



CHAPTER IV

DEVELOPMENT OF A CARBON AEROGEL COMPOSITE FILM FOR GAS SENSORS

4.1 Abstract

New organic aerogel was synthesized via thermal curing reaction of a novel type of phenolic resin called polybenzoxazine. The subsequent carbon aerogel (CA) was generated by pyrolysis of the organic aerogel at high temperature under inert atmosphere. Further activation of CA resulted in an activated CA. The CA and activated CA have surface area of 466 m²/g and 917 m²/g with uniform mesopore radius of 2.4 nm and 2.5 nm, respectively. New gas sensing conductive polymer composites, fabricated from poly (vinyl alcohol) and polybutadiene filled with polybenzoxazine-based CA, have been investigated for organic vapor detection. The experimental results showed that high polar poly (vinyl alcohol) gave a higher response to high polar solvent, ie. water, and moderate polar solvent, ie. Acetone, but a lower response to low polar solvent, ie. n-hexane and toluene. On the other hand, the response of non-polar polybutadiene was excellent to n-hexane and toluene but not to water and acetone. Moreover, CA polymer composites showed better gas response compared to graphite polymer composites since CA is a nano-porous material, which has a high adsorption capacity. Moreover, CA polymer composites showed good reproducibility as the electrical resistance came back to the original value when they were exposed to N₂ gas. This study shows that CA composite films have potential to be used as gas sensors.

Keyword: Composite/ Conductive filler/ Carbon aerogel/ Polybenzoxazine

4.2 Introduction

Recently, gas sensing polymer composites have broadened the application of conductive polymer composites such as electronic noses [4]. The sensing behavior of these polymer composites can be explained by the mechanism that the conductive networks formed by connection of filler particles through out the insulate polymer matrix. Sorption of organic vapors into the polymer provides the swelling of the matrix phase leading to the separation of the inter-particle path of filler in which cut the conducting circuits [39]. As a result, the resistance increases sharply. Previously, the conductive fillers utilized to produce gas sensors have been concentrated on carbon blacks [15, 23], carbon nanotubes [43] and graphite [18].

Carbon aerogel (CA) is one of the unique carbon materials which have nano size pores with highly cross-linked structure. It has been applied in many applications including waste water treatment [12], supercapacitors [47] and advance catalyst supports [29] due to their properties of large surface area resulting in high adsorption capacity and their controllable pores size. The crosslink density of organic aerogel is one of the most importance characteristics. Since high crosslink density not only provides high structural stability after solvent is removed but also provides high char yield to construct the CA after pyrolysis [25].

Polybenzoxazine, as a novel type of phenolic resin has recently been developed. This polymer has many fascinating characteristics such as low water adsorption, dimensional stability, and near-zero shrinkage. Polybenzoxazine can be easily prepared from inexpensive material; phenols, formaldehyde, and primary amine. According to the wide variation of raw materials, they have tremendous molecular-design flexibility. Furthermore, polybenzoxazine can be polymerized without strong acid or base catalysts and without generating by-product and volatile [1, 6, 13]. Consequently, polybenzoxazine is promising for organic and carbon aerogel preparation.

In order to realize the advantages of CA described above, the purpose of this work is to fabricate and characterize the gas sensors made from CA thin film composites and measure its resistivity and gas sensitivity towards different organic vapors.

4.3 Experimental

4.3.1 Materials

Bisphenol-A (Ba) was purchased from Aldrich, Germany. Formaldehyde (analytical grade) was purchased from Merck, Germany. Triethylenetetramine (TETA) was purchased from Fluka, Switzerland. Graphite (< 20 μ m) was purchased from Sigma-Aldrich, Thailand. Polybutadiene (PB) (M_w=40,000) was purchased from Dow Chemical, USA. Polyvinyl alcohol (PVA) (M_w=30,000-70,000) was purchased from Fluka, USA. Toluene (analytical grade), dimethylformamide (analytical grade), n-hexane and acetone (analytical grade) were purchased from Lab-scan, Thailand.

4.3.2 Equipment

The FT-IR spectrum of benzoxazine precursor was obtained using a Nicolet Nexus 670 FT-IR spectrometer. KBr pellet technique was applied in the preparation of powder samples. ¹H-NMR spectra were recorded on a Varian Mercury 300 (300 MHz) instrument, using deuterated dimethyl sulfoxide as solvent. DSC analyses were carried out using a Perkin-Elmer DSC 7 instrument. The samples were heated from 30 ° to 300 °C at a heating rate of 10 °C/min under a N₂ atmosphere with a flow rate of 10 ml/min. TG-DTA curve was collected on a Perkin-Elmer Pyris Diamond TG/TGA instrument. The sample was loaded on the platinum pan and heated from 30° to 900 °C at a heating rate of 20 °C/min under N₂ flow of 50 mL/min. HITACHI S-4800 scanning electron microscope was used to observe the surface morphology of polybenzoxazine-based aerogel and carbon aerogel. The specimens were coated with platinum under vacuum before observation. N₂ adsorption-desorption isotherms were obtained at -196 °C on a Quantachrome Autosorb-1. Samples were degassed at 250 °C for 15 hr in a vacuum furnace prior to analysis. Surface areas were calculated using the BET equation. The pore size distributions were constructed based on Barrett, Joyner and Halenda (BJH) method, using the adsorption branch of the nitrogen isotherm. Electrical resistance of conductive composite polymers membranes were measured using a digital multimeter (KEITHLEY 2700).

4.3.3 Methodology

4.3.3.1 *Preparation of Carbon Aerogel*

Carbon aerogel was obtained by three main which including preparation of benzoxazine precursor, preparation of organic aerogel, and preparation of carbon aerogel from organic aerogel. The details of these steps are as follows:

4.3.3.1.1 Preparation of Benzoxazine Precursor

Benzoxazine Precursor was prepared by mixing Bisphenol-A (2.31 g), triethylenediamine (1.74 g), and formaldehyde (3.28 g) in a 1:1:4 molar ratio. Dimethylformamide (15 g) was used as a solvent. The reaction was cooled in an ice bath and mix continuously for 1 hour until homogenous solution was perceived.

4.3.3.1.2 Preparation of Organic Aerogel derived from Benzoxazine Precursor

The mixture was poured into vessels and sealed tightly. The vessels were kept at an ambient condition overnight and partially cured at 80 °C for 3 days; consequently, highly cross-linked polymer was achieved. Then cross-linked wet gel was dried with supercritical carbon dioxide ($T_c=45$ °C; $P_c=7.5$ MPa). Finally that, dried gels were fully cured in an oven at temperature of 140 °C, 160 °C, 180 °C for 2 hours each and 200 °C for 3 hours, resulting in organic aerogel.

4.3.3.1.3 Preparation of Carbon Aerogel derived from Benzoxazine Precursor

CA was obtained by pyrolysis of organic aerogels in a quartz reactor using the following ramp cycle: 30 °C to 250 °C for 60 min, 250 °C to 600 °C for 300 min, 600 °C to 800 °C for 60 min and held at 800 °C for 60 min. The system was carried out in N₂ flow at 700 cm³/min. Finally, activation of CA was carried out in CO₂ at 900 °C, in order to have more surface area.

4.3.3.2 *Characteristics of Polybenzoxazine and Carbon Aerogel Derived from Polybenzoxazine*

The structural characteristics of polybenzoxazine-based aerogel were investigated using FTIR and ¹H-NMR. Thermal properties were measured using DSC and TG/DTA. Morphology was observed by SEM. Furthermore, surface area and pore distribution were measured using SAA.

4.3.3.3 Preparation of Composite Conductive Polymer Films for Gas Sensors

The CA and activated CA were triturated in a mortar; the average diameter of particle size was less than 180 μm . Then the CA and activated CA were dried at 100 $^{\circ}\text{C}$ in an oven overnight before use. The composite conductive polymer membranes were prepared by a four-step process. In the first step, the filler was introduced into 1 ml of solvent. Water and toluene were used as solvent for PVA and PB, respectively. The mixture was violently stirred for 3 hrs. and ultrasonically dispersed for 15 min. The second step involved the preparation of polymer solution by dissolving polymer in solvent. During the third step, 15 % of polymer solution was added into filler mixture which was then stirred overnight. Finally in the fourth step, the rest polymer solution was added into the filler mixture and stirred for 2 hrs. Then the films were fabricated by spin-coating technique on an interdigitated electrode. For comparison, the composite polymer films with graphite as a conductive filler were also manufactured by the same process.

The interdigitated electrode was fabricated by thermal evaporation of Al (100 nm) and Au (80 nm) on a glass slide (Figure 4.1) with a gap size between fingers of 200 μm .

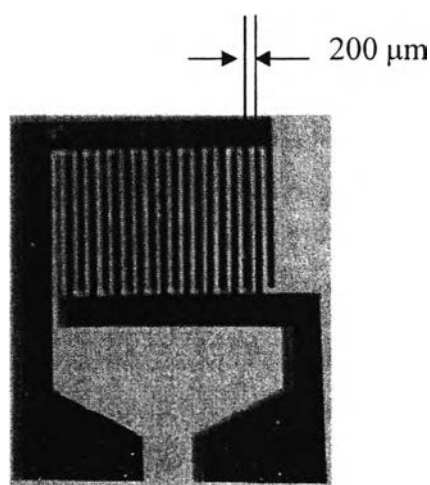


Figure 4.1 Interdigitated electrode.

4.3.3.4 Electrical Response Measurements of Conductive Composite Films for Gas Sensors

The testing steps started from obtaining a baseline resistance (R_b) by allowing only pure nitrogen gas to flow into the test chamber at a flow rate of 300 ml/min. Then an analyte gas vapor was carried by nitrogen gas through the test chamber in which a sensor was kept. Then the maximum of electrical resistance (R_m) of sensor was measured using a digital multimeter. Figure 4.2 shows the scheme of the electrical measurement.

