CHAPTER IV
DEVELOPMENT OF NOVEL CARBON FOAM DERIVED FROM PHENOL-ETHYLENEDIAMINE BENZOXAZINE PRECURSOR

4.1 Astract

Carbon foam is prepared by using phenol-ethylenediamine benzoxazine as an organic precursor and azodicarbonamide (AZD) as a blowing agent. The effects of AZD concentration and polymerization rate on the porous structure and density of phenol-ethylenediamine benzoxazine have been investigated. From DSC results, it has been found that the exothermic peaks of organic foam have shifted to lower temperature when the AZD concentration is increased. It is believed that AZD also acts as a catalyst for benzoxazine ring-opening polymerization.

Keyword: phenol-ethylenediamine, benzoxazine, organic foam, azodicarbonamide, AZD, blowing agent, catalyst, carbon foam

4.2 Introduction

Carbon foam which is a porous and sponge-like carbon material has recently attracted great attention because of their light weight and potential tailorability of their physical properties [1-5]. The applications of carbon foams include thermal management, electrodes, catalyst supports and filters, owing to their novel features, such as adjustable thermal conductivity and electrical conductivity, high porosity, microwave absorption, supercapacitors, low thermal expansion coefficient, high-temperature tolerance, etc [5-7].

Carbon foam has been successfully produced by using different types of precursors including thermosetting polymers, coal, polyimides, olive stones, pitches, etc [3,5,8,9,10]. Benzoxazines can be thermally activated and do not require acid or base catalysts for ring-opening polymerization [11]. The unique chemistry provides tremendous opportunities for molecular design and offers a number of inherent processing benefit including low melt viscosity, no volatile release upon curing, rapid property development, and low overall shrinkage [11]. Benzoxazine monomers are readily synthesized, either in solution [12] or by a patented melt-state process [12] through the Mannich condensation of a phenolic derivative, formaldehyde, and amine. In this study, carbon foam was made from polybenzoxazine which is a novel class of phenolic resins that possesses high crosslinking density. Additionally, polybenzoxazine has high aromatic content with strong chemical bonds resulting in high mechanical and thermal stability properties [11]. Carbon foam can be easily prepared by using benzoxazine as a precursor and azodicarbonamide (AZD) as a blowing agent.

4.3 Experimental

4.3.1 Materials

Benzoxazine precursors was prepared by using phenol, ethylenediamine (EDA) and paraformaldehyde as reactants. Phenol (C_6H_5OH, analytical grade, 99% purity) was purchased from Panreac Company. EDA ($C_2H_8N_2$, analytical grade, 99% purity) was purchased from Fluka Company. Paraformaldehyde (CH_2O, reagent grade, 95% purity) was purchased from Fluka Company. Azodicarbonamide (ADC or AZD, $C_2H_4O_2N_4$) used as blowing agent was purchased from A.F Supercell Co, Ltd.. The structure of AZD is shown in Scheme I.
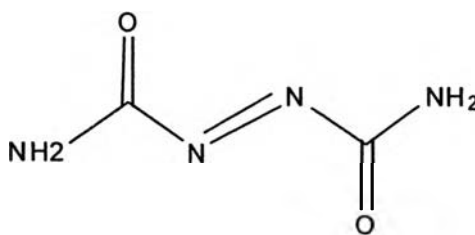
Azodiacarbonamide (AZD)
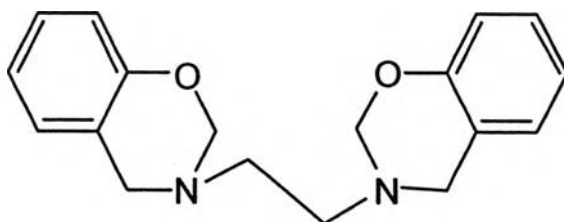
Scheme I

4.3.2 Measurements

The FT-IR spectra of P-eda were obtained by using a Nicolet Nexus 670 FT-IR spectrometer. KBr pellet technique was applied in the preparation of powder samples. TGA curves were collected on a TA Instrument TGA Q50 instrument. The samples were loaded on the platinum pan and heated from $30°$ to $850°C$ at a heating rate of $10°C/min$ under N_2 flow of 90 ml/min. Scanning electron microscope (SEM), JEOL/JSM model 5200, was used to observe the surface morphology of organic and carbon foam. The specimens were coated with gold under vacuum before the observations. DSC analyses were carried out using a Perkin-Elmer DSC 7 instrument. The samples were heated from $30°$ to $280°C$ at three different heating rates of 1.00, 2.00 and $3.00°C/min$ under a N_2 atmosphere with a flow rate of 20 ml/min N_2 to investigate the effect of heating rate on the morphology of organic and carbon foam. An Instron Universed testing machine was applied to measure the compressive

strength of organic foams. The tests were conducted according to ASTM D-1621-00 and the specimens in cylinder shape for compressvie strength studies. All specimens were prepared at a conducted at a crosshed speed of 2.50 mm min^{-1} at room temperature. A surface area and pore size of carbon foam was determined using the BET method. These characterizations are based on the physical adsorption of nitrogen gas through the Autosorb-1 Gas Sorption System (Quantachrome Coporation) at liquid nirogen temperature of 77 K. Before starting characterization, Carbon foam samples were shaped cubic samples and was weighted for about 50 mg each samples. The specific surface area and pore size of carbon foam were obtained from twenty-point nitrogen adsorption and desorption isotherm plot.

4.3.3 Methodology

4.3.3.1 Preparation of Phenol-ethylenediamine (P-eda) based Benzoxazine Monomer.

P-eda based benzoxazine monomer used in study was synthesized from phenol, ethylenediamine and para-formaldehyde with the mole ratio 2:1:4, respectively. The reactants were mixed and heated at 110°C for one hour until viscous yellowish liquid was obtained [12]. The structure of 1,2-di-(2H-benzo[e][1,3]oxazine-3(4)-yl)ethane or Phenol-ethylenediamine (P-eda) benzoxazine monomer is shown in scheme II.

