

CHAPTER VI
**IMPROVEMENT IN THE PORE STRUCTURE OF POLYBENZOXAZINE-
BASED CARBON XEROGELS THROUGH A SILICA TEMPLATING
METHOD**

6.1 Abstract

Polybenzoxazine (PBZ) is synthesized by a facile quasi-solventless method within 1 h of synthesis time and less than 24 h of gelation time without any need of heating, and used as a carbon xerogel precursor. The pore structure of polybenzoxazine-based carbon xerogel is improved by using silica nanoparticles as hard templates. A mesoporous carbon xerogel with uniform pore is successfully synthesized. TGA, energy dispersive X-ray analysis, and field emission scanning electron microscope are used to confirm the successful incorporation of silica template into the microstructure of PBZ xerogel. Depending on the amount of silica template loading (10-50% w/w), the specific surface area of carbon xerogel is improved to 518-899 m²/g, comparing to that of reference carbon xerogel of 362 m²/g. The standard adsorption isotherm of carbon xerogel is changed from type I to type IV after silica templating method is used. Extremely large amounts of meso- and total pore volume of 1.04-4.26 cm³/g and 1.34-6.05 cm³/g, respectively, are obtained for carbon xerogel by the current method. In addition, the amount of micropore volume in carbon xerogel is not affected by silica template.

6.2 Introduction

Recently, mesoporous carbon has become an attractive research topic due to its versatility to be used in many applications such as catalyst support for fuel cell [1, 2], electrode for supercapacitors [3], and adsorbent [4]. Various carbon sources have been used to synthesize meso-structured carbon via a silica templating method, for example: furfuryl alcohol [3], resol [4], gaseous benzene and acetylene via CVD method [1, 5], sucrose [6], and resorcinol-formaldehyde (RF) [7-9]. However, some materials and methods have some drawbacks, such as difficult to control vapor phase of gaseous benzene and acetylene via CVD method [1, 5], the need of acid catalyst for polymerization of sucrose [5, 6], and low molecular design flexibility of starting materials for furfuryl alcohol, resol, and sucrose [3-5, 6]. In this work, we proposed the new type of phenolic resin called polybenzoxazine (PBZ) as a carbon precursor.

Polybenzoxazine (abbreviated as PBZ) was selected as a carbon source due to its exceptional properties, including low water adsorption, no need of adding initiators or catalyst for polymerization, near-zero volumetric change upon polymerization, no release of volatile during polymerization, and high molecular design flexibility by changing amine and phenol derivatives leading to different properties [10-14]. Moreover, the shorter preparation time with fewer steps is required to obtain PBZ-based carbon [15-19].

In 2009, PBZ-based carbon aerogel derived from bisphenol-A – aniline benzoxazine (hereinafter abbreviated as BA-a) was first introduced by Lorjai et al. [18] who found that their carbon showed the microporous property with pore diameter of about 1 nm. Furthermore, the surface area and total pore volume of their carbon aerogel was around 384-391 m²/g and 0.21 cm³/g, respectively.

PBZ-based carbon aerogel was further reported by Katanyoota et al. in 2010 [15]. They found that the PBZ-based carbon aerogel derived from bisphenol-A – tetra benzoxazine (hereinafter abbreviated as BA-teta) gave the surface area of 368 m²/g and total pore volume of 0.34 cm³/g with 3.67 nm in the average pore diameter. In addition, it showed good performance as an electrode for supercapacitor compared with those of PBZ-based carbon aerogel derived from BA-a. As shown in these studies, by varying different types of amines, porous carbons with different

microstructure were obtained. In addition, there are other PBZ-based carbon aerogel works published as well [20-25].

Even though the polybenzoxazine synthesis has been found to be much simpler, the surface area and pore volume obtained from PBZ-based carbon were still lower than those of RF-based carbon [7-9, 15-25]. In this work, an easy colloidal silica templating method was used to improve the porous properties of PBZ-based carbon xerogels. The effects of colloidal silica loading content on the microstructure of PBZ-based carbon xerogels were also investigated.

