, respectively, from the mixture suspensions in formic acid/*N*-methyl pyrrolidone mixed solvent. They were characterized and utilized as the sensing materials for water vapor. Some of them, relatively dull to moisture, were exposed to vapor of chemicals generally found in lacquer: acetone, methyl ethyl ketone (MEK), methanol, and toluene in the range of 0 – 20 vol% depending on evaporation rate of each chemical.

Adding 3A zeolite affected the appearance and properties of Ny20_PPy13_3A50 film and electrospun fibers. The film had higher porosity, as compared to Ny20_PPy13 film. The fibers were bigger and had lower specific conductivity by 2 - 3 orders of magnitudes, as compared to that of Ny20_PPy13 fibers. When compared with the PPy pellet, Ny20_PPy13 electrospun fiber bundle showed ca. 1000 times higher sensitivity toward water vapor. With 3A zeolite added, the response toward water vapor of Ny20_PPy13_3A50 electrospun fiber bundle was only ca. 3 times higher than that of pure PPy. Ny20_PPy13_3A50 film and PPy_3A50 pellet had sensitivity ($\Delta\sigma/\sigma i \times 100$) toward methanol as high as 2422 % (SD = 333 %) and 107 % (SD = 6 %), respectively at 5.6 vol% vapor. At the same vapor concentration, methanol decreased the specific electrical conductivity of PPy pellet by 7.8 % (SD = 0.3 %) and of Ny20_PPy13_3A50 fiber bundle by 0 %. Each sensing material had different characteristics toward different chemicals. This work is an attempt to search for the suitable sensing elements for the vapors in lacquer. Finally, we also provide and discuss the justifications for selecting proper additives, compositions, and fabrication conditions for these sensing materials, especially the electrospinning technique.

Exclusive Summary

This work reports the serial studies on development of a conductive polymer in the form of nanofibers for toxic gas sensor application. The target chemicals were acetone, methyl ethyl ketone (MEK), methanol, and toluene. They are the common components of lacquer, the important compound for interior decoration and many industries. These chemicals lead to both health problem and fire accident. The aim is to investigate new sensing materials with high sensitivity, high selectivity, and fast response time. Chemically synthesized polypyrrole (PPy) which possesses many advantages, e.g. ease of synthesis, high conductivity, and high environmental stability, has been selected as the model conductive polymer. Improvement of its poor selectivity has been investigated by adding various additives in to PPy (Part II). PPy pellet and pellets, films and nanofibers of PPy composites with suitable additive and compositions were prepared (Part III). They were explored as humidity sensors (Part IV). Only some suitable sensing materials were further investigated as chemical sensors (Part V). Parts I-V are summarized below. They are presented as manuscripts in this report.

In Part I, the preliminary study has been carried out to observe the possibility in using nanofibers from an electrospinning process as chemical sensors, in the form of fiber bundle. The electrospun fiber bundle of polypyrrole/polystyrene (PPy/PS) blend has been prepared by means of electrospinning process. It has been investigated as a sensing material for acetone vapor. Its electrical sensitivity ($(\sigma_{acetone} - \sigma_{air})/\sigma_{air} \times 100\%$) toward saturated acetone vapor was -37.7 % (SD = 1.4). That was ca. 20 % larger than that of the cast film sample at the same composition. However, it required 45-50 min to reach the equilibrium signal (t_{eqb}) which is ca. 20 min longer than that of the film. This could be claimed to a larger specific surface area of the fibers because the times needed to reach 10 % of the full response were approximately the same. However, the deviation in data was quite large. Higher performance electrometer and smaller Teflon exposing chamber were needed for better experimental results. A high performance electrometer was later available in Part III. A Teflon chamber and flow system were designed and ready to operate in Parts VI and V.

In Part II, various materials, i.e. non-polar polymers, water-soluble polymer, zeolites with various pore sizes and properties, and a desiccant, have been used as additives for PPy for humidity sensor application. All samples were in the form of hydraulic-pressed pellet with thickness of 50 +/- 5 μm. Adding the inert additives did not affect the electrical response pattern of PPy toward water liquid, but it changed the response magnitude. Adding zeolites and desiccants into PPy changed both the response characteristic and the magnitude from those of pure PPy. PEO and SiO_2 shortened t_{eqb}. Zeolites delayed the response time and enhanced the decrement in specific electrical conductivity of the materials with infinite t_{eqb}.

In Part III, suitable compositions of a mixture of PPy, nylon6 (Ny), and 3A zeolite (3A) in formic acid/*N*-methyl pyrrolidone mixed solvent (Ny20_PPy13_3A50) have been investigated. Conditions for an electrospinning process of the mixture, e.g. applied voltage, speed of rotating grounded collector, have been identified. The obtained fibers were chemically, morphologically, and electrically characterized and their properties were compared to those of PPy pellet, PPy_3A50 pellet, Ny20_PPy13 film, Ny20_PPy13_3A50 film, Ny electrospun fibers, and Ny20_PPy13 electrospun fibers. Adding 3A altered the appearance and the properties of Ny20_PPy13_3A50 film and electrospun fibers. The film with 3A had higher porosity. Bigger electrospun fibers were obtained with 2 - 3 orders of magnitude lower specific electrical conductivity, relative to those of Ny20_PPy13 electrospun fibers.

In Part IV, PPy in the form of hydraulic-pressed pellet, and its composites with 3A and Ny, i.e. PPy_3A50 pellet, Ny20_PPy13_3A50 film, and Ny20_PPy13_3A50 fiber bundle have been investigated as a sensing material for water vapor. When compared with the pellet of pure PPy, the electrospun Ny20_PPy13 fibers showed ca. 1000 times higher electrical sensitivity ($(\sigma_{x\%RH} - \sigma_{N2,3\%RH})/\sigma_{N2,3\%RH} \times 100\%$) toward water vapor. With 3A zeolite added, the response toward water vapor of Ny20_PPy13_3A50 fibers was only ca. 3 times higher than that of pure PPy.

In Part V, PPy pellet, PPy_3A50 pellet, Ny20_PPy13_3A50 film, and Ny20_PPy13_3A50 fiber bundle have been investigated as the sensing materials for vapor of acetone, MEK, methanol, and toluene. Note that Ny20_PPy13 film and Ny20_PPy13 fiber bundle were not employed in this work. It was because the sensitivity of the latter toward water was too high. Ny20_PPy13_3A50 film and PPy_3A50 pellet had electrical sensitivities ($(\sigma_{\text{chemical x ppm}} - \sigma_{N2,3\%RH})/\ \sigma_{N2,3\%RH} \times 100\ \%$) toward 5.6 vol% of methanol vapor as high as 2422 % (SD = 333 %) and 107 % (SD = 6 %), respectively. At the same vapor concentration, methanol decreased the specific electrical conductivity of PPy pellet by 7.8 % (SD = 0.3 %) and of Ny20_PPy13_3A50 fiber bundle by 0 %. Each sensing material had different characteristics toward different chemicals. This is one of the attempts to search for the suitable sensing elements for the vapors from lacquer.

Output ที่ได้จากโครงการ

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Polypyrrole/Polystyrene Electrospun Fiber as Sensor for Acetone Vapor

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Abstract

The polypyrrole-based sensor with high surface area has been developed by the electrospinning process. The bundle of micro-scale fibers of polypyrrole/polystyrene (PPy/PS) blend is successfully used as the sensor for acetone. Its electrical sensitivity, $(\sigma_{acetone} - \sigma_{air})/\sigma_{air}$ x 100%, toward saturated acetone vapor was -37.7 % (SD = 1.4). It was ca. 20 % larger than that of the cast film sample with the same composition. However, it required 45-50 min to reach the equilibrium signal (t_{eqb}) which is ca. 20 min longer than that of the film. This could be claimed to a larger specific surface area of the fiber bundle because the times needed to reach 10 % of the full response were approximately the same.

Keywords: Polypyrrole, Polystyrene, Electrospinning process, Chemical sensor, Acetone

1. Introduction

The electrospinning process is an effective method to produce fibers with a diameter in the range of microns to nanometers [1-3]. The potential applications of this technique concerns with the use of large specific surface, e.g. filter, catalyst, and sensor technologies. Some conductive polymers, e.g. polyaniline, have been electrospun successfully in forms the blends with other polymers with high electrospinability [3]. In our previous publication [4], the blends of PPy with some insulating polymers, e.g. PS, were found to enhance the selectivity of acetone vapor over acetic acid vapor and moisture. In this work, the electrospun fiber of PPy/PS blend is expected to induce higher sensitivity as compared to the film at the same composition. Acetone, a flammable composition in lacquer, was a target chemical vapor.

2. Experimental

2.1 Preparation of PPy, PS fiber bundle, PPy/PS fiber bundle, and PPy/PS films

The pellets of PS (Aldrich, melt index = 3.4, Mn = 9.5E04, MWD = 2.7) were commercially available whereas the powder of PPy was synthesized from pyrrole monomer (AR grade, Fluka) with an oxidant (ammonium persulfate, AR grade, Aldrich) to monomer molar ratio of 1:1 and a dopant (□-naphthalene sulfonic acid, AR grade, Fluka) of 1:12. The polymerization conditions were described elsewhere [5]. The solution of 10 %w/v PS in NMP (AR grade, Lab-scan) and the well-dispersed suspension of 10 % PS and 10 % PPy in NMP were obtained after stirring for 5 - 7 days. By means of the electrospinning, electrospun fiber bundle of PS and PPy/PS blend were collected on a rotating grounded collector surrounded with a sheet of aluminum foil. The speed of the collector was as low as 250 rpm to prevent the appreciable draft generated from the rotating collector. The solution or slurry was stocked in the glass syringe connected with a spinneret. The spinneret was a 4.5 mm-inner diameter, 1 cm-long, stainless steel needle. An applied voltage was 15 kV and the distance between the spinneret tip and the grounded rotating collector was 10 cm. The sample was driven by flowing N_2 into the syringe with the rate of 720 ml/min.

The electrospinning process was carried out at room temperature for 30 min. The collected fibers (Figure 1a) were gathered to be a bundle of fibers as shown in Figure 1b. The same PPy/PS suspension was also used to prepare films from solution casting process. All electrospun fiber bundles and cast films were vacuum dried at room temperature overnight before the characterization.

2.2 Characterization

The electrospun fibers of PPy/PS and the cast film were characterized by a termogravimetric analyzer, TGA to determine the solvent residue and any change in a thermal degradation which might have been caused by a high-voltage process of electrospinning. 1-2 mg of sample was heated at the rate of 10 °C/min from room temperature to 700 °C under N_2 atmosphere. A scanning electron microscope, SEM was used to characterize the surface morphology of the samples at an accelerating voltage of 20 or 25 kV and at magnifications of 100, 500 or 10,000. Their specific conductivity values, □, were measured by a custom-made four-point probe conductivity meter [6]. Si and SiO_2 sheets with known resistance values were used in the probe calibration. The suitable current was applied to each sample to maintain its Ohmic behavior and avoid the Joule heating effect. Once the fiber bundle was pressed by the probe during the conductivity measurement, it became denser. Its thickness values at the pressed areas were measured by a thickness gauge (Peacock, model PDN 12N) with a resolution of 0.001 mm.

2.3 Acetone Vapor Detection

The flow system for testing the sensor response consisted of a humidity-control set (the water container and the desiccant), an acetone container, and an exposure chamber which contained a four-point probe and a thermohygrometer (Cole-Parmer, model P-03313-86) inside. The temperature during an experiment was 31 ± 1°C and the relative humidity was 50 ± 10 %RH. The acetone in the container was vaporized by flowing into a closed loop system for at least 30 min before feeding it to the exposure chamber. The saturated vapor concentration of acetone in air at 31°C is

39 vol% [7]. The equilibrium changes in the specific conductivity of the samples were monitored and reported as $\%\Delta\sigma$ which is $(\sigma_{acetone} - \sigma_{air}) / \sigma_{air}$ x 100 %.

3. Results and Discussion

3.1 Properties of PS fiber bundle, PPy/PS fiber bundle, and PPy/PS films

Figures 2a - 2d show SEM photographs of PS fibers and PPy/PS fiber bundle. There are significant changes in the fibers after adding PPy: 1) the highly beaded structure (bead-widths = 1 – 1.7 μm) changed to be a less beaded structure of PS but still contained PPy particles instead (widths = 1 – 3 μm); 2) the fiber diameters increased from 0.05 – 0.25 μm to 0.24 – 0.66 μm; and 3) the fiber bundle showed more preferred alignment. Figure 2e shows the surface of a bundle of PPy/PS fiber bundle. It has larger surface area as compared with the PPy/PS cast film (Figure 2f).

Figure 3a shows thermograms of PPy powder, PS pellets, PPy/PS fibers, and PPy/PS films. The weight losses during the temperature up to 280°C were attributed to the losses in moisture content and NMP solvent. The amount of NMP in PPy/PS fibers, and PPy/PS films was calculated by subtracting the weight loss in this range of the sample from the weight loss of the simulated thermogram, as shown in Figure 3b. The simulated thermogram is obtained by assuming there is 50% PS and 50% PPy, and there is no NMP. The calculated NMP residues are comparable for both PPy/PS fibers and PPy/PS films (2.8 – 2.3 wt%). Note that the thermograms of the blend fibers and the blend film are nearly identical.

The thickness values of the pressed PPy/PS fiber bundle and the PPy/PS film were also comparable: they were 0.013 – 0.020 and 0.015 – 0.020 cm, respectively. Over 400 min, their specific conductivity values remained stable at 3.5E-05 S/cm (SD = 1.1E-05 S/cm) and 3.5E-05 S/cm (SD = 6.3E-06 S/cm), for the fiber bundle and the film, respectively. The specific conductivity of the PPy/PS fiber bundle showed a positive drift after this period of time.

Here are some proposed reasons for the changes in fiber morphology after adding PPy. Since PPy partially swells and dissolves in NMP, some portion of NMP was absorbed by PPy particles and there was less amount of NMP to dissolve PS. In other words, the concentration of PS in the suspension increased by adding PPy. As reported by Fong et al. [2] and Megelski [8], the higher polymer concentration, the bigger fiber diameter expected along with lesser bead formation. During travelling to the grounded collector, each part of the highly charged solution jet repels each other. This causes jet swirling which tremendously reduces jet diameter before drying and depositing on the collector. The fibers with smaller diameter and poor orientation would be obtained. The poorer orientation of smaller PS fibers has been driven from the swirling of the highly charged jet. In the case of PPy/PS fibers which possess bigger diameter and better alignment, the presence of PPy reduced the swirling. This result might be caused by the conductive properties of PPy which can store the charges, or the increase in an apparent PS concentration which increases the jet viscosity and makes swirling more difficult.

The low percentage NMP residues in both samples reflect the fact that NMP solvent can not be totally removed by any process at room temperature. Nevertheless, the comparable NMP residues cancel out the effect of the difference in solvent residue, which might lead to the difference in sensing performance of those two samples. The almost identical thermograms of these two imply that the electrospinning is a non-destructive process.

Indistinguishable specific conductivity values of the fiber bundle and the film of PPy/PS suggest that PPy and PS were not destroyed during the high-voltage process. The measurement of the thickness of the pressed bundle of fiber bundle, instead of a spongy bundle, solves the problem of a negative error in specific conductivity as reported by Norris et al. [3].

3.2 Sensitivity of PPy/PS Fiber Bundle and PPy/PS Films Toward Acetone

The decrements in the specific conductivity of PPy/PS fiber bundle and PPy/PS films were found during an exposure to the saturated acetone vapor in the air at 31 ± 1 ^{o}C and at 50 ± 10 %RH, but with different magnitudes. $\%\Delta\sigma$ was as large as

–38 % (SD = 1.4 %) for the electrospun fiber bundle whereas it was –25 % (SD = 11 %) for the cast film. The times needed to reach 10 % of the full response were approximately the same: 5 - 12 min for electrospun fiber bundle and 0 – 10 min for the film. However, the times needed to reach equilibrium electrical signal (t_{eqb}) were 45-50 min for the fiber bundle and 8 – 15 min for the film.

A larger $\%\Delta\sigma$ and a much longer t_{eqb} of the electrospun fiber bundle are attributed to its larger surface area, as observed by SEM. Larger surface area provides a greater attack sites, polaron and bipolaron [4], for acetone to attack. This is supported by their times needed to reach 10 % of the full response that were approximately the same.

4. Conclusion

The submicron fiber bundle of PPy/PS blend were successfully electrospun from NMP solution. It could be used as the sensor for acetone vapor with the ca. 13 % larger electrical response than the cast film sample. However, it requires the ca. 20 min longer t_{eqb}. This could be claimed to a larger specific surface area of the fiber bundle, as revealed by SEM, because the times needed to reach 10 % of the full response were approximately the same. The t_{eqb} of the PPy/PS electrospun fiber bundle will be improved if the bundle is spongier.

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Figure captures

Figure 1

a) The collected PS fibers on a part of Al foil surrounding the rotating collector; and b) PS fiber bundles.

Figure 2

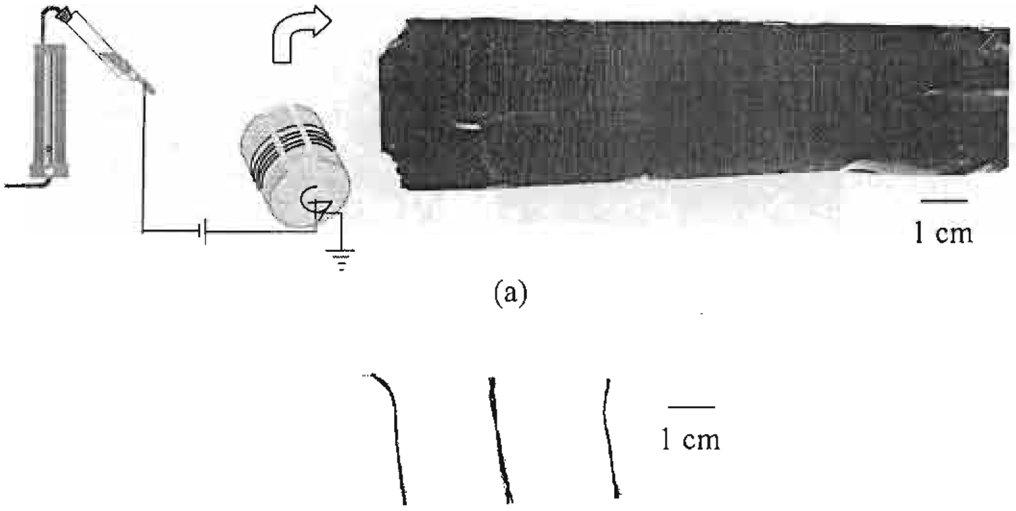
The SEM micrographs of: a) PS fibers at 500 magnifications; b) and at 10000 magnifications; c) PPy/PS fibers at 500 magnifications; d) and at 10000 magnifications, e) a bundle of PPy/PS fibers at 100 magnifications, and f) the surface of PPy/PS cast film at 3500 magnifications.

Figure 3

a) The TGA termograms of (——) PS, (– – –) PPy, (- - - -) PPy/PS fibers, (··········) PPy/PS film, and (– · · –) the simulated TGA termogram of 50 % PS + 50 % PPy as compared to PPy/PS fibers and PPy/PS film.

