CHAPTER IV
MORPHOLOGICAL DESIGN OF POLYBENZOXAZINE
BY SOFT TEMPLATING METHOD

4.1 Abstract

Nanoporous material, especially porous carbon can be synthesized via many methods. However, some methods produced a broad pore-size distribution which might not be appropriate for certain application that required selective pore size. To overcome this drawback soft-template synthesis method, facile synthesis, has been used. Polybenzoxazine, a new type of phenolic resins that provided properties over conventional novolac and resole type of phenolic resin was used as a carbon precursor to synthesize carbon gel and triblock co-polymer, Pluronic P123, was used as a template. Polybenzoxazine-based carbon xerogel with different properties were obtained by varying different synthesis parameters including solvents, concentrations of polybenzoxazine and concentrations of surfactant, etc. The specific surface area and micropore volume could be improved by varying the concentration of surfactant and optimizing the surfactant concentration to get the highest specific surface area and large micropore volume was achieved. In addition, the condition which the carbon with highest specific surface area was reported after varying pyrolysis temperature and CO_2 activation treatment. After activation under CO2 at 900 $^\circ$C, the specific surface area and micropore volume were about four times higher than that of polybenzoxazine-based carbon xerogel without activation process. The resulting carbon can be classified as microporous carbon and can be used for gas adsorption/separation process.

Keywords: polybenzoxazine/porous carbon/soft-templating method

4.2 Introduction

Nowsaday, porous materials have been extensively studied and used in various applications such as water purification, gas separation, catalytic support, electrode material for energy stroage devices, thermal insulator, etc. Generally, porous structure can be classified into three types according to the IUPAC; microporous (< 2nm), mesoporous (2-50 nm) and macroporous (> 50 nm). One of the porous materials that is currently in high demand is porous carbon. Not only because its excellent properties such as light weight, high surface area, high porousity, high thermal stability, high char yield and low density, but also its availability. [1]

Many materials have been used as percursors for synthesis of porous carbon material, particularly, resocinal-formaldehyde (RF). But, using this has some drawbacks which are multi-step to complete the process, needed of harsh catalyst for polymerization and releaseing by-product during polymerization. [2] In this work, polybenzoxazine (PBZ) was used as a precursor to synthesis carbon precursor. Polybenzoxazine can overcome drawbacks of RF polymer because of its easier preparation, no need of harsh catalyst for polymerization, no volatile of toxic by-product released during polymerization.

Porous carbon has been prepared by many processes: for example; hard-templating method, emulsion, surface templating, etc. But, some methods produce broad pore-size distribution which might not be appropriate for the applications that required selective pore size. In order to control the pore structure, template synthesis method which can be classified into two types; hard-templating and soft-templating, has been investigated. [3]

The hard template requried multi-step as follows; (a) the preraration of a porous template with control porosity; (b) the impregnation of suitable carbon precursor by wet impregnation or chemical vapor deposition or a combination of both methods, (c) polymerization and carbonization of carbon precursor to generate an organic/inorganic composite, (d) removing the inorganic template such as silica by using acid (HF) or base (NaOH) to obtain porous carbon. During the template removing process, the porous carbon must withstand several harsh processes such as

high-temperature treatment and strong acid or base (NaOH/HF), which usually reconstructed the pore structure causing the pores to become disorder. [4]

So, an alternative approach is the soft-templating synthesis by using surfactant. Soft-templating has many advantages such as easy to control the pore structure, less steps to prepare, no hazardous chemical involved, etc. [5]

In this work, we aim to design and control the pore structure of porous carbon by using soft-template to obtain high surface area, or nanosphere carbon and studying the effect of synthesis parameters such as solvent, concentration of surfactant, pyrolysis and activation temperatures on the microstructure of the resulting porous carbon.

4.3 Experimental

4.3.1 Materials

Dimethylformamide (DMF) N, N-dimethylformamine (DMF, 99.8%, RCL Labscan, Thailand), 1,4-Dioxane (99.8%, RCL Labscan, Thailand), Isopropanol ($(CH_3)_2CHOH$, 99.5%, Univar, New Zealand) Bisphenol-A (BPA, 97%, Aldrish, USA), Formaldehyde (37% in water, Merck, Germany) Tetraethylenepentaamine (TEPA, 95%, Aldrish, USA) Poly (ethylene glycol)-poly (propylene glycol)-poly(ethylene glycol) (Pluronic P123, 96%, Aldrish, Germany), UHP grade nitrogen (N_2, 99.999% purity, Praxair, Thailand), HP grade carbon dioxide (CO_2, 99.996% purity, Praxair, Thailand), were used without further purification.

4.3.2 Equipment

4.3.2.1 Fourier Transform Infrared Spectroscopy (FT-IR)

The functional groups related to structure of carbon precursors investigated by using FT-IR technique. The FT-IR spectra of fully-polymerized benzoxazine xerogel and as synthesized benzoxazine xerogel were obtained by using a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of 400-4000 cm^{-1}. KBr pellet technique was applied in the preparation of powder samples.

4.3.2.2 Thermogravimetric Analysis (TGA)

TG-DTA curves were collected on a Perkin-Elmer Pyris Daimond TG/DTA instrument. 5 mg of sample was loaded on the platinum pan and heated from 30 to 900°C at a heating rate of 10 °C/min under N_2 flow of 50 ml/min.

4.3.2.3 Differential Scanning Calorimetry (DSC)

DSC analysis were carried out using a Perkin-Elmer DSC 7 instrument. The sample was first heated from 30°C to 300 °C by heating rate 10°C/min under a N_2 atmosphere with a flow rate of 20 ml/min.

4.3.2.4 Scanning Electron Microscope (SEM)

Microstructure and surface morphology of porous carbon material was observed by a Scanning electron microscope (SEM; HITACHI TM3000). The specimens were coated with platinum under vacuum before observation to make them electrically conductive.

4.3.2.5 Surface Area Analyzer (SAA)

BET surface area and pore size distribution of all carbon xerogel were calculated from the nitrogen adsorption isotherms at 77K using a Quantachrome/Autosorb-1. Surface area analyzer based on the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods, respectively.

4.3.2.6 Wide Angle X-Ray Diffraction (WAXD)

Wide Angle X-Ray Diffraction (WAXD) was performed on a Rigaku Smartlab$^{®}$ with a scanning speed of 2 °/min and $CuK\alpha$ source ($\lambda= 0.154$ Å) in a range of $2\theta = 5-80°$ to determine the XRD pattern of carbon in variation parameters.

4.3.3 Methodology

4.3.3.1 Synthesis of Polybenzoxazine Precursor

Polybenzoxazine precursors were synthesized by dissolving Pluronic P123 in which varied the concentration was varied in different types of solvent (N, N,-dimethylformamide, Isopropanol, 1, 4-Dioxane (see in table 3.1, 3.2, 3.3)) in glass bottles and stirred until the clear solution was obtained. Bisphenol-A (2.28 g.) was added into the P123 solution and stirred until the clear solution was obtained. Next formaldehyde solution (3.24g) was added into the bisphenol-A solution. The solution was kept under low temperature by using ice bath. After that tetraethylenepentamine (1.89 g) was added dropwise into the mixture and stirred continuously for approximately 1 hour while the reaction was cooled with the ice bath until transparent yellow viscous liquid was obtained. The molar ratio of bisphenol-A: formaldehyde:TEPA was 1:4:1. The synthetic reaction is shown in Figure 3.1. Then, the precursor was filled in a vial and placed in an oil bath at 80°C for 24 hr. to get benzoxazine gel. The benzoxazine gels were cut into a small pieces and then dried at ambient temperature follow by placing in an oven at 80°C for 2 hr., 100°C for 1 hr., 200°C for 1.30 hr., and 220°C for 15 min.
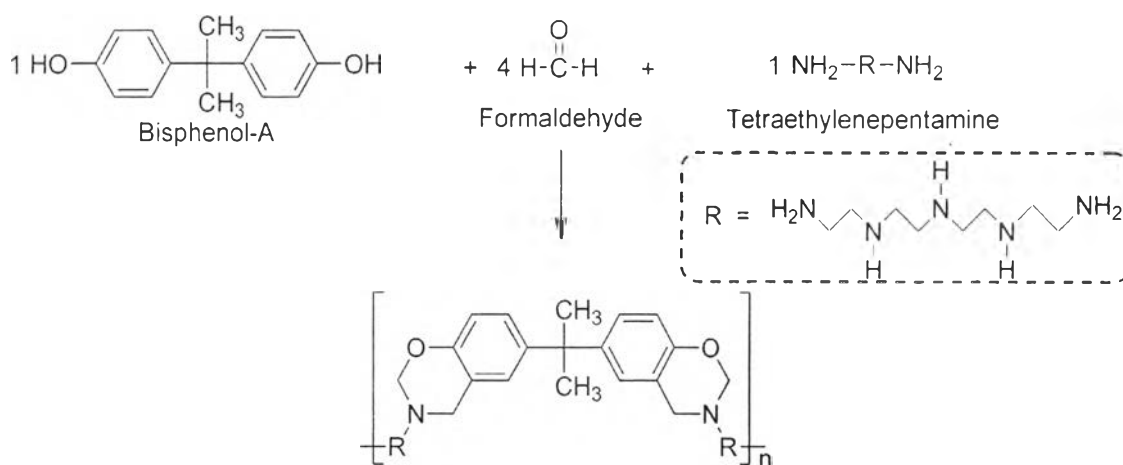