Phenol-ethylenediamine (P-eda) benzoxazine monomer

Scheme II

4.3.3.2 Preparation of Organic Foam

P-eda monomer was mixed with various AZD contents (0-40 wt%) through dry-mixing method. The mixtures were cured in an oven at 30 to 210°C. In order to study the effect of heating rate on the morphology fo organic and carbon foams, the heating rate varied from 0.50-3.00°C/min were employed [13].

4.3.3.3 Preparation of Carbon Foam

Carbon foam was prepared by pyrolysis of the organic foam in a quartz reactor. The pyrolysis took place in a furnace under the nitrogen flow at 600 ml/min using the following ramp cycle : 30 to 250°C in 60 min, 250 to 600°C in 300 min, 600 to 800°C in 60 min, and hold at 800 °C in 60 min. Then the furnace was cooled down to room temperature under nitrogen atmosphere [13].

4.4 Results and Discussion
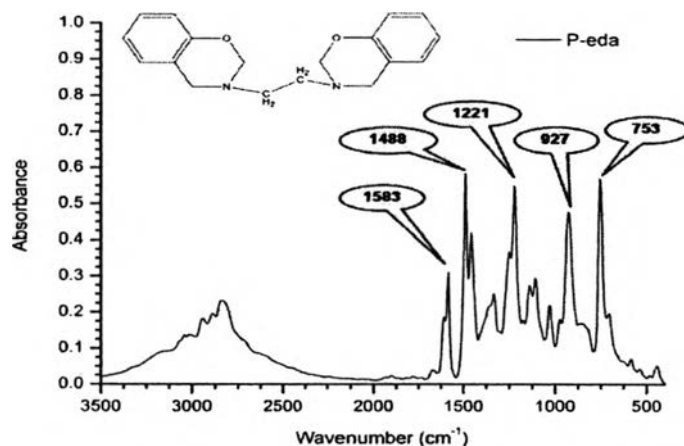
4.4.1 FTIR study

Figure 4.1 FTIR spectrum of P-eda benzoxazine monomer.

FTIR spectrum of P-eda benzoxazine monomer is shown in Figure. 4.1. The symmetric C-N-C stretching mode can be found in the region of 740 to 830 cm^{-1}. The C-O-C antisymmetric stretching and CH_2 wagging of oxazine functionality appeared in the region of 1221 and 1583 cm^{-1}. Additionally, the characteristic absorption peaks assigned to the trisubstituted benzene ring and the out of plane bending vibration of C-H were observed at 1488 and 927cm^{-1}, respectively described by Dunkers et al. [14].

4.4.2 Morphology of Organic Foam

(a)

(b)

(c)

(d)
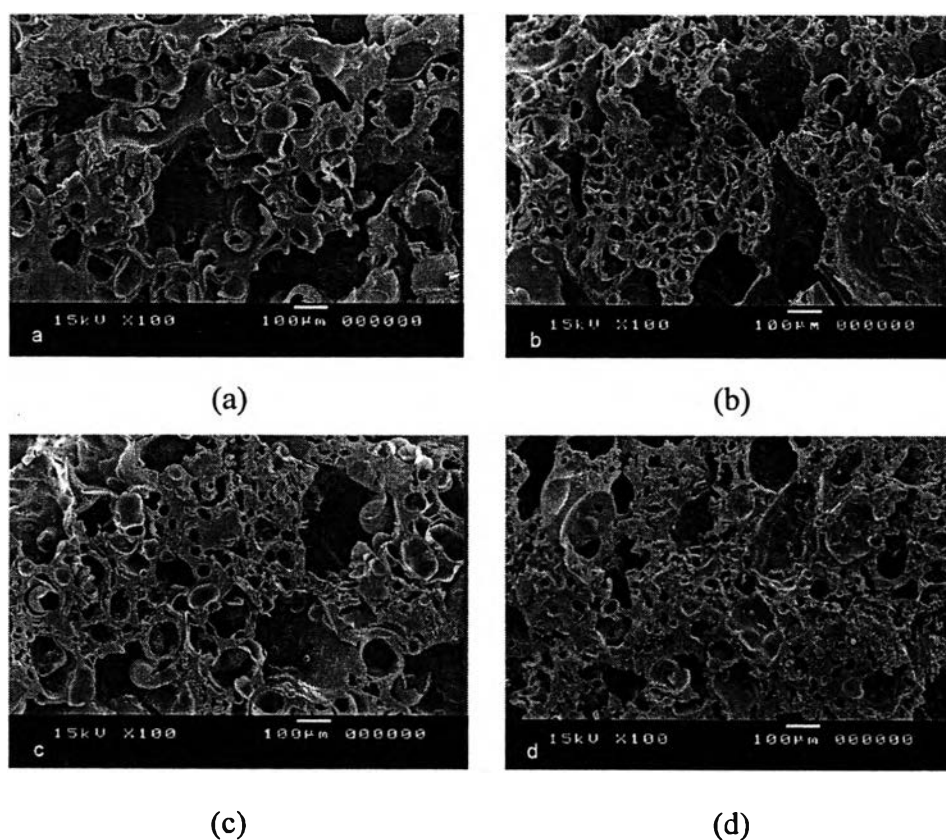
Figure 4.2 SEM micrographs of organic foam with: 1 (a), 5 (b), 10 (c), and 20 wt% (d) of AZD prepared at the heating rate of 3.00°C/min.

In order to determine the optimal processing condition, the heating rate was fixed at 3.00°C/min while the AZD concentrations were varied from 1-20 wt%. It appeared that at the high loading contents of AZD, the porous structure of organic foam was more homogeneous.

