

CHAPTER IV

MORPHOLOGICAL DESIGN OF POLYBENZOXAZINE-BASED CARBON BY SOFT TEMPLATING METHOD

4.1 Abstract

Porous materials, especially porous carbon have received much attention in the past decade because of their indispensable applications in energy storage and conversion, catalysis, adsorption, and others. Template method is the preparation of carbon materials with controlled architecture and relatively narrow pore size distribution. Two types of templates, classified as soft template or hard template, are used as molds to form porous materials. However, the drawbacks of hard template are multi-step and high cost. Which may cause a barrier to industrial applications. So, in this research, we report a facile process to synthesized porous carbon by using soft template method. Polybenzoxazine, a novel phenolic resin was used as a carbon precursor and triblock copolymer, Pluronic P123 was used as a template. The morphology of carbon particles could be design by adjusting the concentration of P123. The results from SEM micrographs showed that the carbon from polybenzoxazine/6.000%P123 composite exhibited a rod-like structure. Moreover, this research also study the effect of activation process by CO₂ at 900 °C in order to increase the specific surface area of the resulting carbon.

Keyword: polybenzoxazine/soft-template method

4.2 Introduction

The International Union of Pure and Applied Chemistry (IUPAC) defined porous materials into three types based on their pore size: microporous (pore size < 2 nm), mesoporous (2-50 nm), and macroporous (>50 nm). Due to their advantages, such as thermal conductivity, electrical conductivity, chemical stability, and low density. Porous materials have been extensively studied and used in various applications, such as water purification, catalyst support, electrode material for energy storage devices etc [1].

In general, porous carbon material made from catalytic activation and carbonization usually show the disordered structures with wide pore size distribution because of the etching process that are difficult to control. In order to generate the ordered structure of porous carbon materials, template synthesis method with controlled architecture and relatively narrow pore size distribution has been widely investigated.

The template synthesis method can be classified into two types, hard and soft template. The hard template carbonization approach, usually involves the following steps: (a) the preparation of a porous template with controlled porosity; (b) the introduction of a suitable carbon precursor into the template pores by wet impregnation, chemical vapour deposition or a combination of both methods; (c) the polymerization and carbonization of carbon precursor to generate an organic-inorganic composite; and (d) the removal of the inorganic template by using HF or NaOH to yield a porous carbon. However, the drawbacks of hard template method are a multi-step and high cost, which may cause a barrier to industrial applications [2].

To reduce the number of preparation steps and the cost involved in producing porous carbon materials, soft-templating method was used in this work. Our strategy is to use an organic-organic interaction between Polybenzoxazine, a thermosetting polymer and block copolymer Pluronic P123, a thermally decomposable surfactant to form a periodic ordered nanocomposite. The organic-organic nanocomposite was pyrolyzed under nitrogen gas at high temperature. The effect of template loading content was investigated. The BET measurement was used to characterize surface area of nanoporous carbon. The morphology was determined

by using SEM. The CO₂ treatment was also used to increase surface area and electrical conductivity of the resulting carbon was also study.

4.3 Experimental

4.3.1 Materials

4.3.1.1 Chemicals:

Polymer Chemicals

- Bisphenol-A
- Formaldehyde
- Tetraethylenepentaamine (TEPA)
- Poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) (Pluronic P123)

Solvents

- Dimethylformamide (DMF)

4.3.2 Equipments

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 using a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of 4000-400 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. The sample was loaded ~5 mg on the platinum pan

and heated from 30 to 900°C a heating rate of 20 °C/min under N₂ 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 and cooled down at a rate of 5°C/min under a N₂ 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 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.

4.3.3 Experimental Procedures

4.3.3.1 Synthesis of Polybenzoxazine Precursor

Polybenzoxazine precursors were synthesized by dissolving Pluronic P123 and bisphenol-A (varied the concentration of P123 in four conditions,(see in Table 5.1)) in *N,N*-dimethylformamide (10 g) in glass bottle and stirred until the clear solution was obtained. Formaldehyde solution (1.20 g) was then 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 4.1. Then, the precursor was filled in a vial and placed in an oil bath at 80°C for 24 hr to generate benzoxazine gel. The benzoxazine gels were cut into a small pieces and then dried at ambient temperature follow by placing in an oven at 100°C in 1 hr, 200°C in 1.30 hr, and 220 in 15 min.