Figure 4

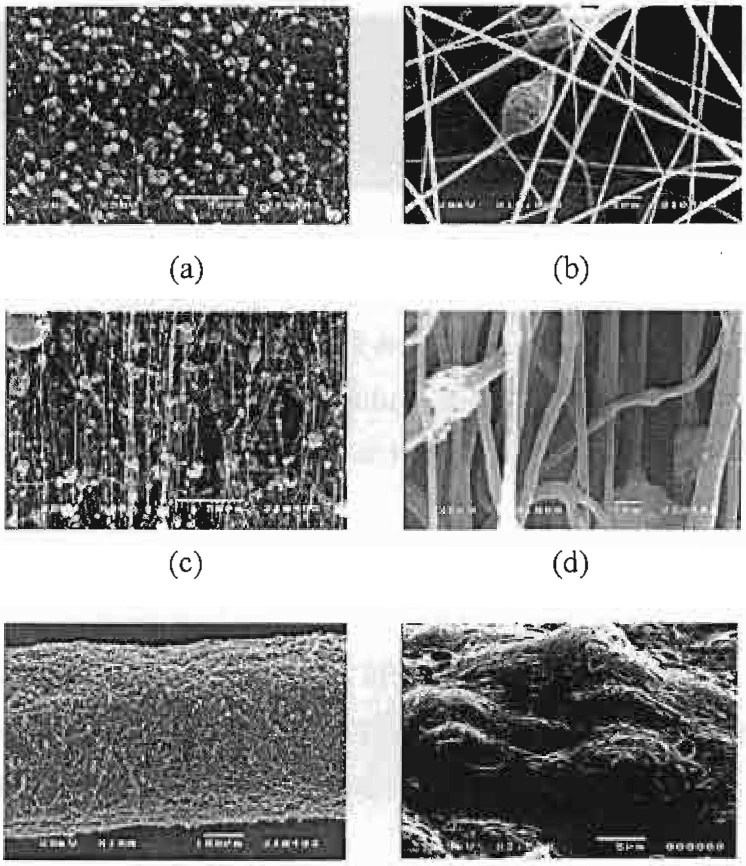
The decrease in the specific conductivity of the of: a) PPy/PS film, and b) PPy/PS fiber bundle.



(a)

(b)

Figure 1

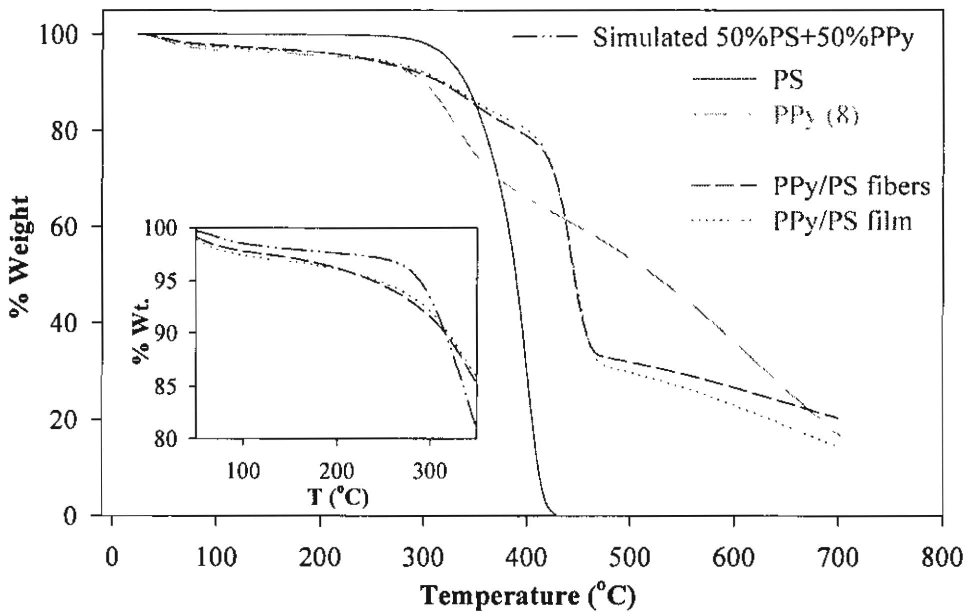


(a) (b)

(c) (d)

(e) (f)

Figure 2



Simulated 50%PS+50%PPy
PS
PPy (8)
PPy/PS fibers
PPy/PS film
% Weight
100
80
60
40
20
0
0
100
200
300
400
500
600
700
800
Temperature (°C)
% Wt.
100
95
90
85
80
100
200
300
T (°C)

Figure 3

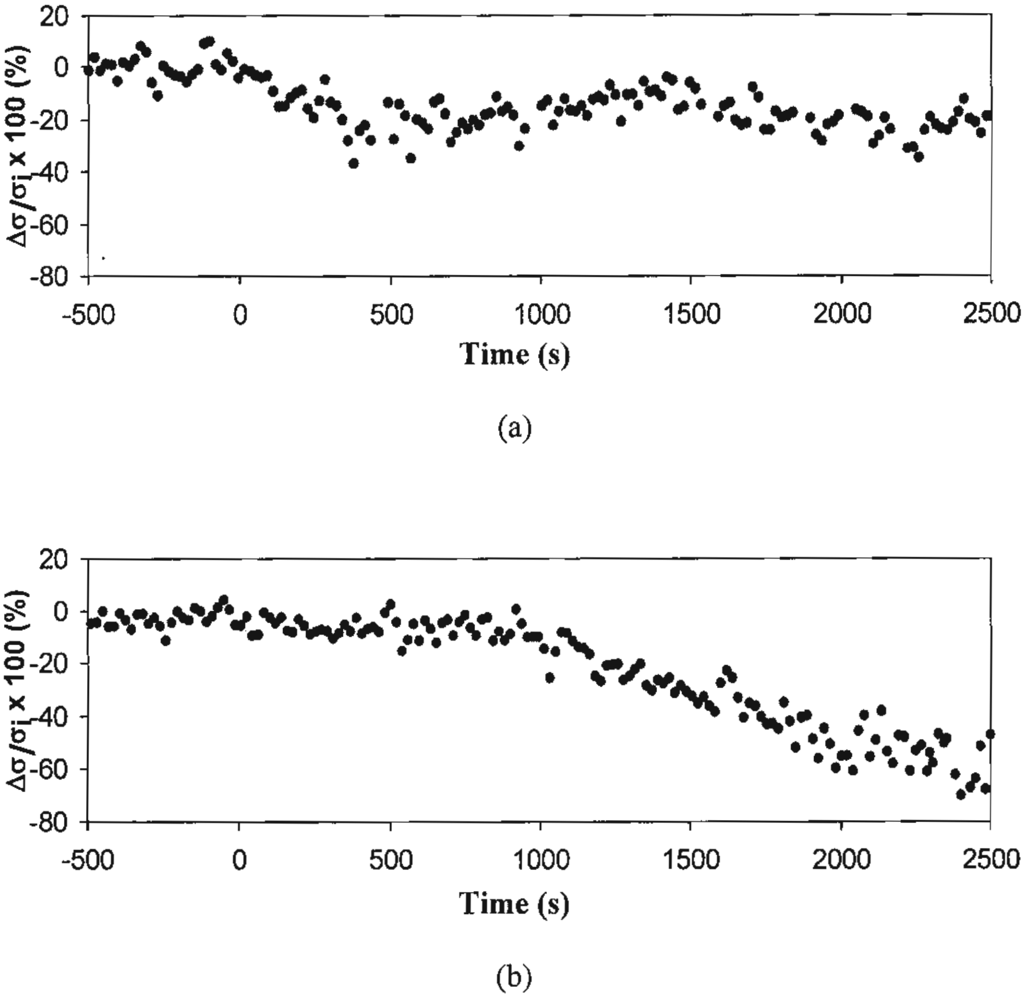

20
0
-20
-40
-60
-80
Δσ/σ$_i$ x 100 (%)
-500
0
500
1000
1500
2000
2500
Time (s)
(a)
20
0
-20
-40
-60
-80
Δσ/σ$_i$ x 100 (%)
-500
0
500
1000
1500
2000
2500
Time (s)
(b)

Figure 4

Utilizing Various Additives In Polypyrrole-Based Humidity Sensor

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Various materials, i.e. non-polar polymers, water-soluble polymer, zeolites with various pore sizes and properties, and a desiccant, have been used as additives for polypyrrole (PPy) for humidity sensor application. It has been found that adding the inert additives did not affect the electrical response pattern but changes the response magnitude whereas adding zeolites and the dessicants changed the response characteristic. PEO and SiO_2 shortened the time the sensor needs to reach the equilibrium. Zeolites delayed the response and seemed to infinitely enhance the sensitivity of PPy toward water.

Introduction In order to develop a simple sensor system which consists of only few sensing elements of conductive PPy, the sensitivity toward an ambient interference, the moisture, should be taken into account. This work focuses on the electrical response patterns of PPy toward liquid water when PPy was mixed with various additives yielding different response patterns toward water.

Experimental PPy was chemically synthesized with pyrrole (monomer): ammonium persulfate (oxidant): α-naphthalene sulfonate (dopant) ratio of 1:1: 0.08 at +/- 0.5 °C under N_2 for 1 hour. The PPy was aged at 50 +/- 5 %RH for 20 days before the experiments. The addivitives, that are polyethylene (PE), polystyrene (PS), Poly(ethylene oxide) (PEO), silica fume (SiO_2), zeolite 3A, 4A, 5A, Y and 13X were kept at 50 +/- 5 %RH before use. The densities, particle sizes, and surface areas of PPy and all additives were determined by a pycnometer, a mastersizer, and BET, respectively. PPy and additive with the equal volume were ground and mixed together. The mixture was pressed by a hydraulic press at 60 kN into a pellet with a diameter of 1.3 cm and a thickness of 50 +/- 5 μm. Their specific conductivity (σ) values were measured by custom-made four-point probe (square array) conductivity meter, as shown in Figure 1.

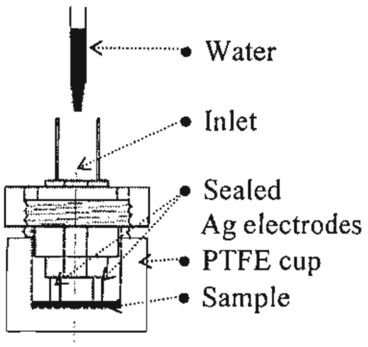

Figure 1. Custom-Made Four-Point Probe

Results and Discussion The sensitivity (percent change in σ relative to the initial σ) toward liquid water of PPy+zeolite changed with age after mixing, so the water responses of all sensing elements in this work were recorded after at least 14 days of mixing. The response patterns of PPy and PPy with various additives toward water are shown in Figure 3. The sensing elements with similar response pattern are described together. ***PPy***: σ of pure PPy suddenly decreased and then gradually increased. It took 700 – 900 seconds to reach the equilibrium signal. The former sudden decrement of σ resulted from the proton (H^+) subtraction whereas the later gradual increment in σ resulted from the hydronium ion (H_3O^+)

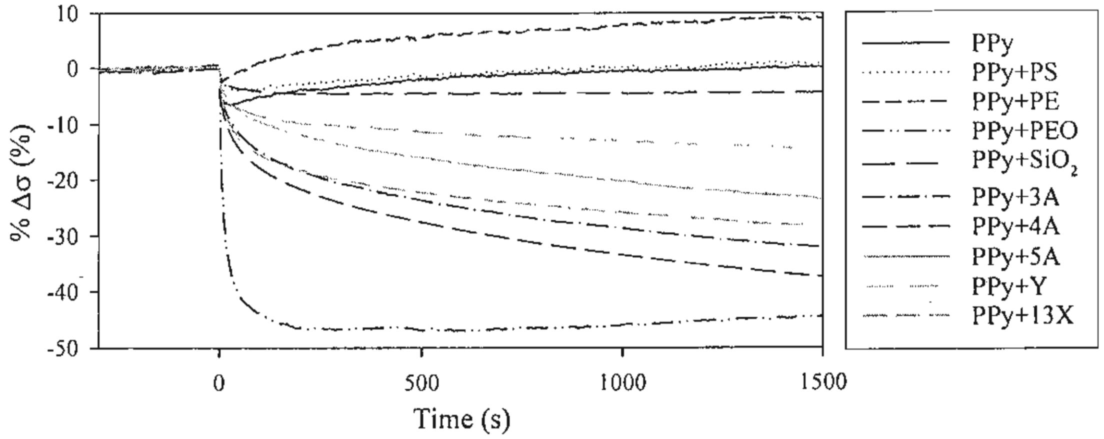

Figure 2. The response patterns of PPy and PPy with various additives toward water

movement in PPy. As investigated by XPS[1], the PPy which was exposed to liquid water showed decreasing of $-NH^{+}-$ and increasing of $-N=$ species. This evident supports the H^+ subtraction interaction. ***PPy mixed with inert additives***: Upon mixing with PE and PS, the response pattern did not change; they sharply decreased and then increased with different magnitudes. The decreases in σ were smaller due to a smaller percentage of active $-NH^{+}-$ sites in PPy. A larger increment in σ of PPy+PE might be due to the hydrophobic nature of PE which freed H_3O^+ to give an ionic conductivity to the sensor. ***PPy mixed with water soluble polymer***: PEO swells in water and increases the distance between conducting PPy particles. σ of PPy+PEO decreasesd suddenly and significantly after the exposure to liquid water. The time needed for equilibrium signal was only ca. 200 s. Most of ions were absorbed, hence no final increment in σ was observed. ***PPy mixed with zeolites***: All zeolites used in this work gave the similar response pattern toward liquid water. They delayed the response and tended to stop H_3O^+ movement. The sensitivity seemed to be infinitely enhanced. The microporous structure of zeolites increased the amount of accessible active $-NH^{+}-$ sites in PPy. Zeolite Y, which has the highest Si/Al ratio and hence the highest hydrophobicity among the others, gave the lowest sensitivity toward liquid water. The long-term sensitivity derivatives, which are the slopes of the response patter from 1000 to 1500 s, of zeolite Y, 13X, and A are -0.3, -0.5, and -0.6 to -0.8 %Δσ/100s. This order is proportional to their Si/Al ratios: 2.43[2], 1.33[3], and ~1. Zeolite 5A has a smaller sensitivity to water than 3A and 4A. The presence of Ca^{2+} in 5A instead of monovalent K^+ and Na^+ in 3A and 4A was responsible for this behavior. ***PPy mixed with other desiccant***: SiO_2 generally absorbs water but does not swell. So σ decrement was not enhanced. With the same reason as the inert additives, PPy+SiO_2 had 50% smaller σ decrement than that of pure PPy. The time needed for equilibrium signal was as short as that of PPy+PEO. SiO_2 absorbs water so there was no final increment in σ.

Conclusion The sensitivity, the response time, the time needed to reach the equilibrium signal, and the long-term sensitivity derivative of PPy can be tailored by utilizing various types of additives.

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Preparation of PPy and Its Composites with Nylon6 and 3A Zeolite as Pellet, Film, and Electrospun Fiber

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Abstract

The suitable conditions for the electrospinning process of composites from solutions containing chemically synthesized and doped conductive polypyrrole (PPy), nylon6 (Ny), 3A zeolite (3A) (Ny20_PPy13_3A50), and formic acid/*N*-methyl pyrrolidone as the solvent have been identified. The obtained fibers, Ny20_PPy13_3A50, were chemically, morphologically, and electrically characterized and their properties were compared to those of PPy pellet, PPy_3A50 pellet, Ny20_PPy13 film, Ny20_PPy13_3A50 film, Ny electrospun fibers, and Ny20_PPy13 electrospun fibers. Adding 3A altered the appearance and the properties of Ny20_PPy13_3A50 films and electrospun fibers. Bigger electrospun fibers were obtained with 2 - 3 orders of magnitudes lower specific electrical conductivity values relative to those Ny20_PPy13 electrospun fibers.

Keywords: Polypyrrole, Nylon6, 3A Zeolite, Electrospinning process

1. Introduction

Nylon is one of the most extensively used polymers in the electrospinning process [1-3]. It has high spinability especially when formic acid (FA), a good solvent, is used as the solvent in the process [3]. With an exception of FA and acetic acid, nylon has good resistance to most solvents. This property has stimulated research interest in the field of sensor technology in which many insulating polymers are blended with conductive carbon black [4-5] or conductive polymers [6] to obtain different swelling behaviors toward target gases or chemicals.

Polypyrrole (PPy) is one of the most stable conductive polymers. P-doped PPy has either a positive or negative electrical response toward electrophilic or nucleophilic gas, respectively. Moreover, its specific electrical conductivity can be reduced by the swelling effect [7], or increased by the ionic conductivity [6]. Its sensitivity is more various than those of carbon black/insulating polymer blends, but on the other hand it has poor selectivity towards a particular gas. There have been several attempts to improve PPy selectivity, e.g., by blending with insulating polymers [6] and zeolites [8].

3A zeolite (3A) exhibits well-known absorption for water and NH_3 [9], not for any other bigger molecules. Mixing 3A with naphthalene sulfonate (NSA) doped PPy alters the electrical conductivity response of PPy toward water liquid [8]. Zeolites can delay the response toward water and obstruct H_3O^+ movement. PPy/zeolite shows the infinite negative response toward liquid water.

The electrospinning process is a tool to produce polymeric fibers with sub-micron diameter, possessing large specific surface areas. Recently, electrospun fibers have been used in various sensor applications [10,11].

This work reports the suitable conditions for the electrospinning process to produce fiber bundles of composites consisting of PPy/NSA, nylon6 (Ny), and 3A, which are expected as promising sensing materials. The FA/*N*-methyl pyrrolidone (NMP) mixed solvent have been introduced instead of pure FA. The obtained fibers were chemically, morphologically, and electrically characterized and properties are compared with those of

PPy pellet, PPy_3A50 pellet, Ny20_PPy13 film, Ny20_PPy13_3A50 film, Ny electrospun fibers, and Ny20_PPy13 electrospun fibers.

2. Experimental

2.1 Synthesis of conductive PPy, pelletizing, aging, and characterization

PPy was chemically synthesized with pyrrole monomer (AR grade, Fluka): ammonium persulfate (APS: AR grade, Aldrich) as the oxidant: α-naphthalene sulfonate (α-NSA: AR grade, Fluka) as the dopant at the mole ratio of 1:1: 0.17. In 213 ml deionized water, 23.40 ml freshly low-pressure distilled pyrrole and 12.98 g α-NSA were suspended and dissolved, respectively. The solution had been stirred at 0 +/- 0.5 °C under N_2 for 30 min before the reaction was allowed to start. A solution of 77.21 g APS in 370 ml deionized water was then added to the mixture solution slowly for a period of 4 hr. After adding the oxidant, the reaction was allowed to proceed for another 1 hr to minimize possible polymer degradation. The black precipitate was collected and washed alternatively with deionized water and methanol for several times. The synthesized *in-situ* doped PPy was dried in a vacuum oven at room temperature, 26 +/- 1 °C, for a period of 2 days.

Three of PPy pellets were prepared by a hydraulic press at $8/\pi(0.75)^2$ kN/cm^2 and aged at 50 +/- 5 %RH and at room temperature, 26 +/- 1 °C, until its specific electrical conductivity (σ) value, as measured by an electrometer (Keithley model 6517A), reached an acceptable equilibrium value. The probes were custom-made two-point probes, made of PTFE and Au wires, designed for pellets and films, as shown in Figure 1a. PPy were chemically characterized by Fourier-transform infrared spectroscopy (FTIR: Bruker model FRA 106/S) at the resolution of 4 cm^{-1} for 32 scans, and morphologically characterized by a scanning electron microscope (SEM, JOEL model JOEL 520) at the accelerating voltages of 15 or 20 kV and at the magnification of 5,000 or 20,000 times.

2.2 Preparation of electrospun Ny fibers: effects of Ny solution concentration and applied voltage

5, 10, 15, and 20 g nylon6 (Ny: MW= 32,000 Da) were dissolved in 100 ml formic acid (FA: 98% AR grade, BDH) to prepare Ny solutions namely Ny05, Ny10, Ny15, and Ny20, respectively. They were electrospun at the applied voltage of 15 kV, the distance between charged spinneret and grounded Al foil collector was 5 cm, a 25G stainless steel spinneret with a length of 1 cm, and the solution feeding rate of 0.1 ml/hr. The suitable range of concentration for the electrospinning process under these conditions was identified from morphological appearances. A concentration of Ny solution at a selected concentration of 15 %w/v was then electrospun at various applied voltages: 10, 15, 20, 25, and 30 kV. A suitable applied voltage, 15 kV, was then chosen from the obtained fiber morphology and from experimental safety aspects.