6.3 Experimental

6.3.1 Materials

Main-chain type benzoxazine polymer (abbreviated as MCBP) was synthesized by the Mannich polycondensation of bisphenol-A (abbreviated as BA, 97%, Aldrich), formaldehyde (37%, Merck Limited, Germany), and triethylenetetramine (abbreviated as teta, 85%, Facai Group Limited, Thailand) using dioxane (analytical grade, Labscan Asia Co., Ltd., Thailand) as a solvent. The polycondensation reaction and ring-opening polymerization of benzoxazine polymer is shown in Figure 6.1. Cationic surfactant, hexadecyltrimethylammonium bromide [$\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{Br})(\text{CH}_3)_3$, CTAB, >99.8%], used as stabilizer, was purchased from Fluka. LUDOX AS-40 colloidal silica solution (40%) with particle size of 24 nm was purchased from Aldrich. Ethyl alcohol (>98%) was purchased from J.T.-Baker. Hydrofluoric acid (HF, 48%) was purchased from Merck Limited, Germany. All chemicals were used without further purification.

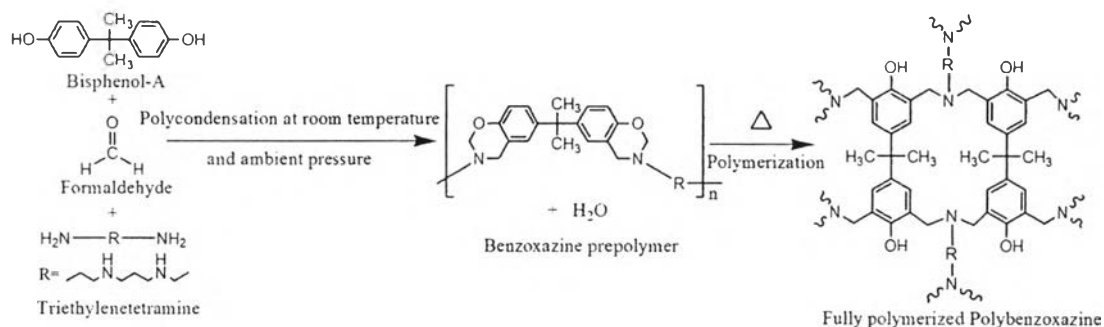


Figure 6.1 Polycondensation reaction and ring-opening polymerization of benzoxazine.

6.3.2 Synthesis of polybenzoxazine-based xerogels (PBZ-based xerogels) in the presence of silica nanoparticle

To prevent the aggregation of silica nanoparticles, CTAB-stabilized colloidal silica solution was prepared following the method proposed by Han and Hyeon [8]. Five gram of CTAB was dissolved to 100 mL of LUDOX AS-40 colloidal silica solution and was then continuously stirred at 50 °C for 20 min until cloudy mixture of CTAB-stabilized colloidal silica was obtained.

To synthesize PBZ-silica composites, a quasi-solventless method adopted from the solventless method proposed by Ishida [26] was employed. The MCBP was synthesized from BA, tetra, and formaldehyde at the molar ratio of 1:1:4. MCBP derived from bisphenol-A and tetra was hereinafter abbreviated as MCBP(BA-tetra). The solid concentration of MCBP(BA-tetra) solution was constant at 25% w/w. BA was dissolved in dioxane and magnetically stirred for 20 minutes. Then, CTAB-stabilized colloidal silica was mixed and stirred for 20 minutes. Afterwards, formaldehyde was added and additionally stirred for 20 minutes. Finally, tetra was slowly dropped into the mixture and continuously stirred for 1 h at ambient condition until the yellow mixture was obtained. The reaction was completed within an hour comparing to those of conventional polybenzoxazine synthesis method [27]. The obtained mixture was sealed in a glass vial and left for 24 h to form the wet PBZ-silica gel composite. The obtained mixture was further heated in an oil bath at

80 °C for 1 day to strengthen PBZ-silica composite gel. The PBZ-silica composites were taken out from the glass vial and cut into a cubic shape. All residual stabilizer and solvent in the PBZ-silica composites were removed by Soxhlet technique using ethyl alcohol as a carrier phase under condensation temperature of 10 °C and heating temperature of 100 °C for 24 h. After that, the PBZ-silica composites were heated at 90 °C for 24 h to remove all the residual ethyl alcohol.