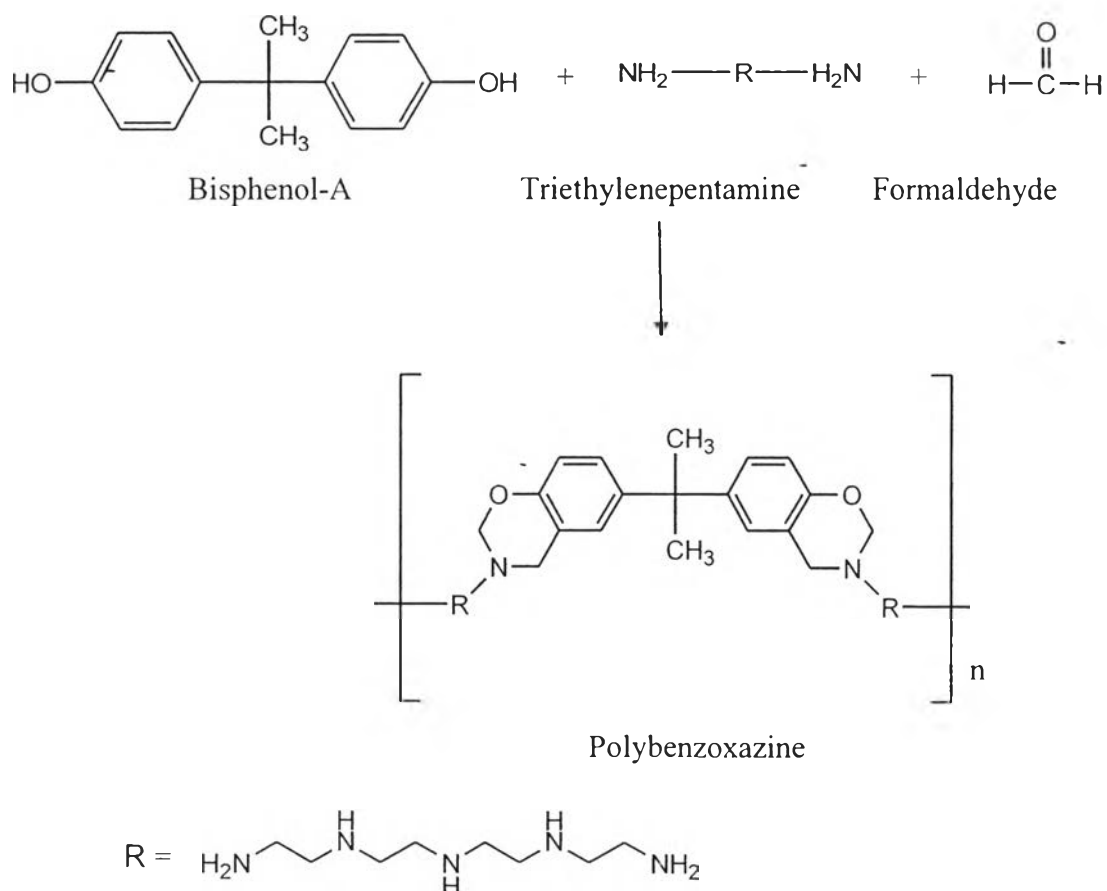


Figure 4.1 Preparation of polybenzoxazine precursor.

Table 4.1 Template loading content of each sample

Sample name	Molar ratios
0.188% P123	0.0013 P123 : 0.695 bisphenol A
0.375% P123	0.0026 P123 : 0.695 bisphenol A
0.750% P123	0.0052 P123 : 0.695 bisphenol A
1.500% P123	0.0104 P123 : 0.695 bisphenol A
3.000% P123	0.0208 P123 : 0.695 bisphenol A
6.000% P123	0.0416 P123 : 0.695 bisphenol A

4.3.3.2 Preparation of Porous Carbon

Polybenzoxazines were pyrolyzed under nitrogen flow rate of $500 \text{ cm}^3/\text{min}$. The heating profile was as follows: heating from room temperature to $200 \text{ }^\circ\text{C}$ in 60 min, 200 to $600 \text{ }^\circ\text{C}$ in 360 min, 600 to $800 \text{ }^\circ\text{C}$ in 120 min, and holding at $800 \text{ }^\circ\text{C}$ for 120 min and finally cooling down to room temperature.

Activated porous carbon was prepared by carbonization of carbon xerogel with carbon dioxide at $900 \text{ }^\circ\text{C}$ for 180 min.