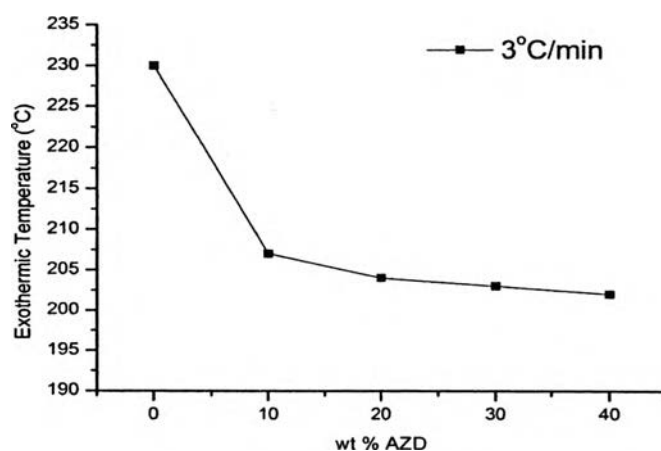### 4.4.3 Effect of AZD Concentrations on Thermal Behaviors of P-eda Benzoxazine Monomer

Figure 4.3 Maximum exothermic temperatures as a function of AZD concentrations.

Thermal behaviors of P-eda based organic foam were investigated by DSC. The concentration of AZD varied from 0-40wt% so that these results were covered and achieved for the interpretation. The exothermic temperatures were shifted to lower temperature as the AZD concentrations were increased as shown in Figure 4.3.

Ghosh *et al.* [15] found that acetic acid could be used as a curing agent for benzoxazine polymerization. Petrakoon *et al.* [16] observed the release of isocyanic acid when AZD was exposed to heat as shown in scheme III. Hence, in this study, isocyanic acid generated from the decomposition of AZD acted as a blowing agent as well as a curing agent for P-eda polymeriazation. Additionally, 10 wt% of AZD was
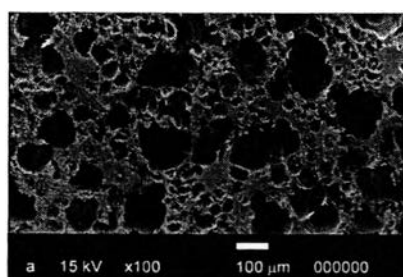
an appropriate concentration since no significant change was observed when AZD content was higher than 10 wt%.
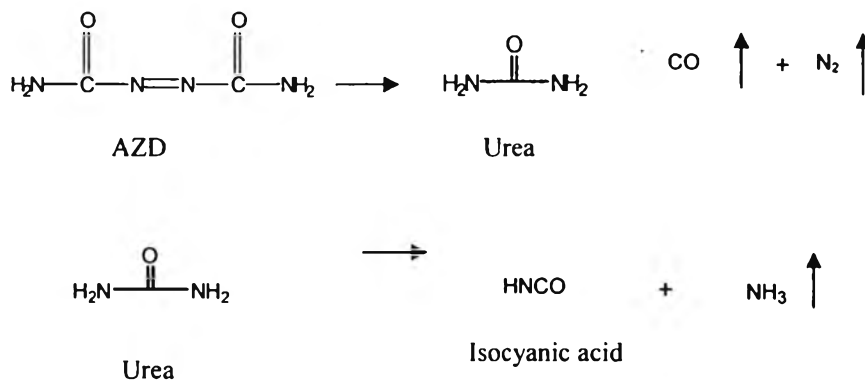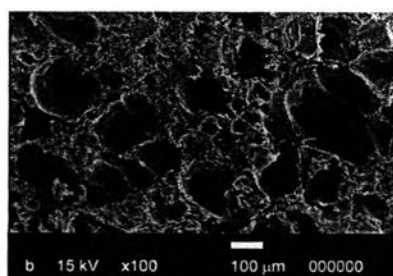

Decomposition reaction of AZD
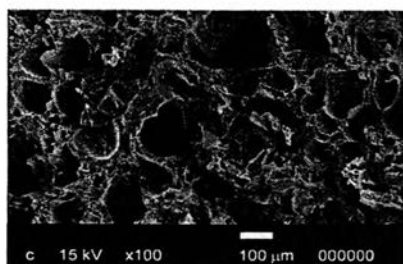
Scheme III

4.4.4 Effects of Heating Rates on Morphology of Organic Foam
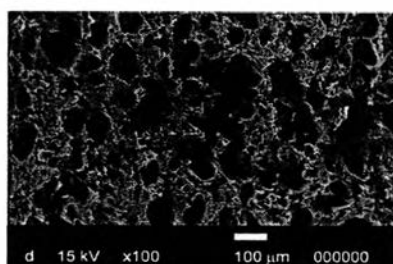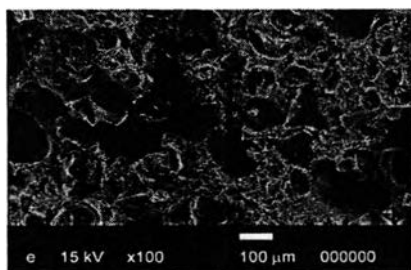

(a)

(b)

(c)

(d)

(e)

Figure 4.4 SEM micrographs of organic foams with 10 wt% of AZD; 0.50(a), 0.75(b), 1.00(c), 2.00(d) and 3.00(e) °C/min.

10 wt% of AZD was chosen for further studies due to the obtained results. Moreover, this loading content is more economical for a large scale production. The effect of heating rate on the morphology of foam was investigated by varying the heating rate from 0.50-3.00°C/min. These results are shown in Figure 4.4(a)-(e). It appeared that at the 0.50-1.00°C/min (a)-(c), the large pores were separated. On the other hand, when the heating rates of 2.00 and 3.00°C/min were used, some large pores were fused together and the over all pores structure was non homogenous. The thermosetting resin reaction had to use the time for creating network as described by Horvat et al. [17]. The degree of bond conversion depended on the time. More time in polymeriazation was equal to giving the energy to every area of material so this material looked nice and more homogeneity.

