CHAPTER IV
HIGH PERFORMANCE HYBRID COMPOSITE CONDUCTIVE FILM: DEVELOPMENT TOWARDS SMART MATERIALS FOR GAS SENSOR APPLICATIONS

4.1 Abstract

Polymer composite thin film used for gas sensor applications with a new type of conductive filler called "carbon aerogel" in a polydimethylsiloxane (PDMS) matrix was fabricated and characterized. The resistivity changes of the composite films when exposed to different analytes, viz. tetrahydrofuran, acetone and methanol, were investigated. It is found that different types of polybenzoxazines, used as organic precursors for carbon aerogel preparation have no significant effect on the response of the sensor to the analytes. Compared with commercially available graphite/PDMS composites, the carbon aerogel/PDMS composites show better gas responsivity. By mixing only 8 wt% of our carbon aerogel, the percolation threshold is obtained while the graphite, normally used as the conductive filler, is required as much as 30 wt% to attain the percolation threshold.

Keywords: Gas sensors; Composite; Conductive filler; PDMS; Carbon aerogel; Polybenzoxazine

4.2 Introduction

Gas sensors made from polymer composite thin film have already shown their potential ability as sensing elements in commercial electronic noses [1, 2]. The simplicity of signal transduction and the low material cost of the detector make them attractive. The principle of composite polymer vapor sensors is basically to exploit the gas absorption properties of an insulating polymer whose electric properties are modulated by the conductive filler. The response of the sensor to an analyst is measured as a change in the resistance of the sensor. As the analyst diffuses into the polymer composite, the polymer swells, causing the dispersed conductive fillers to move farther apart from each other, resulting in a decrease of the conductivity or an increase of the resistance which can be detected by the sensor [3–5].

In this study we fabricated and characterized gas sensors with a new type of filler called "carbon aerogel" from polybenzoxazine based precursor using polydimethylsiloxane (PDMS) as the polymer matrix. Carbon aerogel (CA) is a novel nano-sized porous carbon material with highly cross-linked structure. They have been applied in many aspects, such as electrode materials for supercarpacitors and rechargeable batteries, adsorbents, chromatographic packing, advanced catalyst support, environmental protection, and so on, due to their properties of low mass density, a large amount of mesopores, high surface area and high-electrical conductivity [6–13].

Generally, carbon aerogel can act as both conductive filler and molecular sieve that allows certain type of gas to pass through the carbon aerogel containing thin film [14]. Carbon aerogel has greater advantages over the activated carbon because the porous structure of carbon aerogel can be tailored for desired applications [15]. On the other hand, carbon nanotube is expensive; hence, the filler is not appropriate for commercial applications at the moment [16, 17].

4.3 Experimental

4.3.1 Materials

Bisphenol-A (BPA) was purchased from Aldrich, Germany. Formaldehyde (analytical grade) was purchased from Merck, Germany. Para-formaldehyde (commercial grade) was purchased from BDH Laboratory Supplies.

Triethylenetetramine (TETA) was purchased from Fluka, Switzerland. Aniline (commercial grade) was purchased from Panreac Quimica SA Company. Sylgard 184 Silicone Elastomer Kit (PDMS) was purchased from Dow corning. Graphite (commercial grade) was purchased from Merck. Xylene (commercial grade) was purchased from Carlo Erba Reagenti. 1,4-Dioxane (analytical grade), acetone (commercial grade), tetrahydrofuran (analytical grade) and methanol (analytical grade) were purchased from Lab-scan, Thailand.

4.3.2 Measurements

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. ^{1}H 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 N_2 atmosphere with a flow rate of 10 ml/min. TG-DTA curve was collected on a Mettler Toledo TGA/SDTA 851e 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 N_2 flow of 50 mL/min. Scanning electron microscope, JEOL/JSM model 5200, was used to observe the surface morphology of polybenzoxazine-based aerogel and carbon aerogel. The specimens were coated with gold under vacuum before observation. Transmission electron microscope, JEOL model JEM-2100, was used to observe the porous structure of carbon aerogel. The samples were prepared using the ultramicrotome. N_2 adsorption-desorption isotherms were obtained at -196°C on a Quantachrome Autosorb-1. Samples were degassed at 250°C during 12 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 resistivity of carbon aerogel-PDMS and graphite-PDMS composite films were measured using KEITHLEY 8009 electrometer to find the percolation threshold.