Figure 4.1 Preparation of polybenzoxazine precursor.

Table 4.1 Template loading content of each sample in N, N-dimethylformamine

Concentration of PBZ precursor	Sample name	Concentration of surfactant (Pluronic P123)	Molar ratio P123:BPA
20 %	20%PBZ/DMF	-	-
	20%PBZ/1%P123/DMF	1 %	0.0032:0.323
	20%PBZ/3%P123/DMF	3 %	0.0096:0.323
	20%PBZ/5%P123/DMF	5 %	0.0161:0.323
	20%PBZ/6%P123/DMF	6 %	0.0194:0.323
	25%PBZ /DMF	-	-
	25%PBZ/1%P123/DMF	1 %	0.0043:0.0430
	25%PBZ/3%P123/DMF	3 %	0.0129:0.0430
	25%PBZ/5%P123/DMF	5 %	0.0215:0.0430
	25%PBZ/6%P123/DMF	6 %	0.0258:0.0430
	25%PBZ/7%P123/DMF	7 %	0.0301:0.0430
	25%PBZ/8%P123/DMF	8 %	0.0344:0.0430
	25%PBZ/9%P123/DMF	9 %	0.0387:0.0430
	25%PBZ/10%P123/DMF	10 %	0.0430:0.0430
	25%PBZ/12%P123/DMF	12 %	0.0516:0.0430
	25%PBZ/15%P123/DMF	15 %	0.0645:0.0430
	25%PBZ/18%P123/DMF	18 %	0.0774:0.0430
	25%PBZ/20%P123/DMF	20 %	0.0860:0.0430
	25%PBZ/22%P123/DMF	23 %	0.0989:0.0430
	25%PBZ/25%P123/DMF	25 %	0.1075:0.0430
30 %	30%PBZ/DMF	-	-
	30%PBZ/3%P123/DMF	3 %	0.0166:0.054
	30%PBZ/6%P123/DMF	6 %	0.0326:0.054

Table 4.2 Template loading content of each sample in Isopropanol

Concentration of PBZ precursor	Sample name	Concentration of surfactant (Pluronic P123)	Molar ratio P123:BPA
20 %	20%PBZ / IP	-	-
25 %	25%PBZ/ IP	-	-
	25%PBZ/3%P123/ IP	3 %	0.0107:0.359
	25%PBZ/6%P123/ IP	6 %	0.0215:0.359
	25%PBZ/10%P123/ IP	10 %	0.0359:0.359
	25%PBZ/12%P123/ IP	12 %	0.0431:0.359
	25%PBZ/15%P123/ IP	15 %	0.0538:0.359
30 %	30%PBZ/ IP	-	-
	30%PBZ/6%P123/ IP	6 %	0.0276:0.461
	30%PBZ/10%P123/ IP	10 %	0.0461:0.461
35 %	35%PBZ/ IP	-	-

Table 4.3 Template loading content of each sample in 1, 4-dioxane

Concentration of PBZ precursor	Sample name	Concentration of surfactant (Pluronic P123)	Molar ratio P123:BPA
35 %	35%PBZ/Dioxane	-	-
	35%PBZ/6%P123/Dioxane	6 %	0.0444:0.740
	35%PBZ/7%P123/Dioxane	7 %	0.0518:0.740
	35%PBZ/8%P123/Dioxane	8 %	0.0592:0.740
	35%PBZ/12%P123/Dioxane	12 %	0.0888:0.740
	35%PBZ/15%P123/Dioxane	15 %	0.1110:0.740

4.3.3.2 Preparation of Carbon Xerogel

Polybenzoxazines were pyrolyzed under nitrogen flow rate of 500 cm^3/min under different final temperatures (800 °C, 850 °C, 900 °C, 1000 °C).The heating profile was as follows: heating from room temperature to 200°C in 60 min, 200 to 600°C in 360 min, 600 to final temperature in 120 min, and holding at final temperature for 120 min and then cooling down to room temperature.

4.3.3.2.1 Preparation of Activated Carbon Xerogel

Activated carbon xerogel was prepared by carbonization of carbon xerogel with carbon dioxide atmosphere at 900 °C for 180 mins.

4.3.3.2.2 CO₂ Adsorption

Activated polybenzoxazine porous carbon with highest surface area was test the adsorption application by loading 0.1 g. of sample into the stainless steel adsorption chamber which was heated by the furnace in order to reach the adsorption temperatures. He gas was used as a purge gas in this study. The adsorption processes were carried out by using high purity CO_2 gas.

4.4 Result and Discussion

4.4.1 The Chemical Structure of the Precursors

The structure of benzoxazine precursor was examined by FT-IR. The asymmetric stretching of C-O-C (1230-1236 cm^{-1}), asymmetric stretching of C-N-C (1020-1240 cm^{-1}) and CH_2 wagging of oxazine (1360-1380 cm^{-1}) were observed. Additionally, the characteristic absorptions assigned to trisubstituted benzene ring at 1491-1500 cm^{-1} and out-of-plane bending vibrations of C-H at 920-950 cm^{-1} were detected [6]. After polymerized at 220°C, the intensity of those characteristics absorption bands at 940 cm^{-1} and 1491-1500 cm^{-1} decreased because the ring opening polymerization was completed as shown in Figure 4.2 (a)
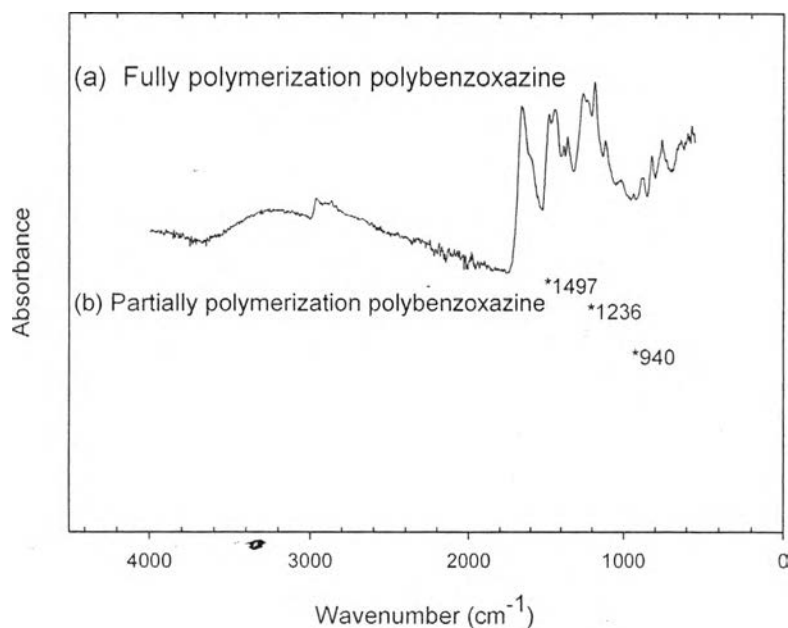
Figure 4.2 FTIR spectrum of benzoxazine precursor and polybenzoxazine.