4.4.5 Effects of AZD Concentrations and Heating Rates on Thermal Behaviors of P-eda Benzoxazine Monomer
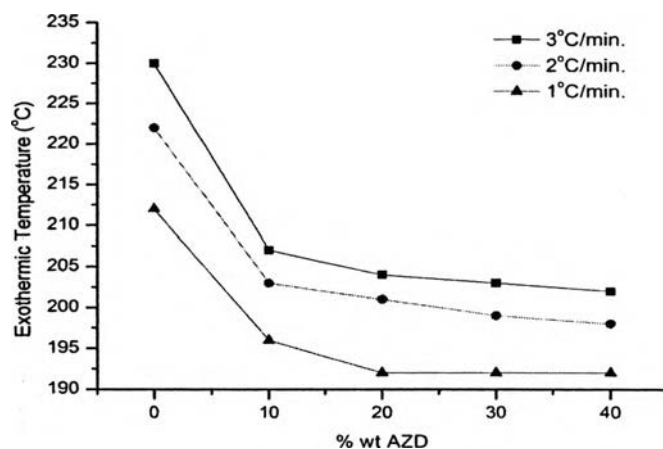

Figure 4.5 Maximum exothermic temperatures as a function of AZD concentrations.

As shown in Figure 4.5, the maximum exothermic temperatures were shifted to lower temperatures when the heating rate was decreased. This might be because at lower heating rate, molecules received energy gradually and more evenly. Moreover, energy can be transferred from one molecule to another. As a result, the polymerization took place at lower temperature. Figure 4.5 showed that the change of the heating rates affected the decrease of the exothermic temperature more significantly than AZD. The optimal heating rate for fabricating organic foam was 1.00 °C/min fabrication. Moreover, the suitable concentrations of AZD for organic foam fabrication were 10 and 20 wt%. Furthermore, it was found that at each AZD concentration, the effect of lower heating rate on the decrease of the exothermic temperature was more pronounce.
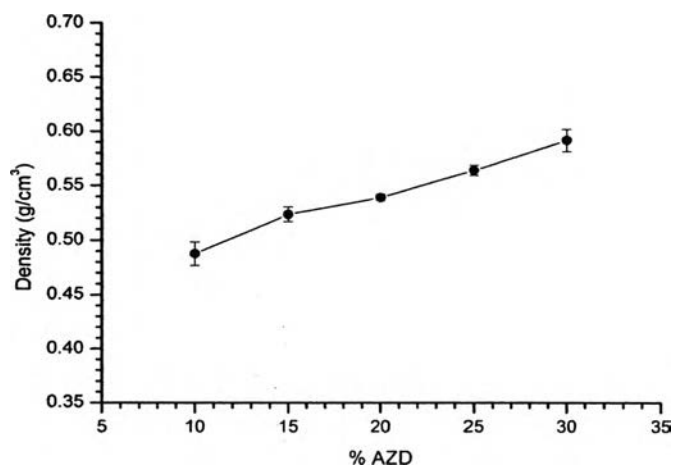
4.4.4 Physical Property of Organic Foams

Figure 4.6 Effect of AZD contents on the density of organic foams (prepared at the heating rate of 1.00 °C/min).
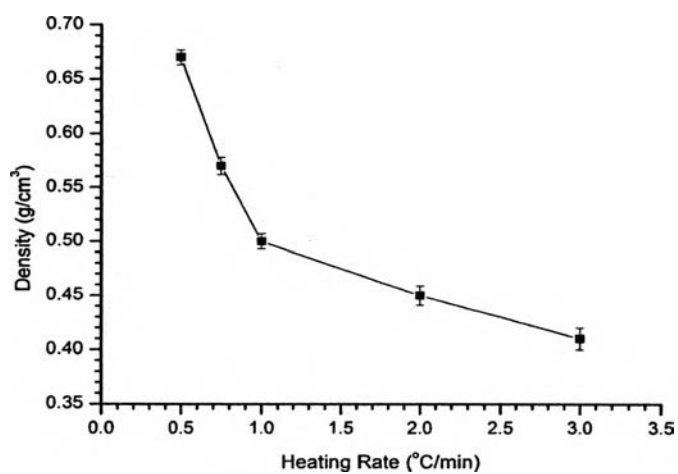

Figure 4.7 Effect of heating rates on the density of organic foams (prepared with 10 wt% of AZD).

The effect of AZD contents on the density of organic foams were investigated as shown in Figure 4.6. The organic foams were prepared at the heating rate of 1.00 °C/min. The result showed that the density of organic foams was increased slightly when the AZD concentration was increased. This is because more residues which was urazole, hydrazodicarbonamide, and cyanuric acid were generated at higher AZD concentration as described by Pentrakoon et al[16].