4.3.3 Methodology

4.3.3.1 Preparation of Carbon Aerogel Derived from Benzoxazine Precursor

Polybenzozaxine precursors were synthesized by dissolving bisphenol-A (4.52 g) in dioxane (20 ml) with stirring continuously, followed by adding formaldehyde (6.48 g) and triethylenetetramine, respectively. The mixture was stirred continuously while the reaction was cooled with an ice bath for 1 hr until the homogeneous viscous liquid was obtained. The mole ratio of bisphenol-A: formaldehyde:diamine was 1:4:1. The precursors were then heated in an oven at 80°C for 72 hr in a closed system to evaporate excess solvent, followed by fully curring oranic aerogel by step cure in an oven at 140°, 160°, 180°C for 2 hr at each temperature and 200°C for 3 hr. After step-curring, carbon aerogels were prepared by pyrolysis of the organic aerogels in a quartz reactor. The pyrolysis took place in a furnace under nitrogen flow at 700 cm^3/min using the following ramp cycle: 30° to 250°C for 60 min, 250° to 600°C for 300 min, 600° to 800°C for 60 min and held at 800°C for 60 min. Then the furnace was cooled down to room temperature under nitrogen atmosphere.
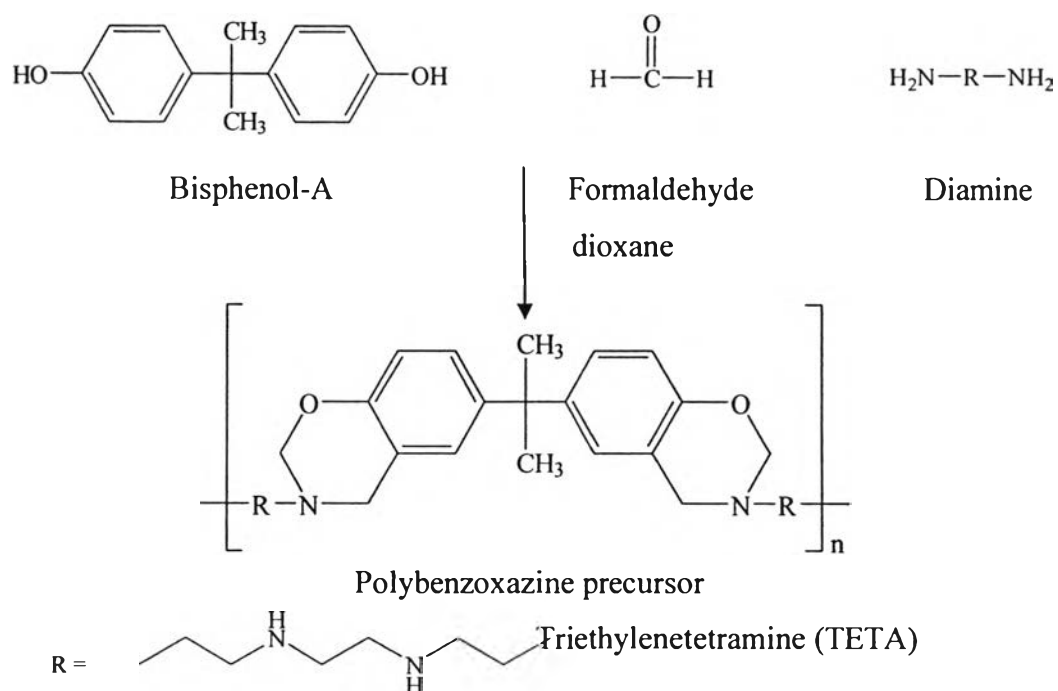

Bisphenol-A   Formaldehyde   Diamine
                     dioxane

Polybenzoxazine precursor

R =   Triethylenetetramine (TETA)

Figure4.1 Preparation of polybenzoxazine precursor.

    4.3.3.2 Synthesis of Carbon Aerogel from Polybenzoxazine Prepared from Monomer

        The benzoxazine monomers were synthesized from bisphenol A, aniline, and paraformaldehyde at a 1:2:4 molar ratio were mixed together and heated at 110°C for 1 hr until the mixture became transparent pale yellow color. Benzoxazine solutions were prepared from 40 wt% benzoxazine monomer in xylene solvent. The mixtures were transferred into vials and sealed before placing in an oven set at 130°C for 96 hr for the pre-curing process. The aerogels were step-cured in an oven at 160°, 180°C for an hour at each temperature and 200°C for 2 hr, respectively. After step-curing, carbon aerogels were prepared by pyrolysis of the organic aerogels in a quartz reactor. The pyrolysis took place in a furnace under nitrogen flow at 500 cm^3/min using the following ramp cycle: 30° to 250°C for 60 min, 250° to 600°C for 300 min, 600° to 800°C for 60 min and held at 800°C for 60 min [18].

    4.3.3.3 Characteristics of Polybenzoxazine and Carbon Aerogel Derived from Polybenzoxazine

        Structural characteristics of polybenzoxazine-based aerogel were investigated using FTIR and ^{1}H-NMR. Thermal properties were measured using DSC and TG/DTA. Morphology was observed by SEM. Porous structure of polybenzoxazine-based aerogel was characterized by TEM. Furthermore, surface area and pore distribution were measured using SAA.