6.3.3 Polymerization and carbonization process

The PBZ-silica composites were placed in an oven for step-polymerization at 160 °C and 180 °C for 3 h at each temperature, and 200 °C for 15 minutes to achieve the fully-polymerized PBZ xerogels [15, 17]. Then, fully-polymerized PBZ-silica composites were carbonized under nitrogen flow of 600 cm³/min, using the following cycle steps: 30–250 °C for 1 h, 250–600 °C for 5 h, 600–800 °C for 1 h and held at 800 °C for 2 h, and the oven was then cooled to room temperature under nitrogen atmosphere [15, 17]. Finally, carbon-silica composites were obtained.

6.3.4 Etching process

Removal of silica nanoparticle from carbon-silica composites was done by using the method proposed by Kim et al. [28]. 15% of HF solution was prepared in the mixture of 50water:50ethyl alcohol. In order to remove silica nanoparticles, carbon-silica composites were etched by the as-prepared 15% HF solution which was stirred by a magnetic stirrer for 24 h. The resulting samples were washed with distilled water under vacuum suction until pH became neutral. The washed samples were then heated at 100 °C for 24 h to remove water. Finally, the meso-structured carbon xerogels derived from PBZ were obtained. All methodologies are summarized in Figure 6.2.

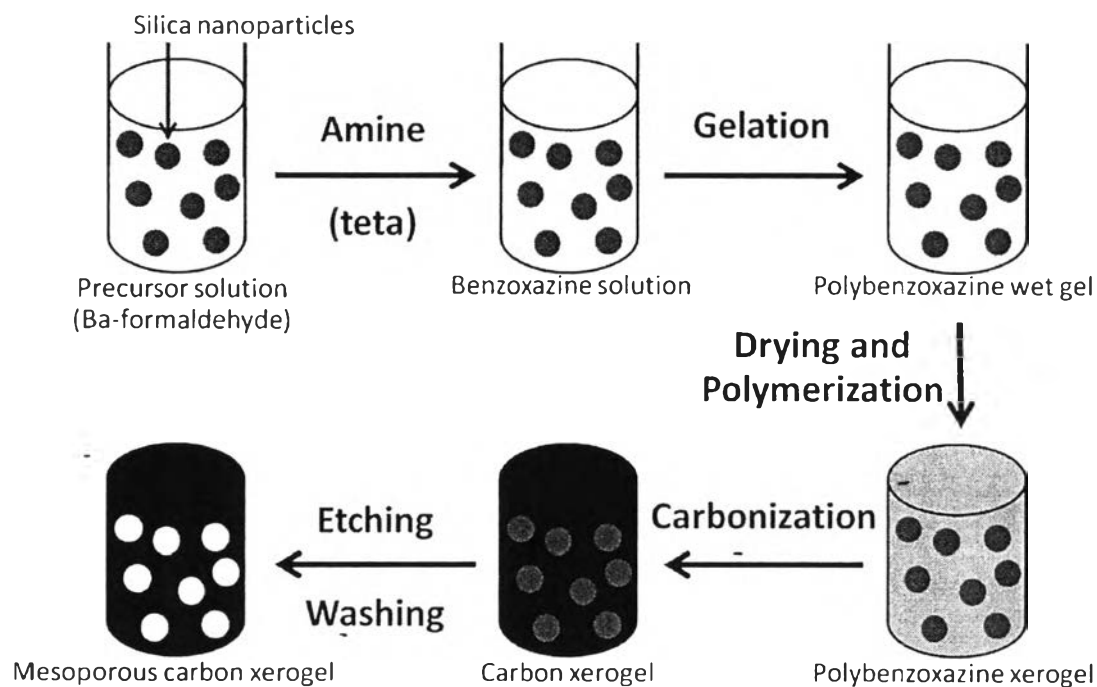


Figure 6.2 Schematic illustration of synthesis process.

6.3.5 Preparation of reference carbon xerogel

Reference carbon xerogel was prepared following the method described in section 2.2 and 2.3 but without the addition of silica nanoparticles. To study the effects of HF treatment on pore structure of reference carbon xerogel, the reference carbon xerogel was treated as same as the method described in section 2.4 as though silica nanoparticles had been removed. The reference carbon treated with HF was hereinafter abbreviated as C-HF.