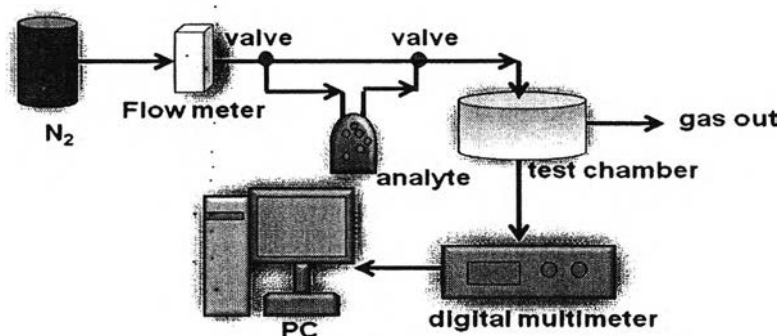


Figure 4.2 The scheme of the electrical measurement.

4.4 Results and Discussion

4.4.1 Characterization of Polybenzoxazine-based Aerogel

The structure of polybenzoxazine was examined by FT-IR and 1H NMR. IR spectra of the polybenzoxazine are shown in Figure 4.3.

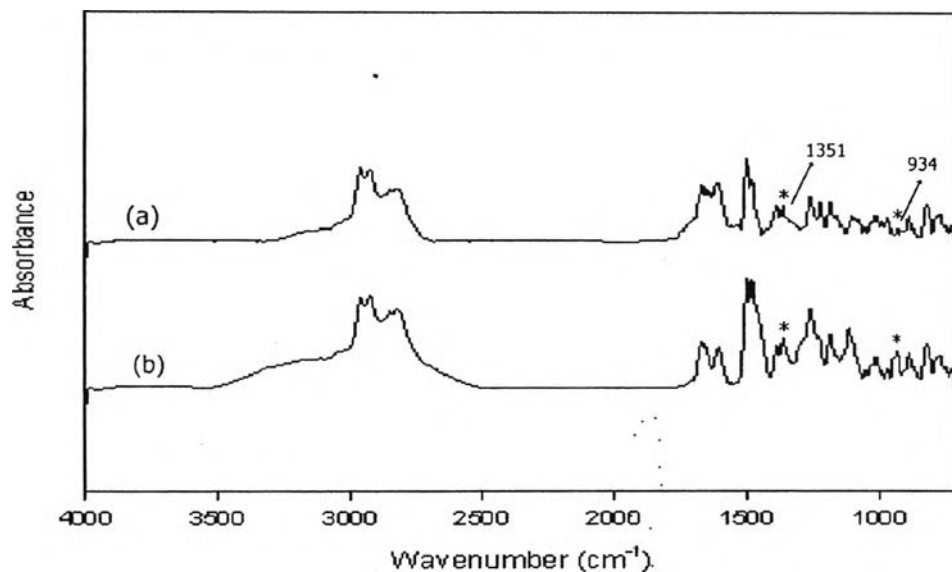


Figure 4.3 IR spectra of (a) fully cured polybenzoxazine (b) partially cured polybenzoxazine.

The characteristic absorption bands at 1252 cm^{-1} (asymmetric stretching of C-O-C of oxazine), 1190 cm^{-1} (asymmetric stretching of C-N-C), 1351 cm^{-1} (CH_2 wagging of oxazine), 1524 cm^{-1} (stretching of trisubstituted benzene ring), and 944 cm^{-1} (out of plane bending vibrations of C-H) were observed, indicating that precursors containing benzoxazine backbone in structure was obtained. These results were well agreed with the results observed by Dunkers and Ishida [6].

By the end of the curing at 200°C , the intensity of the bands of CH_2 wagging of oxazine (1351 cm^{-1}) and out-of-plane bending vibration of C-H (944 cm^{-1}) was decreased. These results also correspond to the result reported by Takachi and coworkers [39] who suggested the completion of ring-opening polymerization of polybenzoxazine was attained.

The $^1\text{H-NMR}$ spectrum of polybenzoxazine is shown in Figure 4. 4.

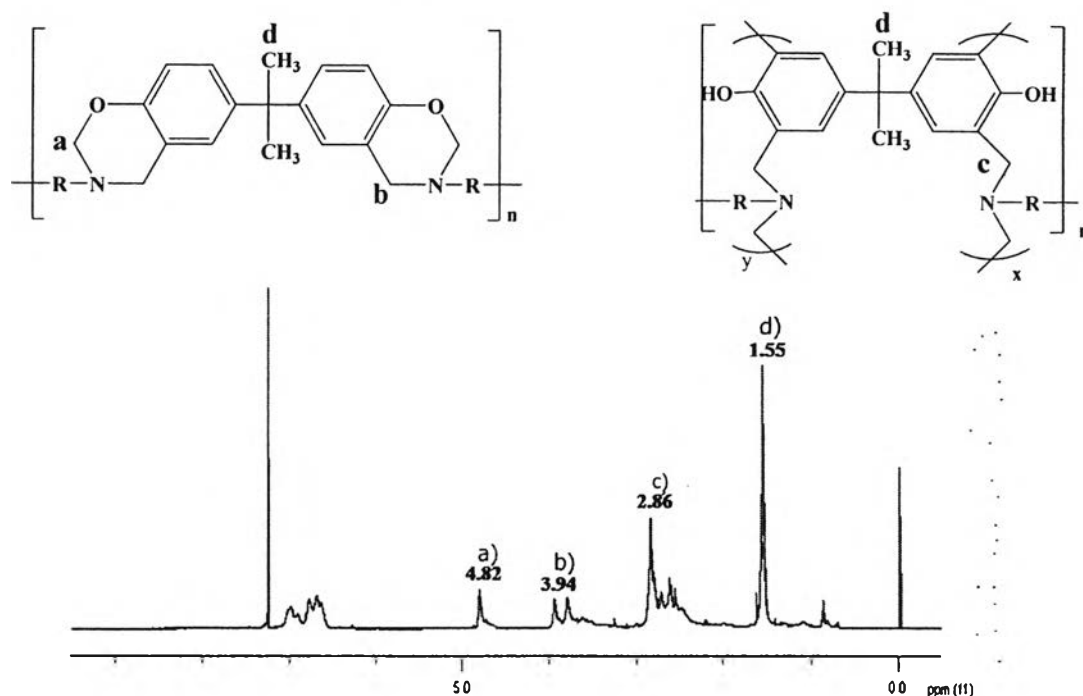


Figure 4.4 ^1H -NMR spectrum of polybenzoxazine.

The characteristic peaks assignable to methylene (O-CH₂-N) and methylene (Ar-CH₂-N) of oxazine functionality were observed at 4.82 and 3.94 ppm, respectively. The methyl protons of bisphenol-A showed peak at 1.55 ppm. The methylene protons of opened-ring of polybenzoxazine were also observed at 2.86 ppm. The results correspond to those of Ning and Ishida [30] that confirmed benzoxazine precursor was obtained.

The progress of ring-opening polymerization of the precursors was also observed by DSC. Figure 4.5 shows DSC thermograms of polybenzoxazine.

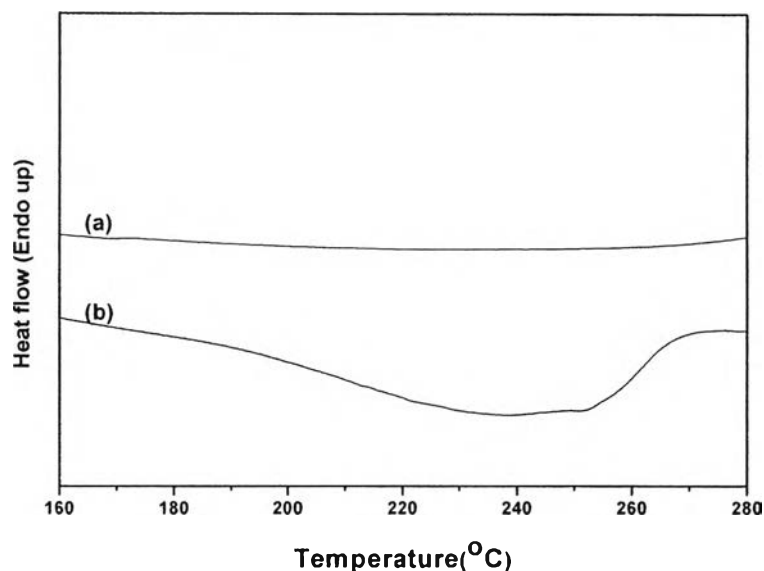
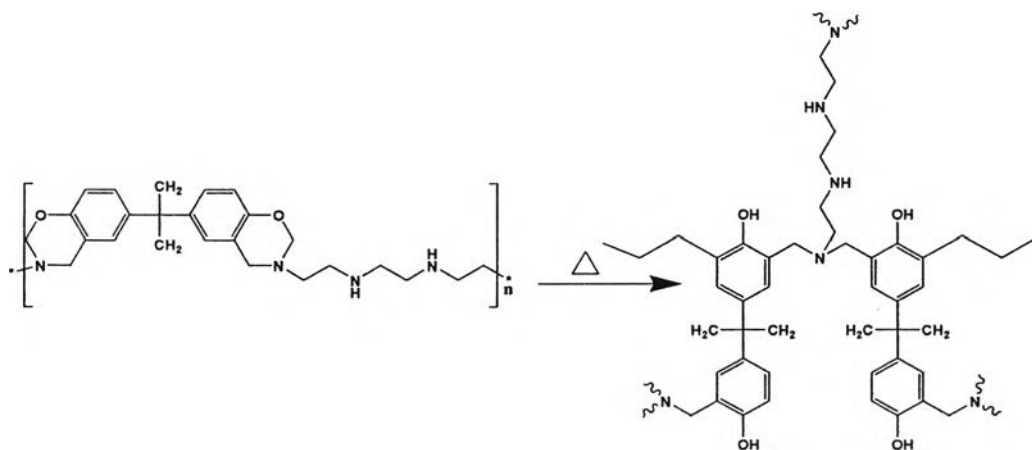


Figure 4.5 DSC profiles of (a) fully cured benzoxazine precursor (b) partially cured benzoxazine precursor.