4.4.2 Thermal Behaviors of Precursors

The progress of ring-opening polymerization of the precursors was monitored by DSC. The DSC thermogram shows the exotherm around 256°C as shown in Figure 4.3 due to the ring opening polymerization of cyclic benzoxazine precursor. The amount of exotherm decreased with the increase of heat treatment temperature. After the precursor was fully polymerized, the exotherm completely disappeared showing that the ring-opening of oxazine was completed [7].
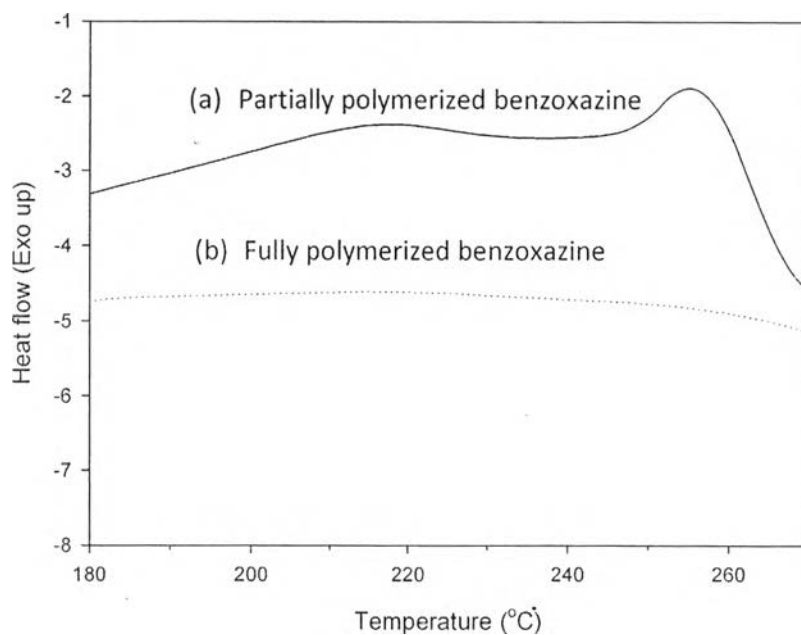
Figure 4.3 DSC thermograms of partially-polymerized and fully-polymerized benzoxazine.

But. in case of using different solvent system. The DSC thermograms were different (Fig 4.4). However. all systems gave exotherm peak around 256 °C corresponding to the ring opening of benzoxazine precursor.
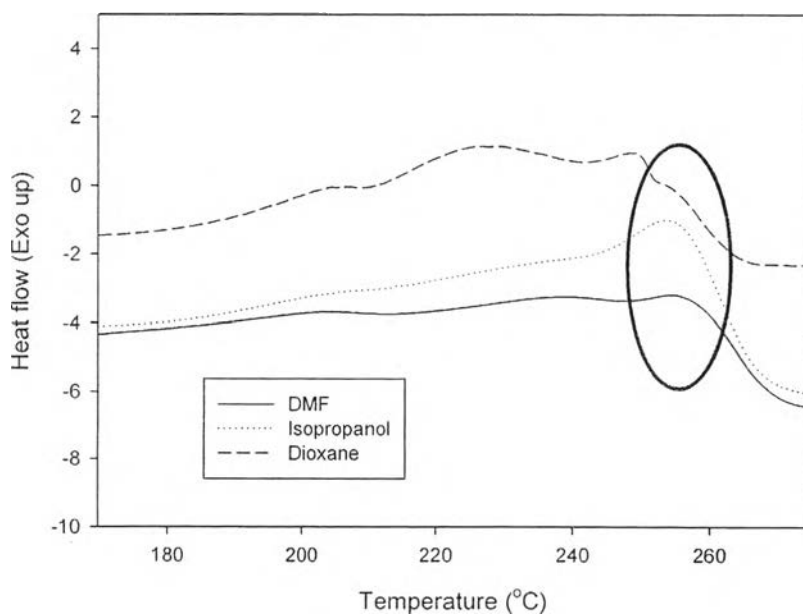

Figure 4.4 DSC thermograms of polybenzoxazine precursor in different solvent.
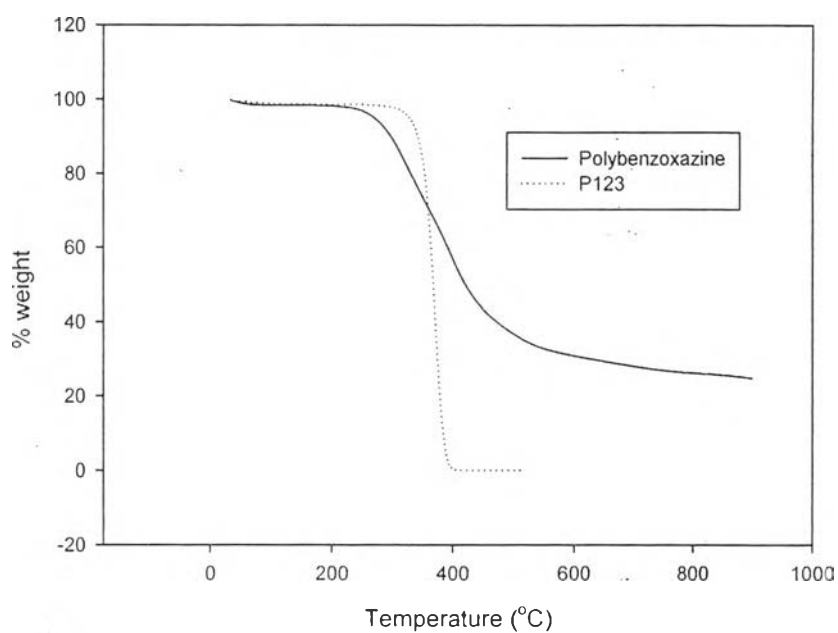
Figure 4.5 TGA thermogram of polybenzoxaine precursor and Pluronic P123.

As a reference, TGA curves of polybenzoxazine and Pluronic P123 were displayed in Fig. 4.5. The decomposition temperature of polybenzoxzine began at 267 °C with the maximum mass loss rate in the temperature range of 267 to 600 °C. The result was in accordance with our previous study [6]. On the other hand, the TGA curve of P123 suggest that P123 composes significantly from 300 °C to 400 °C and there is no char yield left from the decomposition of P123, including that the P123 could be easily removed upon heating at 400 °C in N_2 atmosphere.
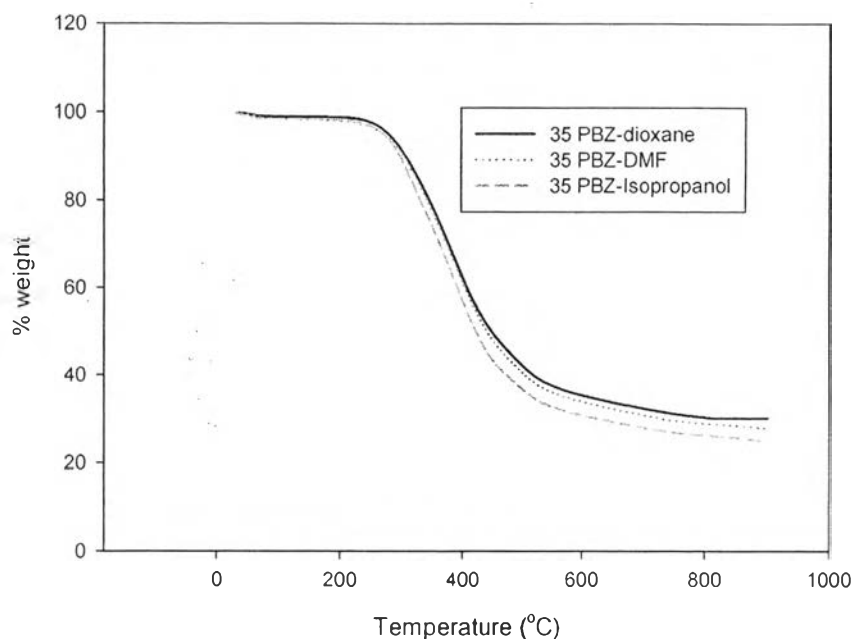
Figure 4.6 TGA thermograms of polybenzoxazine in different solvents