6.3.6 Characterizations of microstructure and morphology of PBZ-based carbon xerogels

The skeletal density (ρ_s) of samples was measured by gas pycnometer (Ultracycrometer, Quantachrome Instrument). The mass (m) and volume (V) of samples were measured and the bulk density (ρ) was calculated from the following formula.

$$\rho = m/V \quad (1)$$

Morphology and microstructure of carbon xerogels were observed by field emission scanning electron microscope (FE-SEM, Hitachi/S-4800 model). The Energy dispersive X-ray analysis (EDX, Hitachi/model S-4800), operated at 20 keV, was used to confirm the successful incorporation of silica nanoparticles into polybenzoxazine xerogel. Thermal stability and residual mass of both polybenzoxazine xerogel and polybenzoxazine xerogel-silica composites were observed on a Mettler Toledo TGA/SDTA 851e instrument, where the sample was loaded on a platinum pan and heated from room temperature to 900 °C at a heating rate of 10 °C/min under N₂ atmosphere with a flow rate of 50 cm³/min. Quantachrome-Autosorp1-MP was used to determine the pore properties of the as-prepared samples. Approximately 0.1 g of carbon xerogel was degassed at 250 °C for 15 h to remove all the adsorbed species. The specific surface area (S_{BET}) was calculated by BET algorithm (Brunauer-Emmett-Teller) [29]. Micropore volume (V_{mic}) was analyzed by t-plot method [30]. Mesopore volume (V_{mes}) and mesopore size distributions were analyzed by BJH (Barrett-Joyner-Halenda) algorithm [31, 32]. Macropore volume (V_{mac}) and total pore volume were calculated according to the Wu et al.'s method [33, 34], in which the total pore volume was determined from the following equation: $V_{total} = (1/\rho) - (1/\rho_s)$ where ρ is the bulk density and ρ_s is the skeletal density. Macropore volume was determined by the subtraction of total pore volume from micro- and meso- pore volume – obtained from N₂ adsorption at -196 °C – as shown in the following equation [33, 34]: $V_{mac} = V_{total} - V_{meso} - V_{micro}$. In the case of the purely microporous sample (standard isotherm of type I), the total pore volume (V_{total}) is equal to micropore volume (V_{micro}).

6.4 Results and Discussion

6.4.1 Characteristics and morphologies of PBZ-based organic/carbon xerogels assembled with silica nanoparticles

The chemical structure of the benzoxazine which was a main-chain type benzoxazine polymer derived from bisphenol A and teta, hereinafter abbreviated as MCBP(BA-teta), was confirmed by FTIR and ^1H NMR as described in more details in our previous work [17]. Interestingly, by using a quasi-solventless method adopted from the solventless method proposed by Ishida [26], the reaction of MCBP(BA-teta) was completed within an hour comparing to those of conventional polybenzoxazine synthesis method which took 5 h [27].

Polybenzoxazine (PBZ)-based carbon xerogels were synthesized by using colloidal silica as a hard template as described in the experimental section. The loading of colloidal silica was varied in the range of 10-50% w/w with respect to polybenzoxazine concentrations. The schematic illustration of the experimental procedure and the goal of this study are illustrated in Figure 6.2. Figure 6.3 shows the char yield of polybenzoxazine xerogel and the composite yield of polybenzoxazine xerogels incorporated with silica nanoparticles by various silica nanoparticle loadings. It was found that polybenzoxazine xerogel has about 30 % char yield after carbonization. After the assembly of polybenzoxazine xerogel with silica nanoparticles, the percentage of composite yield was expectedly increased with increasing amount of silica nanoparticle loadings to 47%, 53%, 59%, 73%, and 75% for 10%, 20%, 30%, 40%, and 50% of silica nanoparticle loadings, respectively. From the results of composite yield in Figure 6.3, it is suggested that the silica nanoparticles were successfully incorporated into polybenzoxazine xerogel before converting to carbon xerogel under inert atmosphere. However, at the silica loading of 40% and 50%, the composite yield of as-synthesized polybenzoxazine xerogel was slightly different – about 73% and 75%, respectively. This phenomenon might be explained by the excess amount of silica nanoparticles loading, in which silica nanoparticles could not be totally encapsulated by polybenzoxazine when the amounts of the silica loadings exceeded 40% w/w. Therefore, the composite yield of

as-synthesized polybenzoxazine at silica loadings of 40% and 50% w/w would be slightly different.