The exotherm onset corresponding to the ring-opening polymerization of partially cured benzoxazine precursor was observed at 160 °C. The exotherm peak disappeared after the precursor was fully cured, showing that ring-opening of oxazine was completed. The possible structure of polybenzoxazine is depicted in Scheme 4.1.



Scheme 4.1 Possible structure of polybenzoxazine precursors and the cured resin.

The thermal stability of polybenzoxazine-based organic aerogel was investigated by TGA (Figure 4.6). Polybenzoxazine began to decompose at 225°C with the maximum mass loss rate in the temperature range between 250° and 600°C. The rate of mass loss became slower after 600°C, and no obvious mass loss was observed beyond 800°C. The values of 5 and 10% weight loss temperatures were 295 and 325 °C, respectively and the char yield was 39 %wt.

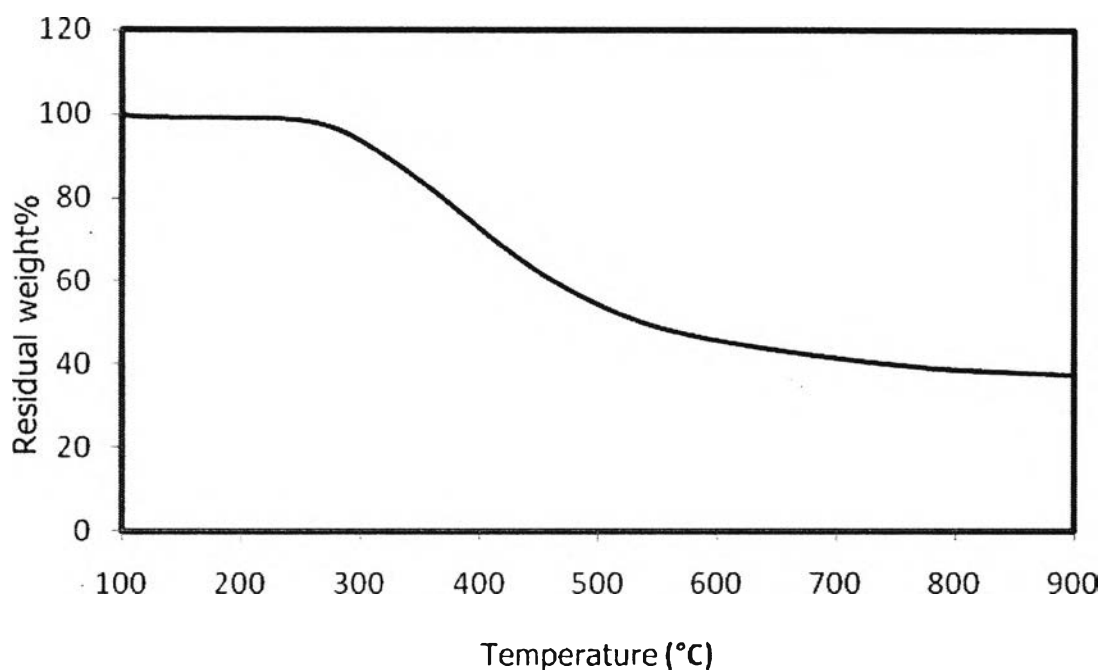


Figure 4.6 TGA thermogram during the pyrolysis of the polybenzoxazine-based organic aerogel.

Lorjai and coworker [26] reported the char yield of polybenzoxazine aerogel is higher than the bulk polybenzoxazine due to polybenzoxazine aerogel has the contiguous microporous in its structure. Therefore, the primary products decomposed within the porous structure and travel in longer retention time. This porous structure cause high opportunity for secondary reaction to form the secondary compounds resulting in formation of char with non-reactive.

Figure 4.7. shows SEM micrographs of the organic aerogel and carbon aerogel which exhibit the 3D interconnected particles into a network with continuous opened-macropore. However, in case of organic aerogel, the denser porous

structure was obtained. Since during pyrolysis process, some organic moieties in organic aerogel structure were decomposed resulting in sparser in carbon aerogel.

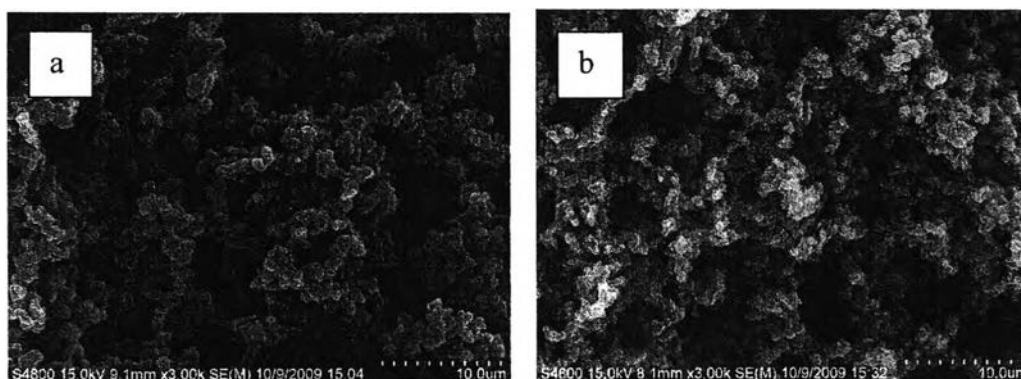


Figure 4.7 SEM micrographs of (a) organic aerogel and (b) carbon aerogel.

Figure 4.8 shows the X-ray diffraction (XRD) pattern of polybenzoxazine-based carbon aerogel. The broad peaks at $2\theta = 23^\circ$ and 43° correspond to the interlayer spacing (d_{002}) and stacking height ($L_{c,002}$) of graphitic carbon material [24], suggesting that the prepared carbon aerogel contained some ordered structure.

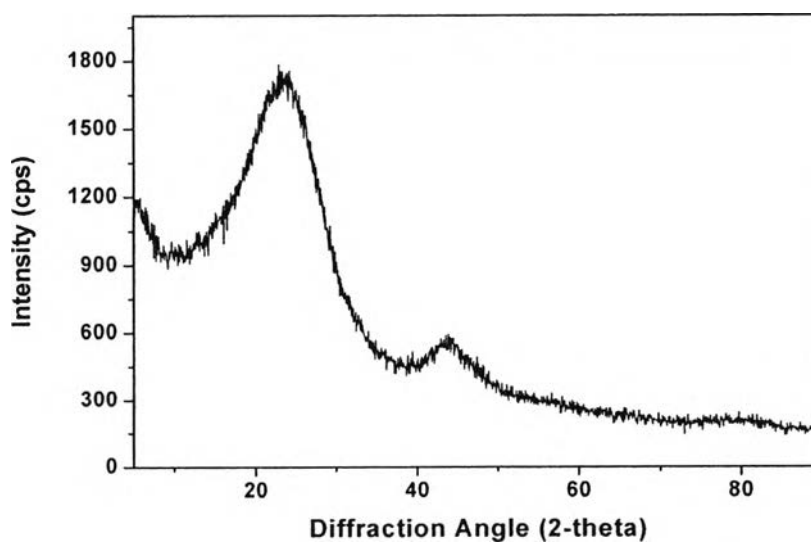


Figure 4.8 XRD pattern of polybenzoxazine-base carbon aerogel.

4.4.2 Conductive films morphology

4.4.2.1 *Microscale surface analysis by optical microscopy (OM)*

Conductive films microscale morphology of activated CA was observed by optical microscopy (Figure 4.9). These images provide a general view of CA composite conducting network microstructure which was built by interconnection of CA in the insulating polymer. Consequently, electrons can circulate via this percolated structure. It is obvious that increasing CA content increases the network of filler. As a result, the conductance of composite film was increased.