2.3 Preparation of Ny_PPy blend films: percolation in Ny_PPy blend

Various amounts of PPy were added into Ny solution with the selected concentrations to produce the Ny_PPy blend suspensions with PPy:Ny volume ratios between 0.01 - 1.00. The blend would be named Ny_PPy01 for the PPy:Ny volume ratio of 0.01, for example. Blend films were cast by means of solution casting. 0.8 ml of the suspension was smeared on 22 x 22 mm^2 glass slide cover. The covers were floated on the water while air-drying, in order to produce the uniform film thickness. The specific conductivity of the dried films was measured to determine the percolation value. Ny_PPy solutions at volume ratios above the percolation threshold were then used further.

2.4 Preparation of PPy_3A composite pellets: percolation in PPy_3A composites

Dried 3A zeolite (3A: Aldrich) was mixed with PPy at 3A:PPy volume ratios between 0.01 – 1.00. The composites would be named PPy_3A01 for the 3A:PPy volume ratio of 0.01, for example. Our previous experiment [8] showed that once 3A particles were added into PPy, the specific electrical conductivity of the PPy_3A50 composite pellet decreased continuously with time and reached an equilibrium value after about 20 aging days. So, in this experiment, the mixtures were left in 20 ml vial tube for 40 days after which zeolite particles were expected to fully absorb water from PPy. Their pellets were prepared by means of the hydraulic press as described above. The pellets electrical conductivity values were measured in order to determine the percolation ratio of the composite. 3A and PPy_3A composite with a suitable ratio below the percolation were used in the preparation of pellets for the morphological characterization by SEM.

2.5 Preparation of electrospun fibers of Ny, Ny_PPy and Ny_PPy_3A: effects of the rotational speed of collector and the duration of process

Our preliminary results showed that the pure FA could not be used as the solvent to electrospin Ny_PPy blend successfully. The obtained fiber mat was completely white, indicating the absence of PPy in these fibers. Hence, the mixed solvent of FA and N-methyl pyrrolidone (NMP: AR grade, Fluka) which can partially dissolve PPy was then introduced instead of pure FA. However, NMP is a poor solvent for Ny. Only a solution with FA:NMP weight ratio of 3:1 or volume ratio of 2.575:1 or higher can dissolve Ny at 20 %w/v completely. This minimum ratio was selected for further experiment since the higher NMP is added into the solution, the higher amount of PPy can be introduced into the composite. The maximum PPy concentration that could disperse well in NMP was 12 wt.%. When the suspension of PPy in NMP was mixed with Ny15 and Ny20 solutions, the blends PPy:Ny volume ratios were 0.176:1 and 0.132:1, respectively. They were called Ny15_PPy18 and Ny20_PPy13. Since continuous detachable electrospun fibers could not be obtained from Ny15_PPy18, while those of Ny20_PPy13 could be detached from the fiber mat on Al foil after immerging in deionized water and dried by lint-free tissue paper, only Ny20_PPy13 and Ny20_PPy13_3A50 suspensions in the mix solvent were used to cast films and for electrospining.

The electrospinning process of the chosen solutions was carried out under these conditions: applied voltage of 15 kV, the distance between charged spinneret and grounded Al foil collector of 5 cm, using a 21G stainless steel spinneret length 1 cm, and the solution feeding rate of 0.1 ml/hr. Note that the spinneret size is bigger than that in section 2 in order to eliminate the clogging problem frequently found in Ny_PPy solution. In order to collect well-aligned fibers, which can be rolled up to be a bundle with a uniform thickness, the stay-still Al foil collector was replaced by a home-made rotating Al drum of variable speeds (0-1200 rpm) with a diameter of 7.5 cm. To prevent excessive accumulation of fibers for the SEM characterization, only 5 min was allowed for the process. A suitable rotating speed of the drum was determined and set from fiber morphological appearances.

Even though one would expect a greater numbers of fibers collected with the longer period of electrospinning time and the specific electrical conductivity of fibers should remain the same, practically, there are some limitations in the experiment, e.g. the probe design. So, the suitable time required for the electrospinning, at particular conditions, was determined from the fiber bundle size required and the corresponding specific electrical conductivity. The probe for electrospun fiber bundle is shown in Figure 1b: it was used the same conductivity meter as in the case of pellets and films.

2.6 Measurement of specific conductivity of Ny_PPy_3A electrospun fibers and related materials

Prior to preparing the pellets of PPy, 3A, and PPy_3A50 by means of the hydraulic press mentioned above, their powders were weighted to control the pellet thickness to be 0.06 - 0.07 cm. The films of Ny20, Ny20_PPy13, Ny20_PPy13_3A50 from FA/NMP mixed solvent were cast as described above. The film thickness was controlled to be 0.06 - 0.07 cm by controlling the suspension volumes used. The electrospun fibers of Ny20_PPy13, Ny20_PPy13_3A50 from FA/NMP mixed solvent were prepared by the conditions described in section 5. The fiber bundle thickness was controlled by the electrospinning time as investigated above.

The specific conductivity values of PPy pellet, Ny film, 3A pellet, Ny20_PPy13 film, Ny20_PPy13_3A film, Ny20_PPy13 fiber bundle, and Ny20_PPy13_3A50 fiber bundle were measured by the custom-made two-point probe conductivity meter designed for pellets and films, as shown in Figure 1a, or for fiber bundles, as shown in Figure 1b.

3. Results and Discussion

3.1 Synthesis of conductive PPy, pelletizing, aging, and characterization

Figures 2a and 2b shows σ and the change in specific electrical conductivity values ($(\sigma_x - \sigma_{x-1}) / \sigma_{x-1} \times 100$) of PPy pellets as functions of aging day (x), respectively. Its initial specific electrical conductivity values were 65-80 S/cm. The values decreased appreciably during the first 10 days. The specific electrical conductivity values reached equilibrium values at 39-40 S/cm when its age was 20 days, after which the percent changes in specific electrical conductivity values were less than +/- 2.5%, as compared to those of the previous days.

The FT-IR spectrum of PPy at the wavenumber higher than 2000 cm^{-1} is featureless with a positive drift due to the presence of a large electronic peak at ~1 eV (8066 cm^{-1}), as shown in Figure 3b. The board band at ~3500 cm^{-1} belongs to N-H stretching [12]. The hygroscopic characteristic of PPy suggests the presence of H_2O which broadens the N-H peak. The peaks at 1157 and 607 cm^{-1} indicate the presence of sulfonate dopant [13]. Figures 3c-3f are described below. The globular structure of the chemically synthesized PPy powers can be seen by SEM micrographs shown in Figure 4a.

3.2 Electrospun Ny fibers: effects of Ny solution concentration and applied voltage

Figure 5 shows the scanning electron micrographs at 20,000x and at the accelerating voltage of 20kV of electrospun Ny fiber mat from Ny solution in FA at the concentrations of 5 (Ny05), 10 (Ny10), 15 (Ny15), and 20 (Ny20) %w/v. The appearances suggest that the suitable range of concentration for the electrospinning process for Ny used in our work should be 10-20 %w/v. At 15 %w/v, the obtained fibers are slightly bigger (0.08 – 0.17 μm) than those at 10 %w/v (0.04 – 0.15 μm) due to a greater mass of Ny drawn from the reservoir even the volume flow rate (of the solutions) was kept constant. The fibers seem to have polydipersity in diameters when the concentration is 20 %w/v (0.05 – 0.22 μm), the concentration at which the solidified solution often clogged at the spinneret tip. This penetrable obstacle at the tip manifested itself as an irregular multiplehole spinneret in which Ny solution leaked. These factors lead to the large variation in fiber diameters obtained.

Ny15 fibers were electrospun at various applied voltages. Figure 6 shows their SEM micrographs. Even though the appearances of these fibers are not significantly different, the sound of air discharging during the electrospinning experiment when the applied voltage was larger than 15 kV (electric field density = 15 kV/5 cm) limited the safe applied voltage to be 10-15 kV.

Figure 3a shows FT-IR spectrum of the ground electrospun Ny fibers. The peaks at 3300 cm^{-1} and at 1640 cm^{-1} are evidences of the N-H and C=O in amide linkage of Ny, respectively. The peak positions are the same as those of a standard nylon. This result demonstrates the harmless nature of the electrospinning process.

3.3 Ny_PPy blend films: percolation in Ny_PPy blend

The specific electrical conductivity values of Ny15_PPy films and Ny20_PPy films with various PPy:Ny volume ratios are shown in Figure 7. Both sets of data show the same trend. At the ratios lower than 0.1, the film conductivity values are approximately the same as that of Ny film. The electrical conductivity values sharply increases with the volume ratio above 0.1. Thus, PPy:Ny volume ratio of 0.1 is the percolation point.

3.4 PPy_3A composite pellets: percolation in PPy_3A composites

Figure 8 shows the specific conductivity values of PPy_3A pellets at various 3A:PPy volume ratios. The percolation is as high as ca. 0.75. The volume ratio of 0.5 (PPy_3A50) was used in subsequent experiments because of its sufficiently high electrical conductivity obtained and a large volume of 3A allowed in order to investigate the improved properties of PPy.

The SEM micrograph of PPy_3A50 pellet is shown in Figure 2b. 3A particles appear to be well dispersed in the PPy_3A50 pellet. The particles are well preserved through grinding and hydraulic pressing. The FT-IR spectrum of 3A is shown in Figure 3c. The most intense peak is at 983 cm^{-1} with its shoulder at 1107 cm^{-1}. They are assigned to the asymmetrical stretching mode of O-T-O where T = Si or Al [14]. The peak of symmetrical stretching mode of O-T-O appears at 653 cm^{-1} whereas the peak of T-O bending of TO_4 tetrahedra appears at 453 cm^{-1}. The peak at 546 cm-1 indicates the vibration of linkage between the tetrahedral building units. The broad peak at 3257-3685 cm^{-1} indicates the presence of Si-O-H [12] and O-H under H-bonding condition with the adsorbed water [14].

3.5 Electrospun fibers of Ny, Ny_PPy and Ny_PPy_3A: effects of rotational speed of collector and duration of process

When compared with the electrospun Ny20 fibers from pure FA solvent (Figure 2c), once the FA/NMP mixed solvent was used to electrospin Ny20, the fibers became more irregular in shape and were contaminated by drops of the solution (Figure 2d1). The fibers had a higher regularity with less impurity at the edges of fiber mat (Figure 2d2) where the distance between solution spinneret and the grounded collector was longer. In both solvents, the electrospun Ny20 fiber from FA/NMP mixed solvent contained a large portion of fibers with bead-on-string morphology.

Figures 4e and 4f show the morphology of Ny20_PPy13 film and Ny20_PPy13_3A50 film, respectively. The higher surface porosity upon adding 3A might be caused by the absorption of solvent and water (98% FA) by 3A zeolite. The film with 3A dried faster, leaving a high degree of porosity. There were no 3A particles found at the film surface.

Figures 4g and 4h show the morphology of electrospun fiber mats of Ny20_PPy13 and Ny20_PPy13_3A50, respectively. Upon adding 3A, the fibers became larger in diameter, the number of the bead was lower whereas the size of the bead was bigger. The 3A zeolite particles were rarely seen from the SEM micrographs. Some of the 3A particles were covered with Ny and became larger by Ny film. Since the film with 3A dried faster, the as being electrospun jet with 3A also dried faster. It can be expected if the solution jet dries faster during the electrospinning process, the jet whipping and jet swirling, which reduce fiber diameter, are terminated sooner. This explains why bigger fibers were found in the electrospun Ny20_PPy13_3A50 fibers.

With increasing rotating drum speed from 0 – 1200 rpm, the electrospun Ny20_PPy13_3A50 fiber alignment became more ordered until the speed reached 500 rpm after which the alignment could not be further improved (Figure 9). Moreover, at high rotating speeds, the drum generates a draft repelling the injected solution jet. The rotating speed of 500 rpm was then used in the next experiment. Note that the fiber morphology of Ny20_PPy13_3A50 fibers at 0 rpm was as normal as shown in Figure 4h. Figure 9b shows fibers that were climbing up on the jet when the fiber mat was too thick: the conductive-grounded collector was covered by the fiber mat. This necessitated the use of the rotating collector.

As shown in Figure 10, when the electrospinning process was as short as 30 - 90 min, the specific electrical conductivity values of the electrospun Ny20_PPy13 fibers varied since the bundle was too thin to fit the custom-designed probe. At the process time of 150 - 180 min, the specific conductivity values of the bundles were 5 orders of magnitude higher than those at 30 - 90 min. This is due to the geometry of the probe which fits perfectly to the bundle with diameters between 0.05 - 0.07 cm. Even though the bundle thickness increases with increasing the electrospinning time, at the time longer than 210 min, the thickness has a high variation. If the fiber mat that had been collected on the rotating drum was too thick, there appeared to be a difficult task of rolling the fiber mat into the uniform bundle. Moreover, at too long period of electrospinning time, the bundles were too thick whereas the contact areas between the electrodes and the bundles could not increase any further due to the probe geometry. In other words, the measured resistivity remained the same whereas the sample thickness was larger. This results in the decline of the bundle's specific conductivity at electrospinning time larger than 180 min. Therefore, the optimum time for the electrospinning process of Ny20_PPy13 with the specific drum and probe is 150-180 min.

For Ny20_PPy13_3A, the specific conductivity of the electrospun fiber bundle was much lower than that of Ny20_PPy13 and independent from the process duration. The thickness increased with the process duration, but it required a longer time to reach the same bundle thickness as that of Ny20_PPy13. This could be explained that there should be less Ny and PPy came out from the spinneret as compared to the amount of Ny and PPy in Ny20_PPy13 suspension, at the same feeding rate and electrospinning time, because the presence of added 3A particles. However, there were no evident for this explanation. From the experiment, the time of 340 min was required to obtain Ny20_PPy13_3A fiber bundle with ~ 0.06 cm thick.

Figures 3e and 3f show the FT-IR spectra of Ny20_PPy13_3A50 film and fiber mat, respectively. The former is dominated by the spectrum of PPy whereas the latter is dominated by the spectrum of Ny. In both cases, the spectrum peak of 3A is diminished. This is not surprising since the added amount of 3A was only 6.6 vol.% of Ny. This corresponds to what we found in SEM micrograph of the composite; 3A particles were rarely seen and some of them were coated by Ny matrix.

3.6 Specific conductivity of Ny20_PPy13_3A50 fiber bundle and related materials

The specific conductivity values of PPy, Ny film, 3A pellet, Ny20_PPy13 film, Ny20_PPy13_3A film, Ny20_PPy13 fiber bundle, and Ny20_PPy13_3A50 fiber bundle are shown in Figure 11. The equilibrium specific electrical conductivity of PPy_3A50 is 1-2 S/cm; that is 2 orders of magnitude lower than that calculated by the volume fraction rule: $(\sigma_{PPy}+0.5\sigma_{3A})/1.5$ or ~26 S/cm. The specific electrical conductivity values of the Ny20_PPy13 film and the electrospun fibers of Ny20_PPy13 are 8E-05 and 3E-05 - 1E-04; they are 5-6 orders of magnitude lower than those calculated from $(\sigma_{Ny}+0.13\sigma_{PPy})/1.13$ which is ~3.3 S/cm. Upon adding 3A, the film of Ny20_PPy13_3A50 had the specific electrical conductivity of 2E-05 S/cm. This value is 6 orders of magnitude lower than that calculated from $(\sigma_{Ny}+0.13\sigma_{PPy}+0.066\sigma_{3A})/1.196$ or ~3 S/cm). The specific conductivity is much lower in the case of Ny20_PPy13_3A50 electrospun fibers; it was 9 orders of magnitude lower than that calculated by the volume fraction rule.

In PPy_3A50 pellet, 3A particles probably adsorbed water molecules from PPy and increased the free volume in PPy, allowing more oxidation induced by air. These factors decreased ion conductivity and obstructed the pathway lengths of polaron and bipolaron, respectively. Hence the specific conductivity of PPy is lower than that calculated. In the film of Ny20_PPy13 blend, Ny acted as a continuous phase. Some PPy particles were surrounded by Ny thin film, shielding conductive PPy from the conductivity meter. Hence the specific electrical conductivity of the film is much lower than expected. The reduction in the specific conductivity of the electrospun fibers from the same Ny20_PPy13 suspension might be caused by the less density of the bundle as reported by Norris *et. al.* [15] in the case of polyaniline/PEO fiber mat. However, this small reduction suggests the harmless nature of the electrospining process. As evidenced by FT-IR spectra, the presence of PPy is dominant in Ny20_PPy13_3A50 film whereas the presence of Ny is dominant in Ny20_PPy13_3A50 electrospun fibers. This corresponds to a much lower value in specific electrical conductivity of the latter.

4. Conclusion

The electrospun fibers of Ny_PPy_3A were successfully collected as fiber bundles with a diameter of 0.05-0.06 cm and with a specific conductivity between 10E-07 – 10E-08 S/cm. The fiber morphology was bead-on-string, their diameters were in the range of 0.25-1.25 μm. The suitable conditions for composite composition were: the concentration of Ny solution of 20 wt.% in FA/NMP mixed solvent, Ny:PPy:3A volume ratio of 1000:132:66, and the FA:NMP volume ratio of 2575:1000. The suitable conditions for the electrospinning process were: the applied voltage of 15 kV, the distance between spinneret and grounded collector of 5 cm, the rotating drum speed of 500 rpm, and the duration of the electrospinning process of 340 min.

5. Acknowledgements

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Figure captures

Figure 1	The custom-made two-point probe designed for: a) pellets and films; and b) electrospun fiber bundles, with 2 stainless steel springs inside.
Figure 2	a) the specific conductivity; and b) the change in specific conductivity (as compared to the adjacent previous day) of PPy pellets, as a function of aging time.
Figure 3	FTIR spectra of: a) ground Ny fibers; b) PPy powder; c) 3A powder; d) Ny20_PPy13 fibers free standing fiber mat; e) ground Ny20_PPy13_3A50 film; and f) Ny20_PPy13_3A50 free standing fiber mat.
Figure 4.	SEM micrographs at 5,000x, 15kV of: a) PPy pellet; b) PPy_3A50 pellet; c) electrospun Ny fibers from FA solution; d1) electrospun Ny fibers from FA/NMP solution at the center of the fiber mat; and d2) at 1.5 cm from the center of the fiber mat; e) Ny20_PPy13 film; f) Ny20_PPy13_3A50 film; g) electrospun Ny20_PPy13 fibers from FA/NMP solution; h) electrospun Ny20_PPy13_3A50 fibers from FA/NMP solution.
Figure 5	The scanning electron micrographs at 20,000x, 20kV, of the electrospun results from Ny solution in FA at the concentrations of: a) 5; b) 10; c) 15; and d) 20 %w/v.
Figure 6	The scanning electron micrographs of electrospun Ny from 15 %w/v Ny solution in FA at the applied voltages of: a) 10; b) 15; c) 20; and d) 25 kV.
Figure 7	The specific conductivity of: (o) Ny15_PPy films; and (Δ) Ny20_PPy films with various PPy:Ny volume ratios.
Figure 8	The specific conductivity of PPy_3A pellets with various 3A:PPy volume ratios.
Figure 9	Scan images and SEM micrographs of Ny20_PPy13_3A50 fibers from the section 6 with various rotating drum speeds: a) and b) 0; c) and d) 100, e) and f) 300; g) and h) 500; i) and j) 800; and k) and l) 1200 rpm.
Figure 10	Thickness and specific conductivity of Ny20_PPy13 and Ny20_PPy13_3A50 fiber bundles collected during various electrospinning process durations.
Figure 11	The specific conductivity of Ny20_PPy13_3A50 fiber bundle and related materials.