From Figure 4.6, different in weight% loss was observed by using different solvents. Polybenzoxazine from dioxane solvent has highest char yield followed by DMF and isopropanol, which might be due to the different morphology obtained when different solvents were used. By using dioxane as a solvent, denser morphology was observed. The denser morphology implies closer packing of structures leading to ability of polybenzoxazine to resist higher temperature.
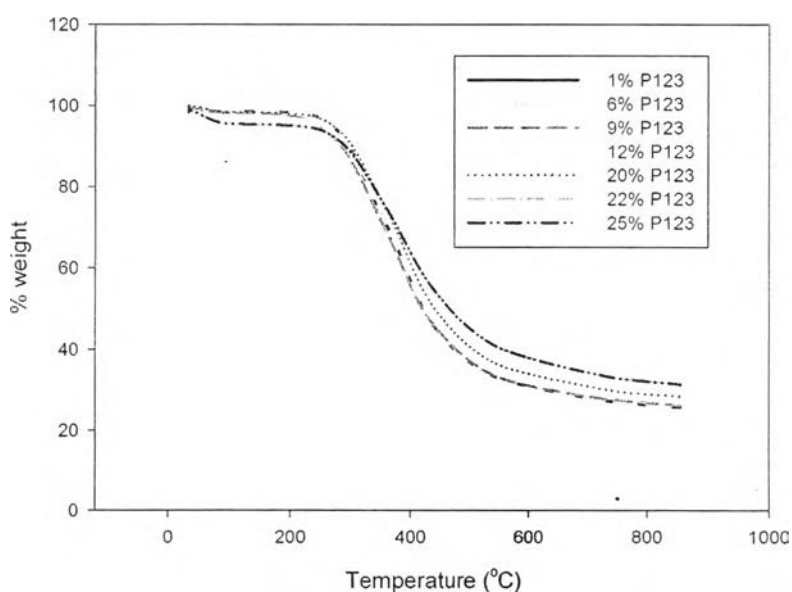

Figure 4.7 TGA thermograms of polybenzoxazine/P123 composites.

From Fig. 4.7 the TGA thermograms of polybenzoxazines with various amount of surfactant did not show significantly change of char yields. Hence, we can confirm that P123 did not effect to amount of char [8]

4.4.3 Morphology of Polybenzoxazine Based Porous Carbon

4.4.3.1 Effect of Resin Concentrations on Morphologies of Polybenzoxazine based-porous Carbon

The most important parameter affecting the pore structure during phase separation is the difference in solubility parameters between solvent and polymer. The gelation time of the sol–gel process is related to the rate of cluster growth [9]. During the gelation process, the molecular weight of benzoxazine resin increased, resulting in the formation and growth of benzoxazine clusters. Finally, gelation was achieved by connecting the benzoxazine clusters which was surrounded by the solvent [10]. The solvent is removed by an ambient pressure drying method, resulting in the creation of pores. Hence. the morphology of the polymeric gel depended on the difference in solubility parameter between the solvent and polymer. At higher benzoxazine concentration. particles had because more agglomerated causing higher chance of benzoxazine monomers to react with each other as shown in Fig 4.8c and 4.8d
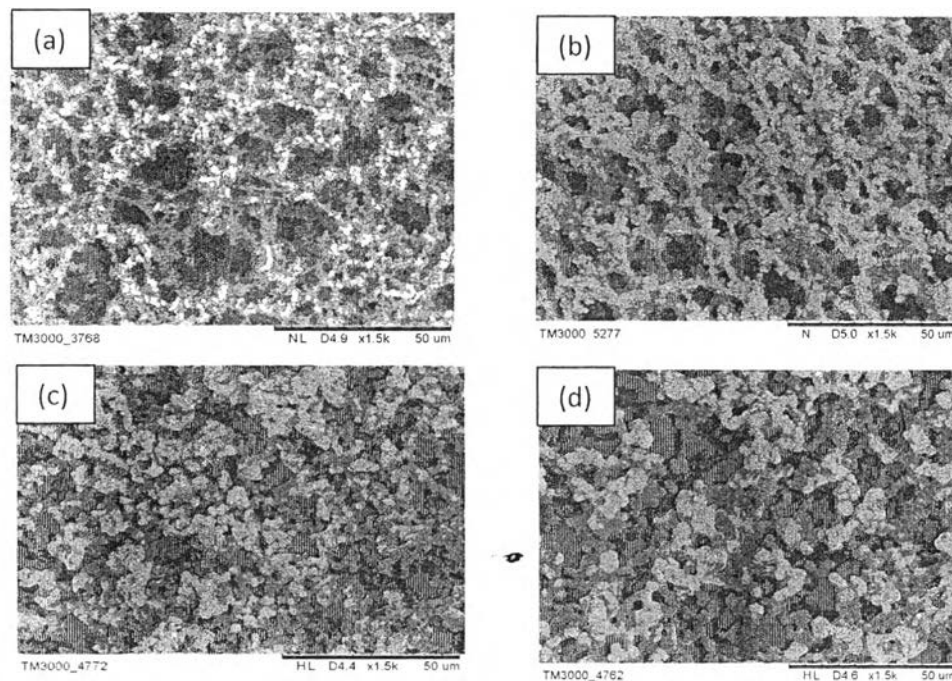
Fig 4.8 SEM micrographs of carbon xerogel using DMF as a solvent (a.) 20 wt%
(b.) 25 wt% (c.) 30 wt% (d.) 35 wt% of benzoxazine.

4.4.3.2 Effect of Solvents on Morphologies of Polybenzoxazine based-porous Carbon

In this work, three solvents were used in the sol-gel process including DMF, dioxane and isopropanol. The concentration of benzoxazine was kept at 25 %wt because we aim to generate smaller rod shape of polybenzoxazine following the senior work. To produce the polybenzoxazine organogel baesd-porous carbon, all benzoxazine solution were left in an oil bath at 80 °C for 1 day to form yellow and opaque polybenzoxazine organogel. After 1 day in an oil bath, polybenzoxazine gel was dried and pyrolyed at 800 °C under inert atmosphere. Lastly polybenzoxazine organogel baesd-porous carbon was observed by SEM to investigate the microstructure. It was found that the dioxane system gave denser morphology than that synthesized in DMF, while the isopropanol system gave spherical structure. The difference in morphology   (Figure 4.8) might be caused

by different of solubility parameters between polybenzoxazine and solvents. From the solubility parameter concept is based on the heat of vaporization proposed by Hildebrand et al. [11]

$$\frac{\Delta E_{mix}}{\varnothing_1 \varnothing_2} = V_m (\delta_1 - \delta_2)^2 \qquad \text{----------------- (1)}$$

$$\delta = \left[\frac{\Delta E_{vap}}{V_m}\right]^{1/2} \qquad \text{----------------- (2)}$$

Where δ_1 and δ_2 = solubility parameter (which are polymer and solvent, respectively in this work)

V_m = average molar volume based on mole fraction

Φ_1 and Φ_2 = volume fraction of material 1 and 2

ΔE_{mix}= energy of mixing and ΔE_{vap}= heat of vaporization

Therefore, the difference in solubility parameter can be used to predict the miscibility between polybanzoxazine and solvent. The universal solubility parameter of DMF, dioxane and isopropanol are 12.1, 10.0 and 8.8 $(cal/cm^3)^{1/2}$, respectively.