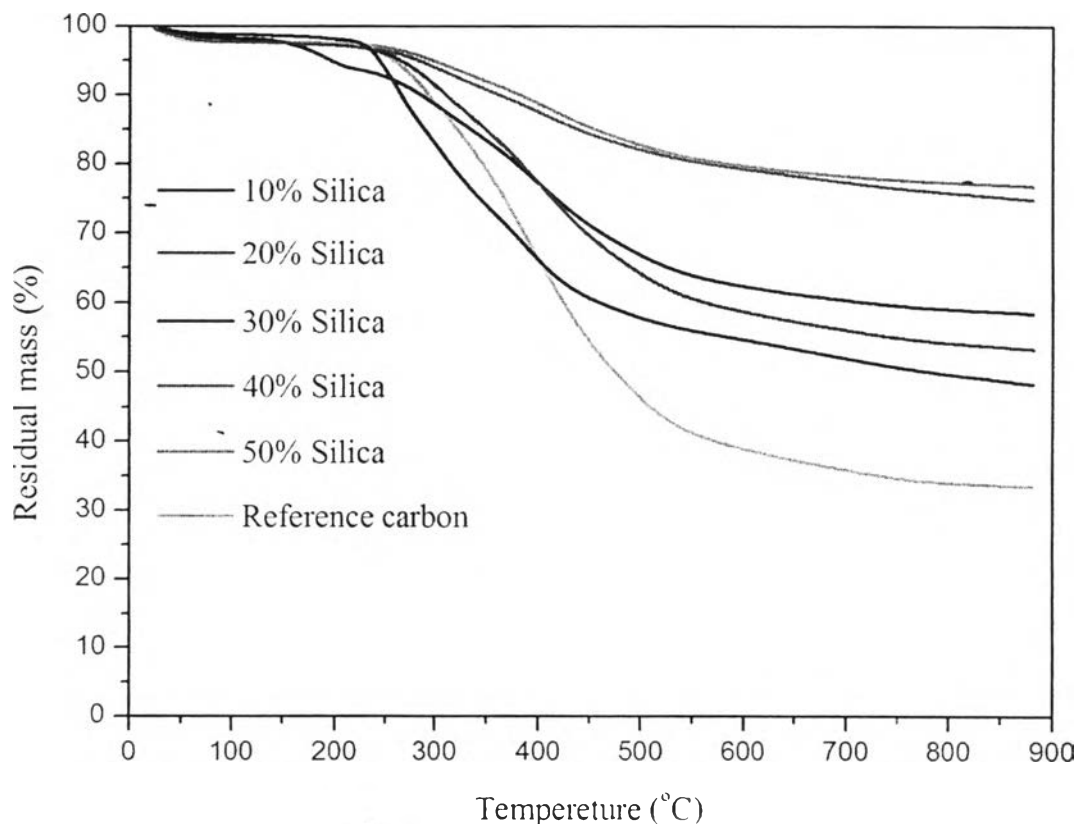


Figure 6.3 Percentage of composite yield of polybenzoxazine xerogel synthesized by using various amounts of silica loading as template.

The EDX technique was used to confirm the successful incorporation of silica nanoparticles into polybenzoxazine xerogel. Figure 6.4 shows the EDX spectrum of polybenzoxazine-based carbon xerogel assembled with 30% w/w of silica nanoparticles. Three elements were detected in the EDX spectrum, including oxygen, carbon, and silica, confirming the presence of silica nanoparticles in the microstructure of polybenzoxazine-based carbon xerogel. However, the percentage of silica in carbon xerogels measured by EDX technique is not reported since EDX technique is not appropriate to quantify the percentage of silica in these carbon xerogels, where silica aggregations occurred.