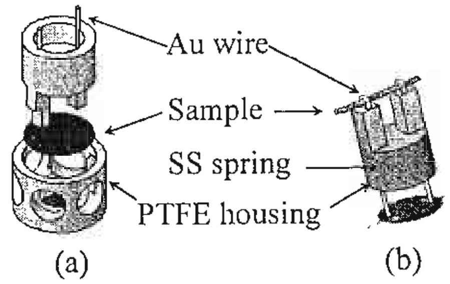


Figure 1

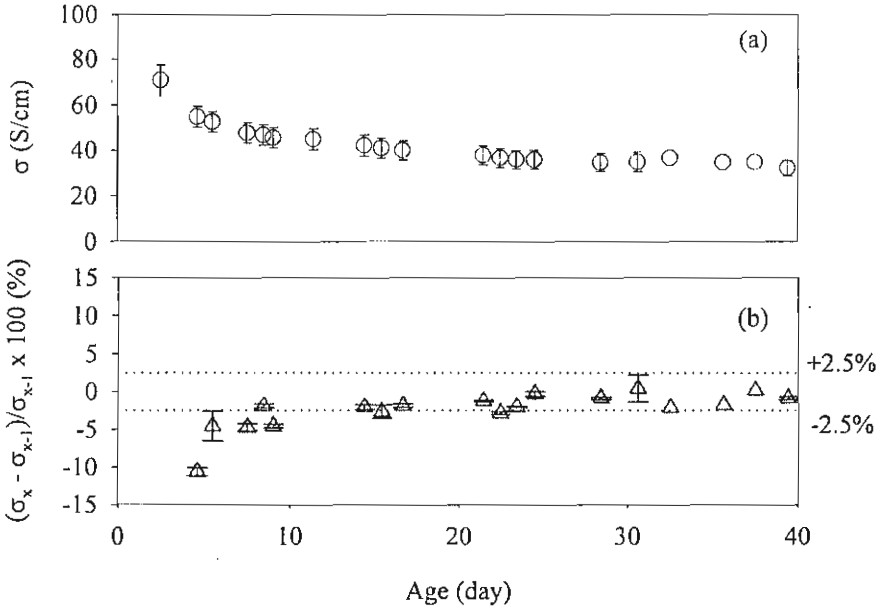

100
80
60
40
20
0
σ (S/cm)
(a)
15
10
5
0
-5
-10
-15
(σx - σx-1)/σx-1 x 100 (%)
(b)
+2.5%
-2.5%
0
10
20
30
40
Age (day)

Figure 2

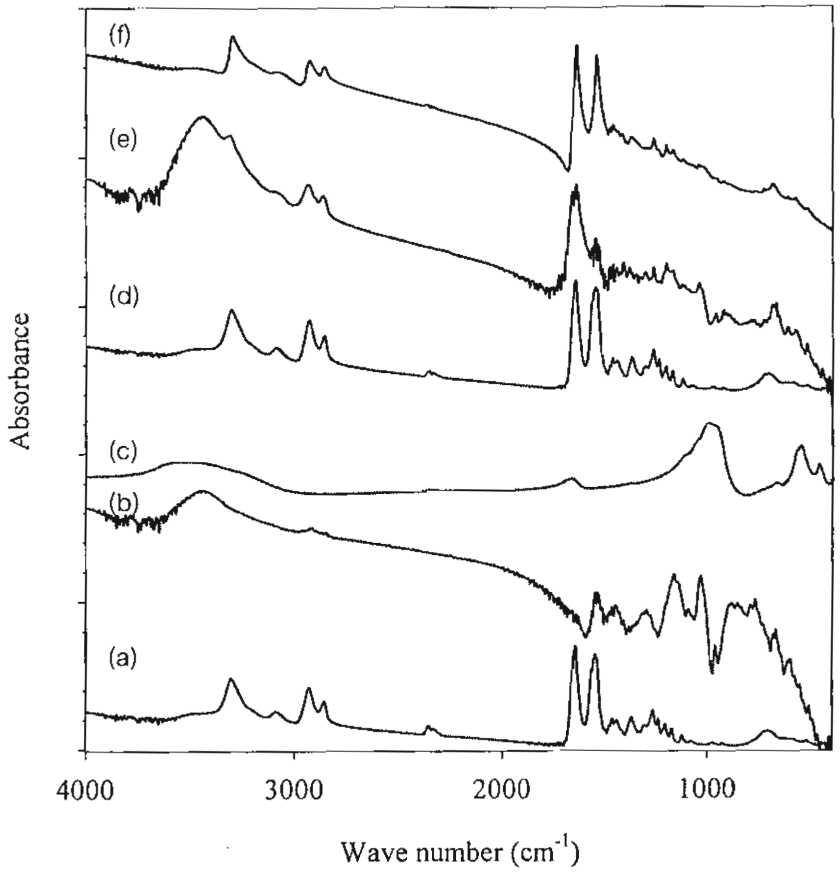


Figure 3

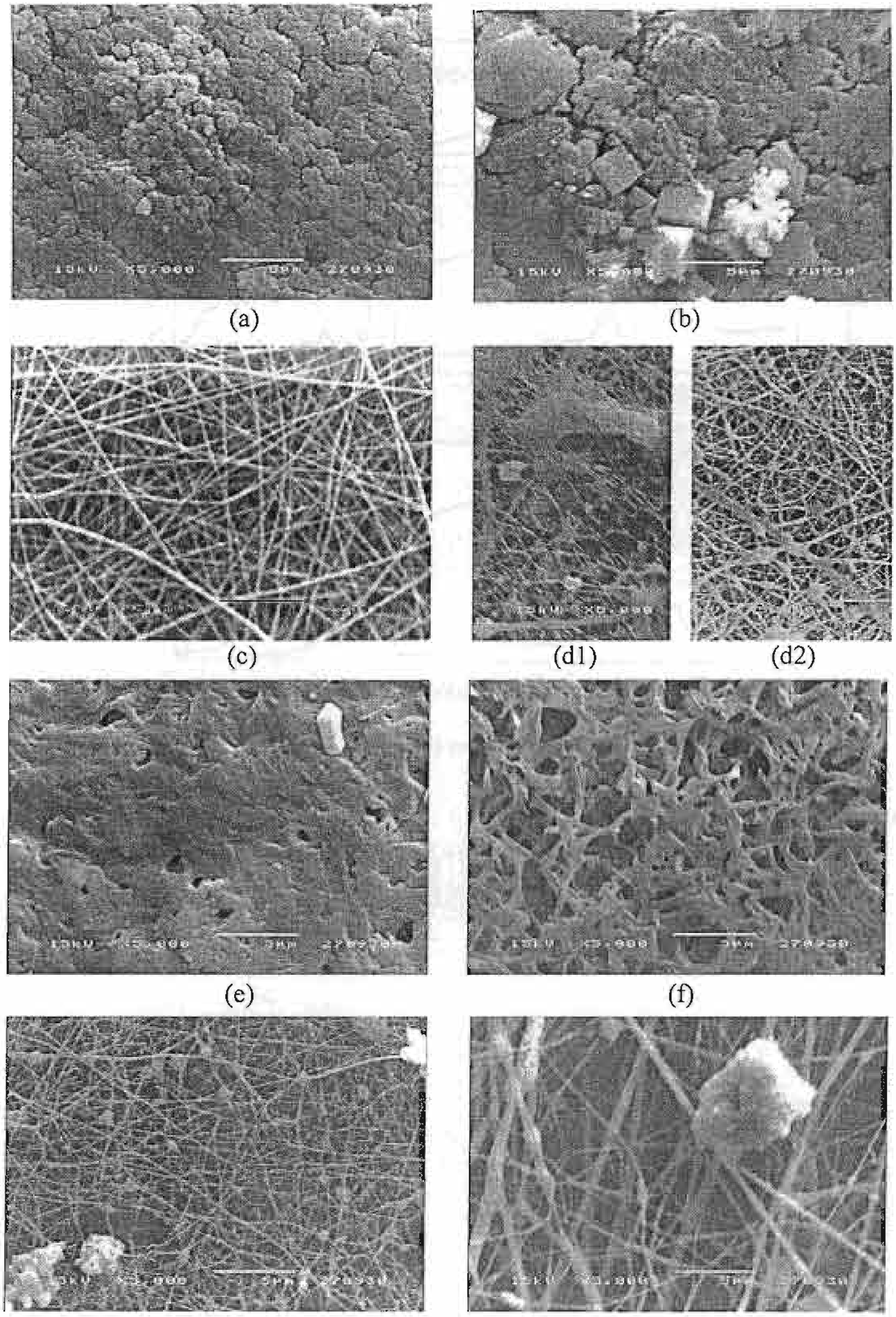
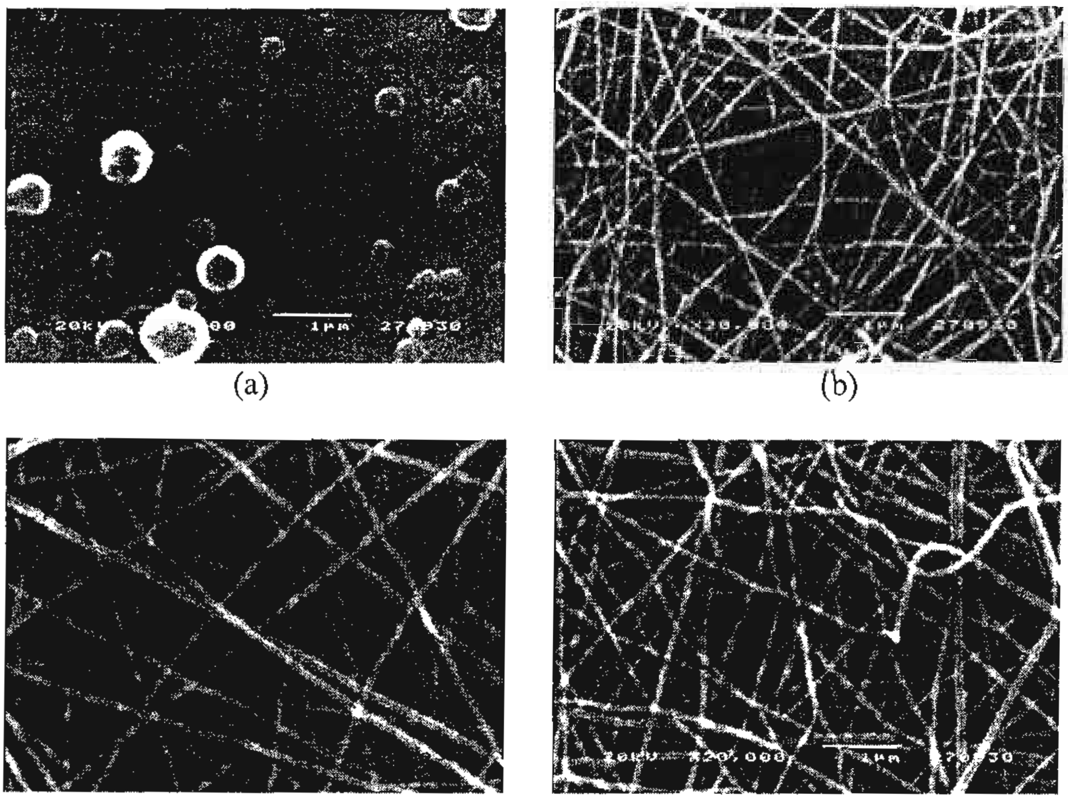

(a) (b) (c) (d1) (d2) (e) (f) (g) (h)

Figure 4



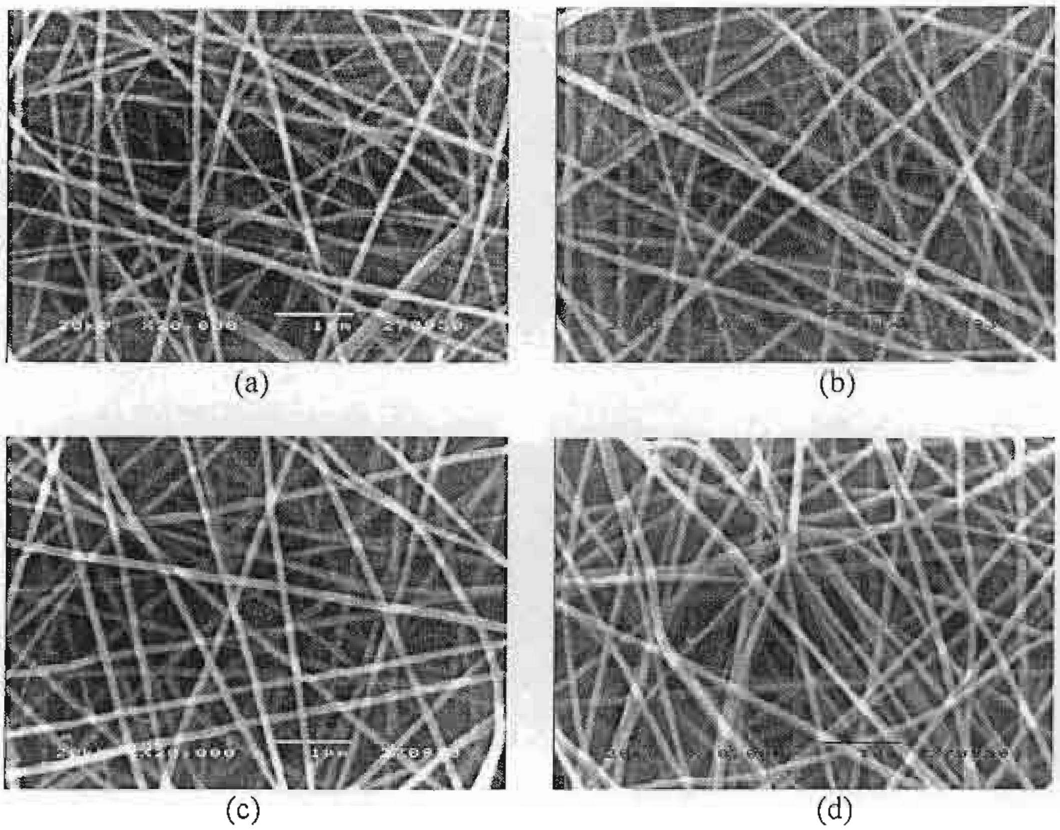
(a)

(b)

(c)

(d)

Figure 5



(a) (b) (c) (d)

Figure 6

ใบแทรก

Correction of Part III, figures 7, 8, and 10

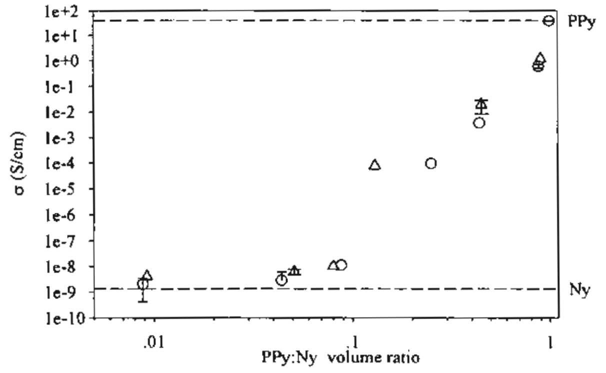


Figure 7

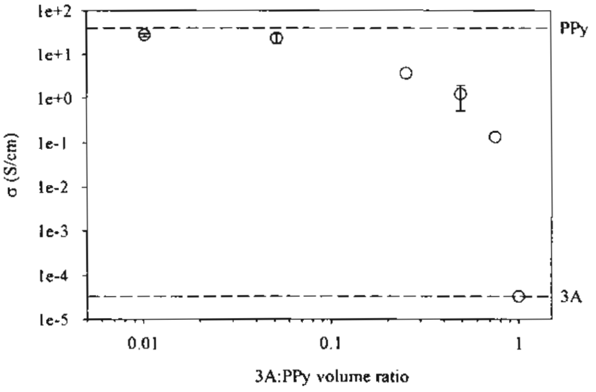
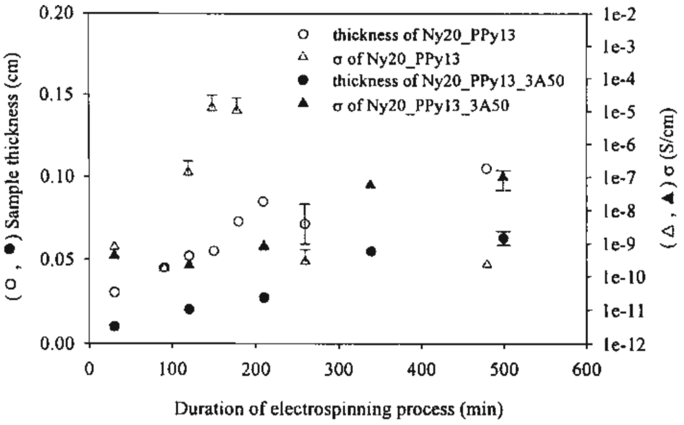


Figure 8



0.20
0.15
0.10
0.05
0.00
(○ , ●) Sample thickness (cm)
0
100
200
300
400
500
600
Duration of electrospinning process (min)
1e-2
1e-3
1e-4
1e-5
1e-6
1e-7
1e-8
1e-9
1e-10
1e-11
1e-12
(△ , ▲) σ (S/cm)
○ thickness of Ny20_PPy13
△ σ of Ny20_PPy13
● thickness of Ny20_PPy13_3A50
▲ σ of Ny20_PPy13_3A50

Figure 10

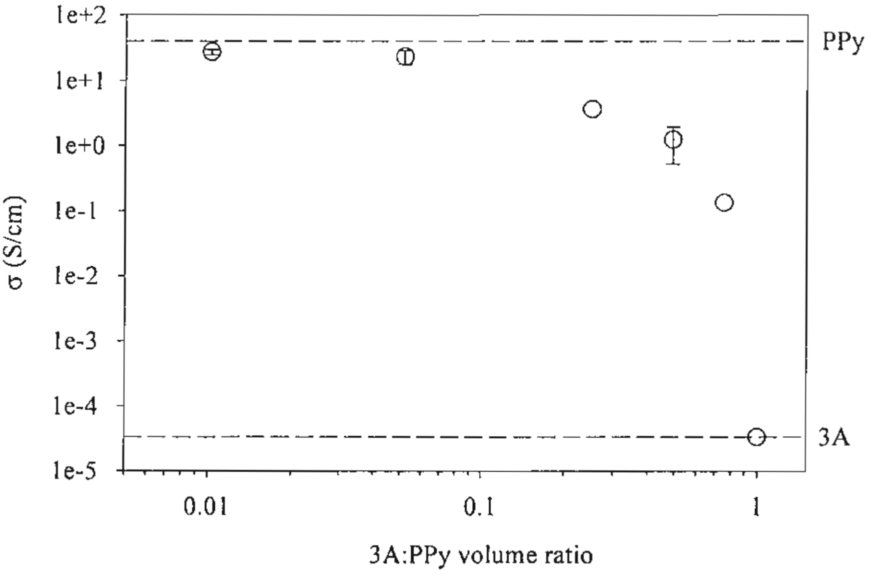

1e+2
1e+1
1e+0
1e-1
1e-2
1e-3
1e-4
1e-5
σ (S/cm)
PPy
3A
0.01
0.1
1
3A:PPy volume ratio