4.4 Results and discussions

4.4.1 The Chemical Structure of the Precursors

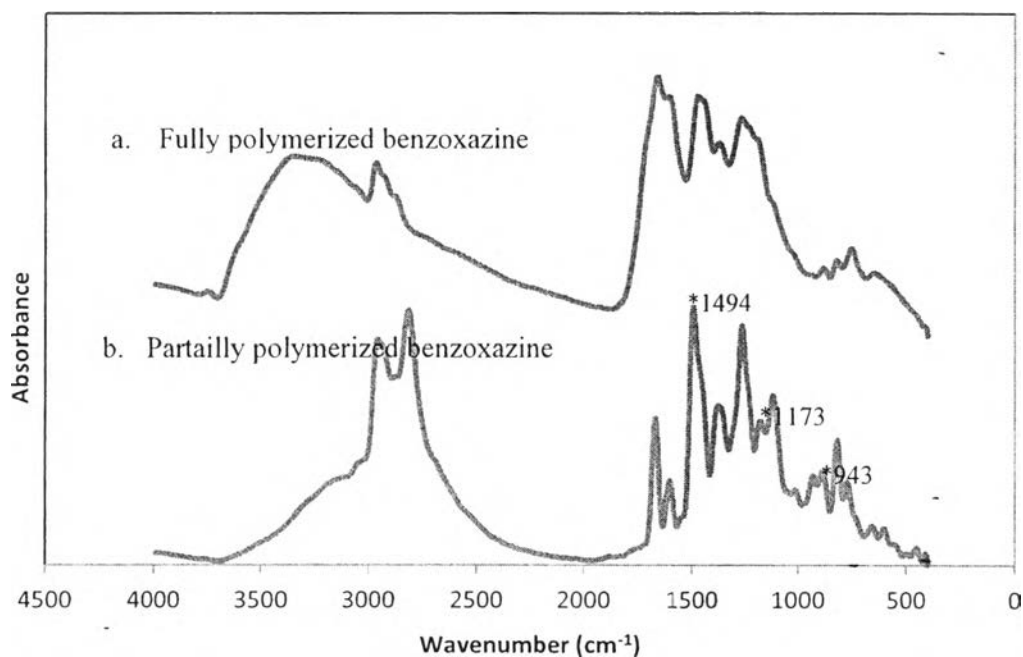


Figure 4.2 FT-IR spectrum of polybenzoxazine precursors.

The structure of benzoxazine precursor was examined by FT-IR spectra. The asymmetric stretching of C-O-C ($1230\text{-}1236 \text{ cm}^{-1}$), asymmetric stretch of C-N-C ($1020\text{-}1240 \text{ cm}^{-1}$), CH_2 wagging of oxazine ($1360\text{-}1380 \text{ cm}^{-1}$) were observed. (Fig 4.2) Additionally, the characteristic absorptions assigned to trisubstituted benzene ring at $1491\text{-}1500 \text{ cm}^{-1}$ and out of plan bending vibrations of

C-H at $920\text{-}950\text{ cm}^{-1}$ were detected. After polymerized at 220°C , the intensity of those characteristic absorption bands decreased because the ring opening polymerization was completed as shown in Figure 4.2(a) [3].

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 polymerization, the exotherm completely disappeared showing that the ring-opening of oxazine was completed [3].

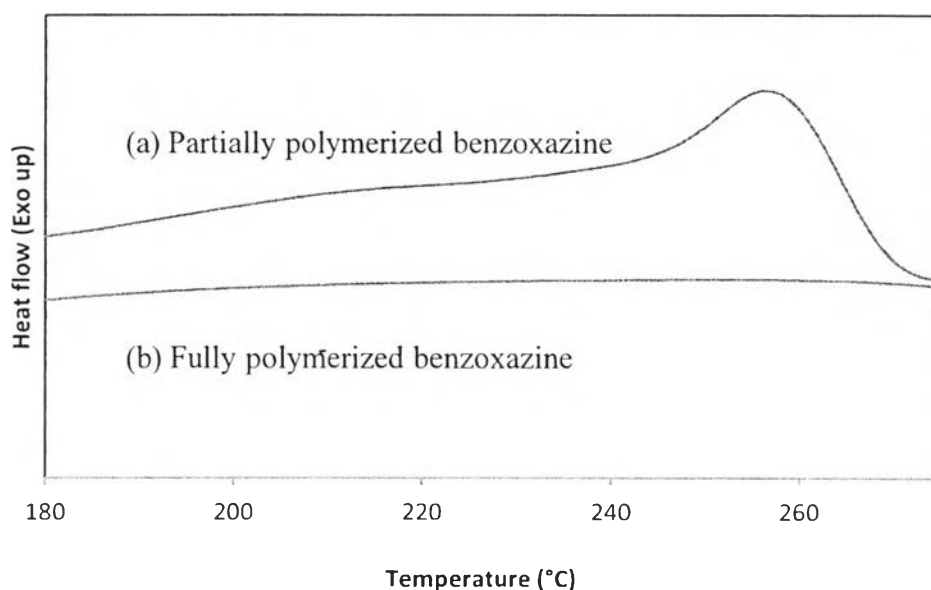


Figure 4.3 DSC thermograms of polybenzoxazine precursor.

In the binary mixture system, the curing exotherms of benzoxazine monomer and the block copolymer Pluronic P123 are shown in Figure 4.3. The studied compositions were observed at 0.188%, 0.375%, 0.750%, 1.500%, 3.000%, and 6.000% P123. It is obviously seen that the exothermic peaks of the neat benzoxazine is located at 220°C whereas the exothermic peaks of Polybenzoxazine/Pluronic P123 composite at 0.188%, 0.375%, 0.750%, 1.500%,

3.000%, and 6.000% P123 are 256, 256, 257, 257, 256 and 257 °C respectively.

After curing at 220°C, the exotherm peak were disappear, this mean that the mixture of benzoxazine/Pluronic P123 were fully polymerized.