    4.3.3.4 Preparation of Polydimethylsiloxane Composite Conductive Films

        Polydimethylsiloxane composite conductive films were prepared by mixing three types of conductive fillers; carbon aerogel derived from Ba-TETA (abbreviated as CA_{TETA}), carbon aerogel derived from BA-a (abbreviated as CA_{Ba}) and graphite with polydimethylsiloxane at various concentrations. The mixtures were then stirred continuously for 10 min until the conductive fillers are well dispersed. The mixtures were then cast on the glass plates with the film thickness of 1 mm. Finally, the films were kept at 80°C for 24 hr, yielding PDMS conductive composite films.

4.3.3.5 <u>Electrical Response Measurements of Polydimethylsiloxane</u>
<u>Composite Conductive Films</u>

Electrical resistivities of CA_{TETA}/PDMS, CA_{Ba}/PDMS and graphite/PDMS composite films were measured using KEITHLEY 8009 electrometer to determine the percolation threshold. Adsorption measurements of composite films in organic vapors were carried out as follows: firstly, the samples were kept in a vacuum cavity before flowing saturated organic vapor, produced directly from the organic solvent located at the bottom of a seal gas vessel, at a temperature of 35°C. The composite films weighing approximately 10 mg were used to evaluate the adsorption behavior of the sample when exposed to several organic vapors. The adsorption quantity (Q_t) of the sample was determined from $Q_t = \Delta m/m_0$, where Δm is the mass increment of the sample in vapors, and m_0 is the original mass.

4.4 Results and Discussion

Unlike the traditional method requiring solvent and long reaction, as first reported by Takeichi *et al.* [19], our polybenzoxazine precursors were prepared by so called "quasi-solventless" method which is our first recovery. Dioxane was used in our method to help the mixing of all reactants to produce polybenzoxazine precursor. Both CA_{TETA} and CA_{Ba} were studied to compare their performances by making as films to investigate their gas sensor capability.

4.4.1 Characterization of Polybenzoxazine-based Aerogel

The chemical structure of benzoxazine precursor prepared from bisphenol-A, formaldehyde and TETA was confirmed using FT-IR and ^{1}H-NMR, as shown in Figures 4.2 and 4.3
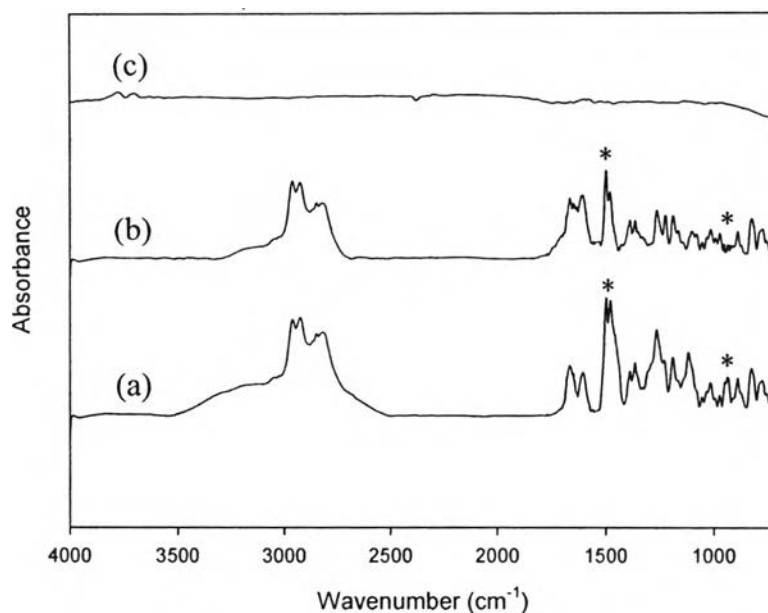
Figure 4.2 FTIR spectra of polybenzoxazine precursor (a), after fully-cured (b), after pyrolysis yielding carbon aerogel (c).

The characteristic absorption bands of the asymmetric stretching of C–O–C (1252 cm⁻¹) and C–N–C (1190 cm⁻¹) were observed. The band at 1351 cm⁻¹ represents CH₂ wagging of oxazine functionality. Additionally, the characteristic absorption bands assigned to the stretching of trisubstituted benzene ring and the out of plane bending vibrations of C–H were detected at 1524 cm⁻¹ and 944 cm⁻¹, respectively. These results were well agreed with the results observed by Takeichi and coworkers (2005) [19].