Figure 7

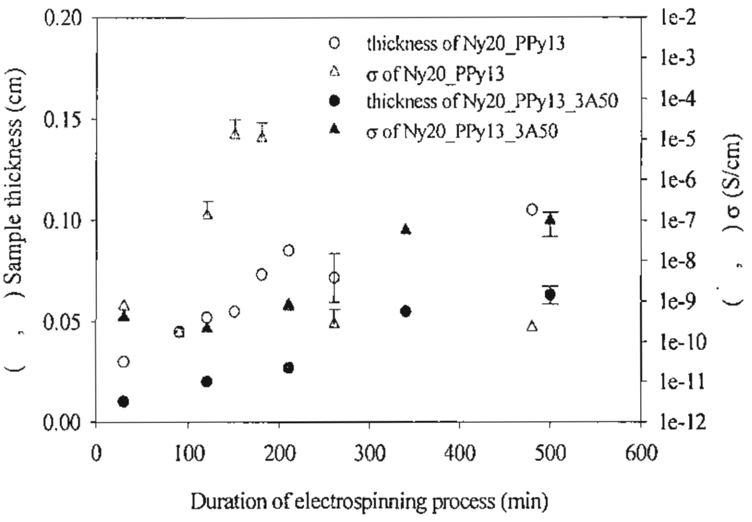

0.20
0.15
0.10
0.05
0.00
(,) Sample thickness (cm)
1e-2
1e-3
1e-4
1e-5
1e-6
1e-7
1e-8
1e-9
1e-10
1e-11
1e-12
(,) σ (S/cm)
0
100
200
300
400
500
600
Duration of electrospinning process (min)
○ thickness of Ny20_PPy13
△ σ of Ny20_PPy13
● thickness of Ny20_PPy13_3A50
▲ σ of Ny20_PPy13_3A50

Figure 8

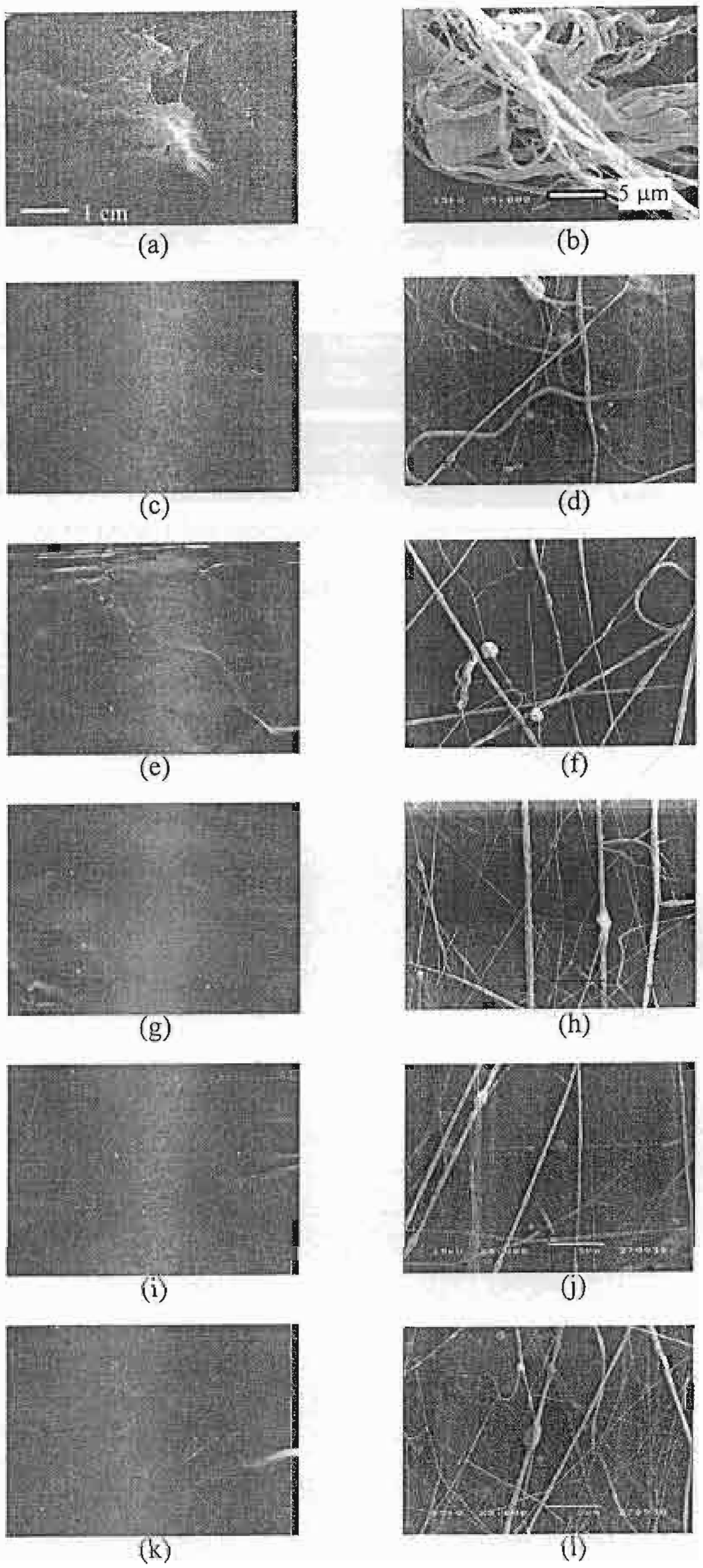


Figure 9

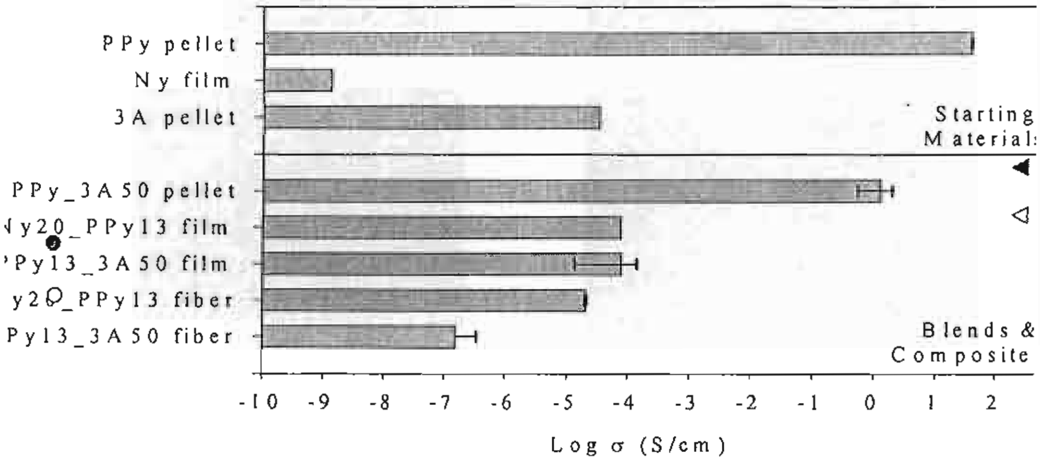

PPy pellet
Ny film
3A pellet
PPy_3A50 pellet
y20_PPy13 film
Py13_3A50 film
y20_PPy13 fiber
Py13_3A50 fiber
Starting
Material
Blends &
Composite
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
1
2
Log σ (S/cm)

Figure 10

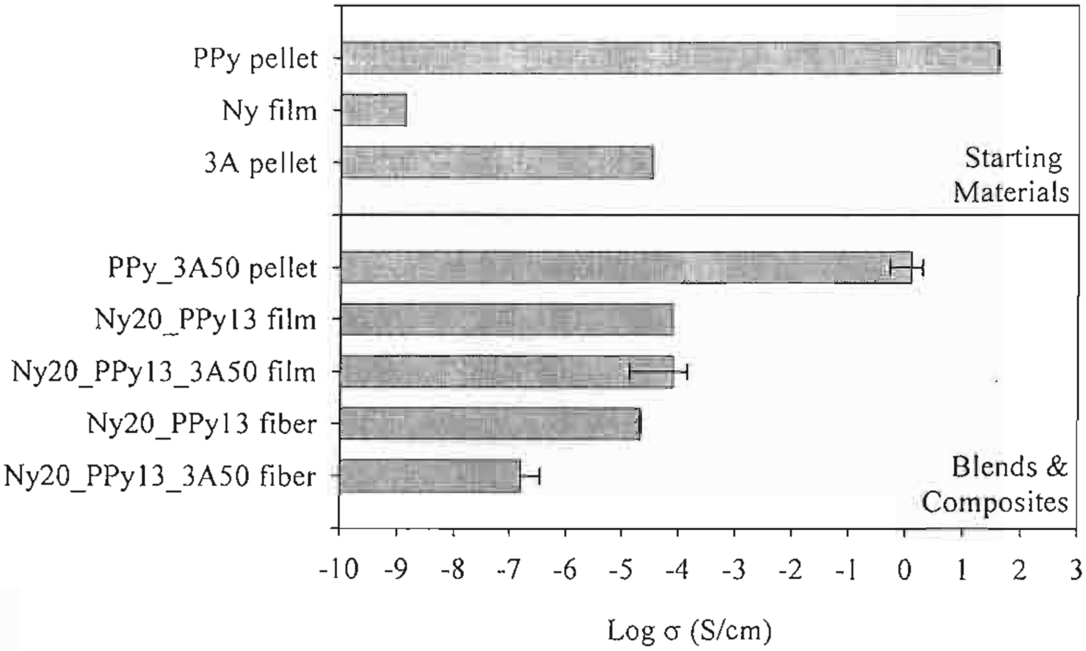

PPy pellet
Ny film
3A pellet
Starting Materials
PPy_3A50 pellet
Ny20_PPy13 film
Ny20_PPy13_3A50 film
Ny20_PPy13 fiber
Ny20_PPy13_3A50 fiber
Blends & Composites
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
1
2
3
Log σ (S/cm)

Figure 11

Polypyrrole and Its Composites as Humidity Sensor: Effects of 3A Zeolite and Fabrication Technique

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Abstract

Chemically synthesized polypyrrole (PPy) in forms of hydraulic-pressed pellet, and its composites with 3A zeolite (3A) and nylon6 (Ny), i.e. PPy_3A50 pellet, Ny20_PPy13 film, Ny20_PPy13 fiber bundle, Ny20_PPy13_3A50 film, and Ny20_PPy13_3A50 fiber bundle have been investigated as the sensing material for water vapor. When compared with the pellet of pure PPy, the electrospun Ny20_PPy13 fibers showed ca. 1000 times higher electrical sensitivity ($\Delta\sigma/\sigma_i$ x 100) toward water vapor. With 3A zeolite added, the response toward water vapor of Ny20_PPy13_3A50 fibers was only ca. 3 times higher than that of pure PPy. These tunable responses initiate the idea of a simple gas sensor consisting of as few sensing materials as possible, where the response toward ambient water could be eliminated.

Keywords: Polypyrrole, Nylon6, 3A zeolite, Composite, Humidity sensor, Electrospinning process

1. Introduction

Conductive polypyrrole (PPy) with different preparation conditions, dopants, and doping levels generally shows different responses toward water vapor. PPy doped with HSO_4^- showed a decrease in specific electrical conductivity as exposed to water vapor, whereas PPy doped with TS^- showed an increase in specific electrical conductivity [1]. In the former case, water reacted with carbenium ions of PPy which reduced charge carrier species in PPy and hence its specific electrical conductivity. For the latter case, water formed the stable complex with TS^- which increased mobility and hence specific electrical conductivity.

In our previous work [2], the specific electrical conductivity of PPy suddenly decreased and then gradually increased when exposed to liquid water. The initial sudden decrement of σ was proposed to be caused by the proton (H^+) subtraction as evidenced by XPS study. The later gradual increment in σ resulted from the hydronium ion (H_3O^+) movement. The mixture of PPy and many zeolites exibited the retarded response toward water liquid and the zeolites obstructed the H_3O^+ movement resulting in the large negative response towards water liquid. For an effective sensing material, the specific surface area is a very important factor for the electrical conductivity sensitivity. Electrospinning process [3] can produce polymeric fibers with diameters in the range of nanometer to micrometer, whereas the specific surface area can reach extremely values.

This work focuses on utilizing chemically synthesized polypyrrole (PPy) in forms of hydraulic-pressed pellet, and its composites with 3A zeolite (3A) and nylon6 (Ny), i.e. PPy_3A50 pellet, Ny20_PPy13_3A50 film, and Ny20_PPy13_3A50 fiber bundle, as the humidity sensing materials. The scope of our work covers the sensor response pattern, the time needed to reach equilibrium specific conductivity, and the sensitivity over a wide range of relative humidity.

2. Experimental

2.1. Materials Preparation

2.1.1. PPy and PPy_3A50 pellets

PPy was chemically synthesized with the mole ratio of pyrrole monomer (AR grade, Fluka): ammonium persulfate (APS: AR grade, Aldrich) as the oxidant: α-naphthalene sulfonate (α-NSA: AR grade, Fluka) as the dopant = 1:1: 0.17. The synthesis details have been described elsewhere [4]. The synthesized *in-situ* doped PPy was dried in a vacuum oven at room temperature, 26 +/- 1 °C, for a period of 2 days: it was aged further at the ambient pressure for 20 days. Dried 3A was mixed with PPy at 3A:PPy volume ratios of 0.5:1.0. The mixture, so called PPy_3A50, was kept in a seal vial tube for another 20 days after which 3A zeolite particles were expected to fully absorb water from PPy [5]. PPy and PPy_3A50 pellets were prepared by a hydraulic press at $8/\pi(0.75)^2$ kN/cm^2. Specific amounts of PPy and PPy_3A50 mixture powders were weighted in as calculated prior to the compression in order to obtain the pellet thickness of 0.06-0.07 cm.

2.1.2. Ny20_PPy13 and Ny20_PPy13_3A films

5 g of nylon6 (Ny: BR HD, MW = 32,000 g/mole) was dissolved in 18.75 g of formic acid (FA: 98% AR grade, BDH) while 0.75 g of PPy was dispersed in 6.25 g of *N*-methyl pyrrolidone (NMP: AR grade, Fluka). Ny solution and PPy suspension were mixed together to obtain the mixture with the Ny:PPy volume ratios of 1000:132 and the FA:NMP volume ratio of 2575:1000. The mixture is called Ny20_PPy13. When 2 g of Ny20_PPy13 mixture was mixed with 0.04 g of dried 3A zeolite (3A: Aldrich), the mixture so called Ny20_PPy13_3A50 was obtained. The reason for selecting these materials and compositions had been described elsewhere [4].

The films of Ny20_PPy13 and Ny20_PPy13_3A50 were cast by means of solution casting from Ny20_PPy13 and Ny20_PPy13_3A50 suspensions, respectively. The film thickness obtained was 0.06 - 0.07 cm by controlling the suspension volume used. 0.8 ml of the suspension was smeared on 22 x 22 mm^2 glass slide covers. The film was air-dried at room temperature.

2.1.3. Ny20_PPy13 and Ny20_PPy13_3A fiber bundles

The conditions for the electrospinning process for Ny20_PPy13 and Ny20_PPy13_3A mixtures were: the applied voltage of 15 kV, the distance between spinneret and grounded collector of 5 cm, the rotating drum speed of 500 rpm, and the duration of the electrospinning process, which controlled the bundle diameter, of 180 min for Ny20_PPy13, and of 340 min for Ny20_PPy13_3A.

2.2. Materials Characterization

The specific conductivity (σ) values of samples were measured by an electrometer (Keithley, 6517A) with a custom-made two-point probe made of TPFE and Au wires for pellets and films, as shown in Figure 1a, and for fiber spun, as shown in Figure 1b. The specific electrical conductivity of the samples was previously discussed [4]. The samples were chemically and morphologically characterized as reported earlier [4]. Contact angle measurement has been carried out by KRÜSS model DSA10-Mk2 under ASTMD5725M. At 25°C, 1 microliter of water was dropped from the tip of polypropylene tube onto the middle of sample surfaces, which were PPy pellet and Ny20_PPy13_3A fiber mat on top of an adhesive 25 x 25 mm^2 square frame. The contact angle was calculated and recorded by Drop Shape Analysis program (DSA: version 1.08.0.2) as a function of time to study the absorption behaviors.

2.3. Water vapor detection

The samples, which were held by the probes, were placed in the exposing chamber as shown in Figure 1c. There were 4 samples tested in a particular experiment. The specific electrical conductivity of highly conducting samples would be measured by the custom-made conductivity meter using a DC power supply (Textronix, PS280). The current traveling through the samples were recorded by a data acquisition system (Data Translation, DT2801) interfaced with a personal computer. For the sample with low specific conductivity, an electrometer/high resistance meter (Keithley, 6517A) interfaced with another personal computer was utilized. In both cases, the applied voltage was set at a level so that the current measured obeyed the Ohmic behavior without the Joule heating effect.

A mass flow controller (AALBORG, 0-5 L/min), M in Figure 1c was adjusted to obtain the total flow rate of the system to be 2.0 L/min. Under the 99.99 % N_2 background with 3 +/- 1 %RH, as monitored by a humidity transmitter (Vaisala, type HMD40U) located at the conditioning chamber, the steady state specific electrical conductivity of the samples should be observed for at least 20 minutes prior to the exposure experiment. Valves 2 (V2) and 3 (V3) were adjusted until the relative humidity (RH) in the conditioning chamber reached the desired RH, while the solenoid valve (SV1) was switched to drain the flow out. Once SV1 was switched, the water vapor flowed through the exposure chamber, and the change in specific electrical conductivity was monitored and recorded until it reached a steady state value. The N_2 background with 3 +/- 1 %RH was then switched back through the exposing chamber. After the specific electrical conductivity of the sample recovered its initial value, N_2 with water vapor at the next desired relative humidity was then allowed to flow into the system. The experiments were carried out in the random order: there were no continuous decrement or increment in relative humidity, in order to avoid adding the drift response (if any) to the sole response by mistake.

The investigated parameters are: the response pattern, the time needed for reaching equilibrium specific conductivity (t_{eqb}) at particular relative humidity, and the sensitivity ($\Delta\sigma / \sigma_i \times 100$: σ_i = specific conductivity in N_2 with relative humidity of 3 +/- 1 %RH) over the wide range of relative humidity.

3. Results and Discussion

3.1. Material Characterization

The water adsorption characteristics of PPy pellet and Ny20_PPy13_3A50 fiber mat are shown in Figures 2a and 2b, respectively. PPy pellet had the initial contact angle of ca. 70 degrees. Due to adsorption by the sample, the drop volume and height decreased and the contact angle decreased to ca. 60 degree in 2 minutes. The adsorption was much faster in the case of Ny20_PPy13_3A50 fiber mat where the contact angle decreased from ca. 40 degree to be 10 degree in 2 minutes. The results can be related to sample surface morphologies, as studied by Wannatong *et al.* [4], and shown here in Figure 2. The high porous Ny20_PPy13_3A50 fiber mat adsorbs water at a faster rate.

3.2. Water vapor detection

3.2.1. The sensor response pattern

Figure 3 shows the changes in specific electrical conductivity of samples as the relative humidity was changed from 3 +/- 1 %RH to 60-70 %RH. Note that: 1) the experiments of all samples were not taken at the same time: the experiment of Ny20_PPy13 film and fiber bundle had longer exposure times than others; and 2) the responses of Ny20_PPy13 fiber bundle and of Ny20_PPy13_3A50 fiber bundle were obtained from the electrometer (Keithley 6517A) which had low noise. The response patterns of PPy pellet and Ny20_PPy13_3A50 fiber bundle are shown in the magnified scale as the inset of Figure 3. All sensing materials showed the positive response toward water vapor. The responses were reversible.

Upon exposure to liquid water, Wannatong *et al.* [2,4] found the sudden decrease in specific electrical conductivity of PPy pellet followed by the gradual increase in specific conductivity. This is due to the H^+ subtraction and the H_3O^+ movement, respectively. In the case of water vapor, there are fundamental differences. Water vapor molecules penetrated into the pellet at a lesser extent than that of liquid water. At the sensor surface, lesser H^+ was subtracted, and hence only the H_3O^+ movement became dominant. This led to the different response patterns of our materials towards water vapor at 60-70 %RH where only increments in specific electrical conductivity were found.