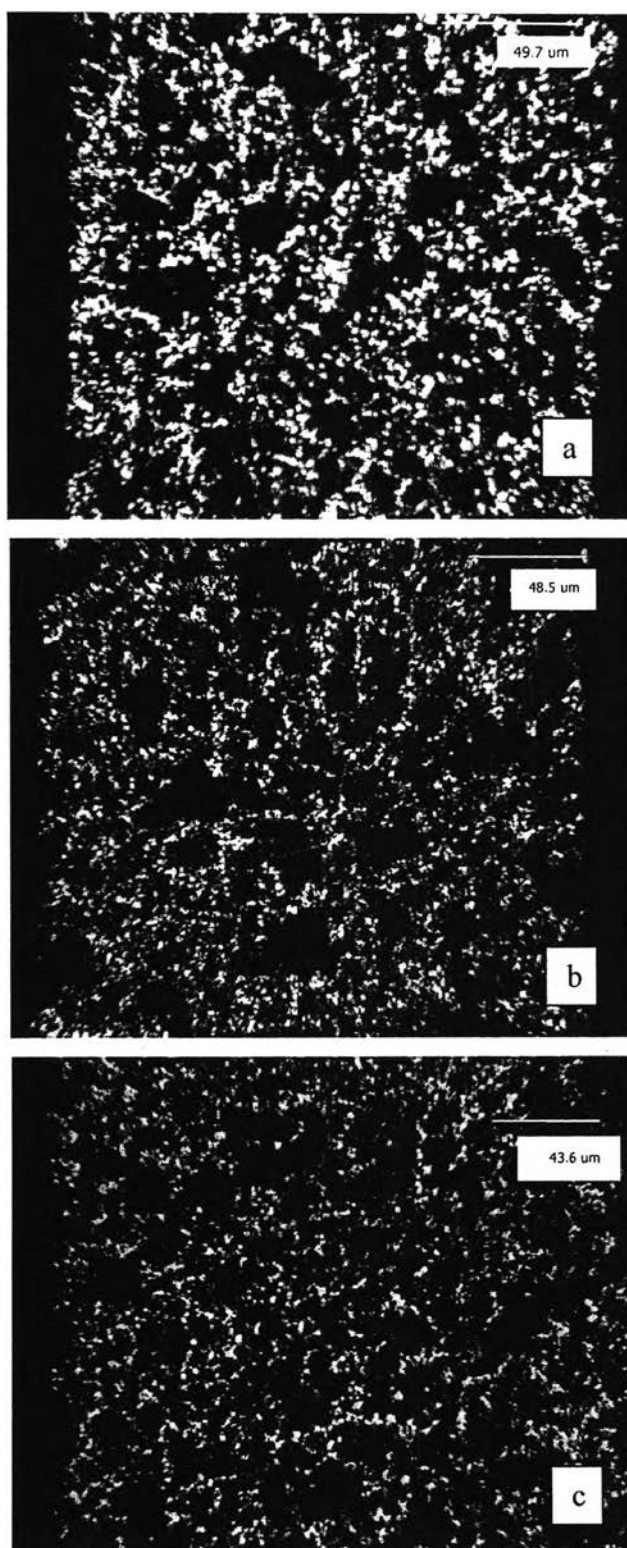


Figure 4.9 Microscale morphology of a) 32 wt% of activated CA in PB b) 38 wt% of activated CA in PB c) 47 wt% of activated CA in PB observed by optical microscope.

4.4.3 Electrical Response Characterization of Conductive Composite films

Common polymers are generally insulators. When the presence of CA approaches to a critical quantity in which at least one conductive path formed throughout the matrix, the electrical conductivity increases due to the effect of percolation threshold [43]. Figure 4.10 shows the relationship between electrical resistance of the composites and the content of conductive fillers. As can be seen, there is a sharp decrease in the resistance starting at 90 wt% of graphite in PB, 24 wt% of CA in PB, and 32 wt% of activated CA in PB, indicating the formation of percolating networks. However, the amounts of additive were higher when compared with the previous report [41]. Since the conductive fillers interconnect only orthogonal plane, say xy in pseudo-two-dimension system (2D), whereas the interconnect path can also be formed in the z direction in pseudo-three-dimensional system (3D) [17] resulting in the higher content of filler in thin film was required for percolating formation in 2D.

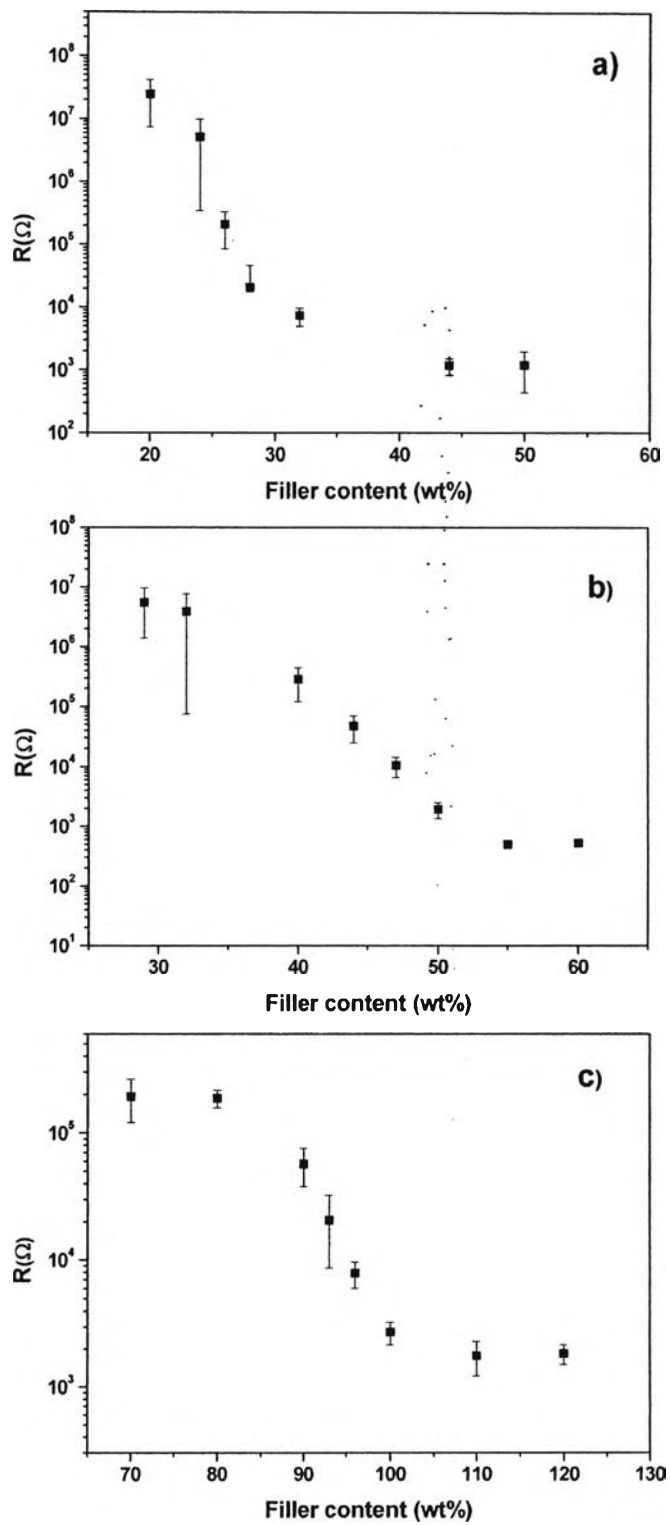


Figure 4.10 Electrical resistance of polybutadiene filled with a) CA b) activated CA c) graphite.

In order to further examine the gas sensitivity and electrical response of each sensor to various organic vapors of CA/PB composites to demonstrate gas sensing composite performance, the response ($dR/R_b = (R_m - R_b)/R_b$) of the composites with various filler contents in toluene vapor was evaluated. (figure 4.11). The highest point appeared at 28 wt%, 44 wt% and 96 wt% of loading CA, activated CA and graphite in PB, respectively. These loading contents of conductive fillers were higher than the percolation threshold. These results are similar to that of the multi-walled nanotube/polystyrene composites reported by Zhang *et al.* [43]. When the content of conductive filler in composite is low, the tunneling effect contributes to the composite conduction beside the direct inter-filler contact. During the composite was exposed to organic vapor, the increase in resistance due to the separation of the conductive paths built by the direct inter-filler contact has to be less significant. In case of high conductive filler content, the excessive fillers causes filler aggregation resulting in the difficulty of conductive path destruction. Only at certain filler content, the conductive networks are mainly built by the direct inter-filler contact, which are easy to be separated by the swelling of polymer matrix resulting in the maximum response of the composite.