For carbon xerogel in dioxane, the longer gelation time (table 4.4) implies that the solubility parameter of polybenzoxazine precursor is close to that of dioxane. From smaller difference solubility parameter lead to good miscibility that gives the difficult of phase separation. As a result, benzoxazine particle have time to rearrange, forming denser morphology and creating smaller amounts of pore as shown in Fig 4.10 (a)

In case of using DMF as a solvent, the shorter gelation time (table 4.4) imply that the larger difference in solubility parameter between benzoxazine precursor and DMF lead to poor miscibility or easy phase separation of benzoxazine from DMF, generating looser morphology (Fig 4.10 (b))

However, in case of using isopropanol as a solvent, interestingly the spherical particles were obtained (fig 4.10 (c)) without using any surfactant and there has many work of other that can get spherical micelle by using this solvent [12]. According to like-dissolve-like concept, methyl groups of isopropanol turned in and had benzoxazine precursor inside and the hydroxyl group outside. Therefore, isopropanol acted like surfactant to generate spherical particles of polybenzoxazine. (Fig 4.9)

Table 4.4 Gelation time of polybenzoxazine in different solvents

Types of solvent	Gelation time
Dioxane	7 hours
DMF	15 minutes
Isopropanol	5 hours

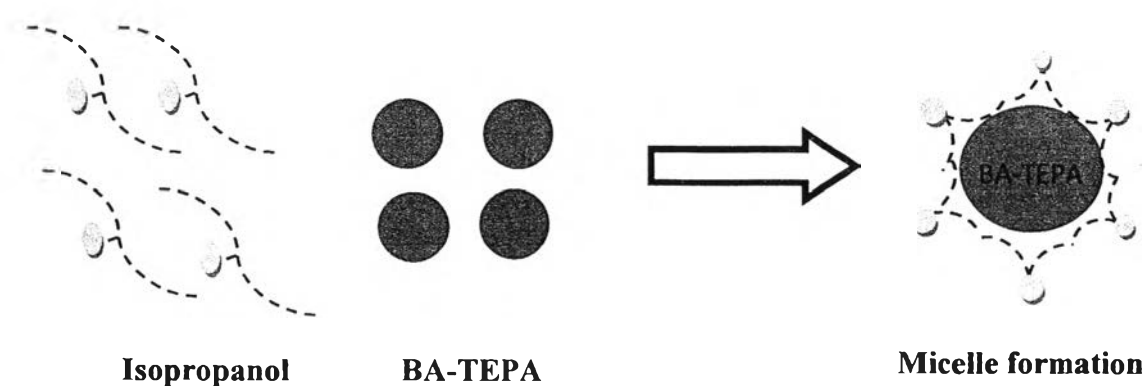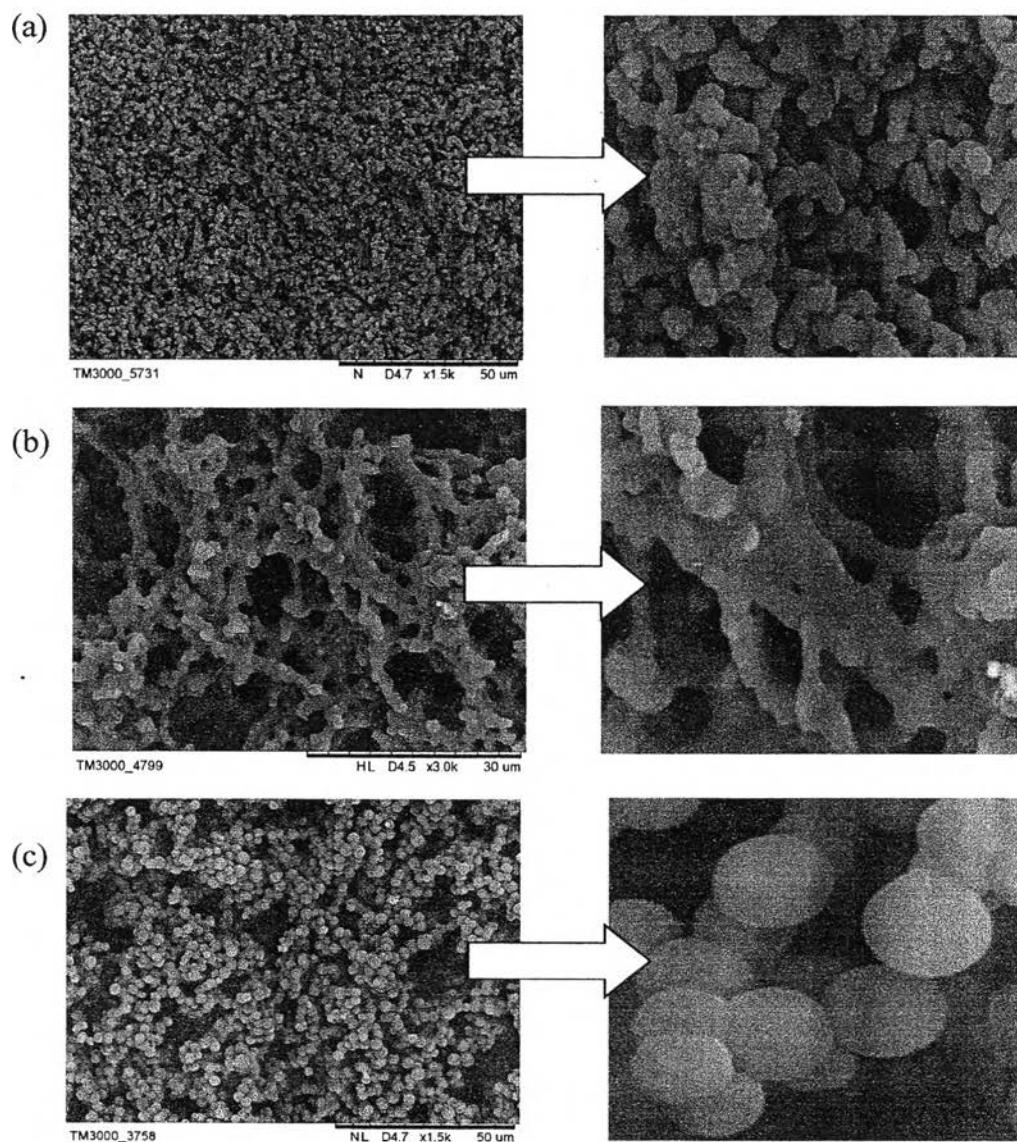**Isopropanol**   **BA-TEPA**   **Micelle formation**

Fig 4.9 Schematic micelle formation of isopropanol.

4.10 (a) carbon xerogel in dioxane, (b) in DMF and (c) in isopropanol.

4.4.3.3 Effect of Surfactant on Morphologies of Polybenzoxazine

Polybenzoxazine based carbon xerogel were synthesized by using Pulonic P123 as a surfactant. The morphologies of polybenzoxazine based carbon xerogel were observed by SEM technique. Figure 4.11 shows the SEM micrographs of polybenzoxazine based carbon xerogel synthesized with different concentrations of P123 from 0% to 25%. All samples shown the 3D-interconnected

structure with particle size about 1-3 micrometers. Fig 4.11a-f show looser morphologies, smaller particles when increase percentage of P123. After increasing the concentration of P123, micelle formation was formed in which polybenzoxazine molecules was sounding by. It was found that the more percentage of surfactant the more micelle formation to surround polybenzoxazine particles giving looser morphology with smaller particles. But, when the P123 concentration increase to 22% and 25% (Fig 4.11g and 4.11h), the denser and more agglomerated carbon particles were observed. The reason might be the conversion of phase between major phase (in this case polybenzoxazine) and minor phase (in this case P123). So, when curing at 220 °C, P123 act as solvent.
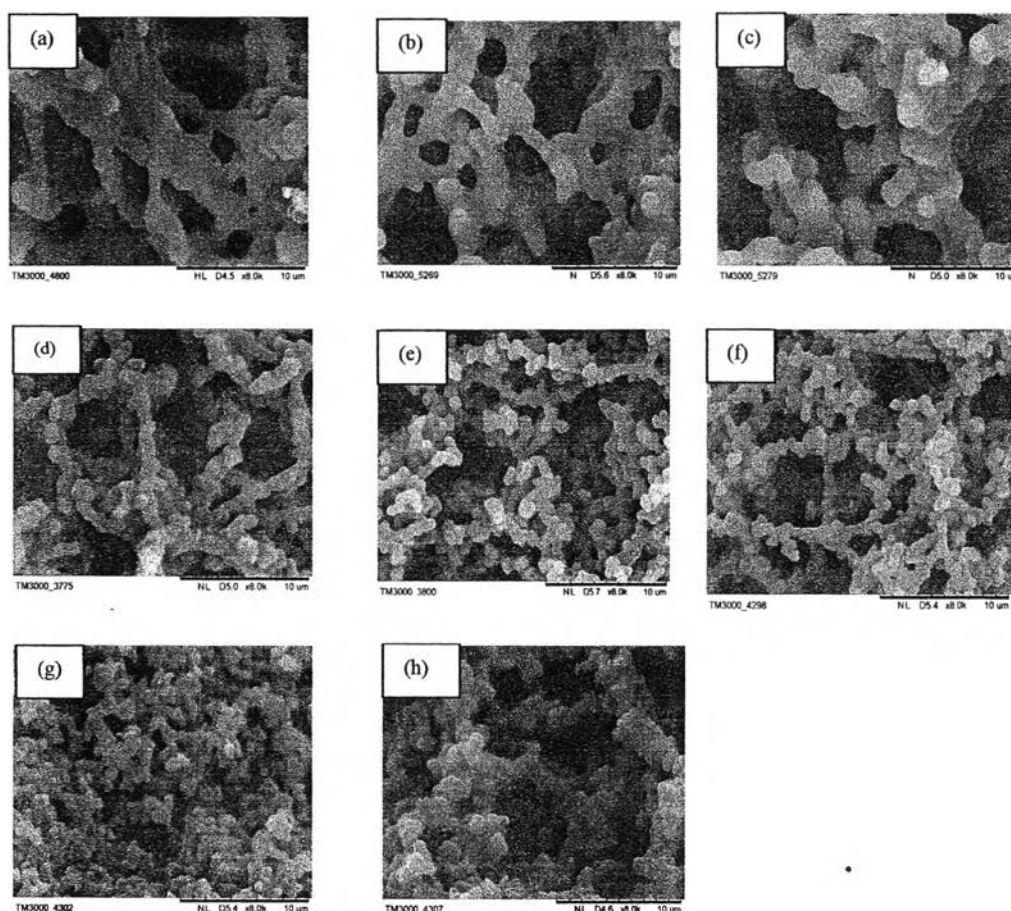