3.2.2. The time sensor needed to reach equilibrium specific conductivity (t_{eqb}) at 60 – 70 %RH

The order of materials with the longest to the shortest t_{eqb} is: Ny20_PPy13 film (at 63.3 %RH) > Ny20_PPy13 fiber bundle (at 63.3 %RH) = Ny20_PPy13_3A50 film (at 66.4 %RH) > PPy pellet (at 60.0 %RH) > PPy_3A50 pellet (at 60.0 %RH) > Ny20_PPy13_3A50 fiber bundle (at 66.4 %RH).

Even thought the relative humidity values of each experiment were not exactly the same since the needle valves (V2 and V3 in Figure 1c) were adjusted manually, there is no trend found from the effect of the differences in the relative humidity of the above materials. Adding 3A into PPy pellet induced a higher porous surface. This explains the faster absorption of water vapor of PPy_3A50 pellet, as compared to PPy pellet. In the case of the cast film, Ny film was coated with 3A particles and the role of 3A was different from the case of pellet. Adding 3A into Ny20_PPy13 blend changed surface morphology of Ny20_PPy13_3A50 film dramatically [4]. It became a fiber-like structure with higher specific surface area and shorter t_{eqb}. In the case of fiber bundles, both Ny20_PPy13 and Ny20_PPy13_3A50 fibers had fast responses. With the same components, materials in forms of fiber bundle show faster t_{eqb} than those in forms of film.

3.2.3. The sensor sensitivity over the wide range of relative humidity

From Figure 3, the order of materials with the lowest to the highest sensitivity, as the relative humidity changed from 3 +/- 1 %RH to 60-70 %RH, is: PPy pellet (at 60.0 %RH) < Ny20_PPy13_3A50 fiber bundle (at 66.4 %RH) < PPy_3A50 pellet (at 60.0 %RH) ~ Ny20_PPy13 film (at 63.3 %RH) < Ny20_PPy13_3A50 film (at 66.4 %RH) << Ny20_PPy13 fiber bundle (at 63.3 %RH). Figures 4a and 4b show sensitivities of all materials over the wide range of relative humidity. The results are described and discussed for each 3 pairs of materials as followed:

A. *PPy pellet and PPy_3A pellet*

As seen in Figure 4a, the response of PPy was significantly altered by adding 3A by the dry mixing process. PPy pellet shows ~ 4% sensitivity at 20 %RH while PPy_3A50 pellet seems to be insensitive to water vapor in the range of 0-20 %RH. PPy pellet continued its exponential response toward water vapor while PPy_3A50 pellet started its exponential response at 20 %RH, with a higher slope. The response of PPy_3A pellet dramatically decreased at relative humidity higher than 60 %RH.

3A adsorbed water molecules attacking the sensor, but it had the limit at very low relative humidity. This led to smaller response of PPy_3A50 as compared to PPy at relative humidity lower than 20 %RH. At 60 %RH, $\Delta\sigma$ values were approximately the same for PPy and PPy_3A50 (avg. 4.2 and 3.6 S/cm, respectively), whereas σ_i of PPy_3A50 was ~ 30 times lower. So the sensitivity of PPy_3A50 which is $\Delta\sigma/\sigma_i$ x 100 was larger by 30 times. This might be called the dilution effect. However, when relative humidity was sufficiently high, the effect was closer to what found in the case of liquid water [5]: 3A prohibited the H_3O^+ movement at PPy_3A50 surface and decreased the response toward water vapor at relative humidity higher than 60 %RH.

B. *Ny20_PPy13 film and Ny20_PPy13_3A50 film*

Figure 4b shows that at relative humidity lower than ~ 30 %RH, Ny20_PPy13_3A50 film had higher sensitivity toward water vapor: its initial slope was higher than Ny20_PPy13 film. After ~ 30 %RH, the slope decreased and the sensitivity became very close to those of Ny20_PPy13 film at relative humidity higher than ~ 55 %RH. Ny20_PPy13 film also had a lower slope beyond this relative humidity.

The SEM micrographs of Wannatong *et al.* [4] showed that surface of Ny20_PPy13_3A50 film was fiber-like which might be caused by the faster drying when 3A particles were added. The larger surface area corresponds to its higher sensitivity at low relative humidity. At higher relative humidity, the prohibition of the H_3O^+ movement by 3A became significant, as discussed above and the response decreased. This sensitivity decrement was compromised by the sensitivity increment induced by high porosity nature of Ny20_PPy13_3A50 film. This explains the sensitivity of Ny20_PPy13_3A50 film at high relative humidity which is close to that of Ny20_PPy13 film without 3A.

C. *Ny20_PPy13 fiber bundle and Ny20_PPy13_3A50 fiber bundle*

Ny20_PPy13 fiber bundle shows the highest slope among the materials in our work. The linear range (in the log scale) started at ~ 30 %RH. Ny20_PPy13_3A50 fiber bundle has the lowest sensitivity among the materials in this work. The linear range (in the log-linear plot) starts at ~ 55 %RH.

Sensing materials in forms of electrospun fibers in this work seem to have a critical concentration of water vapor at which their sensitivity sharply increases. The distance between conducting PPy particles in the composite, in form of fibers is longer than in the forms of film and pellet. A certain water vapor concentration is necessary to induce the ionic conductivity of these fibers. The presence of 3A particles in Ny20_PPy13_3A50 fibers obstruct electronic and/or ionic paths, the required concentration is higher.

D. *Ny20_PPy13 and Ny20_PPy13_3A50 in forms of films and fiber bundles*

As compare Ny20_PPy13 and Ny20_PPy13_3A50 in forms of film and fiber bundle, the form of film had lower saturation water vapor concentration.

This implies a larger specific surface area of electrospun fiber bundle as discussed in form of fiber mat by other research groups [6,7].

To summarize from the above results and discussion, 3A played four possible direct effects to the response of PPy-based sensors toward water vapor. Firstly, 3A scavenged water molecules. This case was found in PPy_3A50 pellet at very low relative humidity where the sensitivity toward water vapor was low. Secondly, 3A obstructed the H_3O^+ movement. This case was found in PPy_3A50 pellet at high relative humidity where the sensitivity toward water vapor was dropped. These first two cases were not found in Ny20_PPy13_3A50 film and fibers where 3A particles were hardly seen from SEM and some were covered by Ny matrix. Thirdly, 3A increased sensor porosity. This case was found in PPy_3A50 pellet where the time needed for reaching equilibrium was shortened. Lastly, 3A obstructed the electronic and/or ionic paths. This case was found in Ny20_PPy13_3A50 fibers where the deflecting point of sensitivity was as high as 55 %RH.

Moreover, there is one possible indirect effect. 3A altered sensor morphology by subtracting water from solvent, thereby changing the rate of material drying. With 3A, Ny20_PPy13_3A50 film dried faster and had a higher porosity whereas the electrospun jet of Ny20_PPy13_3A50 suspension dried faster during travelling to and depositing onto the grounded Al foil. The obtained Ny20_PPy13_3A50 fibers were bigger and their bundles had less density as described previously [4]. Higher porosity of the film led to higher sensitivity and faster response time. Lesser density of fiber spun led to faster response time whereas the sensitivity was limited from the fourth possible direct effect of 3A as described above.

However, the dilution effect which does not affect response ($\Delta\sigma$) but affects sensitivity ($\Delta\sigma / \sigma_i$ x 100) should be also taken into account.

4. Conclusion

3A had both direct and indirect effect to the response of PPy-based sensing materials in this work. In the form of electrospun fibers, the conductive PPy phase was not continuous, sufficiently high relative humidity was needed to exhibit ionic conductivity. With 3A, the electrospun fibers needed higher required water vapor concentration since 3A prohibited the H_3O^+ movement. More experimentally explanation for this is undergoing our group interest.

5. Acknowledgements

This work had been fully supported by the Thailand Research Fund (TRF), grant no. MRG 4780087, and the Conductive and Electroactive Polymer Research Unit (Rachanapiseksompoch Fund, Chulalongkorn University. LW would like to thank the technical staff of The Petroleum and Petrochemical College, Chulalongkorn University for the technical support and students in the research group of A. Sirivat for their help.

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Figure captures

Figure 1. The probes for a) pellets and film and b) fiber bundle, c) the flow system to study the electrical response toward humidity.

Figure 2. Water contact angles and absorption behaviors of: a) PPy pellet; and b) Ny20_PPy13_3A50 fiber mat. The inserts show the drops of deionized water on the samples. The SEM micrographs from Wannatong *et. al.* [4] show the difference in surface morphology.

Figures 3. The response patterns of (····· ···) PPy pellet at 60.0 %RH, (— —) PPy_3A50 pellet at 60.0 %RH, (— — —) Ny20_PPy13 film at 63.3 %RH, (—··—···) Ny20_PPy13 fiber bundle at 63.3 %RH, (- - - -) Ny20_PPy13_3A50 film at 66.4 %RH, and (———) Ny20_PPy13_3A50 fiber bundle at 66.4 %RH. The inset shows the response of (····· ····) PPy pellet and (———) Ny20_PPy13_3A50 fiber bundle in the magnified scale.

Figure 4. The electrical sensitivity (Δσ/σi x 100%) toward relative humidity of: a) PPy and PPy_3A50 pellets; and b) Ny20_PPy13 film and fiber bundle, and Ny20_PPy13_3A50 film and fiber bundle. Note that the sensitivities at 3 +/- 1 %RH were 0 % by definition but they were indicated as 1 % in order to fit the log-scaled plots.

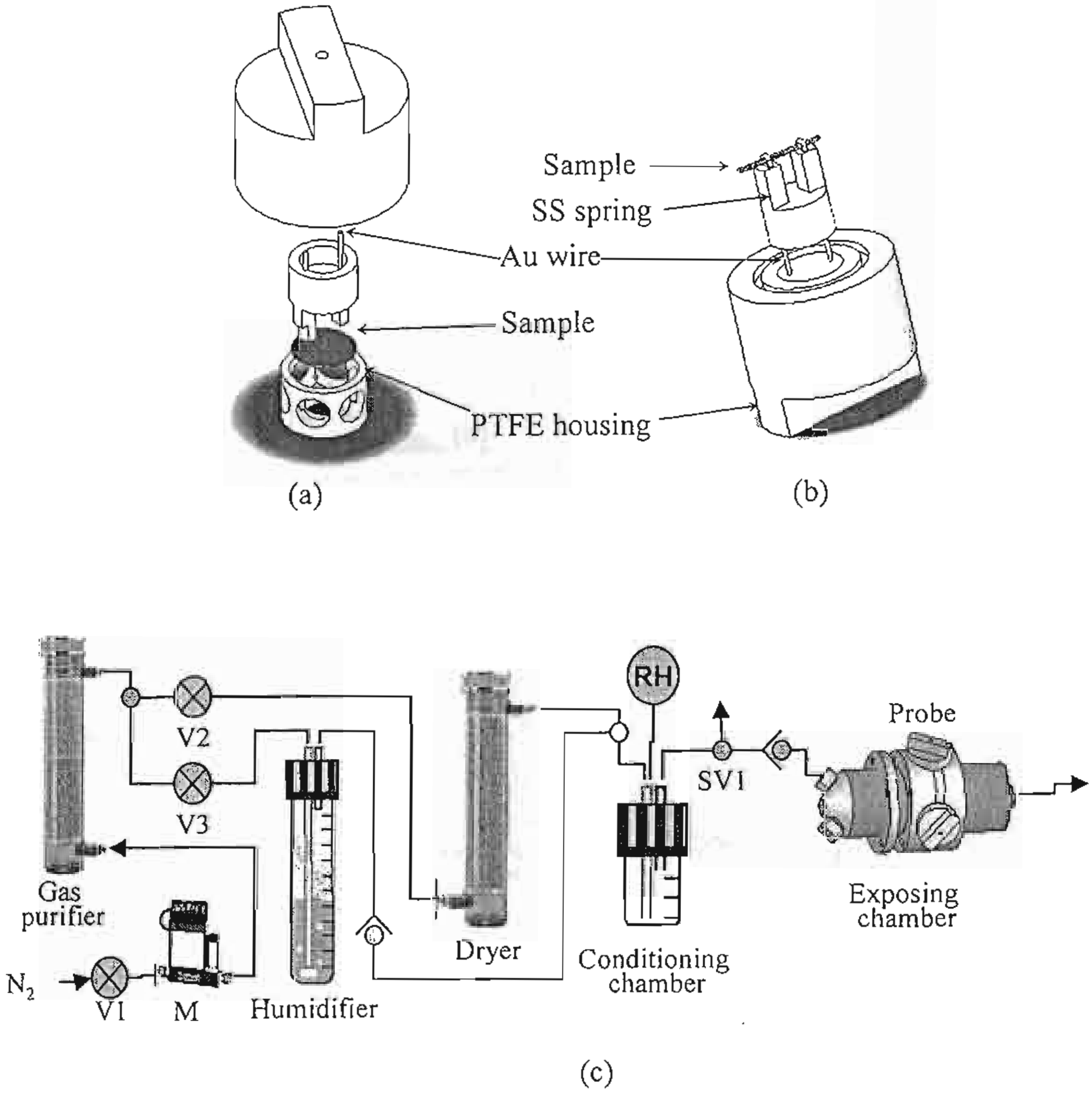

Sample
SS spring
Au wire
Sample
PTFE housing
(a)
(b)
RH
Probe
V2
V3
SV1
Gas purifier
Dryer
Conditioning chamber
Exposing chamber
N_2
V1
M
Humidifier
(c)

Figure 1

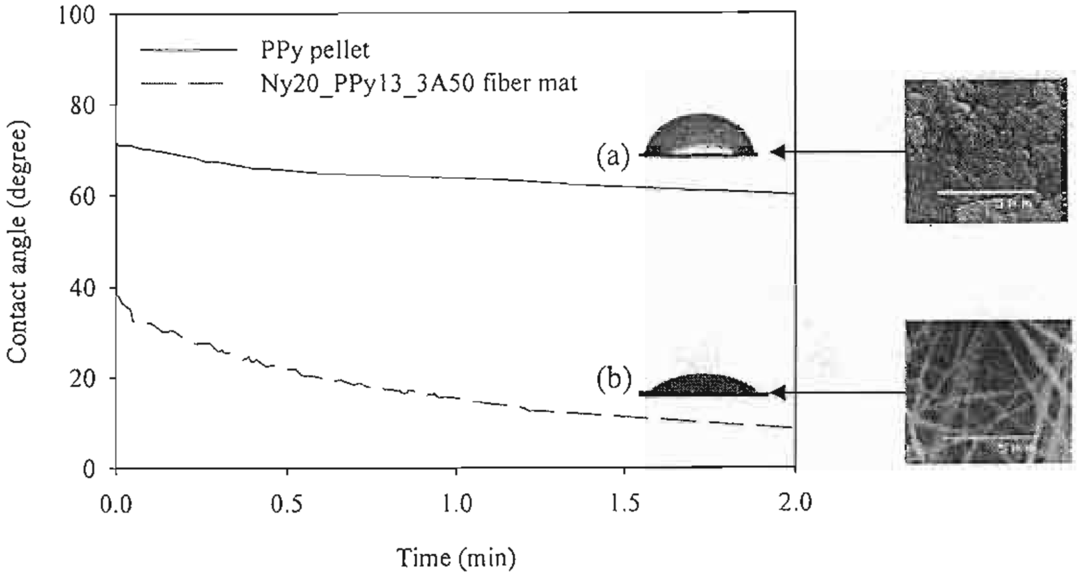
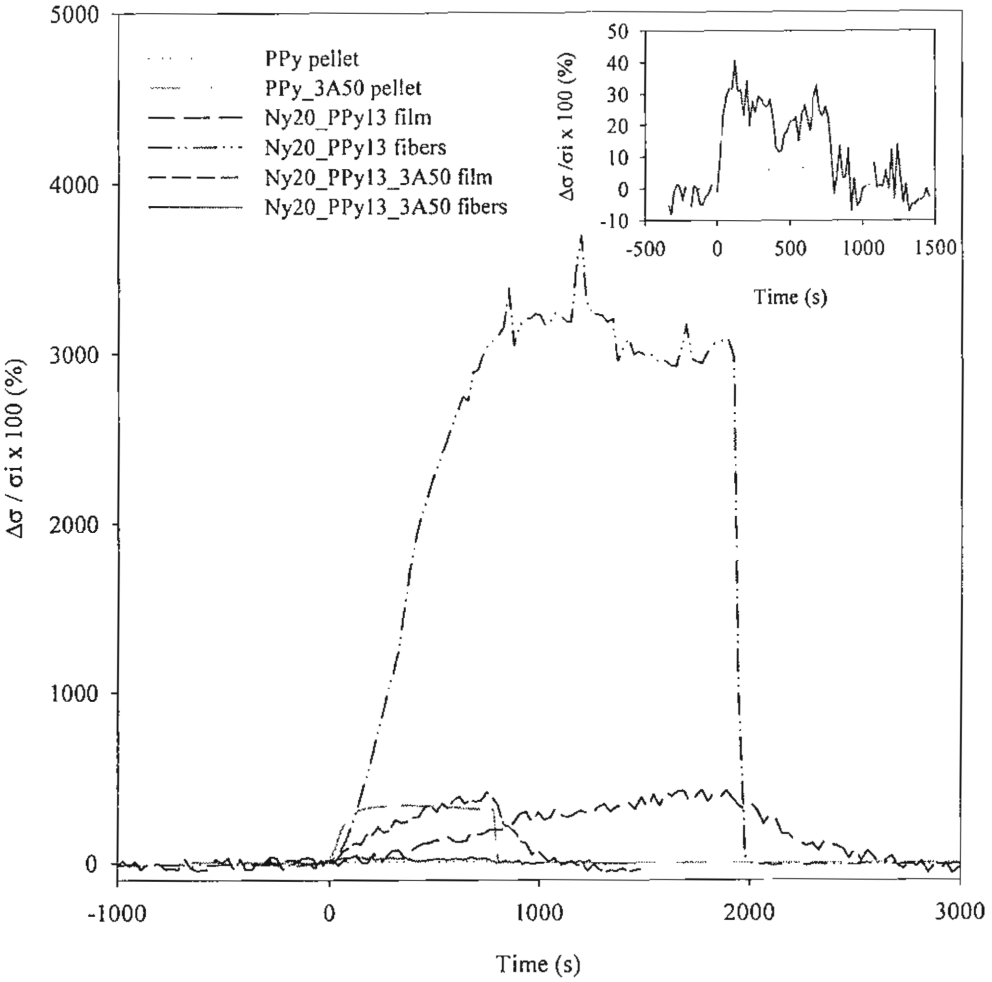
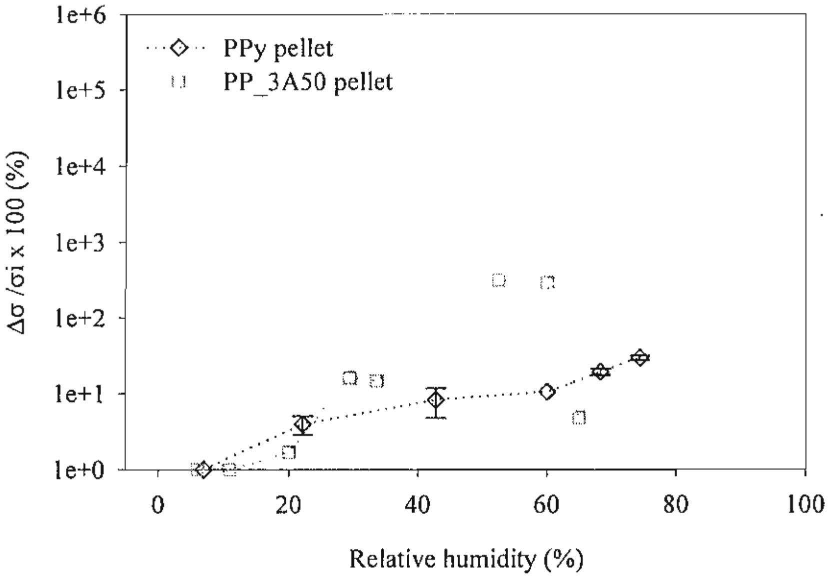