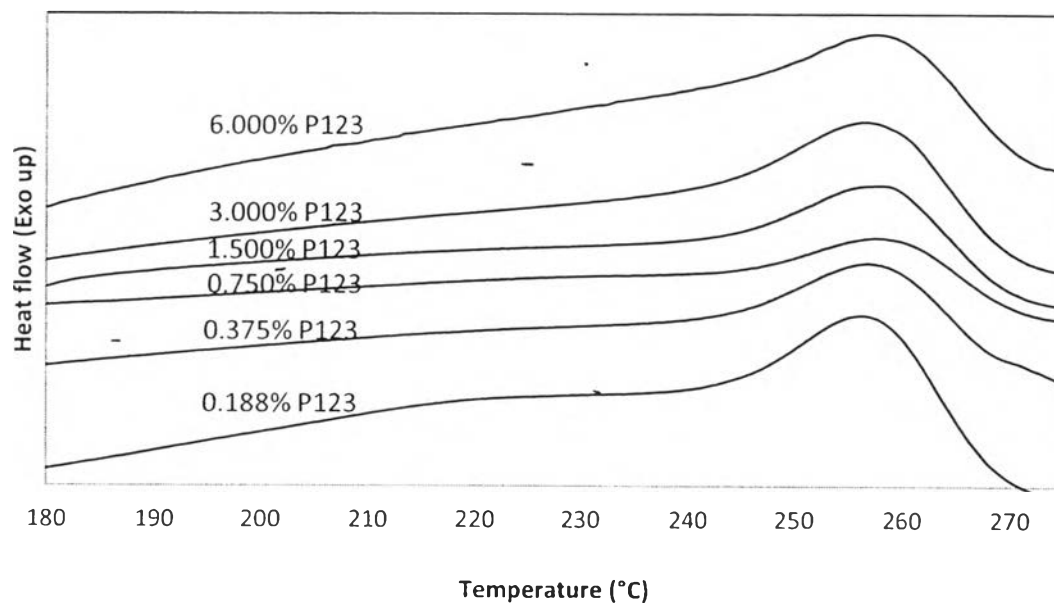


Figure 4.4 DSC patterns of polybenzoxazine/P123 composite at a various compositions: 0.188%, 0.375%, 0.750%, 1.500%, 3.000% and 6.000% P123.

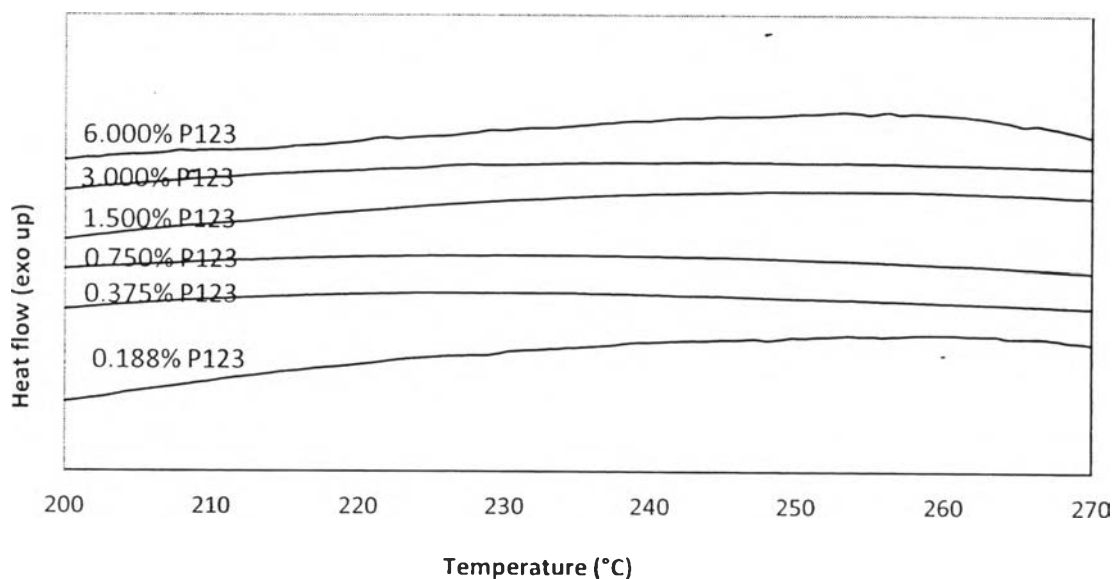


Figure 4.5 DSC patterns of polybenzoxazine/P123 composite at a various compositions: 0.188%, 0.375%, 0.750%, 1.500%, 3.000%, and 6.000% P123 after curing at 220°C.