It was easy to observe the obvious change at 920–950 cm⁻¹ due to the chemical transformation from the benzoxazine precursor to fully-cured aerogel. The characteristic absorption bands of the fully-cured polybenzoxazine disappeared. Moreover, after pyrolysis, the FT-IR spectrum is rather flat due to the loss of all organic moieties. In 2005 Takeichi and coworker [19] also observed the disappearance of this peak by the end of the curing process, suggesting the completion of the ring-opening polymerization.

From the ¹H NMR spectrum, the characteristic peaks assigning to the methylene protons of O–CH₂–N and Ar–CH₂–N in the ring-closed benzoxazine

structure were observed at 4.76 and 3.89 ppm, respectively. The methylene protons of the ring-opened benzoxazine, Ar–CH_2–N; were also observed at 3.68 ppm. The methyl protons of bisphenol-A showed the peaks at 1.55 ppm. The result comfirms that benzoxazine precursor was obtained. The results are in agreement with those of Takeichi and coworkers [19], showing the characteristic peaks of polybenzoxazine precursors derived from Bisphenol-A and ethylene diamine (B-eda), assigning to the methylene protons of O–CH_2–N and Ar–CH_2–N in the oxazine ring observed at 4.86 and 3.97 ppm, respectively. The methyl protons of their bisphenol-A showed the peaks at 1.58 ppm.
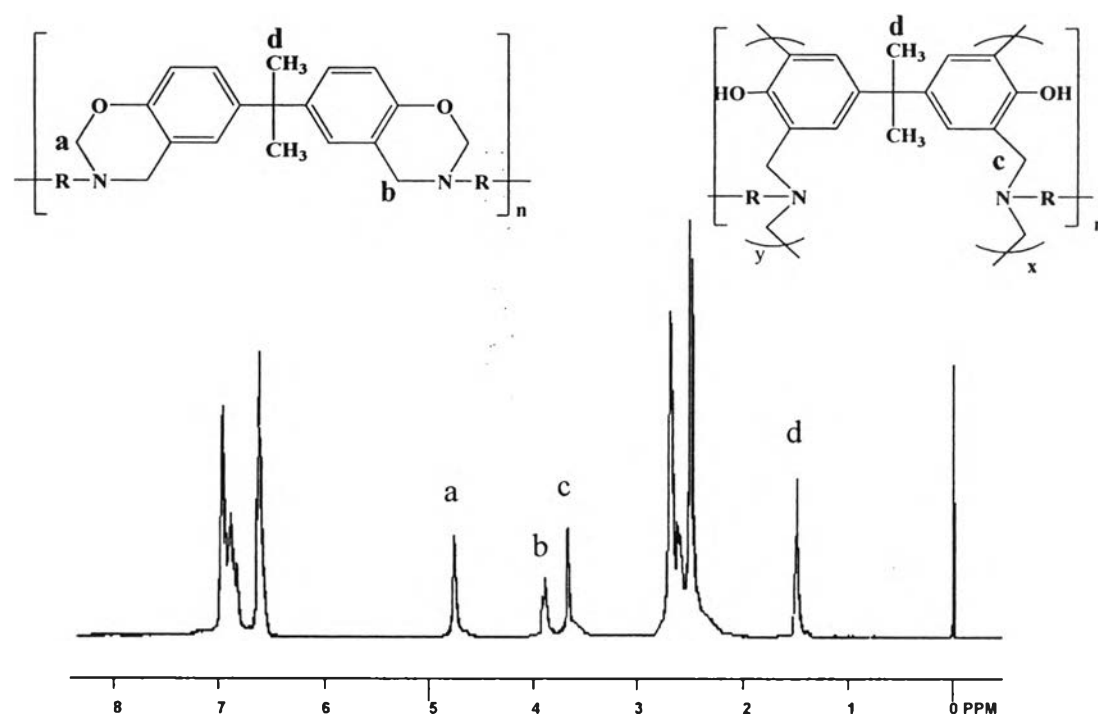

Figure 4.3 ^{1}H-NMR spectrum of partially cured polybenzoxazine.

The DSC thermogram of partially-cured benzoxazine precursor shows the exotherm peak starting at 180°C with a maximum at 245°C attributed to the benzoxazine ring-opening polymerization, as shown in Figure 4.4. After the precursor was fully cured, the exothermal peak disappeared, implying that benzoxazine aerogel was completely cured. Takeichi and coworkers (2005) [19] also found that the exotherm peak of high molecular weight polybenzoxazine precursors