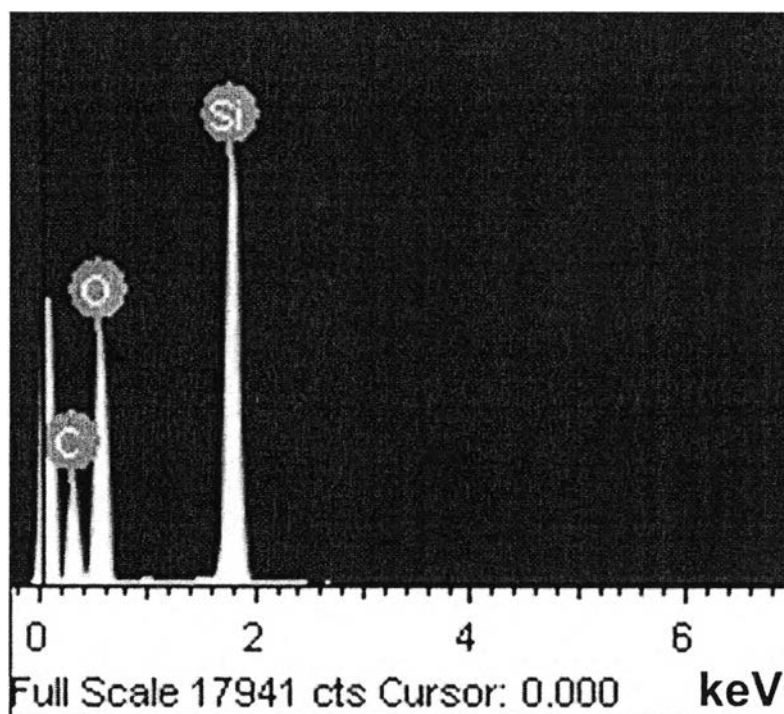


Figure 6.4 EDX spectrum of polybenzoxazine-based carbon xerogel assembled with 30% w/w of silica nanoparticles template.

The morphology of the silica-incorporated carbon xerogel and carbon xerogel after removal of silica nanoparticles was observed using FE-SEM technique. Figure 6.5 shows the SEM micrographs of reference carbon xerogel, silica-incorporated carbon xerogel synthesized at silica concentration of 50% w/w, and carbon xerogel after silica removal. The composite yield from TGA technique (Figure 6.3), the EDX spectrum shown in Figure 6.4, and the SEM micrographs of silica-incorporated carbon xerogel in Figure 6.5b are evidence for the successful incorporation of silica nanoparticle into carbon xerogel structure. Good dispersion of silica nanoparticle in carbon xerogel structure was also observed due to the stabilization of cationic surfactant (CTAB) (Figure 6.5b), although silica nanoparticles were slightly aggregated due to the high silica nanoparticle loading. After the removal of silica nanoparticles by hydrofluoric acid etching, the spherical monolithic cavities with pore diameter of about 24-25 nm were generated, mirroring the particle size of silica templates, as shown in Figure 6.5c. On the other hand, the

morphology of the reference carbon xerogel was quite dense and no meso- and macrostructure was observed by the FE-SEM technique (Figure 6.5a). Hence, the pore in reference carbon xerogel should be micropore (< 2 nm) generated during the carbonization process [35, 36]. The obtained carbon xerogel with pore diameter of about 24 nm, observed in Figure 6.5c, could be used as a catalyst support for certain systems.