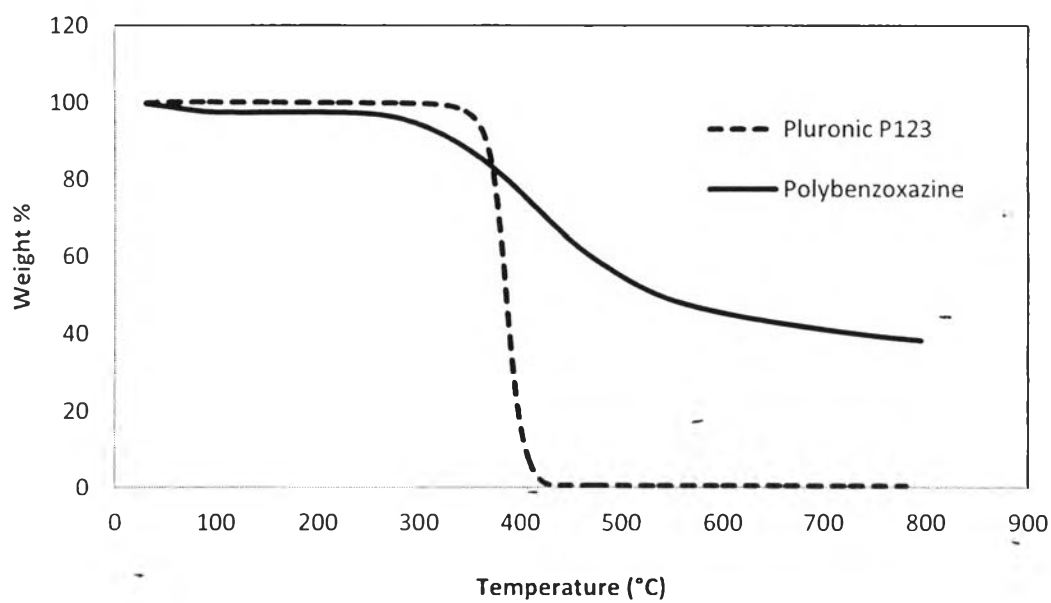


Figure 4.6 TGA thermogram of polybenzoxazine precursor and Pluronic P123.

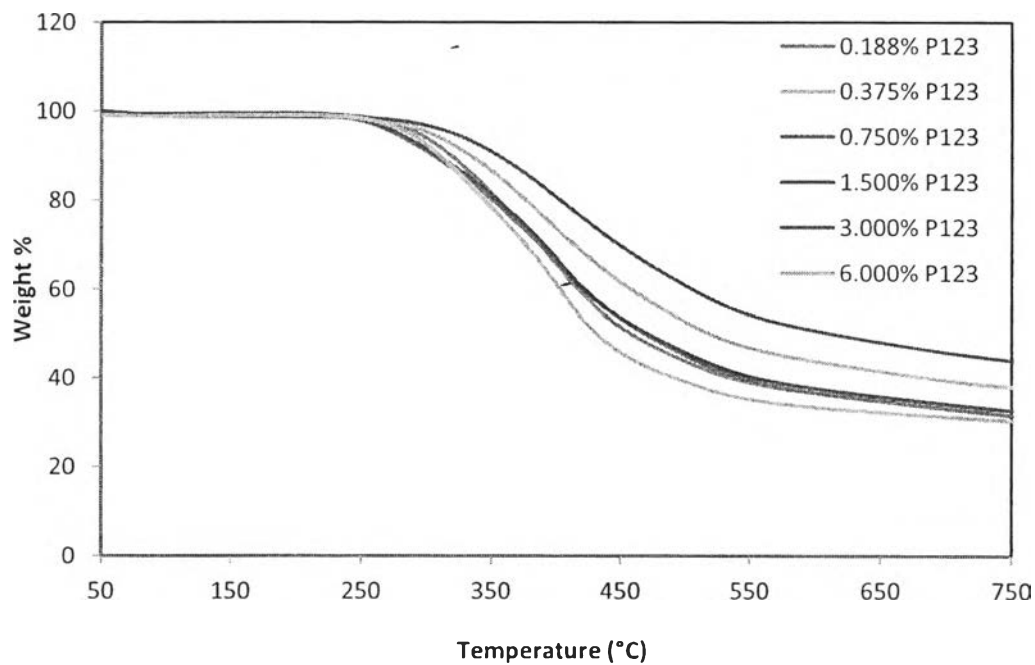


Figure 4.7 TGA thermogram of polybenzoxazine/P123 composite.

As a reference, TGA curves of polybenzoxazine and Pluronic P123 were displayed in Fig. 4.6 The decomposition temperature of polybenzoxazine began at 268 °C with the maximum mass loss rate in the temperature range of 268 to 600 °C. The result was in accordance with our previous study [4]. On the other hand, the TGA curve of P123 suggest that P123 composes significantly from 300 °C to 400 °C and there are no char yield occur from the decomposition of P123, revealing that the P123 could be easily removed upon 400 °C in N₂ atmosphere.

In Fig. 4.7 no obvious weight loss was observed at 300 – 400 °C. The TGA curves are very similar to that of fully polymerized benzoxazine. The decomposition of the P123 is the least affected, as the benzoxazine is localized in the P123 domain. The P123 chain is tangled with benzoxazine because of the interaction between P123 and polybenzoxazine [5].