100
80
60
40
20
0
Contact angle (degree)
PPy pellet
Ny20_PPy13_3A50 fiber mat
(a)
(b)
0.0
0.5
1.0
1.5
2.0
Time (min)

Figure 2

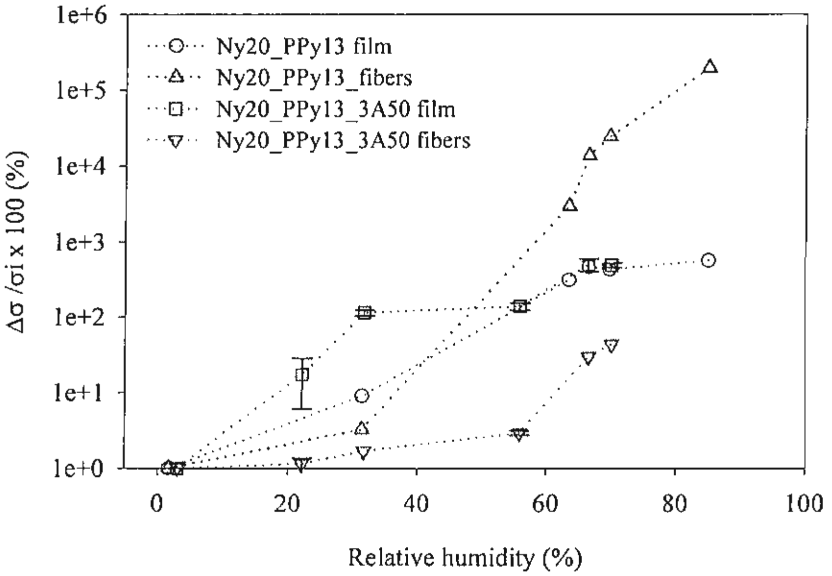


PPy pellet
PPy_3A50 pellet
Ny20_PPy13 film
Ny20_PPy13 fibers
Ny20_PPy13_3A50 film
Ny20_PPy13_3A50 fibers
Δσ / σi x 100 (%)
5000
4000
3000
2000
1000
0
-1000
0
1000
2000
3000
Time (s)
Δσ /σi x 100 (%)
50
40
30
20
10
0
-10
-500
0
500
1000
1500
Time (s)

Figures 3


PPy pellet
PP_3A50 pellet
Δσ /σi x 100 (%)
1e+6
1e+5
1e+4
1e+3
1e+2
1e+1
1e+0
0
20
40
60
80
100
Relative humidity (%)

(a)


Ny20_PPy13 film
Ny20_PPy13_fibers
Ny20_PPy13_3A50 film
Ny20_PPy13_3A50 fibers
Δσ /σi x 100 (%)
1e+6
1e+5
1e+4
1e+3
1e+2
1e+1
1e+0
0
20
40
60
80
100
Relative humidity (%)

(b)

Figure 4

Polypyrrole and Its Composites as Sensor for Chemicals in Lacquer

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Abstract

Pressed pellet of chemically synthesized polypyrrole (PPy) and PPy composite with 3A zeolite (3A) and nylon6 (Ny): i.e. PPy_3A50 pellet, Ny20_PPy13_3A50 film, and Ny20_PPy13_3A50 fiber bundle have been investigated as the sensing material for four chemical vapors that are the common components of lacquer: acetone, methyl ethyl ketone (MEK), methanol, and toluene. Ny20_PPy13_3A50 film and PPy_3A50 pellet had sensitivity ($\Delta\sigma/\sigma_i$ x 100) toward methanol as high as 2422 % (SD = 333 %) and 107 % (SD = 6 %), respectively at 5.6 vol% vapor. At the same vapor concentration, methanol decreased the specific conductivity of PPy pellet by 7.8 % (SD = 0.3 %) and of Ny20_PPy13_3A50 fiber bundle by 0 %. Each sensing material had different characteristics toward different chemicals. This work is an attempt to search for the suitable sensing elements for the vapors in lacquer.

Keywords: Polypyrrole, Nylon6, 3A zeolite, Composite, Chemical sensor, Lacquer, Electrospinning process

1. Introduction

Conductive polypyrrole (PPy) is one of the most promising conductive polymers for many applications due to its ease of synthesis, high conductivity, and high environmental stability [1,2]. Its electrical conductivity is highly tunable by changing synthesis conditions [3], oxidation state [4], counter ions or dopants [5-6], solvents involved in material fabrications [7], chemical treatments [8,9], and heat treatments [9]. As sensor for chemical vapor and liquid, PPy has been blended with insulating polymers [10], and many additives such as zeolites and silica gel [11], in order to improve selectivity. PPy fiber specific surface area can be extremely enhanced when it is electrospun into ultra-fine fibers by the electrospinning process [12]. Recently, there have been a few reports using electrospun fibers of PPy blends as sensing materials for chemicals [13,14].

This work focuses on utilizing PPy and its the composites with 3A zeolite and nylon6 in the forms of hydraulic-pressed pellet, solution-cast film, and electrospun fiber bundle, as chemical sensing materials. The target chemical vapors are the chemical components in lacquer thinner, the major source of fire accident during interior decoration. Even thought there are many types and manufacturers of lacquer thinners, their chemical components can be summarized. They mainly consist of 10 – 50 % ketone (mostly acetone or methyl ethyl ketone (MEK)), 0 – 20 % methanol, 0.5 – 50 % toluene, and 10 – 20 % other distillates [15]. So, the target chemical vapors in this work are acetone, MEK, methanol, and toluene.

The main focus in this work is the electrical conductivity sensitivity of four sensing materials toward four chemical vapors of various concentration at 26 +/- 1 °C, 3 +/- 1 %RH, with N_2 as a carrier gas at 2.0 L/min. The sensitivity is defined as the percent change in specific electrical conductivity relative to the baseline or unexposed value: $(\sigma - \sigma_i) / \sigma_i \times 100\%$. Note that for a serial experiment, σ_i is the electrical conductivity in N_2 with 3 +/- 1 %RH before a particular exposure starts.

2. Experimental

2.1. Materials Preparation

2.1.1. PPy and PPy_3A50 pellets

PPy was chemically synthesized with the mole ratio of pyrrole monomer (AR grade, Fluka): ammonium persulfate (APS: AR grade, Aldrich) as the oxidant: α-naphthalene sulfonate (α-NSA: AR grade, Fluka) as the dopant = 1:1: 0.17. The synthesis details have been described elsewhere [16]. The synthesized *in-situ* doped PPy was dried in a vacuum oven at room temperature, 26 +/- 1 °C, for a period of 2 days: it was aged further at the ambient pressure for 20 days. Dried 3A was mixed with PPy at 3A:PPy volume ratios of 0.5:1.0. The mixture, so called PPy_3A50, was kept in a seal vial tube for another 20 days after which 3A zeolite particles were expected to fully absorb water from PPy [11]. PPy and PPy_3A50 pellets were prepared by a hydraulic press at $8/\pi(0.75)^2$ kN/cm^2. Specific amounts of PPy and PPy_3A50 mixture powders were weighted as calculated prior to the compression in order to obtain the pellet thickness of 0.06 - 0.07 cm.

2.1.2. Ny20_PPy13_3A films

5 g of nylon6 (Ny: MW = 32,000 Da) was dissolved in 18.75 g of formic acid (FA: 98% AR grade, BDH) while 0.75 g of PPy was dispersed in 6.25 g of *N*-methyl pyrrolidone (NMP: AR grade, Fluka). The Ny solution was mixed with the PPy suspension. Then, 2 g of the mixture was mixed with 0.04 g of dried 3A zeolite (3A: Aldrich). The final mixture then contained the components at the Ny:PPy:3A volume ratio of 1000:132:66 and the FA:NMP volume ratio of 2575:1000, so called Ny20_PPy13_3A50. The reason for selecting these materials and compositions had been described elsewhere [16].

The films of Ny20_PPy13_3A50 were cast by means of solution casting from Ny20_PPy13_3A50 suspensions. They were air-dried at room temperature. The required film thickness was 0.06 - 0.07 cm.

2.1.3. Ny20_PPy13_3A fiber bundles

The conditions for the electrospinning process for Ny20_PPy13_3A mixtures were: the applied voltage of 15 kV, the distance between spinneret and grounded collector of 5 cm, the rotating drum speed of 500 rpm, and the duration of the electrospinning process of 340 min. The required thickness was 0.06 - 0.07 cm.

2.2. Materials characterization

The specific conductivity (σ) values of samples were measured by an electrometer (Keithley, 6517A) with custom-made two-point probes made of TPFE and Au wires for pellets and films [17]. The electrical, chemical, and morphological properties of all sensing materials have been previously discussed [16]. Some fruitful information will be mentioned again.

2.3. Chemical vapor detection

The chemicals used in this work were acetone (AR grade, Lab-Scan), methanol (AR grade, Lab-scan), methyl ethyl ketone (MEK: AR grade, Lab-scan), and toluene (AR grade, Lab-scan).

Samples, which were held by the probes, were placed in the PTFE exposing chamber as shown in Figure 1. The solenoid valves, tube connectors, and the tubes which were in contact with chemical vapors were PTFE, polypropylene, and PTEF, respectively, to minimized vapor absorption by the flow system. There could be four or five samples tested in a particular experiment. The specific conductivity of highly conducting samples would be measured by the custom-made conductivity meter with a DC power supply (Textronic PS280). The current traveling through the samples were recorded by a data acquisition system (Data Translation board model DT2801) interfaced with a personal computer. For the sample with low specific conductivity, an electrometer/high resistance meter (Keithley, 6517A) interfaced with another personal computer was utilized. In both cases, the applied voltage was 8.5 V.

The sum of the mass flow rates of N_2 through the exposure chamber (F1 + F2), as measured by two mass flow controllers (AALBORG, 0-5 L/min or 0-200 mL/min), M1 and M2 in Figure 1, was 2.0 L/min. The vapor concentration depends on the ratio of F2 / (F1 + F2), the slope of calibration curve (A) in Figure 2, and solvent molar mass (MW) as followed:

$$\text{Vapor concentration (vol\%)} = \frac{F2\,(A/MW)}{F1+F2}\; MV_{STP}\,(T/273) \times 100 \;\ldots\ldots\ldots\ldots(1)$$

where

F1 and F2 = flow rates of M1 and M2, respectively (L/min)
A = slope of calibration curve (g of chemical loss/min/(L/min))
MW = chemical molar mass (g/mole)
MV_{STP} = molar volume of vapor at STP (22.4 L/mol)
T = experimental temperature (K).

Valves 2 (V2) and 3 (V3) were adjusted until the relative humidity (RH) of 99.99 % N_2 background in the conditioning chamber reaches 3 +/- 1 %RH, as monitored by a humidity transmitter (Vaisala, type HMD40U) located at the background conditioning chamber. When the background condition was reached, solenoid valve 1 (SV1) splited the flow into two flow routes: SV1-M1-exposure chamber-drain and SV1-V4-SV2-SV3-M2-SV4-drain. There was no flow in the route SV1-SV3-M2 because the obstruction of SV3 at that time. V4 was manually set to allow the flow with the mass flow rate of F2, with the assistance of M2. The flow from SV1 then splited into 3 flow routes: SV1-M1-exposing chamber-drain; SV1-V4-SV2-SV5-exposing chamber-drain; and SV1-SV3-M2-SV4-chemical container-SV6-drain. The total mass flow rate through the exposing chamber was F1 + F2 without chemical vapor. M2 was set to F2 and the mass flow rate of N_2 through the chemical container was F2.

When the flows through exposing chamber and chemical container were stable and the steady state specific electrical conductivity of the samples had been observed for at least 20 minutes, the exposure experiment was then started. Three routes of flow were changed to: SV1-M1-exposing chamber-drain; SV1-V4-SV2-SV5-drain; and SV1-SV3-M2-SV4-chemical container-SV6-exposing chamber-drain. The total mass flow through the exposing chamber remained F1 + F2 with chemical vapor of desired concentration. The change of specific conductivity was monitored and recorded until all samples were saturated. SV5 and SV6 would then be switched back to allow the flow of N_2 with no chemical vapor to purge the samples in the exposing chamber. After the specific conductivity of all samples reached the initial values or other stable values, N_2 with the next desired chemical vapor concentration was further switched into the system. The exposures were carried out in the random order: there was no continuous decrement or increment in vapor concentration, in order to prevent adding the drift response (if any) to the total response toward vapor concentration by mistake.

The investigated parameters are the type of response (positive or negative, linear or non-linear) over the whole range of vapor concentrations, and the sensitivity at ca. 3 vol% of each vapor.

3. Results and Discussion

As reported in Wannatong et al. [16], the specific conductivity values of PPy pellet, PPy_3A50 pellet, Ny20_PPy13_3A50 film, and Ny20_PPy13_3A50 fiber bundle were 4.0E+01 (SD = 7.1E-01), 1.2E+00 (SD = 7.1E-01), 7.7E-05 (SD = 6.4E-05), and 1.4E-07 (SD =1.6E-07) respectively.

The sensitivity of four materials toward four chemicals is discussed as followed. Since the investigation of the sensor-chemical interaction is not in the scope of this work, we report only the experimental results with some notices.

3.1. Type of responses toward four chemical vapors in N_2

Acetone vapor

As shown in Figure 3a, PPy pellet and Ny20_PPy13_3A50 fiber bundle show the negative response in conductivity when exposed to acetone vapor whereas PPy_3A pellets and Ny20_PPy13_3A50 film show the positive response.

Ny20_PPy13_3A50 film shows the highest sensitivity toward acetone vapor among the sensing materials used in this work. All of them had the linear responses in the studied concentration range: 0-17 vol%, with some deviations.

MEK vapor

In Figure 3b, Ny20_PPy13_3A50 film has the positive response with the highest sensitivity among all materials. Its response was linear. PPy_3A50 pellet shows small negative response at 3 vol% and small positive response at 5.4 vol% MEK vapor. PPy pellet and Ny20_PPy13_3A50 fiber bundle are insensitive to MEK vapor.

Methanol vapor

Figure 3c shows that PPy pellet was the only sensing material in the work that has the negative response toward methanol vapor. Ny20_PPy13_3A50 film and PPy_3A50 pellet have the positive ones. The former has the highest sensitivity: it is ca. 25 times higher than that of the latter. Ny20_PPy13_3A50 fiber bundle has no response for methanol vapor.

Toluene vapor

As evidenced in Figure 3d, all sensing materials in this work are insensitive to toluene vapor at 0 – 3 vol%. The highest sensitivity belongs to Pyy_3A50 pellet; it is only ca. 1.8 % (SD = 0.4 %) at 3 vol% toluene vapor.

3.2. Electrical sensitivity at 3 vol% of chemical vapors in N_2

Figure 4 shows sensitivity of four sensing materials towards vapor of acetone, MEK, methanol, and toluene, at 3 vol% in N_2. There are both positive and negative responses. The largest response is that of Ny20_PPy13_3A film towards methanol vapor. The second largest is that of PPy_3A50 pellet towards methanol vapor. Ny20_PPy13_3A50 fiber bundle is insensitive to all of chemicals used in this work.

The possible reasons of the positive response (increase in specific conductivity) are the oxidation by the target gas [18], or the formation of stable complex with dopant by the target gas [5], or ionic conductivity [5]. On the other hand, the negative response (decrease in specific conductivity) could possibly be caused by the swelling effect [19], or the reduction [19], or the surface absorption by target gas. Adding insulating polymers into PPy alters the swelling effect and tailors the sensitivity [10] but normally induces the negative response. Among four chemicals in this work, methanol is the best solvent for Ny. Their solubility parameters are 14.5 and 13.5 $(\mathrm{MPa})^{1/2}$, respectively [20]. The film of Ny20_PPy13_3A shows the largest response towards methanol vapor, but it is the positive response. The presence of 3A in the film might be the key but it needs more experimental explanation. For the insensitive Ny20_PPy13_3A50 fiber, the conducting PPy particles are too far from each another; this leads to not only poor specific conductivity of material, but also low sensitivity toward swelling effect. It would not response to methanol that can swell Ny but only to the chemicals that directly affect PPy, i.e. acetone. Acetone reduces doped PPy, as evidenced by UV-Vis [19].

4. Conclusion

The type of response and the sensitivity of PPy can be tailored by making a composite with 3A and Ny. They can also altered with the forms of sensing materials. Methanol shows the highest effect on to sensor conductivity. The response of Ny20_PPy13_3A50 film are 2 orders of magnitude higher than that of pure PPy pellet, with the opposite direction of response. More investigation of interaction mechanism is needed for further development of these materials to be the simplest sensor for chemical vapors in lacquer.

5. Acknowledgements

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Figure captures

Figure 1 The flow system to study the electrical response toward chemical vapor.

Figure 2 Calibration curves of (○) acetone, (△) MEK, (□) methanol, and (◇) toluene.

Figure 3 Sensitivity of four sensing materials toward vapor of: a) acetone, b) MEK, c) methanol, and d) toluene, at various concentrations.

Figure 4 Sensitivity of four sensing materials toward vapor of acetone, MEK, methanol, and toluene, at 3 vol% in N_2.