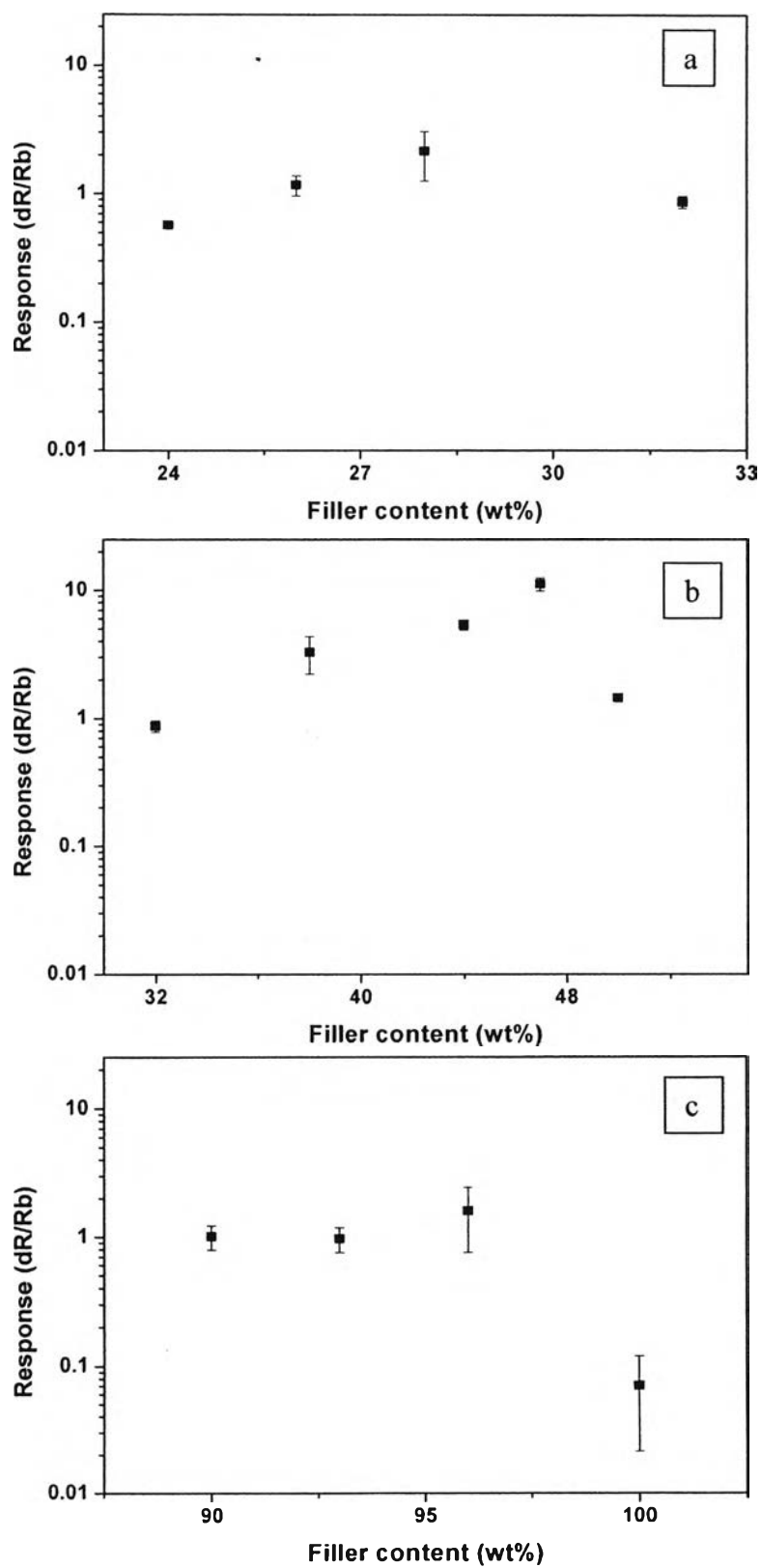


Figure 4.11 Electrical response of a) CA/PB composite b) activated CA/PB composite c) graphite/PB composite with different content of fillers to toluene vapor.

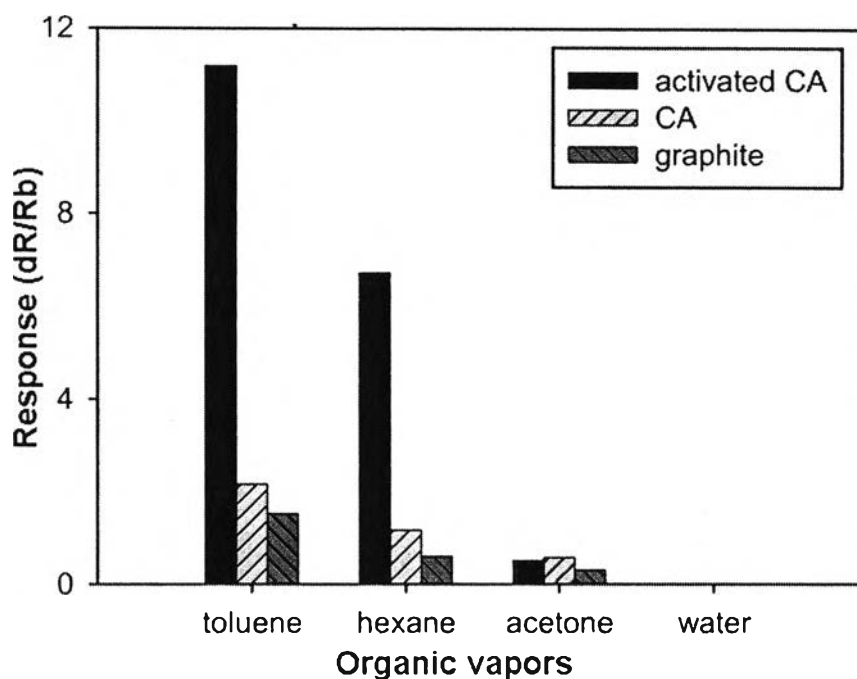


Figure 4.12 Electrical response of composites with different conductive fillers on species of organic solvent vapors.

It is known that the composites showed highest response against toluene vapor at 28 wt%, 44 wt% and 96 wt% of loading CA, activated CA and graphite in PB, respectively. Therefore, the subsequent experiment should be made on the composites with these conductive filler concentrations. The electric response of composites on organic solvents as shown in figure 4.12, comparing to CA/PB and graphite/PB composite, the response of activated CA/PB to three organic vapors was highest. According to the previous reports [19, 42], the adsorption characteristics of filler exerted the importance role on the response of sensor; therefore, the adsorption capacity of composites with different fillers was measured by using ATR-FTIR spectroscopy. Before the composite films were exposed into toluene vapor which was carried by N_2 gas, they were heat for 5 hr. at 70 °C in an oven in order to evaporate remaining organic solvent. Figure 4.13 illustrates the IR spectra of 20 wt% of activated CA in PB composite film. The intensity of each spectrum was normalized by the intensity of the peak at 990 cm^{-1} (=C-H out of plane bending). The peak at 1490 cm^{-1} corresponds to C=C ring stretching of toluene was observed after activated

CA/PB film was exposed into toluene vapor for 5 min. Moreover, the peak intensity was increased with longer exposed time. These results indicated the relative amount of toluene adsorbed by activated CA/PB composites.

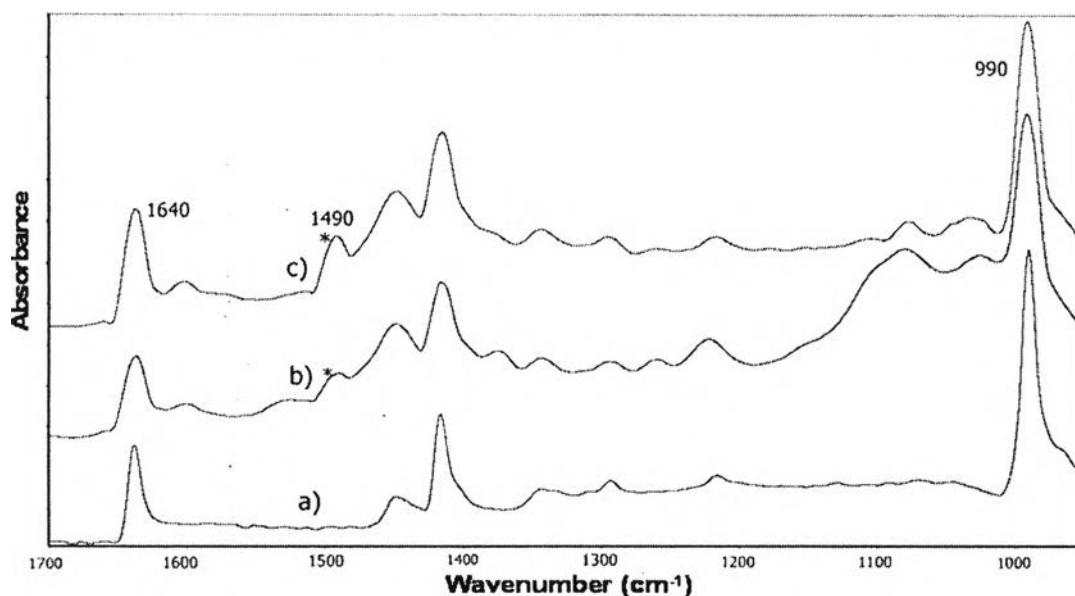


Figure 4.13 Infrared absorbance spectra of 20 %wt of activated CA in PB films a) before exposing to toluene vapor b) after exposing to toluene vapor 5 min c) after exposing to toluene vapor 10 min.

Figure 4.14 shows the comparison of the peak area at 1490 cm^{-1} of pristine PB film and with 20 wt% of activated CA, CA and graphite in PB after exposing to toluene vapor as a function of time. It can be seen that, the peak area of the films increased with the exposure time. Furthermore, the peak area of composite films was higher than that of pristine PB film at the same exposure time. It can be deduced that the adsorption capacity of the filler enhanced the adsorption of the composite film. Moreover, the peak area of activated CA was the highest, indicating that the activated CA/PB composite film adsorbed larger amount of toluene vapor. These results correspond to the work done by Zhang *et al.* [42] who showed that the absorption of CA in organic vapors was higher than that of carbon black resulted in better response of CA/polystyrene composite film to organic gas. Since CA has high adsorption capacity owing to its property of porous material with high surface area

[8,12,20]. The physical characteristic of activated CA compare to other fillers as show as table 4.2.

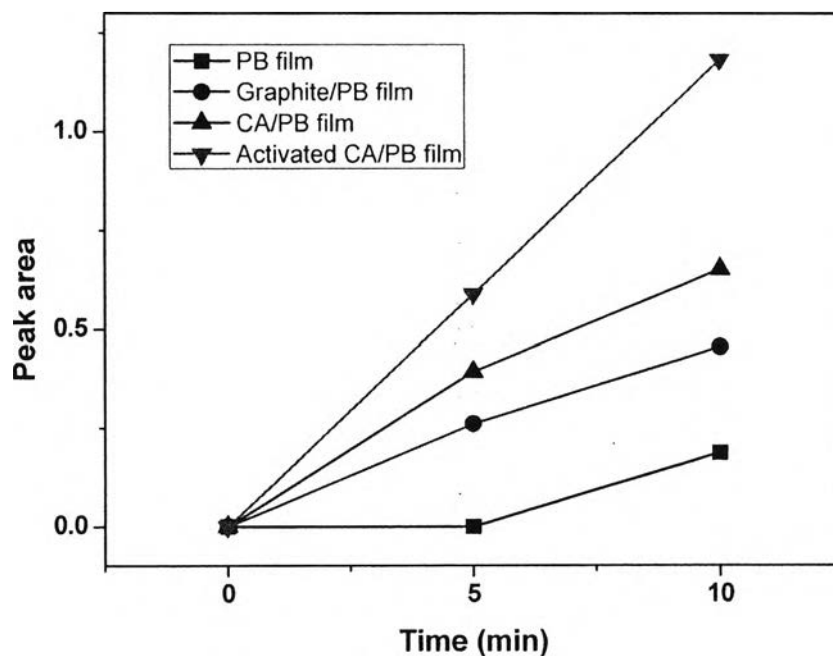


Figure 4.14 The peak area at 1490 cm^{-1} of composite film with different fillers after exposing to toluene vapor as a function of time.