4.4.3 Morphology of Porous Carbon

4.4.3.1 Morphology of Porous Carbon Derived from Polybenzoxazine and Polybenzoxazine/P123 Composite

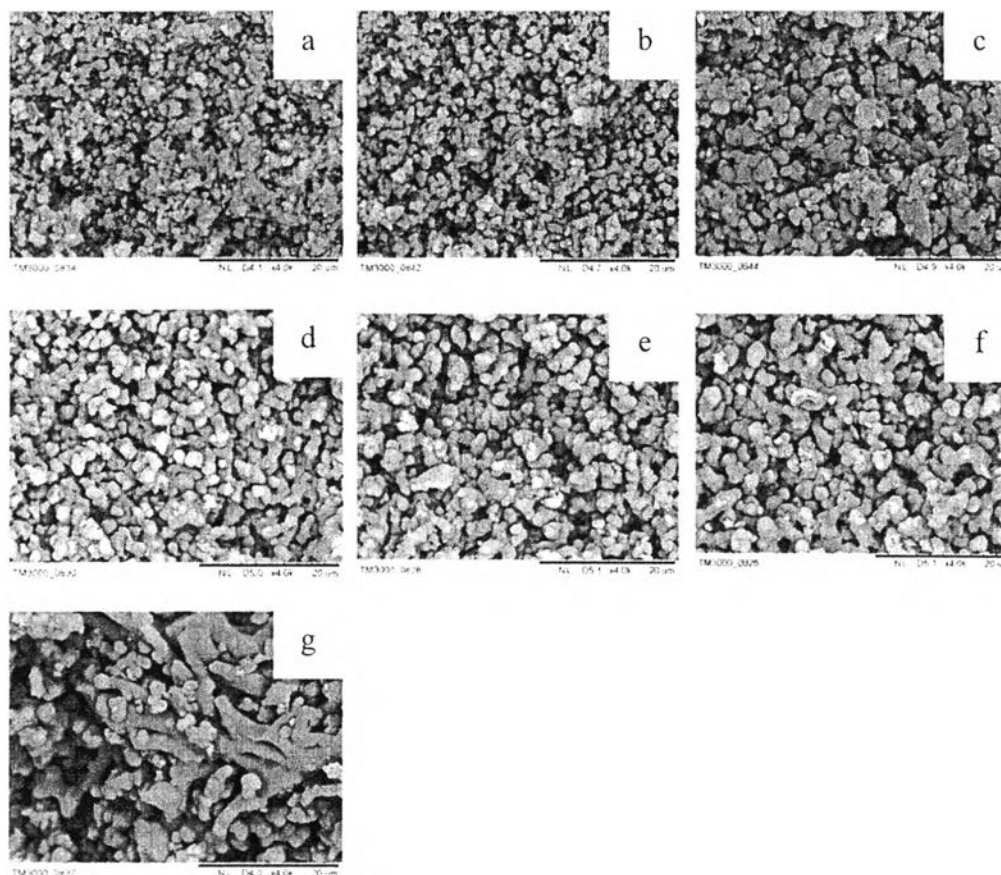


Figure 4.8 Morphology of polybenzoxazine-based porous carbon: (a) carbon xerogel without Pluronic P123 template, (b) carbon xerogel with Pluronic P123 loading 0.188%, (c) 0.375%, (d) 0.750%, (e) 1.500%, (f) 3.000%, and (g) 6.000%.

The morphologies of porous carbon were observed by SEM (Scanning electron Microscope). Fig. 4.8 shows the SEM micrographs of polybenzoxazine based carbon xerogels synthesized at different concentration of P123 from 0.188% to 6.000%. Fig 4.8-a shows the morphologies of porous carbon derived from polybenzoxazine without P123. These carbon particles with the size of about 1 μm are slightly hard to distinguish in shape and form. After increasing the concentration of P123, carbon particles were began to pack with each other, the size was increase,

and show the disordered structure (Fig. 4.8-b,c,d,e). The main reason may be the extremely weak interaction between polybenzoxazine and P123 surfactant [6]. When the concentration of P123 reach to 3.000%, the carbon particles were began to formed to a coral-like shape, with the diameter around 2 μm (Fig 4.8-f). Finally, a rod-like carbon particles were obtained, by increasing the P123 concentration to 6.000% (Fig. 4.8-g).

To explain the formation and the size of carbon particles, the self assembly formation of P123 was used to clarify. After dissolution of P123 into the solvent, the molecules of P123 were form with two hydrophilic head groups toward the solvent and hydrophobic tail group away from the solvent. In this study, polybenzoxazine (BA-TEPA) shows the hydrophobic property and formed inside the interior region of P123 micelle under the driving of hydrogen bond interaction between polybenzoxazine and P123 micelles. Higher concentration of P123 favor the formation of carbon particles with higher curvature. When P123 concentration was 6.000%, rod-like composite micelles were formed. For this trend, we can proved that, the rod-like carbon particles were produce from rod-like micelles of amphiphilic surfactant P123 [7].