Table capture

Table 1 Parameters for calculating vapor concentration from Equation 1

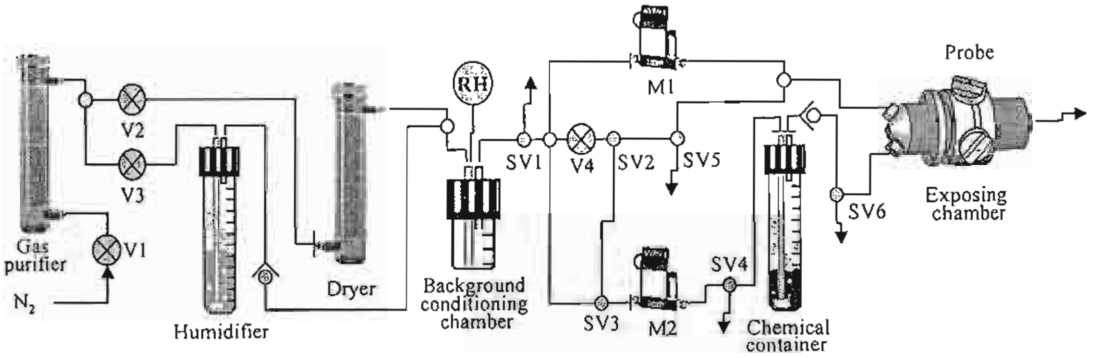

Probe
M1
RH
V2
V3
V1
SV1
V4
SV2
SV5
SV6
Exposing chamber
Gas purifier
N$_2$
Humidifier
Dryer
Background conditioning chamber
SV3
M2
SV4
Chemical container

Figure 1

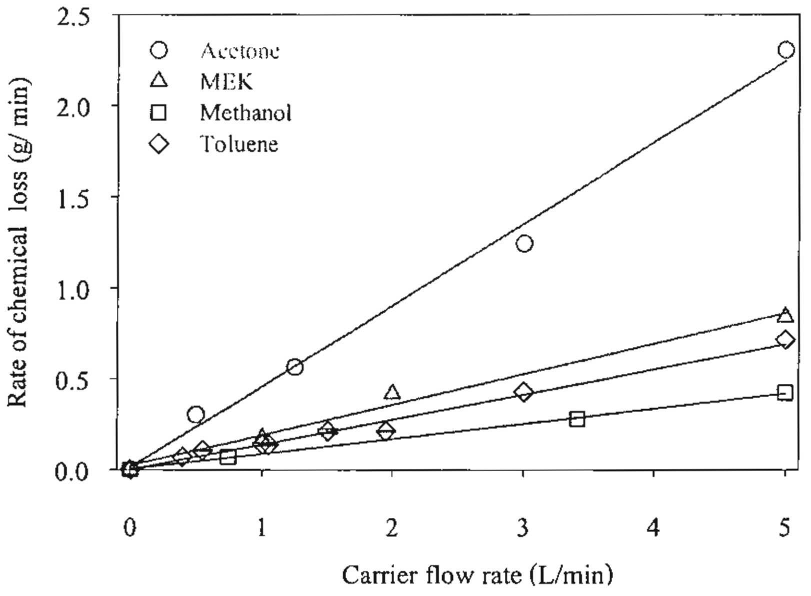
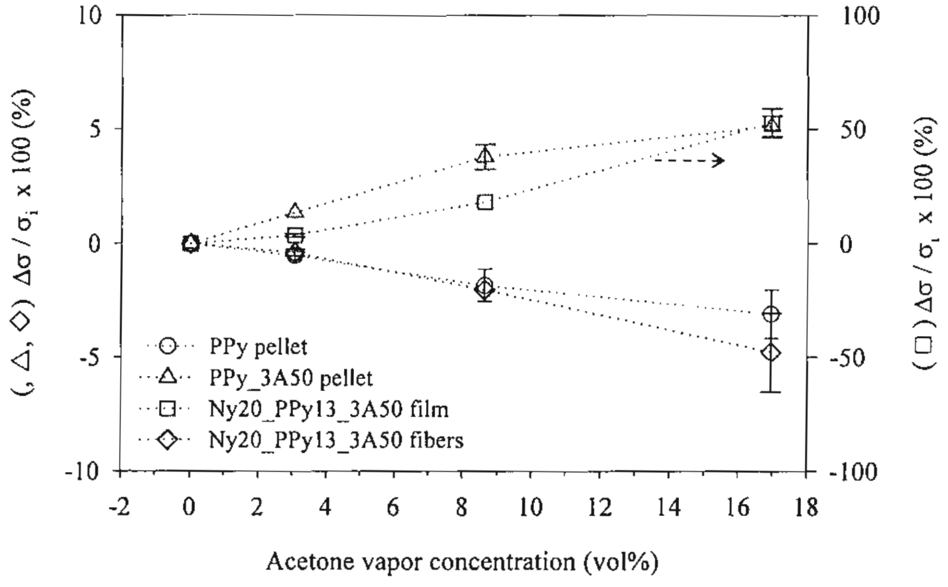
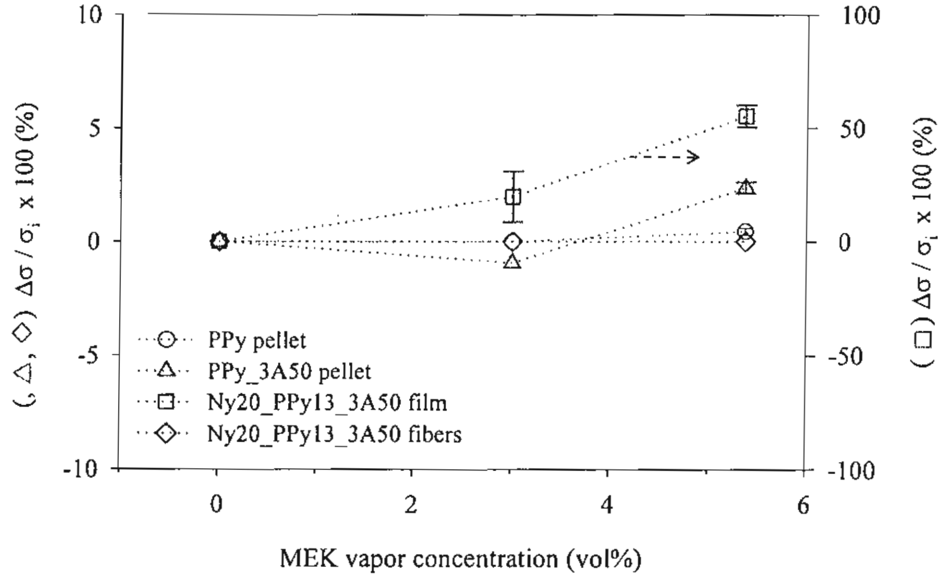

2.5
2.0
1.5
1.0
0.5
0.0
Rate of chemical loss (g/ min)
○ Acetone
△ MEK
□ Methanol
◇ Toluene
0
1
2
3
4
5
Carrier flow rate (L/min)

Figure 2



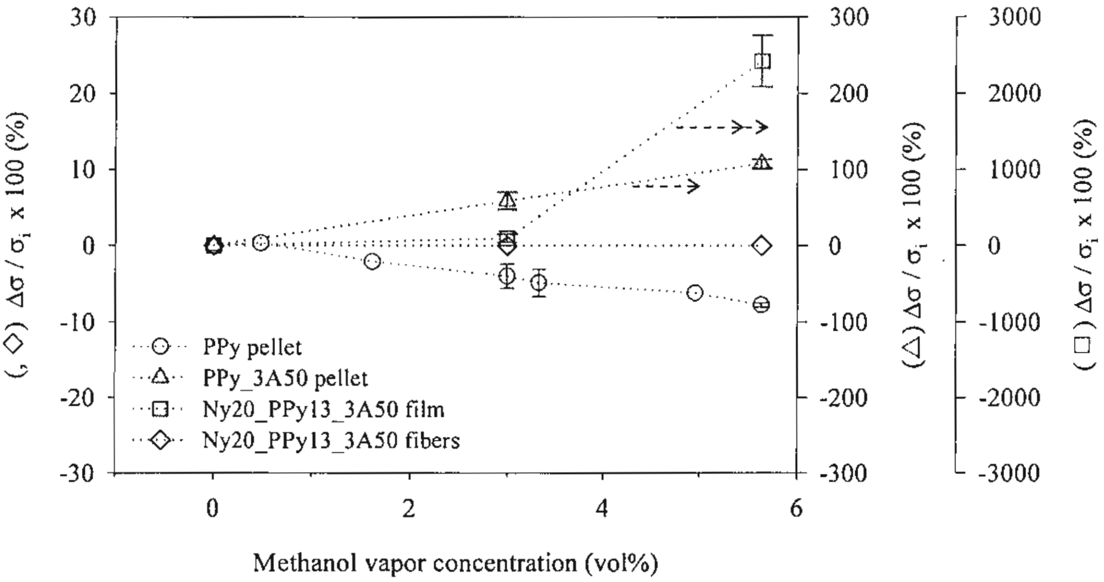
10
5
0
-5
-10
100
50
0
-50
-100
-2
0
2
4
6
8
10
12
14
16
18
(, △, ◇) Δσ / σ$_i$ x 100 (%)
(□) Δσ / σ$_i$ x 100 (%)
Acetone vapor concentration (vol%)
PPy pellet
PPy_3A50 pellet
Ny20_PPy13_3A50 film
Ny20_PPy13_3A50 fibers

(a)

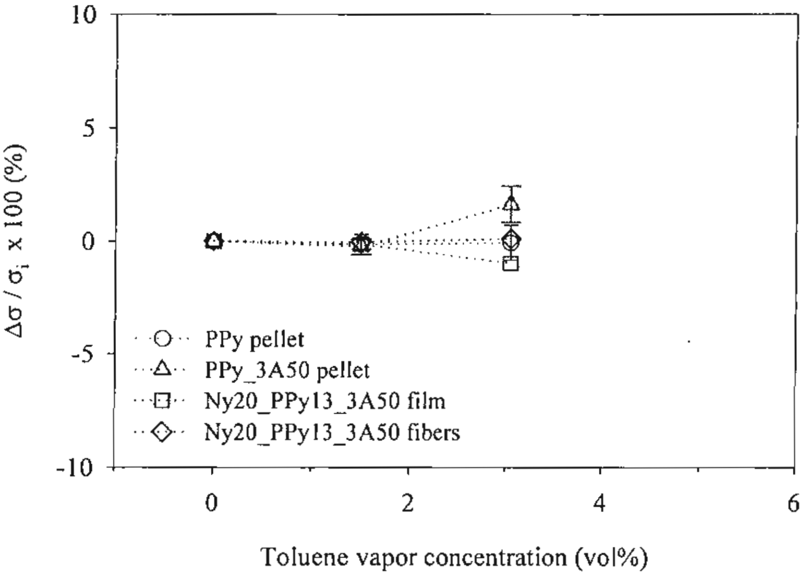


10
5
0
-5
-10
100
50
0
-50
-100
0
2
4
6
(, △, ◇) Δσ / σ$_i$ x 100 (%)
(□) Δσ / σ$_i$ x 100 (%)
MEK vapor concentration (vol%)
PPy pellet
PPy_3A50 pellet
Ny20_PPy13_3A50 film
Ny20_PPy13_3A50 fibers

(b)

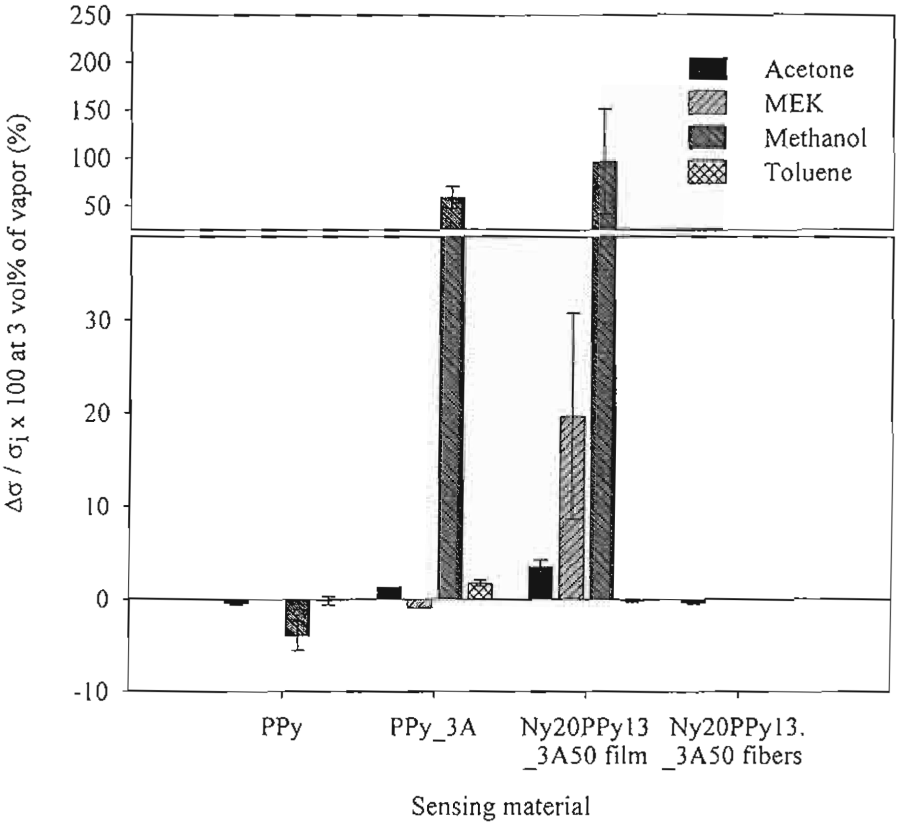

30
20
10
0
-10
-20
-30
(, ◇) Δσ / σ_i x 100 (%)
300
200
100
0
-100
-200
-300
(△) Δσ / σ_i x 100 (%)
3000
2000
1000
0
-1000
-2000
-3000
(□) Δσ / σ_i x 100 (%)
0
2
4
6
Methanol vapor concentration (vol%)
PPy pellet
PPy_3A50 pellet
Ny20_PPy13_3A50 film
Ny20_PPy13_3A50 fibers

(c)


10
5
0
-5
-10
Δσ / σ_i x 100 (%)
0
2
4
6
Toluene vapor concentration (vol%)
PPy pellet
PPy_3A50 pellet
Ny20_PPy13_3A50 film
Ny20_PPy13_3A50 fibers

(d)

Figure 3



250
200
150
100
50
30
20
10
0
-10
Δσ / σi x 100 at 3 vol% of vapor (%)
Acetone
MEK
Methanol
Toluene
PPy
PPy_3A
Ny20PPy13 _3A50 film
Ny20PPy13. _3A50 fibers
Sensing material

Figure 4

Table 1 Parameters for calculating vapor concentration from Equation 1.

Parameter Chemical	A (g of chemical loss / min / (L / min))	MW (g / mol)
Acetone	0.450	58
Methyl ethyl ketone (MEK)	0.174	72
Methanol	0.084	32
Toluene	0.144	92

ภาคผนวก ก.

L. Wannatong and A. Sirivat (2006) Utilizing Various Additives In Polypyrrole-Based Humidity Sensor, Presented at the the 28th Australasian Polymer Symposium.

Australasian Society for Biomaterials

POLYMER DIVISION
Royal Australian Chemical Institute

28th Australasian Polymer Symposium
& Australasian Society for Biomaterials
16th Annual Conference

5 - 9 February, 2006
Rotorua, New Zealand

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P51

Utilizing Various Additives In Polypyrrole-Based Humidity Sensor

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Various materials, i.e. non-polar polymers, water-soluble polymer, zeolites with various pore sizes and properties, and a desiccant, have been used as additives for polypyrrole (PPy) for humidity sensor application. It has been found that adding the inert additives did not affect the electrical response pattern but changes the response magnitude whereas adding zeolites and the dessicants changed the response characteristic. PEO and SiO_2 shortened the time the sensor needs to reach the equilibrium. Zeolites delayed the response and seemed to infinitely enhance the sensitivity of PPy toward water.

Introduction In order to develop a simple sensor system which consists of only few sensing elements of conductive PPy, the sensitivity toward an ambient interference, the moisture, should be taken into account. This work focuses on the electrical response patterns of PPy toward liquid water when PPy was mixed with various additives yielding different response patterns toward water.

Experimental PPy was chemically synthesized with pyrrole (monomer): ammonium persulfate (oxidant): α-naphthalene sulfonate (dopant) ratio of 1:1: 0.08 at +/- 0.5 °C under N_2 for 1 hour. The PPy was aged at 50 +/- 5 %RH for 20 days before the experiments. The addivitives, that are polyethylene (PE), polystyrene (PS), Poly(ethylene oxide) (PEO), silica fume (SiO_2), zeolite 3A, 4A, 5A, Y and 13X were kept at 50 +/- 5 %RH before use. The densities, particle sizes, and surface areas of PPy and all additives were determined by a pycnometer, a mastersizer, and BET, respectively. PPy and additive with the equal volume were ground and mixed together. The mixture was pressed by a hydraulic press at 60 kN into a pellet with a diameter of 1.3 cm and a thickness of 50 +/- 5 μm. Their specific conductivity (σ) values were measured by custom-made four-point probe (square array) conductivity meter, as shown in Figure 1.

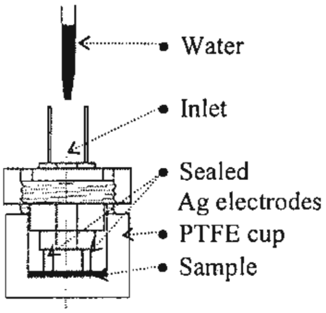

Figure 1. Custom-Made Four-Point Probe

Results and Discussion The sensitivity (percent change in σ relative to the initial σ) toward liquid water of PPy+zeolite changed with age after mixing, so the water responses of all sensing elements in this work were recorded after at least 14 days of mixing. The response patterns of PPy and PPy with various additives toward water are shown in Figure 3. The sensing elements with similar response pattern are described together. ***PPy***: σ of pure PPy suddenly decreased and then gradually increased. It took 700 – 900 seconds to reach the equilibrium signal. The former sudden decrement of σ resulted from the proton (H^+) subtraction whereas the later gradual increment in σ resulted from the hydronium ion (H_3O^+)

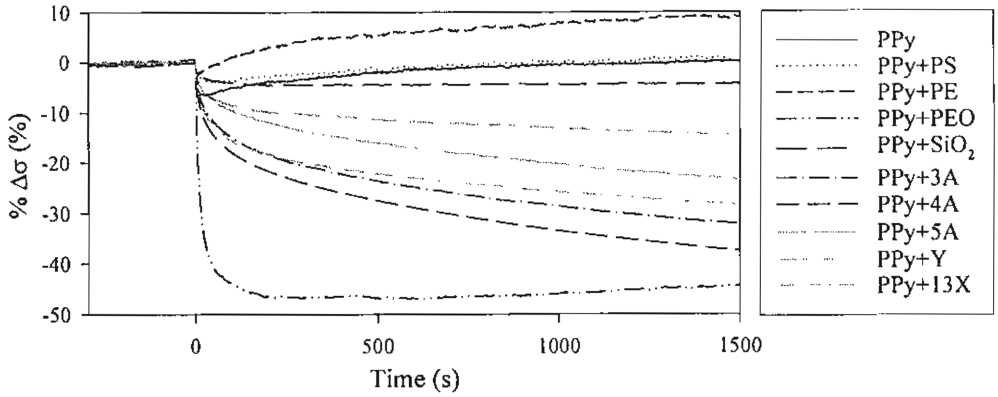

Figure 2. The response patterns of PPy and PPy with various additives toward water

movement in PPy. As investigated by XPS[1], the PPy which was exposed to liquid water showed decreasing of –NH$^+$– and increasing of –N= species. This evident supports the H$^+$ subtraction interaction. ***PPy mixed with inert additives***: Upon mixing with PE and PS, the response pattern did not change; they sharply decreased and then increased with different magnitudes. The decreases in σ were smaller due to a smaller percentage of active –NH$^+$– sites in PPy. A larger increment in σ of PPy+PE might be due to the hydrophobic nature of PE which freed H_3O^+ to give an ionic conductivity to the sensor. ***PPy mixed with water soluble polymer***: PEO swells in water and increases the distance between conducting PPy particles. σ of PPy+PEO decreasesd suddenly and significantly after the exposure to liquid water. The time needed for equilibrium signal was only ca. 200 s. Most of ions were absorbed, hence no final increment in σ was observed. ***PPy mixed with zeolites***: All zeolites used in this work gave the similar response pattern toward liquid water. They delayed the response and tended to stop H_3O^+ movement. The sensitivity seemed to be infinitely enhanced. The microporous structure of zeolites increased the amount of accessible active –NH$^+$– sites in PPy. Zeolite Y, which has the highest Si/Al ratio and hence the highest hydrophobicity among the others, gave the lowest sensitivity toward liquid water. The long-term sensitivity derivatives, which are the slopes of the response patter from 1000 to 1500 s, of zeolite Y, 13X, and A are -0.3, -0.5, and -0.6 to -0.8 %Δσ/100s. This order is proportional to their Si/Al ratios: 2.43[2], 1.33[3], and ~1. Zeolite 5A has a smaller sensitivity to water than 3A and 4A. The presence of Ca^{2+} in 5A instead of monovalent K$^+$ and Na$^+$ in 3A and 4A was responsible for this behavior. ***PPy mixed with other desiccant***: SiO_2 generally absorbs water but does not swell. So σ decrement was not enhanced. With the same reason as the inert additives, PPy+SiO_2 had 50% smaller σ decrement than that of pure PPy. The time needed for equilibrium signal was as short as that of PPy+PEO. SiO_2 absorbs water so there was no final increment in σ.

Conclusion The sensitivity, the response time, the time needed to reach the equilibrium signal, and the long-term sensitivity derivative of PPy can be tailored by utilizing various types of additives.

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