Table 4.1 The physical characteristics of conductive fillers

| Material | Morphology type | Surface area (m^2/g) | Average pore size (nm) | Pore volume (cc/g) |
|--------------|-----------------|--|------------------------|--------------------------------------|
| CA | Powder | 466 | 2.4 | 0.28 |
| Activated CA | Powder | 917 | 2.5 | 0.57 |
| Graphite | Powder | 140 | - | - |

The characteristic resistance of activated CA/PB composites is shown in figure 4.15. The resistance rapidly increased and gave high response when the composite was exposed in organic vapors only for 25 seconds. This exposure time is

shorter than previously report [19, 42], according to the effect of thinner film [16]. The adsorbed gas molecule on the surface of thinner film can penetrated into bulk easier than the thicker film causing the swelling of polymer matrix; therefore, the change of the resistance in thinner film was larger than that of the thicker film. Moreover, the activated CA/PB composites showed a good reproducibility as the electrical resistivity came back to its original value rapidly after exposing to N₂ gas. Thus, polybenzoxazine-based CA is a suitable filler for gas sensing polymer composites.

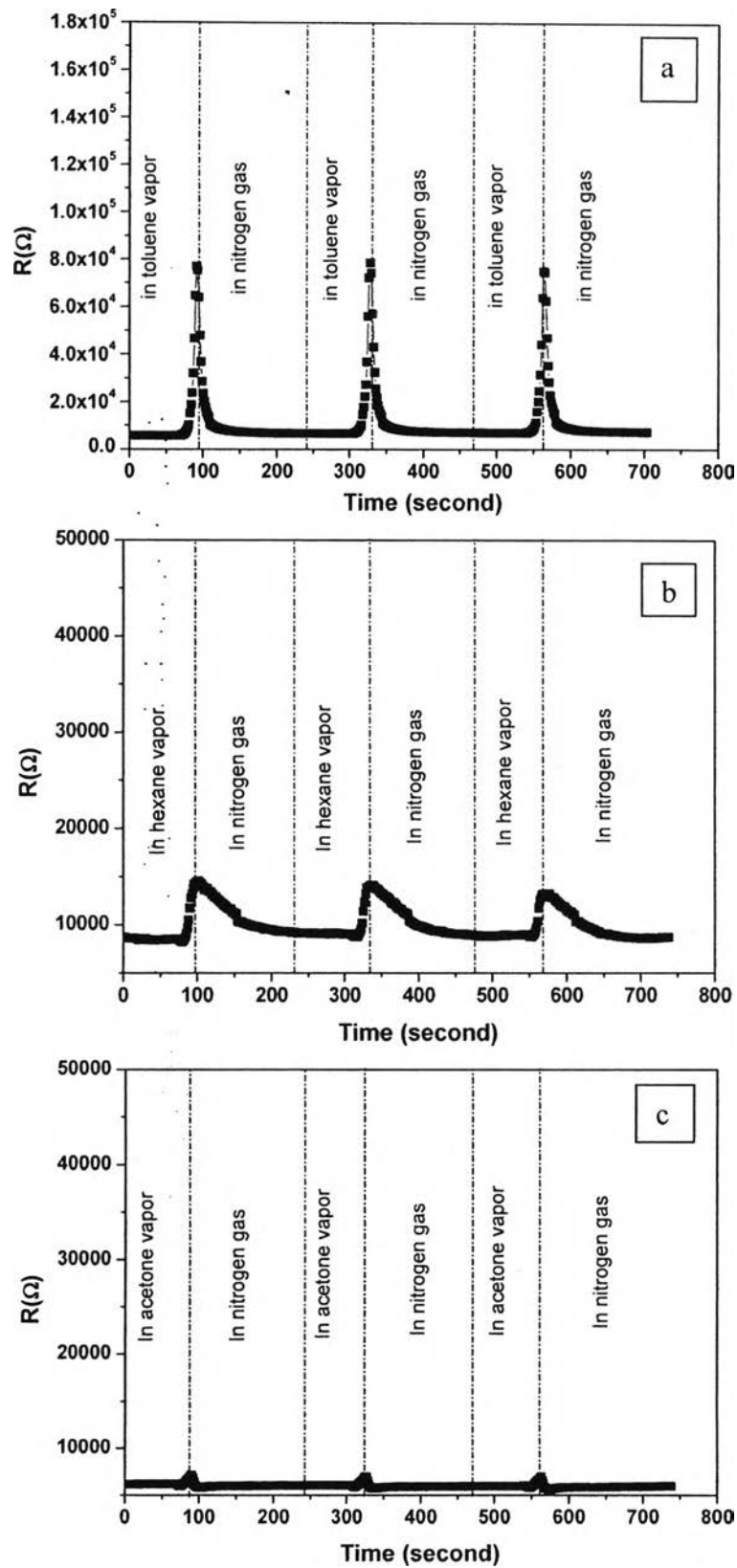


Figure 4.15 Typical cyclic responses of electrical resistance of activated CA filled PB against a) toluene b) hexane c) acetone vapors as a function of time.

Table 4.2 The list of the dielectric constant and polarity index of organic vapors

| Organic vapors | Dielectric constant* | Polarity index** |
|----------------|----------------------|------------------|
| Toluene | 2.38 | 2.4 |
| n-hexane | 1.88 | 0.1 |
| Acetone | 21 | 5.1 |
| Water | 80 | 10.2 |

(*<http://en.wikipedia.org/wiki/solvent>)

**<http://macro.lsu.edu/howto/solvents/polarity%20index.htm>)

The composites possess different responses to different organic vapors providing the composites with selective response. From figure 4.11, the hydrophobic PB composite showed high response to non-polar solvents like toluene and hexane. But its response was low to moderate to acetone, and no response when exposed to high polar solvent such as water. These results correspond to work done by Li *et al.* [19]. They found that the carbon black/polystyrene composites showed high responsiveness to good solvent for the polymer matrix.

Since vapor pressures of organic solvent are quite different under the same condition, to obtain information about the sensitivity of gas sensor in four kinds of organic solvents: toluene, hexane, acetone and water. Their concentrations which were carried out by N₂ gas were calculated by equation (1).

$$PV = nRT \quad (1)$$

Where P is the pressure of the atmosphere, V is the volume of gas vapor, n is the mole of gas vapor, R is the gas constant and T is the temperature at experimental condition. Mole of each gas can be deduced from the difference between the analyst liquid's original weight and its weight subsequent to the release of the N₂ into the analyte reservoir at flow rate of 300 ml/min for 30 min. This enables us to calculate the value of V, the volume of gas vapor. Then the concentration of analyte gas vapor in N₂ gas for 25 sec can be obtained. Table 4.4 shows the concentration of

gas vapors carried out by N₂ at flow rate of 300 ml/min for 25 sec which were exposed in chamber.

Table 4.3 The concentration of organic vapors carried by N₂ gas in the sensor testing

| Organic vapors | Concentration (ppth) |
|----------------|-----------------------|
| Toluene | 3.49×10^1 |
| Hexane | 1.62×10^2 |
| Water | 2.75×10^{-1} |
| Acetone | 2.01×10^{-2} |

The sensitivity of gas sensor to each solvent was calculated according to equation (2) [22].

$$\text{Sensitivity} = \text{Response}/\text{concentration of gas vapor (ppm)} \quad (2)$$

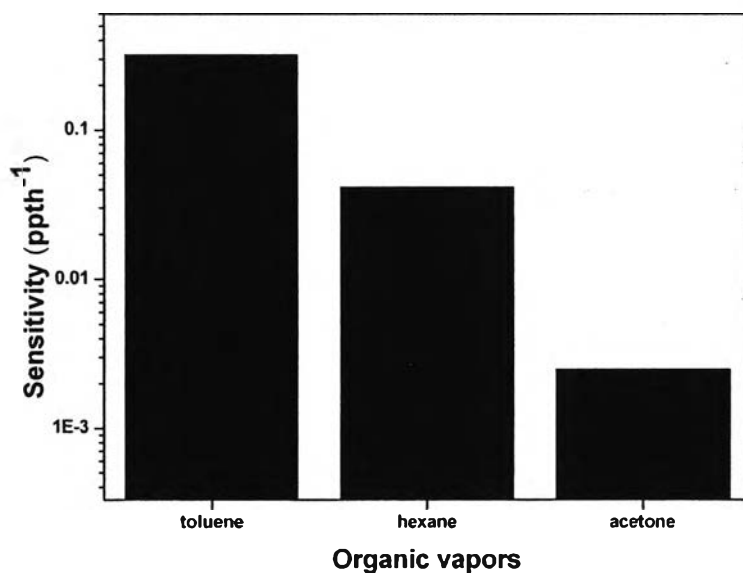


Figure 4.16 Sensitivity of activated CA/PB composite to different kind of organic vapors.

The sensitivity of activated CA/PB composite to various organic vapors is shown in figure 4.16. The activated CA/PB composite which possesses hydrophobic matrix showed sensitivity of $3.20 \times 10^{-1} \text{ ppm}^{-1}$ and $4.14 \times 10^{-2} \text{ ppm}^{-1}$ to non-polar toluene and hexane, respectively. This sensitivity is higher than that of the sensitivity of the composite when it was exposed to higher polar acetone in which the sensitivity of composite was $2.49 \times 10^{-3} \text{ ppm}^{-1}$.