The effect of the heating rate on the density of organic foams was further studied as shown in Figure 4.7. 10 wt% of AZD was used for organic foam preparation. The density of organic foams was increased steeply when the heating rate was in 0.50-1.00 °C/min. Then, the density was gradually increased when the heating rate was in the range of 1.00-3.00 °C/min. The ring-opening polymerization happened quickly at low heating rate as discussed previously. Therefore, the cell walls of organic foams were set early before gas bubble were expanded. The organic foams were thicker and denser. This imply that organic foam was higher density at low heating rate.
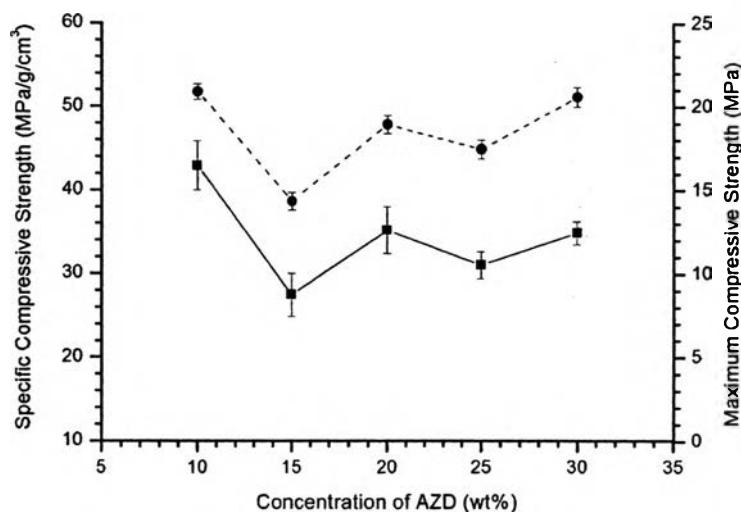
Figure 4.8 Specific compressive strength (SpC) and maximum compressive strength of organic foams at varied concentrations of AZD.
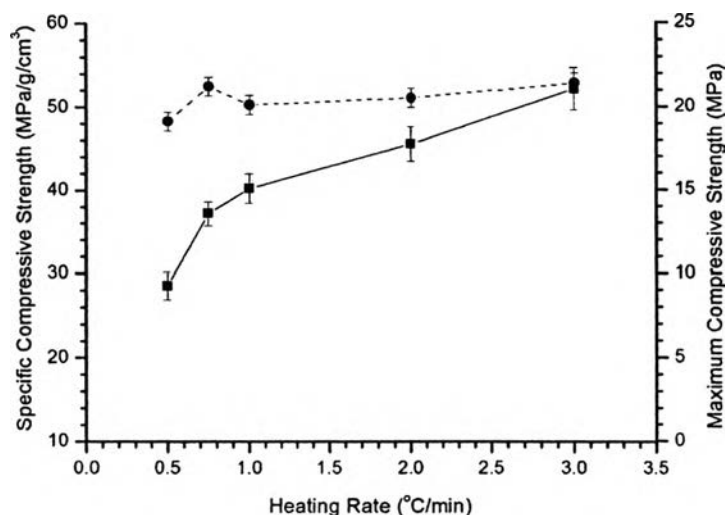
Figure 4.9 Specific compressive strength (SpC) and maximum compressive strength of organic foams with 10 wt% of AZD varied heating rates.

To study the effect of AZD contents on the specific compressive strength (SpC) of the organic foams, 10 to 30 wt% of AZD was used to prepare the organic foam while the heating rate was fixed at 1.00 °C/min. It was found that concentrations of AZD had no signification effect on the compressive strength and as shown in Figure 4.8 since AZD only acted as a curing agent but did not change the crosslink density.

The heating rates showed pronounced effect when the heating rate of 0.50-1.00 °C/min were applied and less effect at higher heating rate because maximum compressive strengths of organic foams in Figure 4.9 were not different significantly but their densities were different enormously. This cause changed their SpCs opposite their densities so at low heating rate occurred low SpC and at high heating rate showed high SpC.
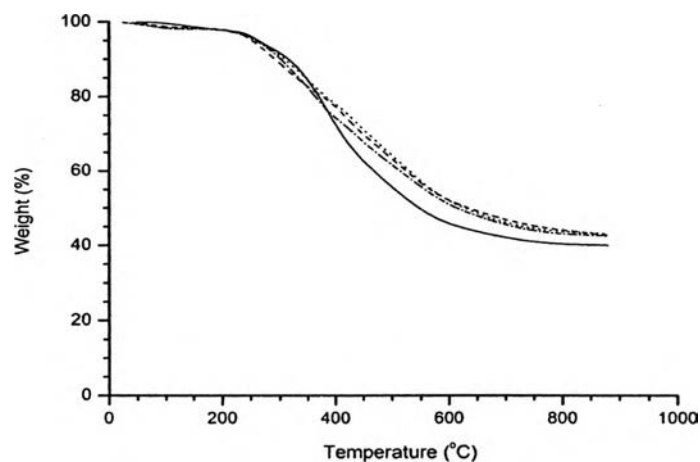
4.4.5 Thermalgravimatic Analysis (TGA)

Figure 4.10 TGA of organic foams prepared at heating rate of 1.00 °C/min and varied contents of AZD.

Table 4.1 Thermogravimetric analysis results of poly(p-eda) and organic foams

Sample	% of char yield
Poly(p-eda)	40
Organic foam with 10 wt% of AZD	45
Organic foam with 20 wt% of AZD	45
Organic foam with 30 wt% of AZD	45

The thermal stabilities of organic foams were investigated by TGA as shown in Figure 4.10. The decomposition of volatile materials from polybenzoxazine precursor start at 250 °C and the maximum rate of mass loss observe between 250 °C and 600 °C. From Table 4.1, Poly(p-eda), 0 wt% of AZD, had about 40% char yeild as described by Allen *et al.* [11] and organic foams included 10-30 wt% of AZD had approximately 45% char yeild.