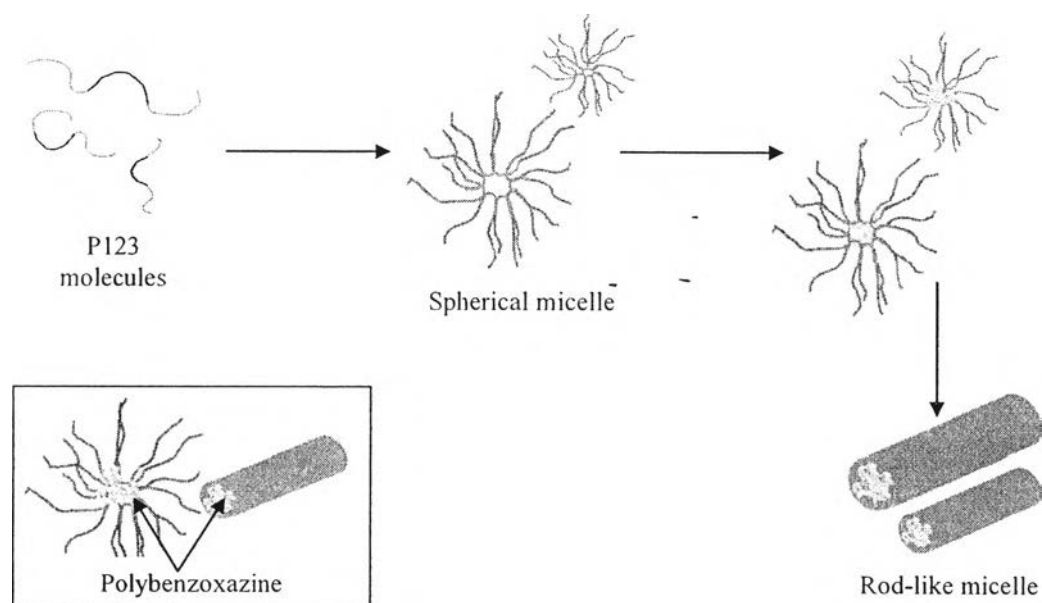


Figure 4.9 Scheme of the benzoxazine-P123 system.

4.4.3.2 Morphology of Activated Porous Carbon

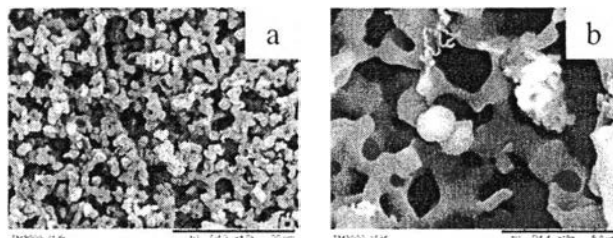


Figure 4.10 Morphology of activated carbon derive from polybenzoxazine/6.000% P123 composite: (a) 4000 magnificant, (b) 15000 magnificant.

SEM micrograph of activated carbon show the hollow structure of carbon particles. Due to the activation process by CO_2 at $900\text{ }^\circ\text{C}$, carbon particles were generated micropore. The results suggest that effect of gasification in a CO_2 atmosphere can produce large surface area and high pore content as we show in Table 4.2.

4.4.4 Surface Characterization of Polybenzoxazine-Derived Porous Carbon

The specific surface area, total pore volume, and average pore diameter of polybenzoxazine-based porous carbon using P123 as a soft template were show in Table 4.2. The surface area was slightly different because of the effect of P123 loading. The carbon xerogel from polybenzoxazine/0.188% P123 composite shows the highest BET surface area of $370.7\text{ m}^2/\text{g}$ with the highest total pore volume of $0.208\text{ cm}^3/\text{g}$. Whereas, polybenzoxazine/6.000% P123 composite-based porous carbon, the BET surface area was decrease to $1.675\text{ m}^2/\text{g}$ with lowest total pore volume of $0.001\text{ cm}^3/\text{g}$. These results imply that P123 can be used to improve the specific surface area and total pore volume by adding in a proper condensation [8].

Table 4.2 Surface area, total pore volume, and average pore diameter of porous carbon prepared from polybenzoxazine and nanoporous carbon derived from polybenzoxazine by using P123 as a soft template

Sample name	Surface area (m ² /g)	V _{total} (cm ³ /g)	Average pore diameter (nm)
Carbon xerogel	337.7	0.193	2.287
0.188% P123	370.7	0.208	2.244
0.375% P123	293.9	0.170	2.310
0.750% P123	199.9	0.145	2.902
1.500% P123	343.9	0.207	2.417
3.000% P123	304.5	0.186	2.447
6.000% P123	337.8	0.183	2.167

Table 4.3 Surface area, total pore volume, and average pore diameter of porous carbon prepared from polybenzoxazine and nanoporous carbon derived from polybenzoxazine by using P123 as a soft template after activated by CO₂ at 900 °C

Sample name	Surface area (m ² /g)	V _{total} (cm ³ /g)	Average pore diameter (nm)
AC-Carbon xerogel	1309	0.704	2.152
AC-0.188% P123	1382	0.749	2.178
AC-0.375% P123	993.3	0.546	2.200
AC-0.750% P123	1118	0.614	2.197
AC-1.500% P123	971.4	0.525	2.163
AC-3.000% P123	1174	0.637	2.172
AC-6.000% P123	1327	0.720	2.137

Activated carbon derived from carbonized polybenzoxazine and polybenzoxazine P123 composite obtained at carbonization temperature of 800 °C by CO₂ activation were prepared. The BET surface area could reach the maximum of 1382 m²/g under the following condition: activation temperature was 900 °C, activation time was 180 min, and CO₂ flow rate was 500 cm³/min [9].