In order to study the response of different polymer matrix to organic vapors, polyvinyl alcohol (PVA) which is hydrophilic nature was chosen for further study. Figure 4.17 shows the relationship between electrical resistance of activated CA/PVA composite and the content of activated CA. The resistance of composite dropped sharply at concentration of activated CA in PVA about 30 wt%. Figure 4.18 shows the response ($dR/R_b = (R_m - R_b)/R_b$) of the composites with various activated CA contents in water vapor. The highest point was observed at 40 %wt of activated CA in PVA. Since it is known that the composites showed highest sensitivity against water vapor at CA contents of 40%. Therefore, subsequent experiment; the measurement of gas sensitivity and electrical response of each gas sensing composite to different organic vapors should be made on the composite with this filler content.

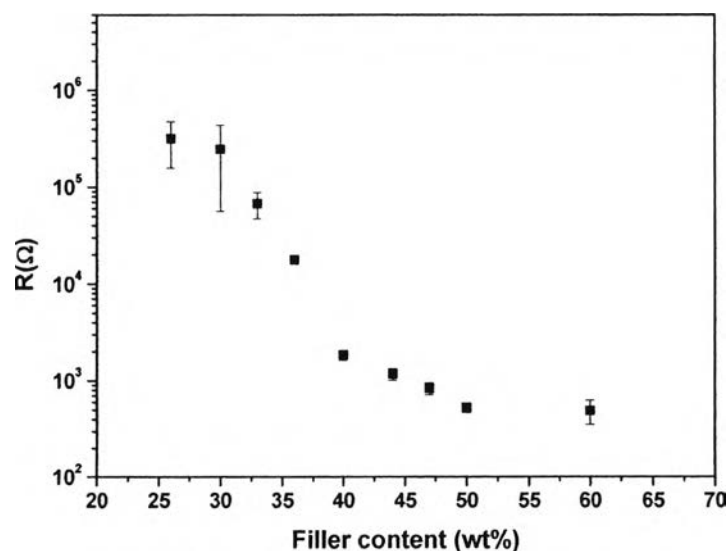


Figure 4.17 Electrical resistance of activated CA/PVA composite with activated CA content.

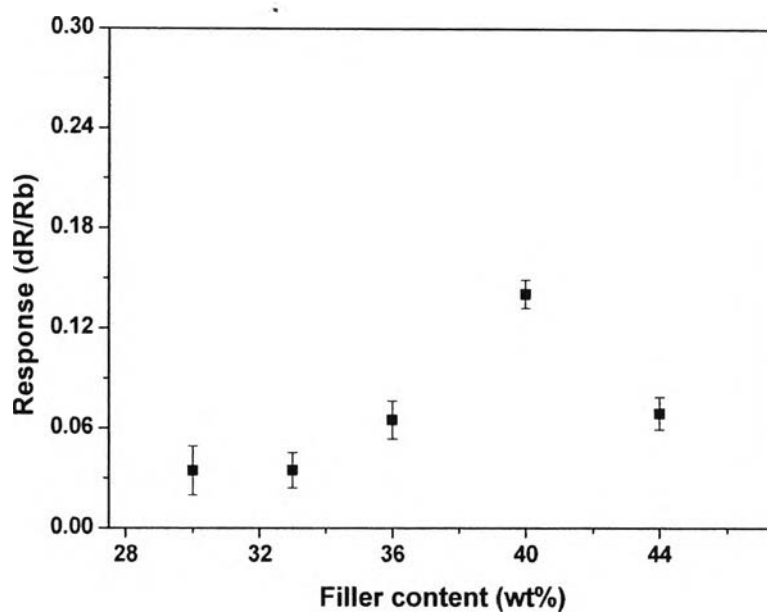


Figure 4.18 Electrical response of activated CA/PVA composite to water vapor with activated CA content.

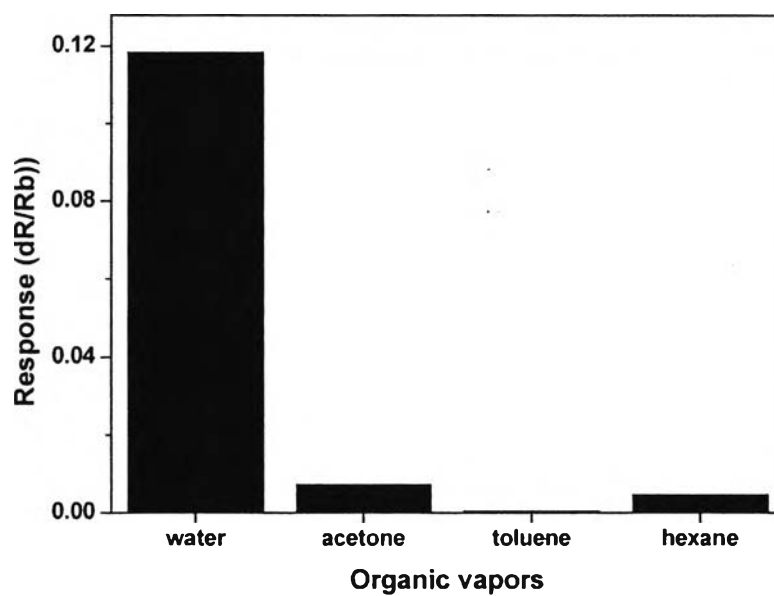


Figure 4.19 Electric response of activated CA/PVA composite on species of organic solvent vapors.

From figure 4.19, clearly the response of the activated CA/PVA composite to high polar water was the highest and moderate to acetone. On the other hand, the composite showed low response to non-polar hexane and no response to non-polar toluene.

The sensitivity of CA/PVA composite to each solvent is shown in figure 4.20. The composite which has hydrophilic PVA as a matrix showed sensitivity of $4.31 \times 10^{-3} \text{ ppm}^{-1}$ to polar water which was higher than the sensitivity of 3.60×10^{-5} and $2.82 \times 10^{-5} \text{ ppm}^{-1}$ when the composite was exposed to lower polar acetone and non-polar hexane, respectively. This result suggested that the good solvent of polymer matrix in the composite caused large swelling in matrix. As a result the gas sensing composite has high sensitivity.

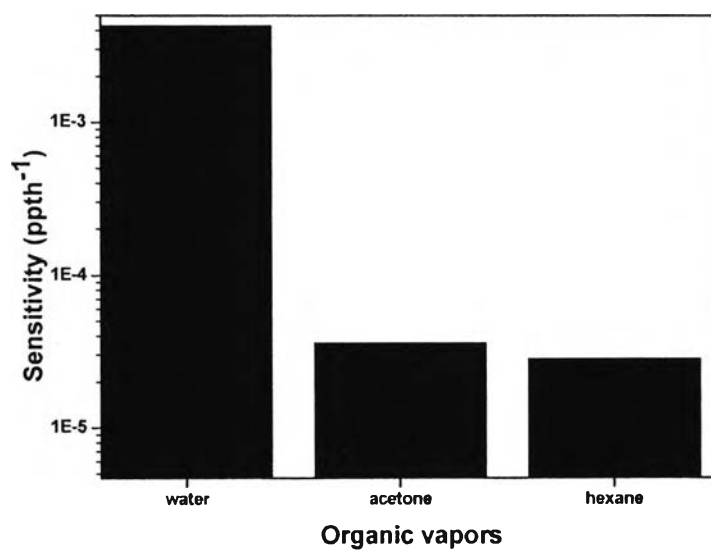


Figure 4.20 Sensitivity of activated CA/PVA composite to different kinds of organic vapors.

4.5 Conclusions

In this study, we have demonstrated the synthesis and characterization of gas sensing materials which were produced by a new type of filler called CA using PVA and PB as matrices. In this work, CA was made from polybenzoxazine based precursor which provides high crosslink density and char yield as 39 %wt to construct CA. In order to have a higher pore volume and surface area, the CA was activated.

On the basis of this study, the following conclusions can be drawn:

1. In the present of activated CA in composite film, the adsorbed gas on composite film was higher comparing to pure polymer film and composite film with graphite as a filler, resulting in the higher responses of this composite upon exposure to organic gas vapors. Further more, the gas sensing material based on activated CA show excellent reproducibility.

2. The response of activated CA/PB films was higher when the composites were exposed to non-polar solvents like toluene and hexane. But their response was low to moderate acetone, and no response with high polar solvent such as water due to the hydrophobic nature of the polymer matrix.

3. The response of activated CA/PVA films were high when the composites were exposed to high polar water was highest and moderate to acetone. On the other hand, the composite showed low response to non-polar hexane and no response to non-polar toluene due to the hydrophobic nature of the polymer matrix.

4.6 Acknowledgements

The authors wish to thank the Petroleum and Petrochemical College, Chulalongkorn University and the Center for Petroleum, Petrochemical, and Advanced Materials for financial support and the National Metal and Materials Technology Center, Thailand for equipments support of this research.