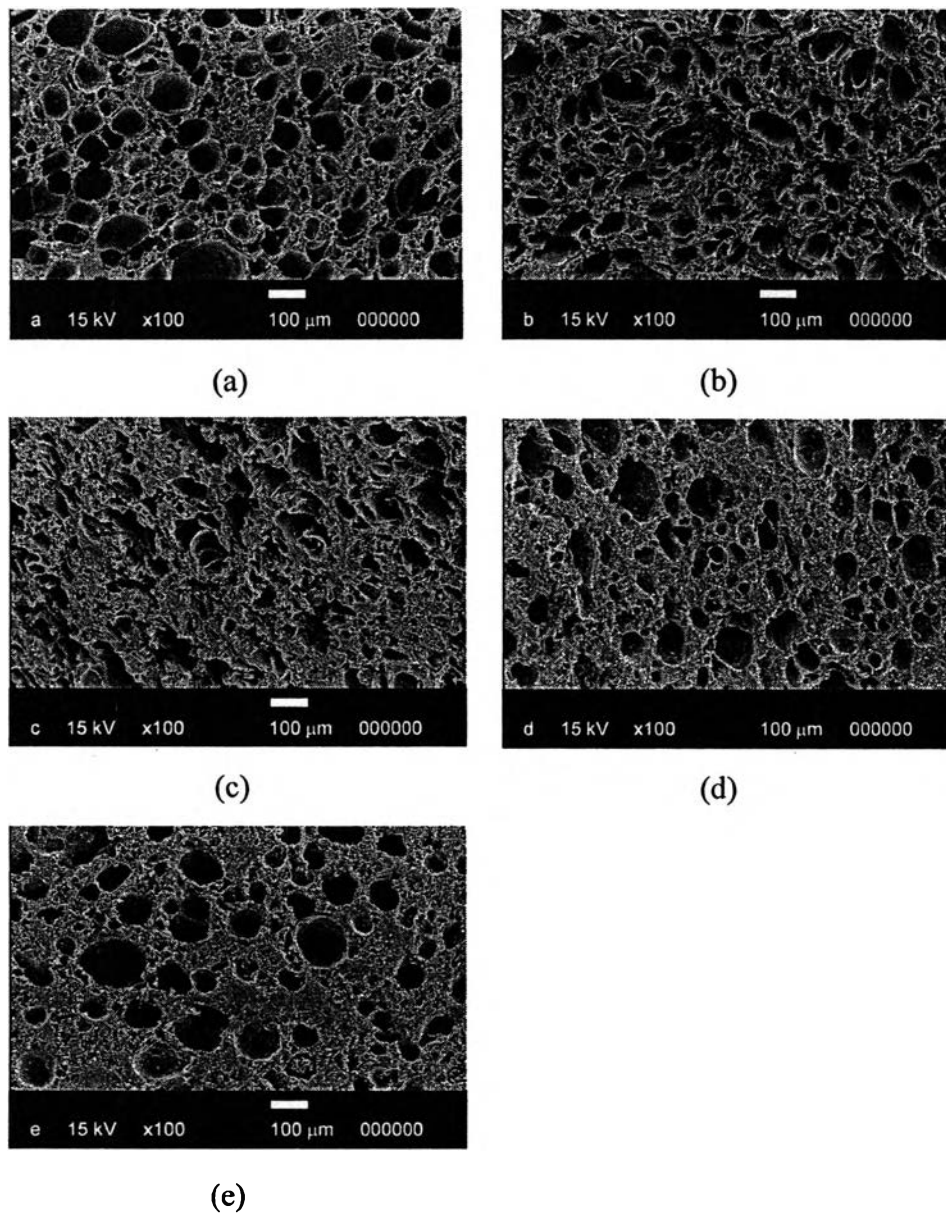### 4.4.6 Morphology of carbon foams

(a)

(b)

(c)

(d)

(e)

Figure 4.11 SEM micrographs of the carbon foams with 10 wt% of AZD (a-e) at various heating rates from 0.50-3.00 °C/min.
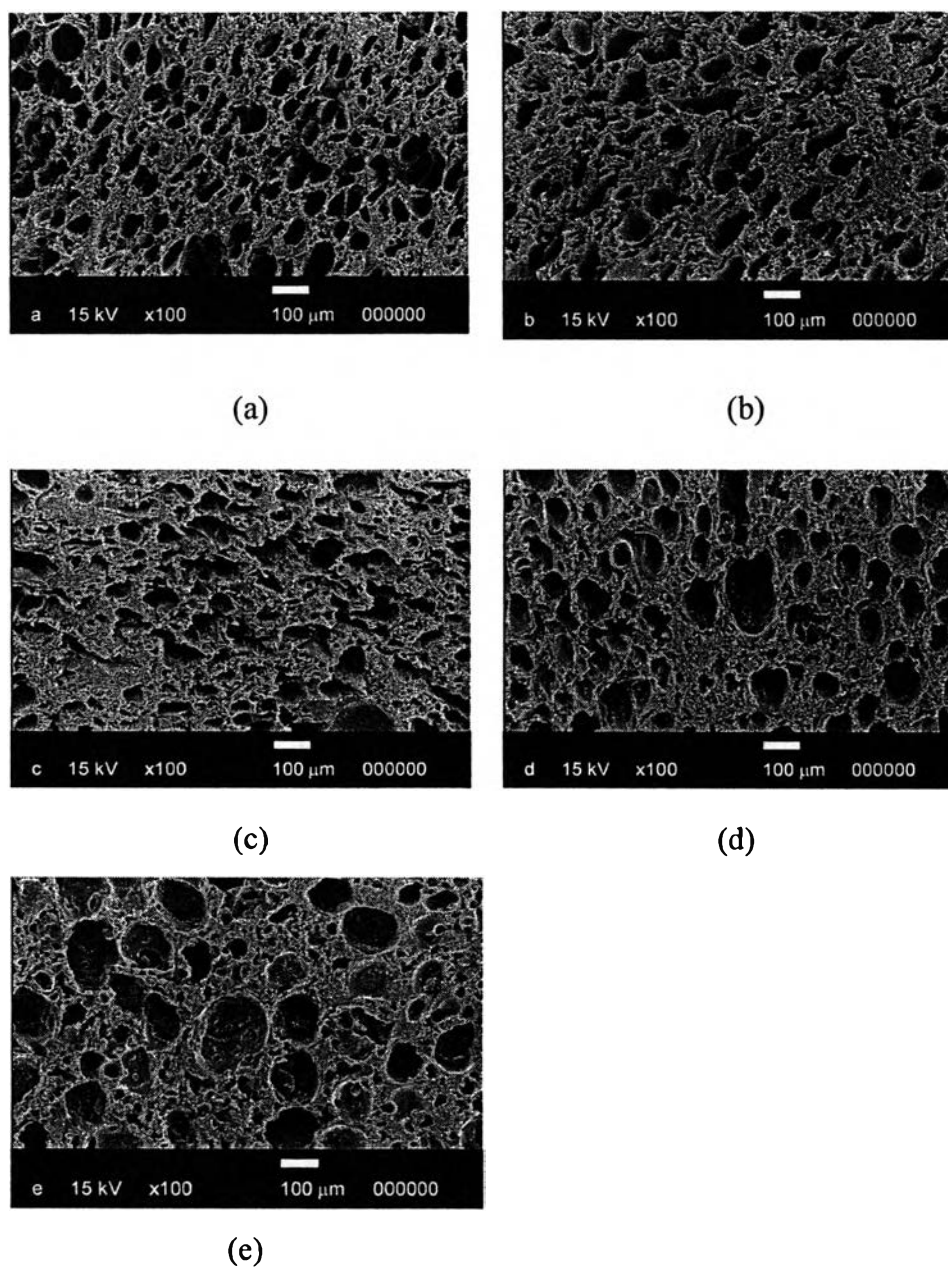
(a)