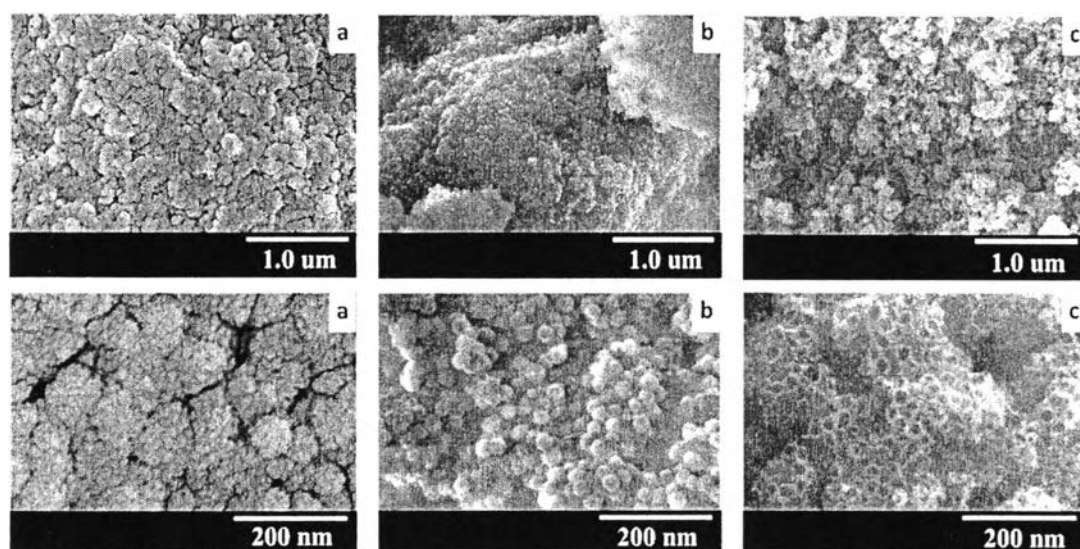


Figure 6.5 Morphology of polybenzoxazine-based carbon xerogel: (a) carbon xerogel without silica nanoparticles template (reference carbon xerogel), (b) carbon xerogel with silica nanoparticles loading of 50% w/w, and (c) carbon xerogel after removal of silica nanoparticles loading of 50% w/w (upper: low magnification, lower: high magnification).

6.4.2 Pore structure of PBZ-based carbon xerogels obtained after removal of silica nanoparticles

Table 6.1 shows the bulk densities and pore properties of carbon xerogels at various conditions. From Table 6.1, it is found that bulk densities of reference carbon xerogel and C-HF are quite high and slightly different, about 0.972 and 0.928 g/cm³, respectively. The high bulk density of reference carbon xerogel corresponds to the dense morphologies observed by FE-SEM technique, as shown in

Figure 6.5a, indicating that few porosity is contained in the structure. When silica nanoparticles were used as hard template, after removal of silica nanoparticles, the bulk densities of carbon xerogels are drastically decreased with increasing silica content: 0.498 g/cm³ for 10% of silica, 0.360 g/cm³ for 20% of silica, 0.293 g/cm³ for 30% of silica, 0.164 g/cm³ for 40% of silica, and 0.149 g/cm³ for 50% of silica. The decrease in bulk density of carbon xerogel is due to the increment of porosity – created by silica nanoparticles template – in the carbon xerogel structure.

Table 6.1 Pore structure of PBZ-based carbon xerogels obtained after removal of silica nanoparticle templates

Sample (% Silica)	Bulk Density (g/cm ³) ±0.01	^a S _{BET} (m ² /g) ±5	^a V _{micro} (cm ³ /g) ±0.05	^a V _{meso} (cm ³ /g) ±0.05	^b V _{macro} (cm ³ /g) ±0.05	^b V _{total} (cm ³ /g) ±0.03	^a APD _{meso} (nm) ±0.5
Reference carbon	0.972	362	0.18	-	-	0.18 ^{a,c}	-
C-HF	0.928	436	0.27	-	-	0.27 ^{a,c}	-
10%	0.498	518	0.24	1.04	0.06	1.34	24
20%	0.360	596	0.27	1.78	0.07	2.12	24
30%	0.293	647	0.26	2.44	0.06	2.76	24
40%	0.164	827	0.39	4.07	0.99	5.45	24
50%	0.149	899	0.36	4.26	1.43	6.05	24

Notes : C-HF: Reference carbon treated with HF; S_{BET}: BET surface area; V_{micro}: micropore volume; V_{meso}: mesopore volume; V_{macro}: macropore volume; V_{total}: total pore volume; APD_{meso}: average mesopore diameter; a: obtained from N₂ adsorption at -196 °C; b: calculated by using Wu et al.'s method [36, 39]; c: the error value is equal to that of V_{micro} due to V_{total}=V_{micro} for microporous sample