derived from Bisphenol-A and methylene diamine (B-mda) was started at 191°C with a maximum at 236°C, and the amount of exotherm decreased with temperature. Moreover, the exotherm completely disappeared after curing at 240°C, suggesting that the oxazine ring was completely opened.
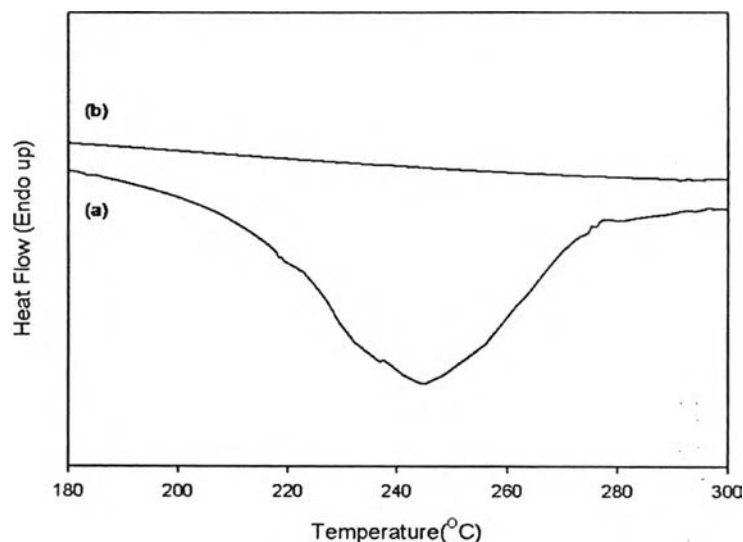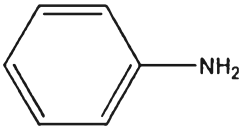

Figure 4.4 DSC thermograms of partially-cured benzoxazine precursor (a) and fully-cured polybenzoxazine (b).

The thermal stability of polybenzoxazine was investigated by TGA. The values $T_{-5\%}$ and char yield are summarized in Table 4.1. PB-a has the highest thermal stability, as expected, because of the high aromatic content, but poly (PB-teta) shows somewhat higher char yield than poly (PB-a) owing to nitrogen groups containing in polymer chain which enable more H-bonding [19].

The TGA thermogram of poly (BA-TETA) is presented in Figure 4.5. It began to decompose at 250°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. Su *et al.* [20] also identified the decomposition of polybenzoxazines through TGA technique, and found that the decomposition was from the degradation of the crosslinking between aliphatic and amines.

Table 4.1 Thermal properties of polybenzoxazines

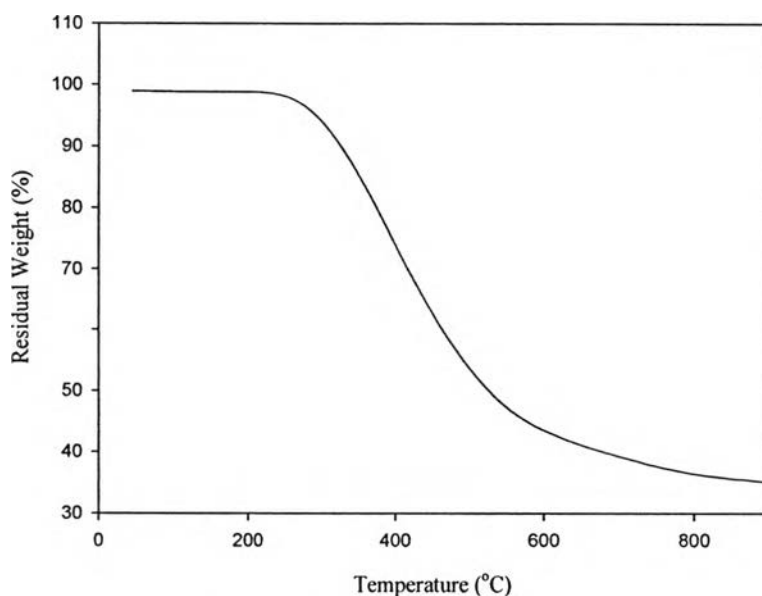| Material	Type of amine	$T_{-5\%}$ (°C)	Char yield (%)
PB-a	[benzene ring]—NH₂	330	25
PB-TETA	NH₂—/\—NH—/\—NH—/\—NH₂	293	37

[a] At 800°C.

Figure 4.5 TGA thermogram during the pyrolysis of the polybenzoxazine.