(b)

(c)

(d)

(e)

Figure 4.12 SEM micrographs of the carbon foams with 20 wt% of AZD (a-e) at various heating rates from 0.50-3.00 °C/min.

The carbon foams derived from organic foams with 10 and 20 wt% of AZD are shown in Figure 4.11 and 4.12. It was found that at lower heating rate, the carbon foams showed denser cell wall, well-distributed pore structure, and smaller pore size. These results were in good agreement with those of organic foams.

4.4.7 BET Analysis

Table 4.2 Surface area of carbon foam made from 20 wt% of AZD

Heating Rate (°C/min)	Surface Area (m²/g)
0.50	379.70
1.00	410.00
2.00	392.00
3.00	393.50

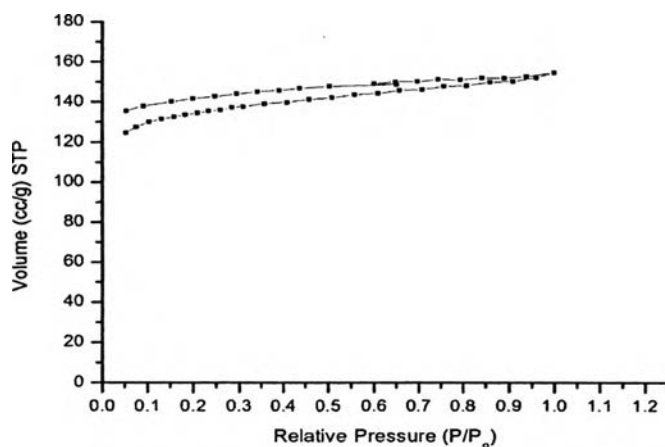### 4.4.8 Nitrogen adsorption-desorption isotherm for carbon foam

Figure 4.13 Isotherm of carbon foam made from organic foam with 20 wt% of AZD and 1.00°C/min.
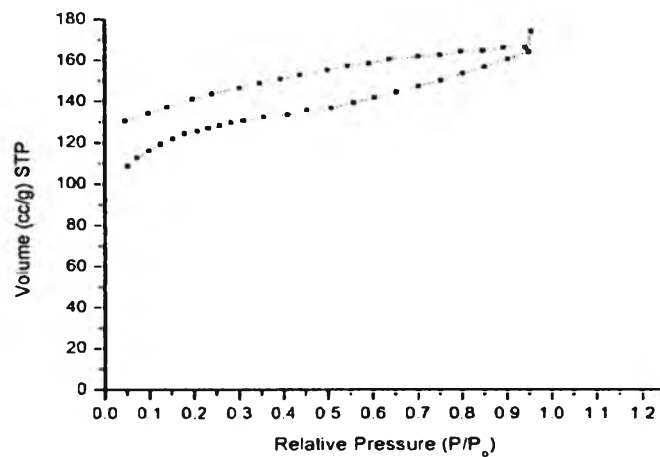
Figure 4.14 Isotherm of carbon foam made from organic foam with 20 wt% of AZD and 3.00°C/min.

The nitrogen adsorption/desorption isotherm on the carbon foams at 77K were shown in Figure 4.13 and 4.14. The mounts of adsorbed and desorbed data were plotted against the relative pressure. Both isotherms of carbon foam were Type I because Type I isotherm must account for the fact that the uptake adsorbed gas hugely due to large space on adsorbent and comes to a limiting value manifested in the plateau. According to the earlier, the pores are so narrow that they cannot accommodate more than a single molecular layer on their walls ; the plateau thus corresponds to the completion of the monolayer. This type of isotherm was designed to characteristic of microporous absorbents as described by Gregg *et al.* [18]. Carbon foam at 1.00°C/min was more uniform than carbon foam at 3.00°C/min since the adsorption data were closed to desorption data each relative pressure according to ideal Type I isotherm. The calculated surface areas were shown in Table 4.2.
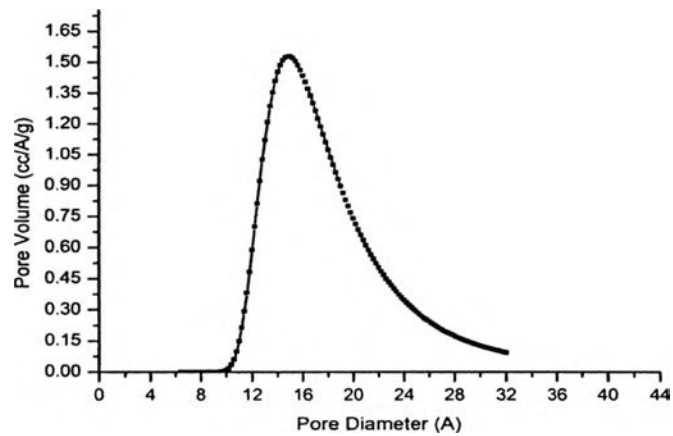
4.4.9 Pore size distribution (PSD) graph