Fig 4.11 Morphology of polybenzoxazine-based porous carbon: (a) carbon xerogel at 25 wt% PBZ without Pluronic P123 template, carbon xerogel at 25 wt% PBZ with Pluronic P123 loading (b)1%, (c) 6%, (d) 9%, (e) 12 %, (f) 20%, (g) 22% and (h) 25%.

However, the spherical nanoparticles (a) was not obtained because of the high reaction activity that enables the rate of polymer to be faster than the rate of micelle formation.
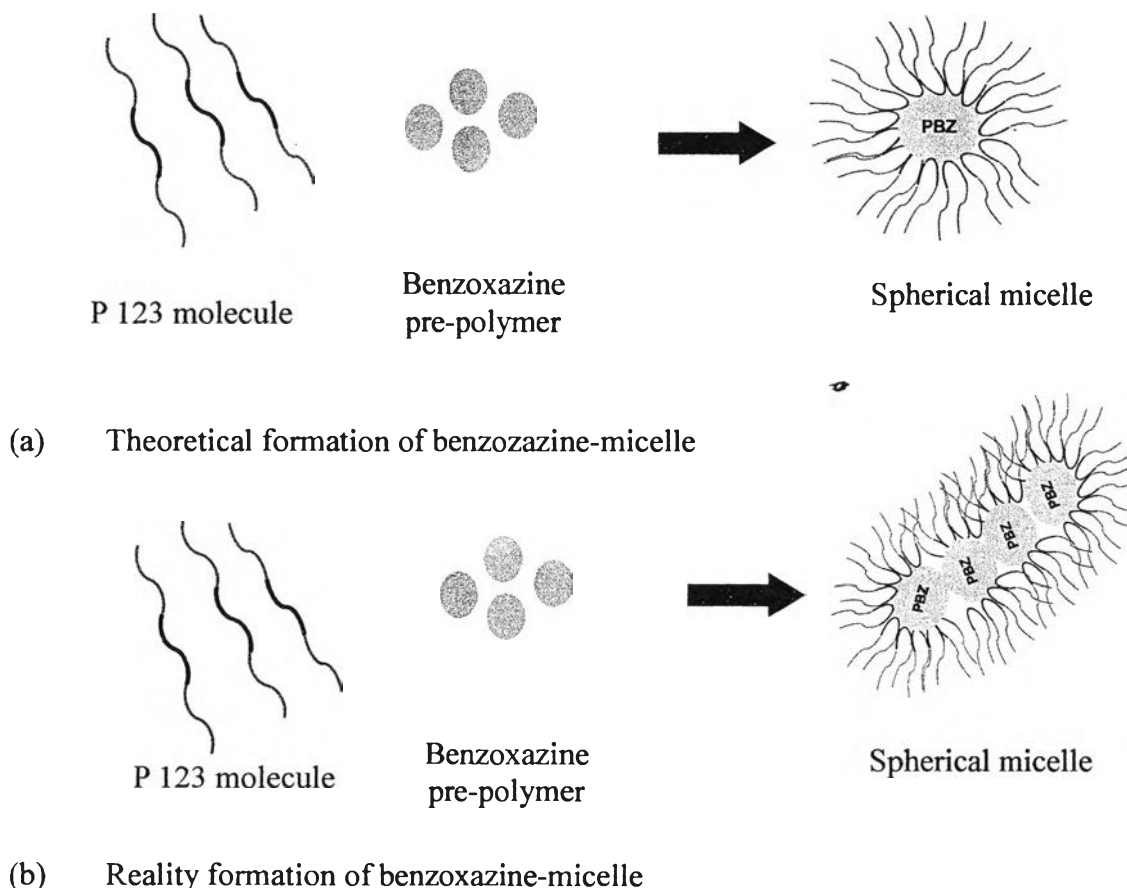

P 123 molecule   Benzoxazine pre-polymer   Spherical micelle

(a)   Theoretical formation of benzozazine-micelle

P 123 molecule   Benzoxazine pre-polymer   Spherical micelle

(b)   Reality formation of benzoxazine-micelle

Fig 4.12 Scheme of the benzoxazine-micelle formation

4.4.4 Surface Characterization of Polybenzoxazine-based Porous Carbon

4.4.4.1 The Effect of Surfactant on the Specific Area Total Pore Volume

The specific surface area, total pore volume, and micropore volume of polybenzoxazine-based porous carbon using P123 as a soft template were show in Table 4.5. The surface area was slightly different because of the effect of P123 loading. The carbon xerogel from polybenzoxazine/6%P123 composite shows the highest BET surface area of 345.0 m^2/g with the highest total pore volume of 0.18 cm^3/g. In case of polybenzoxazine/25%P123 composite-based porous carbon, the BET surface area was decreased to 45.6 m^2/g with the lowest total pore volume

of 0.04 cm³/g. These results imply that P123 can be used to improve the specific surface area and total pore volume by adding in a proper condensation [13]

Table 4.5 The BET analysis of carbon of polybenzoxazine in different P123 loading

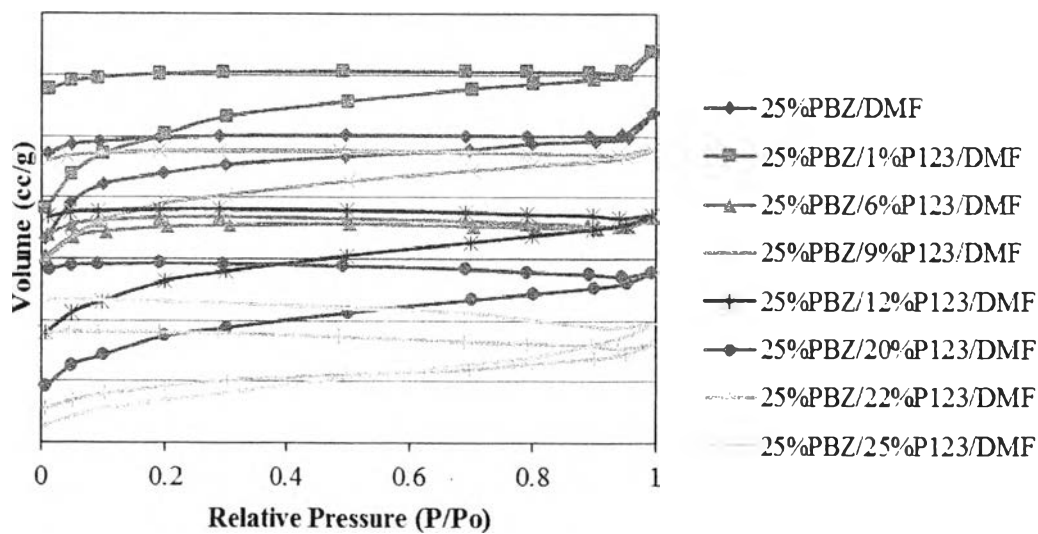| Sample name	S_{BET} (m²/g)	V (cm³/g)	Micropore volume (cc/g)
25%PBZ/DMF	282.4	0.17	0.13
25%PBZ/1%P123/DMF	291.8	0.17	0.14
25%PBZ/6%P123/DMF	345.0	0.18	0.17
25%PBZ/9%P123/DMF	218.3	0.13	0.11
25%PBZ/12%P123/DMF	189.5	0.12	0.10
25%PBZ/20%P123/DMF	172.0	0.11	0.09
25%PBZ/22%P123/DMF	51.6	0.05	0.03
25%PBZ/25%P123/DMF	45.6	0.04	0.03

Fig. 4.13 The N₂ adsorption-desorption isotherms of polybenzoxazine carbon in different P123 loading.