Figure 4.6 shows SEM micrographs of organic aerogel and carbon aerogel. The porous structure was obtained from the removal of the solvent. According to the structure of the organic aerogel, the solid phase presents a smooth continuous polymer network incorporated with open macropores. However, in case of the carbon

aerogel, the denser porous structure of three dimension carbon network containing continuous open macropores was obtained.
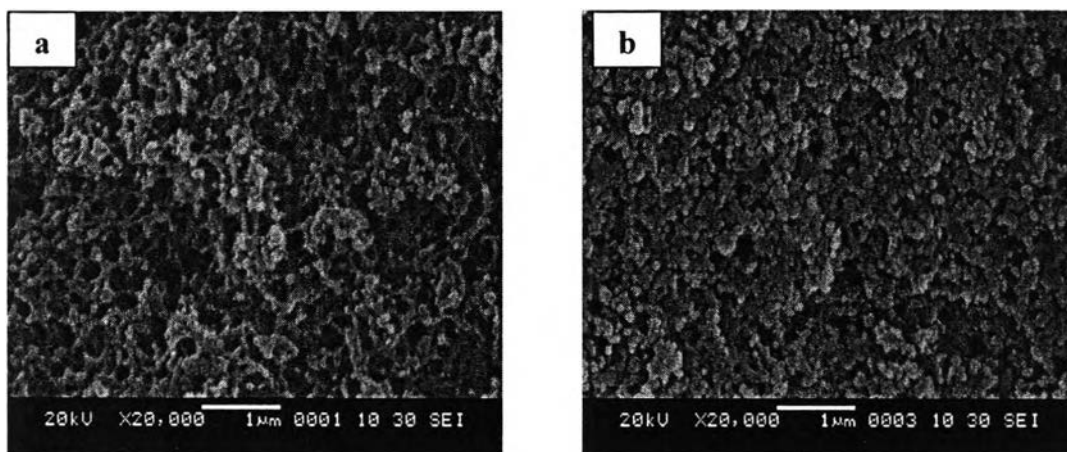

Figure 4.6 SEM micrographs of organic aerogel (a) and carbon aerogel (b).

Kim *et al.* [21] showed that the pore distribution of the resorcinol/formaldehyde resin aerogel was broadly spread with diameters ranging from nanopores to macropores. In our case, TEM observation indicates that carbon aerogels have a three-dimensional nano-network, and the pore size was less than 10 nm, as shown in Figure 4.7.
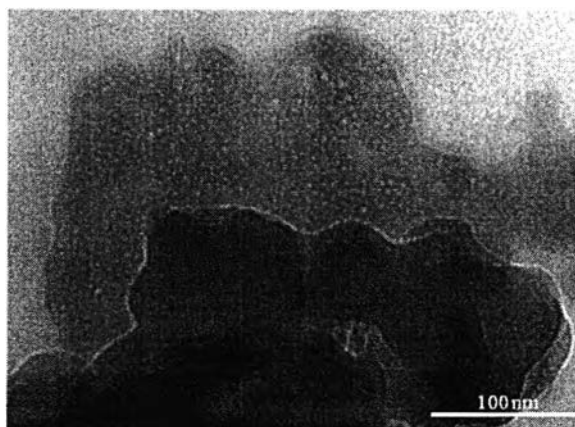

Figure 4.7 TEM photograph of the carbon aerogel.

4.4.2 Electrical Response Characterization of Conductive Composite Films

The electrical variation of composite films, namely, filler type and content, organic gas, when exposed to organic vapors was studied. The gas sensitivity of polymer composites can be determined from their electrical variation in organic vapors. Hence, the electrical conductivities of $CA_{TETA}/PDMS$, $CA_{Ba}/PDMS$ and graphite/PDMS were measured.
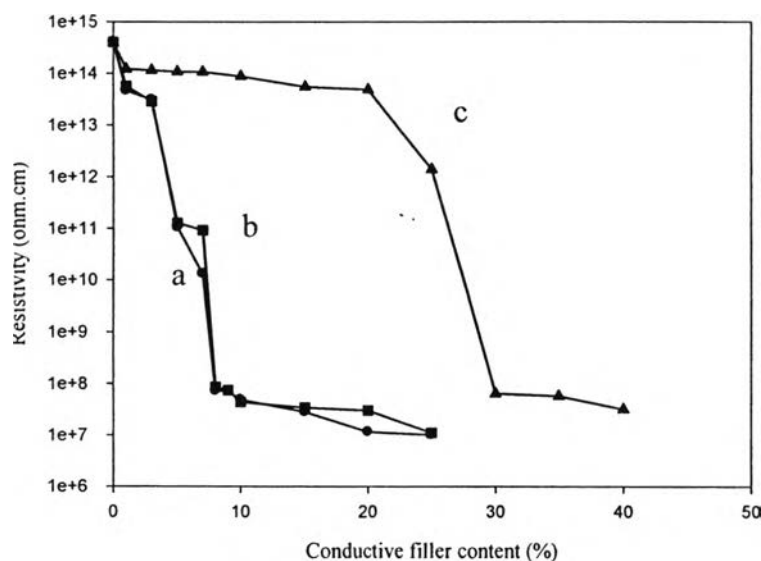

Figure 4.8 The electrical percolation thresholds of different types of conductive filler in PDMS matrix: $CA_{TETA}/PDMS$ (a), $CA_{Ba}/PDMS$ (b) and graphite/PDMS (c).