Fig. 4.11 (a. and b.) illustrates the nitrogen adsorption-desorption isotherm of all sample. According to classification by IUPAC, all sample exhibited the

standard isotherm of type I. Type I represents the characteristics of microporous material. The sorbent has pore smaller than 2-3 nm, the isotherm show this type although multilayer adsorption and capillary condensation occur on the surface of sorbent. But for the porous carbon without activation process, the adsorption is not saturated because of the wide-spread pore diameter [10].

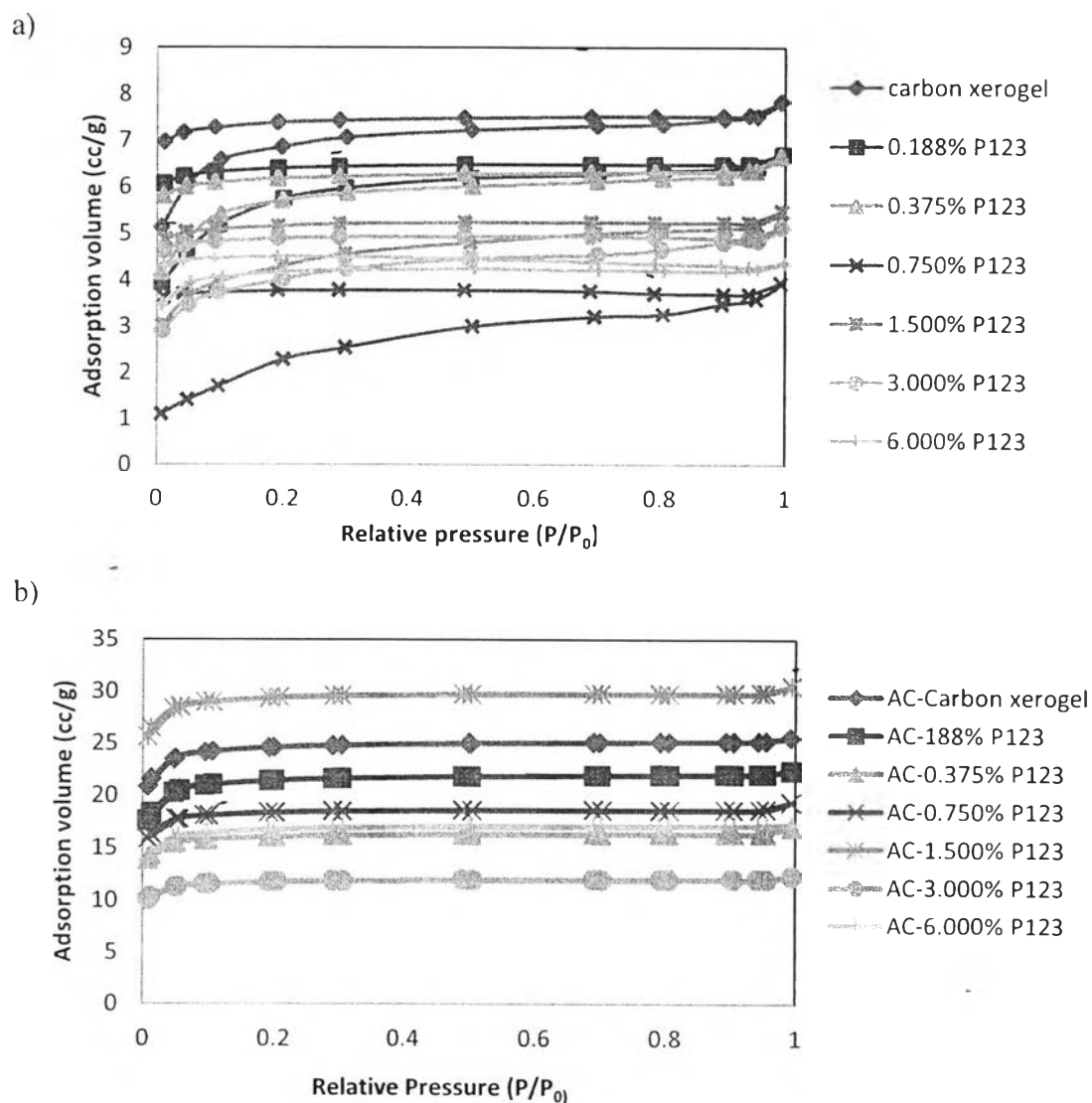


Figure 4.11 N_2 adsorption-desorption isotherms of polybenzoxazine-based (a.) porous carbon and (b.) activated porous carbon using different concentration of P123 template.

Conclusions

Porous carbon derived from polybenzoxazine, which is used the soft templating method is successfully synthesized. By adjusting the concentration of Pluronic P123 template, coral like, and rod like carbon particles were obtained. Moreover, we have reported the surface area and pore volume of porous carbon after activated by CO₂ at 900 °C, BET surface area of activated carbon is about three times higher than the carbon porous carbon without activation process.

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