Figure 4.13 shows the BET isotherms of carbon of polybenzoxazine with different P123 loading. According to the classification by IUPC, all sample exhibited the standard isotherm of type I. Type I represents the characteristics of microporous [14].

4.4.4.2 The Effect of Pyrolysis Temperature and Activation on Specific Surface Area and Total Pore Volume

The specific surface area, total pore volume, and micropore volume of polybenzoxazine-based porous carbon in different pyrolysis temperature were shown in Table 4.6. The carbon xerogel at 800 °C shows the highest BET surface area of 345 m^2/g with the highest total pore volume of 0.15 cm^3/g. Whereas, in case of carbon xerogel at 1000 °C, it was found that the pores were collapsed resulting in the BET surface area was decreased to 1 m^2/g with on pore volume due to increasing the heating rate causing the pore collapse. These results imply that pyrolysis temperature have effect on the specific surface area and total pore volume by adding in a proper condensation [14].

Table 4.6 The BET analysis of porous carbon derivative polybenzoxazine at different pyrolyzed temperatures

Sample name	Pyrolysis Temperature (°C)	Heating rate (°C/min)	S_{BET} (m²/g)	V (cm³/g)	Micropore volume (cc/g)
25%PBZ/6%P123/DMF	800 °C	1.67	345	0.18	0.17
25%PBZ/6%P123/DMF	850 °C	2.08	233	0.14	0.11
25%PBZ/6%P123/DMF	900 °C	2.50	186	0.11	0.09

Table 4.7 The BET analysis of activated carbon of polybenzoxazine at different pyrolysis temperature

Sample name	Pyrolysis Temperature (°C)	Heating rate (°C/min)	S_{BET} (m²/g)	V (cm³/g)	Micropore volume (cc/g)
AC25%PBZ/6%P123/DMF	800 °C	1.67	1,415	0.76	0.66
AC25%PBZ/6%P123/DMF	850 °C	2.08	1,062	0.56	0.51
AC25%PBZ/6%P123/DMF	900 °C	2.50	1,147	0.61	0.55

Table 4.7, carbon derived from carbonized polybenzoxazine and polybenzoxazine P123 composite obtained from carbonization at 800 °C, 850 °C and 950 °C then CO_2 activation at 900 °C for 3 hr. were prepared. The BET surface area reached the maximum of 1400 m²/g under the following condition: activation temperature was 900 °C, activation time was 180 min, and CO_2 flow rate was 500 cm³/min [15].
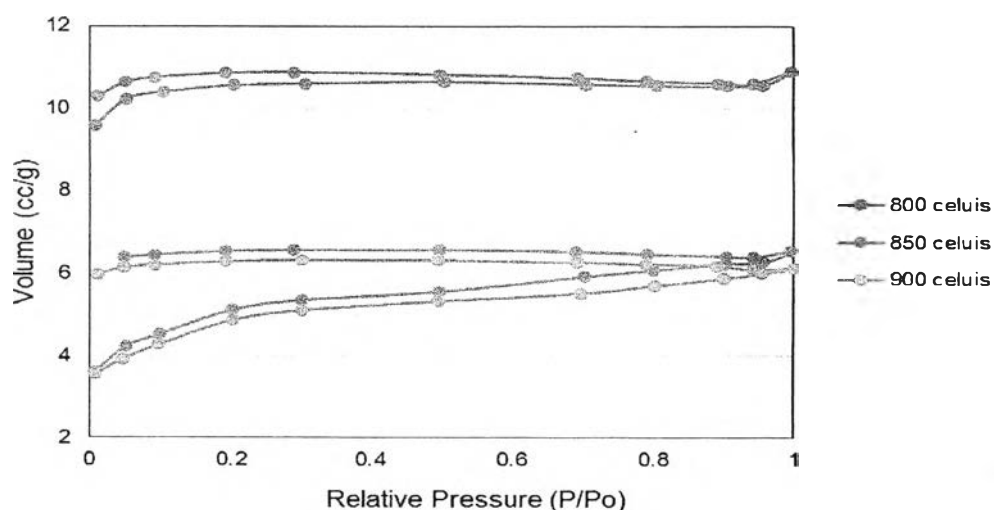

Fig. 4.14 The N_2 adsorption-desorption isotherm of polybenzoxazine carbon using different pyrolysis temperatures.
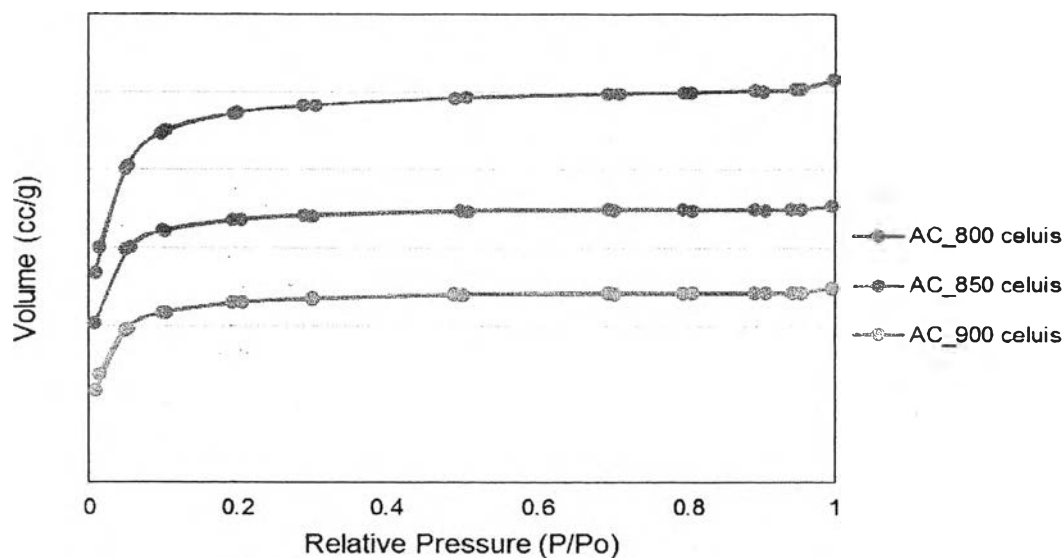
Fig 4.15 The N₂ adsorption-desorption isotherm of polybenzoxazine activated carbon using different pyrolysis temperatures.

The N₂ Adsorption/desorption isotherms of polybenzoxazine carbon and polybenzoxazine activated carbon in Figure 4.14 and Figure 4.15 exhibiting a type I isotherm. It means that all carbon and activated carbon of polybenzoxazine samples has microporous structure. Howe. Non-activated carbons have larger pore diameter than of activated carbons because of adsorption and desorption value. Therefore, activation increase micropore volume and give smaller micropore.