Figure 4.8 shows the electrical percolation thresholds of different conductive filler types in PDMS matrix. We found that different types of polybenzoxazines used as organic precursors for carbon aerogel preparation showed insignificant effect on the electrical percolation threshold. Moreover, only 8 wt% of carbon aerogel was required to attain the threshold, indicating that carbon aerogel, a mesoporous material with high surface area, provides excellent conductivity. As a result, the conductive pathway can be easily built up at relatively low carbon aerogel content. Zhang *et al.* [22] also found similar results, except that carbon aerogel determined in their work was synthesized from resorcinol formaldehyde, and needed upto 17.5 wt% to obtain the threshold. Nevertheless, in case of commercially available graphite, known as a good conductivity source, the content as much as 30 wt% was required in order for

the graphite-filled composite films to reach the threshold. However, the percolation threshold is depended on both filler type and polymer matrix, as described by Kozlowski *et al.* [23].

The physical characteristics in Table 4.2 of the prepared carbon aerogel indicate a mesoporous material with higher surface area when compared with graphite particles. Hence, it is possible for CA_{TETA}/PDMS and CA_{Ba}/PDMS composites to adsorp more organic vapor than graphite/PDMS composites. Figure 4.9 A-C describes the adsorption behaviors of each conductive film system when exposed to saturated THF, acetone, and methanol vapors, respectively.

Table 4.2 The physical characteristics of carbon aerogels and graphite used as conductive fillers

Material	Morphology type	Surface area (m^2/g)	Average pore size (nm)	Pore volume (cc /g)
Ba-TETA	powder	368	3.6	0.3
Ba-A	powder	391	2.4	0.3
Graphite	powder	140	-	-

The adsorption quantities of both CA/PDMS composite systems are higher than that of graphite/PDMS composite. According to the equation shown below, experimentally, adsorbing more organic vapors created bigger swelling of the matrix, causing thinner sample, resulting in higher increment of resistance of the composite.

$$\rho = \frac{22.9}{T} \times \frac{V}{I}$$

Where ρ is resistivity (ohm.cm), V is voltage, I is current, and T is the material thickness (cm).

Therefore, carbon aerogel is better conductive filler than graphite to fabricate the gas sensitive polymer composite. These results are similar to the work done by Zhang *et al.* [22]. They showed that the adsorption of carbon aerogel in

organic vapors was higher than that of carbon black owing to the porosity and higher surface area of carbon aerogel.
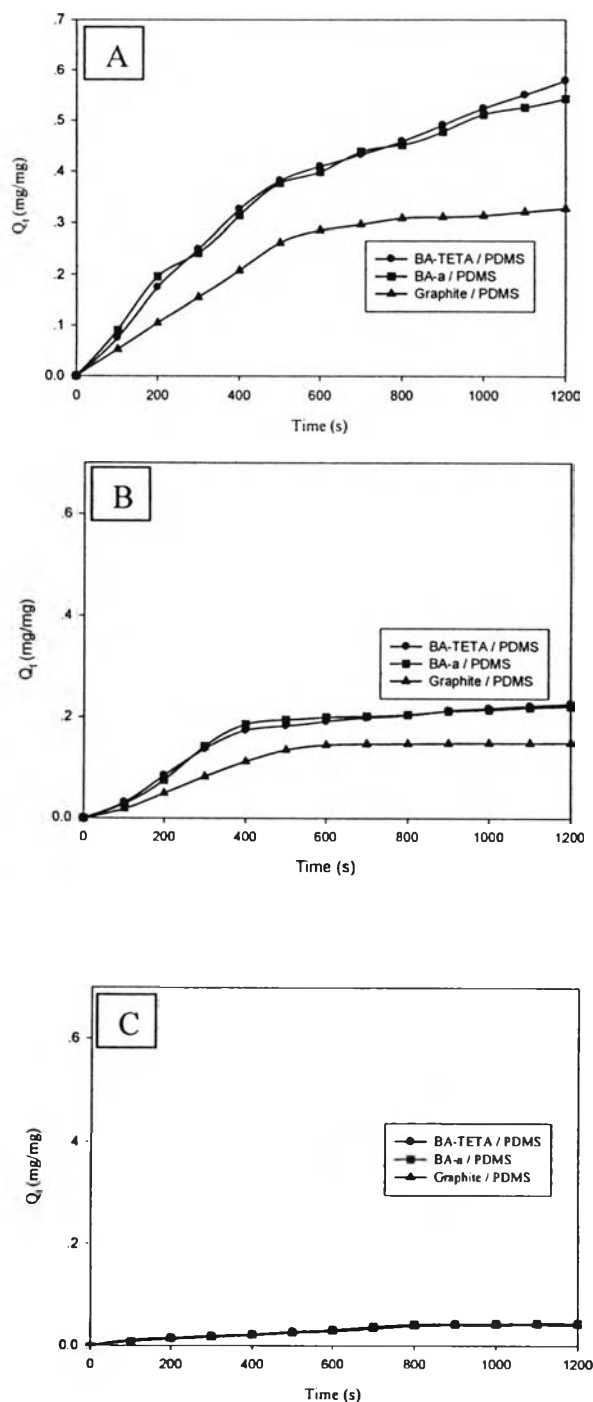