Figure 4.15 PSD of carbon foam made from organic foam with 20 wt% of AZD and 1.00°C/min.
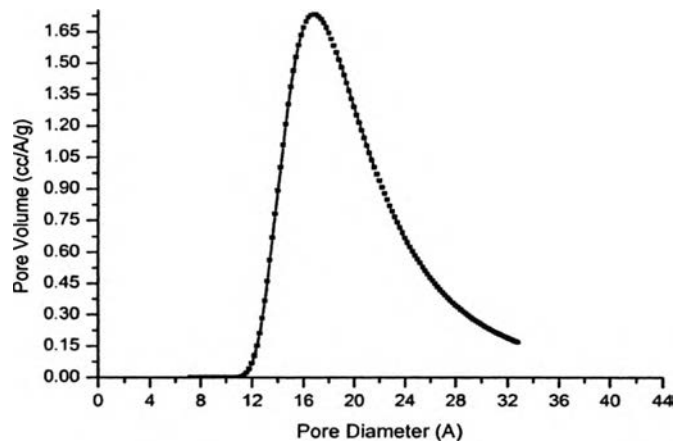

Figure 4.16 PSD of carbon foam made from organic foam with 20 wt% of AZD and 3.00°C/min.

The average pore diameters of carbon foams at 1.00°C/min and 3.00°C/min were 1.5nm, 1.7nm respectively. The pore diameter as 1.5 nm had the highest pore volume 1.53 cc/A/g in Figure 4.15 and The pore diameter as 1.7 nm had the highest pore volume 1.73 cc/A/g in Figure 4.16. These average pore diameters and pore volumes were no different significantly. These results showed that the different heating rate didn't effect the pore diameter. These average pore diameters were in the range of micropore which pore diameter was less than 2 nm as micropore according to Gregg *et al.* This result agreed very well with adsorption/desorption isotherm classification.

4.5 Conclusions

The carbon foams were prepared by using Poly(p-eda) as an organic precursor and AZD as a blowing agent. From the DSC results, it was found that AZD also acted as a curing agent due to the shift of exothermic peaks to lower temperature. The organic foams was more thermal stability and % char of yield than Poly(p-eda). Nitrogen adsorption-desorption isotherm of carbon foam at 1.00°C/min showed characteristic of microporous absorbents and was the highest surface area at 410 m²/g. This result associated with pore size distribution graph which showed pore diameter at 15 nm. Although the heating rate was more effect on macropore, it was effect raredly on micropore from two pore size distribution graphs. Therefore, the heating rate of 1.00 °C/min and 20 wt% of AZD were appropriate for organic and carbon foam preparation.

4.6 Acknowledgements

4.7 References

[1] Wang, X., Zhong, J., Wang Y., and Yu, M. (2006). A Study of the properties of carbon foam reinforced by clay. Carbon, 44(8), 1560-4.

[2] Mehta, R., Anderson, D.P., and Hager, J.W., (2003). Graphite open-celled carbon foams: processing and characterization. Carbon, 41(11), 2174-6.

[3] Chen, C., Kennel, E.B., Stiller, A.H., Stansberry, P.G., and Zondlo, J.W. (2006). Carbon derived from various precursors. Carbon, 44(8), 1535-43.

[4] Mattis, D.C., (2005). Theory of ferromagnetism in carbon foam, Phys Rev B: Condens Mater Mater Phys, 71(14), 144424/1-4/5.

[5] Klett, J.W., Hardy, R., Romine, E., Walls, C., and Burchell, T. (2000). High-thermalconductivity, mesophase-pitch-derived carbon foams: effect of precursor on structure and properties. Carbon, 38(7), 953-73.

[6] Yang, J., Shen, Z., Xue, R., and Hao, Z. (2005). Study of mesophase-pitch-based graphite foam used as anodic materials in lithium ion rechargeable batteries. J Mater Sci, 40(5), 1285-7.

[7] Klett, J.W., Process for making carbon foam. US Patent 6033506; 2000.

[8] Yang, J., Shen Z.M., and Hao Z.B. (2004). Microwave characteristics of sandwich composites with mesophase pitch carbon foams as core. Carbon, 42(8-9), 1882-5.

[9] Inagaki, M., Morishita, T., Kuno, A., Kito, T., Hirano, M., Suwa, T., et al. (2004). Carbon foams prepared from polyimide using urethane foam temple. Carbon, 42(3), 497-502.

[10] Rios, R.V.R.A., Martinez-Escandell, M., Molina-Sabio, M.,. and Rodriguez-Reinoso, F. (2006). Carbon foam prepared by pyrolysis of olive stones under steam. Carbon, 44(8), 1448-54.

[11] Allen, D.J., and Ishida, H. (2006). Physical and Mechanical Properties of Flexible Polybenzoxazine Resins; Effect of Aliphatic Diamine Chain Length. Journal of Applied Polymer Science, 101, 2798-2809.

[12] Ishida, H., US Patent 5,543,516; 1996.

[13] Lorjai, P., et al., Thailand Patent Submitted.

[14] 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, 51, 1061-1074.

[15] Ghosh, N.N., Kiskan, B., and Yagci, Y. (2007). Polybenzoxazine-New high performance thermosetting resin : Synthesis and properties. Progress in Polymer Science, 32,1344-1391.

[16] Pentrakoon, D. and Ellis, J.W. (2005) An Introduction to Plastic Foams, 1stedition, Chulalongkorn University Press.

[17] Horvat, D., Mozina, J., and Diaci, J. (1994). Pulsed photoacoustic studies of thermoset curing reaction. Journal De Physique IV, 4, 249-252 .

[18] Gregg, S.J., Sing K.S.W. (Eds.). (1982) Adsorption, Surface Area and Porosity. London: Academic press.