4.4.5 Order Structure of Polybenzoxazine Based-Porous Carbon

4.4.5.1 Effect of Solvent on Order Structure of Polybenzoxazine Based Porous Carbon

The XRD patterns of polybenzoxazine based-porous carbon by using different solvent (Figure 4.16) and pyrolysis in different temperature (Figure 4.17) showed a single broad peak at 2θ 26.6°, relate to the characteristic peak (002) of graphite at 26.58° [16] suggesting that graphene layers are already formed as parallel layers and another single broad peak at 2θ 44° including the ordering of carbon atoms inside the graphene layer. When dioxane was used as a solvent, the obtained XRD pattern shows the highest intensity, implying higher ordered structure of porous carbon obtained. And comfirm with stacking height (Lc) in Table 4.8.
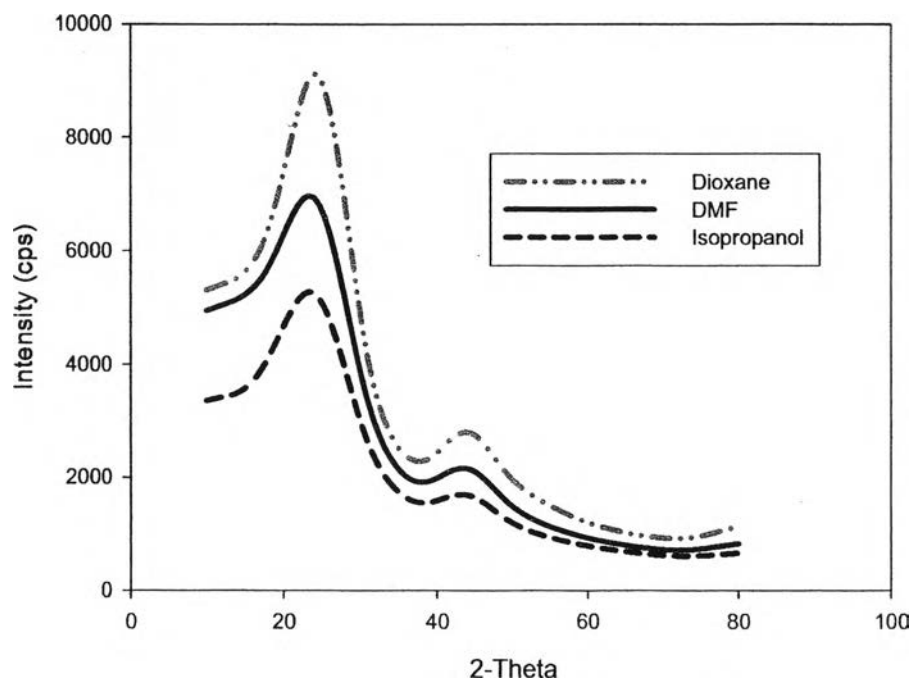
Fig 4.16 XRD pattern of polybenzoxazine based porous carbon in different solvent.

Table 4.8 The stacking height (Lc) of polybenzoxazine based porous carbon in different solvent systems and pyrolysis temperature

Sample name	Pyrolysis Temperature (°C)	Heating rate (°C/min)	Stacking height (Lc)
25%PBZ/Dioxane	800 °C	1.67	0.917
25%PBZ/DMF	800 °C	1.67	0.819
25%PBZ/Isopropanol	800 °C	1.67	0.769
25%PBZ/6%P123/DMF	800 °C	1.67	0.835
25%PBZ/6%P123/DMF	900 °C	2.50	1.019
25%PBZ/6%P123/DMF	1000 °C	3.33	0.981

4.4.5.2 Effect of Pyrolysis Temperature on Order Structure of Polybenzoxazine Based Porous Carbon

The porous carbon pyrolyzed under higher temperature gave higher intensity of the XRD pattern (fig 4.17) due to high temperature can be improve the order structure [17]. Moreover, we can comfirm with **Stacking height (Lc)** (Table 4.8) which increased with increase in carbon content whereas interlayer spacing d_{002} decreased with increase in carbon content, aromaticity and coal rank. [18]. However, when the pyrolysis temperature was increased up to 1000 °C, the intensity of the XRD pattern was obviously decreased which might be due to the structure collapse at this temperature.
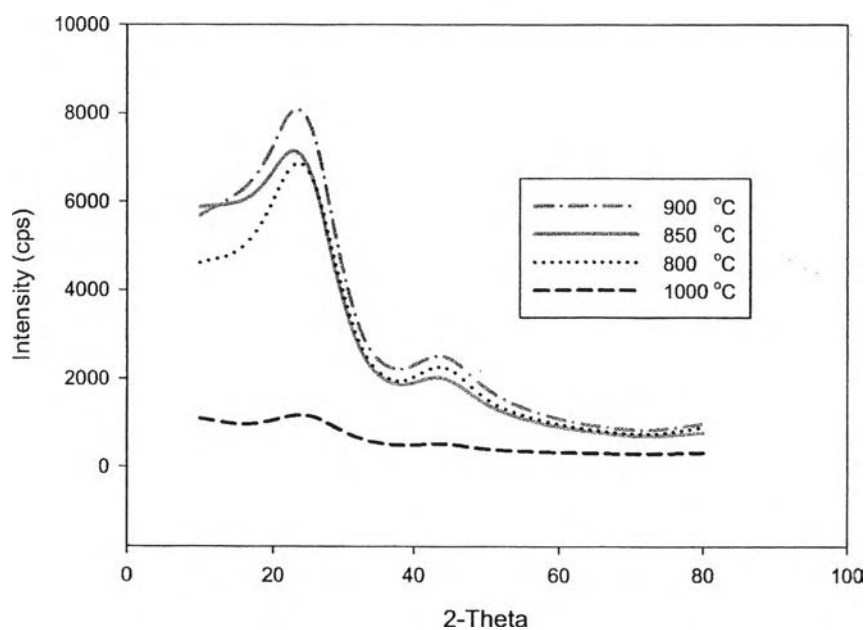

Fig 4.17 XRD pattern of polybenzoxazine based porous carbon in different pyrolysis temperature.

4.4.6 CO₂ Adsorption

The CO_2 adsorption result of activated polybenzoxazine porous carbon which has maximum BET surface area (1400 m^2/g) at 1 ATM compare with Zeolite A and activated carbon from Hauchhum and co-worker [19] work at 35 °C as shown in table 4.8, activated polybenzoxazine carbon give higher amount of CO_2

adsorption. So, activated polybenzoxazine carbon is suitable for the CO_2 adsorption application due to contain large amount of micropore.

Table 4.9 The amount of CO_2 adsorption at 1 ATM

Temperature (°C)	Material	Amount of CO_2 adsorption (mmol/g)
35 °C	PBZ-AC	3.25
	Zeolite 4A	3.07
	AC	2.71

4.5 Conclusion

Porous carbon xerogel was successfully synthesized via soft templating method by using polybenzoxazine as a carbon precursor and triblock copolymer Pluronic P123 as a soft template. Different textural properties were obtained by varying different synthesis parameters which are solvents, concentrations of polybenzoxazine and concentrations of surfactant. The specific surface area and micropore volume could be improved by optimizing the surfactant concentration. All solvents gave porous carbon with the microporous property. Micro-size spherical particles were obtained by using isopropanol as a solvent due to the self-micelle-like formation. In case of using dioxane as a solvent, denser morphology was obtained due to the small difference in solubility parameter between polybenzoxazine and dioxane. Comparing the morphology of polybenzoxazine when synthesized in DMF and dioxane system, looser morphologies with 3D interconnected were obtained in DMF system because of poor miscibility between polybenzoxazine and DMF.

Moreover, we have reported the condition which gave the highest specific surface area and micropore volume by varying pyrolysis temperature and treatment activation under CO_2. After activation under CO_2 at 900 °C, the specific surface area

and micropore volume were about four times higher than that of polybenzoxazine-based carbon xerogel without activation process.

Finally, we have study about CO_2 adsorption by loaded activated polybenzoxazine porous carbon that have highest surface area 0.1 g into the stainless steel adsorption chamber which was heated by the furnace in order to reach the adsorption temperatures. He gas was used as a purge gas in this study. The adsorption processes were carried out by using high purity CO_2 gas.The result shown that the CO_2 adsorption result at 1 ATM compare with Zeolite A and AC from Hauchhum and co-worker work at 35 $^{\circ}$C, activated polybenzoxazine carbon give higher amount of CO_2 adsorption. So, activated polybenzoxazine carbon is suitable for the Co_2 adsorption application due to contain large amount of micropore.

4.6 Acknowledgements

4.7 References

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