Figure 4.9 The dynamic adsorption curves of CA_{TETA}/PDMS, CA_{Ba}/PDMS and graphite/PDMS in saturated THF (A), acetone (B), and methanol (C) vapors.

Table 4.3 The solubility parameter of various solvents

Solvent	Solubility parameter ($cal^{1/2} cm^{-3/2}$)
Poly(dimethylsiloxane)	7.3
Tetrahydrofuran (THF)	9.3
Acetone	9.9
Methanol	14.5

The adsorption quantity based on different organic vapors is in the following order: THF > Acetone > Methanol. The solubility parameter of THF is similar to that of PDMS, as shown in Table 4.3. As a result, THF can be dissolved more easily into PDMS films when comparing with acetone and methanol. Zhang *et al.* [22] determined the adsorption quantity of polystyrene matrix in various organic vapors, and found the dependence of the adsorption quantity on the solubility parameters of both polystyrene and vapors.

To investigate the performance of different conductive fillers for sensor, the sensitivity is necessary to be studied. The sensitivity of the sensor is defined by $\Delta R/R$, where ΔR is the resistivity of the film when exposed to the analyte for 5 min minus the initial resistivity. R is the initial resistivity.

The average data of the $\Delta R/R$ for different gases with different conductive fillers are shown in Figure 4.13. It is revealed that different types of polybenzoxazine used as organic precursor (BA-TETA and BA-a) have no significant effect on the response of the sensor to the analytes. Both CA/PDMS composites showed good resistivity response to many organic vapors such as THF, acetone and methanol. The comparison between the CA/PDMS and graphite/PDMS composites also clearly demonstrates that the former possesses larger resistivity response than the latter.
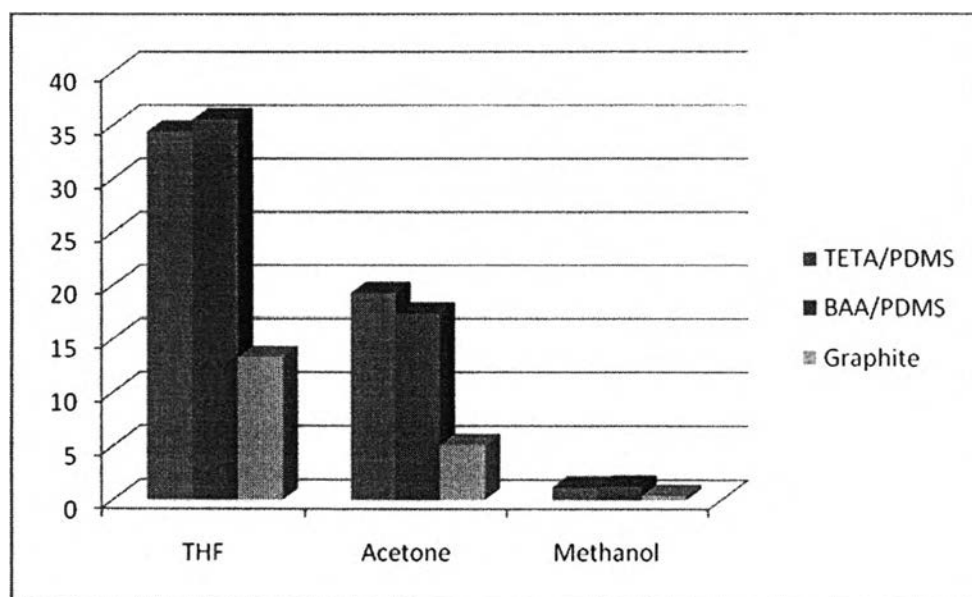
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Figure 4.10 The percentage change of resistivity of each sensor to THF, acetone and methanol

4.5 Conclusions

Different types of polybenzoxazine used as organic precursors for carbon aerogel applications have no significant effect on the response of the sensor to the analysts. By mixing only 8 wt% of the carbon aerogel, the percolation threshold was obtained, showing that carbon aerogel is a mesoporous material with excellent conductivity and high surface area. Both CA/PDMS composites were able to produce large resistivity responsivity against various organic vapors because of adsorbing more organic vapors.

4.6 Acknowledgements

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4.7 References

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