4.7 References

- [1] Agag, T., and Takeichi, T. (2006) High-molecular-weight AB-type benzoxazines as new precursors for high-performance thermosets. Journal of Polymer Science: Part A :Polymer Chemistry, 15, 1878-1888.
- [2] Ardhyanta, H., Wahid, M. W., Sasaki M., Agag, T. Kawauchi, T., Ismail, H., Takeichi, T., (2008) Performance enhancement of polybenzoxazine by hybridization with polysiloxane. Polymer. 49, 4585-4591.
- [3] Burke, W.J., Bishop, J.L., Glennie, E.L.M., and Bauer, W.N. (1965) A new aminoalkylation reaction condensation of phenols with dihydro-1,3-oxazines. Journal of Organic Chemistry, 30, 3423–3427.
- [4] Burl, M.C., Sisk, B.C., Vaid, T.P., Lewis, N.S., (2002) Classification performance of carbon black-polymer composite vapor detector arrays as a function of array size and detector composition, Sensors and Actuators B: Chemical, 87, 130.
- [5] Dong, X.M., Fu, R.W., Zhang, M.Q., Zhang, B., Li, J.R., Rong, M.Z. (2003) Vapor-induced variation in electrical performance of carbon black/poly(methyl methacrylate) composite prepared by polymerization filling. Carbon, 41, 371-374.
- [6] Dunkers, J., and Ishida, H. (1995) Vibrational assignments of 3-alkyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazines in the fingerprint region. Spectrochimica Acta, 51A, 1061-1074.
- [7] Fairén-Jiménez, D., Carrasco-Marín, F., and Moreno-Castilla, C. (2006) Porosity and surface area of monolithic carbon aerogels prepared using alkaline carbonates and organic acids as polymerization catalysts. Carbon, 44, 2301-2307.
- [8] Foster, K.L. Fuerman, R.G., Economy, J., Larson, S.M., and Rood, M.J. (1992) Adsorption characteristics of trace volatile organic compounds in gas

- streams onto activated carbon fibers. American Chemical Society. 4, 1068-1073.
- [9] Ghosh, N.N., Kiskan, B., and Yagci, Y., (2007) Polybenzoxazines-new high performance thermosetting resins: Synthesis and properties. Progress in Polymer Science, 32, 1344-1391.
- [10] Horikawa, T., Hayashi, J., and Muroyama K. (2004) Size control and characterization of spherical carbon aerogel particles from resorcinol-formaldehyde resin. Carbon, 42, 169-175.
- [11] Holly, F.W., and Cope, A.C. (1994) Condensation products of aldehydes and ketones with o-aminobenzyl alcohol and o-hydroxybenzylamine. Journal of the American Chemical Society, 66, 1875-1879.
- [12] Hrubesh, L.W., Coronado P.R., and Satcher Jr., J.H. (2001) Solvent removal from water with hydrophobic aerogels. Journal of Non-Crystalline Solids, 285,328-332.
- [13] Ishida, H. (1998) Versatile Phenolic stands up to the heat. Modern Plastics International, 113(5), 219-220.
- [14] Ishida, H., and Sanders D.P., (2000) Regioselectivity and network structure of difunctional alkyl-substituted aromatic amine-based polybenzoxazines. Macromolecule, 33, 8149-8157.
- [15] Iwata, H., Nakanoya, T., Motohashi, H., Chen, J., Yamauchi, T., and Tsubokawa, N. (2006) Novel gas and contamination sensor materials from polyamide-block-poly(ethylene oxide)-grafted carbon black. Sensors and Actuators B, 113, 875-882.
- [16] Jiang, L., Jun, H., Hoh, Y., Lim, J., Lee, D., and Huh, J., (2005) Sensing characteristics of polypyrrole-poly(vinyl alcohol) methanol sensors prepared by in situ vapor state polymerization. Sensors and Actuators B. 105 132-137.

- [17] Kantor, Y. (1986) Three-dimensional percolation with removed lines of sites. The American Physical Society, 33, 3522-3525.
- [18] Knite, M., Ozols, K., Sakale, G., and Teteris, V. (2007) Polyisoprene and high structure carbon nanoparticle composite for sensing organic solvent vapours. Sensors and Actuators:B, 126, 209-213.
- [19] Li, J.R., Xu, J.R., Zhang, M.Q., and Rong, M.Z. (2003) Carbon black/polystyrene composites as candidates for gas sensing materials. Carbon. 41, 2353-2360.
- [20] Lillo-Rodenas, M.A., Fletcher, A.J., and Thomas, K.M., (2006) Competitive adsorption of a benzene-toluene mixture on activated carbon at low concentration. Carbon. 44, 1455-1463.
- [21] Liu, Y.L., Yu, J.M., and Chou, C.I. (2004) Preparation and properties of novel benzoxazine and polybenzoxazine with maleimide groups. Journal of Polymer Science: Part A :Polymer Chemistry, 42, 5954-5963.
- [22] Li, J., Lu, Y., Ye, Qi, Cinke, M., Han, J., and Meyyappan, M. (2003) Carbon nanotube sensors for gas and organic vapor detection. Nano Letters, 3, 929-933.
- [23] Li, Y., Hong, L., Chen, Y., Wang, H., Lu, Xin., and Yang, M. (2007) Poly(4-vinylpyridine)/carbon black composite as a humidity sensor. Sensors and Actuators B, 123, 554-559.
- [24] Lorjai, P. Chaisuwan, T. Sujitra, W. (2009) Preparation of polybenzoxazine foam and its transformation to carbon foam. Materials Science and Engineering A. 527, 77-84.
- [25] Lorjai, P. Chaisuwan, T. Sujitra, W. (2009) Porous structure of polybenzoxazine based organic aerogel prepared by sol-gel process and their carbon aerogels. Journal of Sol-Gel Science and Technology, 52, 56-64.

- [26] Lorjai, P. Chaisuwan, T. Sujitra, W. Significant Enhancement of Thermal Stability for the Non-oxidative Thermal Degradation of Bisphenol-A/aniline Based Polybenzoxazine Aerogel. submitted.
- [27] Low, H.Y., and Ishida, H. (1999) An investigation of the thermal and thermo-oxidative Degradation of Polybenzoxazines with a reactive functional group. Journal of Polymer Science: Part A : Polymer physics, 37, 647-659.
- [28] Liu, Ning., Zhang, S., Fu, R., Dresselhaus, M.S., and Dresselhaus, G. (2006) Carbon aerogel spheres prepared via alcohol supercritical drying. Carbon, 44, 2430-2436.
- [29] Moreno-Castilla, C., and Maldonldo-Hódar, F.J. (2005) Carbon aerogels for catalysis applications: An overview. Carbon, 43, 455-465.
- [30] Ning, X., and Ishida, H. (1994) Phenolic materials via ring-opening polymerization synthesis and characterization of bisphenol-a based benzoxazines and their polymers. Journal of Polymer Science, 32, 1121-1129.
- [31] Pekala, P.W., Farmer, J.C., Alviso, C.T., Tran, T.D., Mayer, S.T., Miller, J.M., and Dunn, B. (1998) Carbon aerogels for electrochemical applications. Journal of Non-Crystalline Solids. 225, 74-80.
- [32] Pekala, R.W. (1989) Organic aerogels from the polycondensation of resorcinol with formaldehyde. Journal of Material Science, 24, 3221-3227.
- [33] Pérez-Caballero, F., Peikolainen, A.L., and Koel, M. (2008) Preparation of nano structured carbon materials. Proceedings of the Estonian Academy of Sciences, 57(1), 48-53.
- [34] Prabhakaran, K., Singh, P.K., Gokhale, N.M., and Sharma, S.C. (2007) Processing of sucrose to low density carbon foams. Journal of Master Science, 42, 3894-3900.

- [35] Reghunadhan Nair, C.P. (2004) Advances in addition-cure phenolic resins. Progress in Polymer Science, 29, 401-408.
- [36] Reynolds, G.A.M., Fung, A.W.P., Wang, Z.H., Wang, Z.H., Dresselhaus, M.S., Pekala, R.W., (1995) The effects of external conditions on the internal structure of carbon aerogels. Journal of Non-Crystalline Solid, 188, 27-33.
- [37] Shen, J., Wang, J. Zhai, J., Guo, Y., Wu, G., Zhou, B., and Ni, X. (2004) Carbon Aerogel films synthesized at ambient conditions. Journal of Sol-Gel Science and Technology, 31, 209-213.
- [38] Shimizu, Y., and Egashira, M. (1999) Basic aspects and challenges of semiconductor gas sensors, MRS Bull, 24, 18-24.
- [39] Takeichi, T., Kano, T., and Agag, T. (2005) Synthesis and thermal cure of high molecular weight polybenzoxazine precursors and the properties of the thermosets. Polymer, 46, 12172-12180.
- [40] Wu, D., and Fu, R. (2005) Fabrication and physical properties of organic and carbon aerogel derived from phenol and furfural. Journal of Porous Materials, 12, 311-316.
- [41] Wu, D., Fu, R., Zhang, S., Dresselhaus, M.S., and Dresselhaus, G. (2004) Preparation of low-density carbon aerogels by ambient pressure drying. Carbon, 42, 2033-2039.
- [42] Zhang, B., Fong, X., Song, W., Wu, F., Fu, R., Zhao, B. and Zhang, M. (2008) Electrical response and adsorption performance of novel composites from polystyrene filled with carbon aerogel in organic vapors. Sensors and Actuators B, 132, 60-66.
- [43] Zhang, B., Fu, R., Zhang, M., Dong, X., Lan, P., and Qui, J. (2005) Preparation and characterization of gas-sensitive composites from multi-walled carbon nanotubes/polystyrene. Sensors and Actuators B, 109, 323-328.

- [44] Zhang, B., Fu, R., Zhang, M., Dong, X., Wang, L., and Pittman Jr., C.U. (2006) Gas sensitive vapor grown carbon nanofiber/polystyrene sensors. Materials Research Bulletin, 41, 553-562.
- [45] Zhang, R., Lu Y., Zhang L., Liang, X., Wu, G., and Ling, L. (2002) Monolithic carbon aerogels from sol-gel polymerization of phenolic resins and methylated melamine. Carbon, 41, 1660-1663.
- [46] Zhang, S.Q., Wang, J. Shen, J., Deng, Z.S., Lai, Z.Q. , Zhou, B. , Attia, S.M., and Chen, L.Y. (1999) Investigation of the adsorption character of carbon aerogels. Nanostructured Materials, 11, 375-381.
- [47] Zhu, Y., Hu, H., Li, W.C., and Zhang X. (2006) Cresol-formaldehyde based carbon aerogel as electrode material for electrochemical capacitor. Journal of Power Sources, 162, 738-742.