The pore properties of the reference carbon xerogel, C-HF, and silica-templated carbon xerogels were examined by using the nitrogen adsorption/desorption technique. According to classification by IUPAC, the reference carbon xerogel exhibits the standard isotherm of type Ia – as shown in Figure 6.6, in which type Ia represents the characteristics of microporous material with pore of molecular dimension (small micropore) [37]. After the reference carbon xerogel was treated with HF (C-HF), the standard isotherm of C-HF is of type Ia. In addition, Table 6.1 also shows that the amount of micropore volume and specific

surface area are increased from $0.18 \text{ cm}^3/\text{g}$ and $362 \text{ m}^2/\text{g}$ for reference carbon xerogel to $0.27 \text{ cm}^3/\text{g}$ and $436 \text{ m}^2/\text{g}$ for C-HF, respectively. This is because chemical treatment process can increase either micropores or small mesopores, and specific surface area [35]. On the contrary, the carbon xerogel obtained after removal of silica template exhibits the standard isotherm of type IV with H1 hysteresis loop; in which type IV represents the characteristics of mesoporous material and H1 hysteresis loop is associated with the narrow distribution of uniform pore [37]. Therefore, carbon xerogels obtained after the removal of silica template will be hereinafter called mesoporous carbon xerogel. Moreover, at the silica loadings of 10%, 20%, and 30%, the adsorption branch of mesoporous carbon xerogel reached the plateau region at high relative pressure of 0.9, indicating that no large pore was contained in the structure of mesoporous carbon xerogel. Additionally, the adsorption branch of mesoporous carbon xerogel synthesized at silica loadings of 40% and 50% did not reach the plateau region, indicating that some large pores were contained in the structure of mesoporous carbon xerogel.

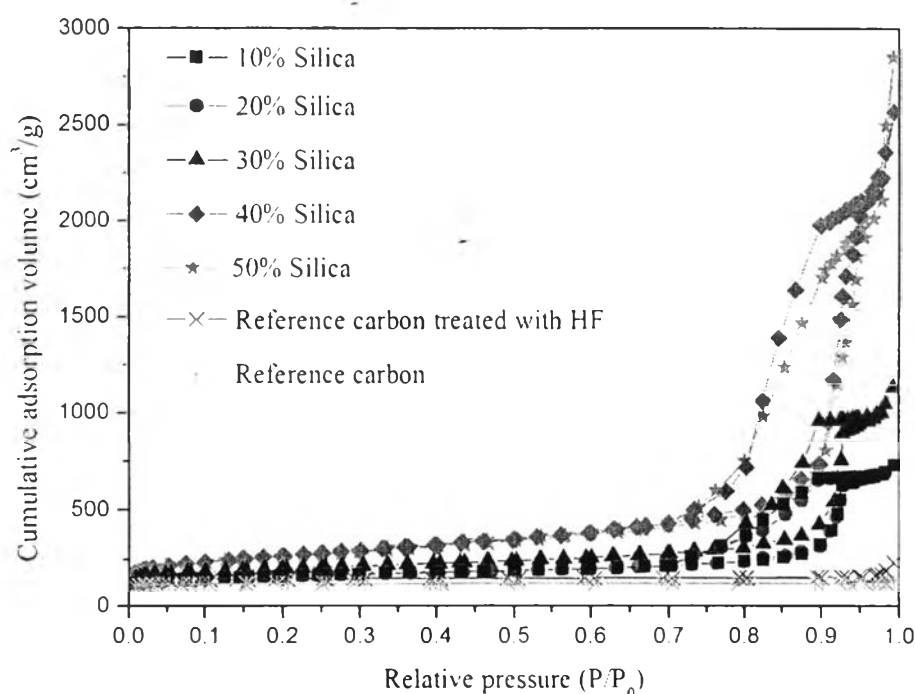


Figure 6.6 Adsorption isotherm of polybenzoxazine-based carbon xerogel obtained after removal of silica nanoparticles.

To clarify the generation of large pores in mesoporous carbon xerogel synthesized at the silica loading of 40% and 50%, the aggregation of silica template was used to explain. At silica loading of 10%, 20%, and 30%, the silica templates were not aggregated due to the stabilization of individual silica particle by the cationic surfactant (CTAB). The amount of silica loading was also in the optimum range for preventing the aggregation. However, at the 40% and 50% loadings, the aggregation of silica templates took place, yielding the large pores.

In 1999, Han and Hyeon synthesized a high surface area porous carbon derived from resorcinol-formaldehyde polymer using silica template without CTAB stabilization [7]. They found that the aggregation of silica templates took place. After that, Han and Hyeon attempted to avoid the aggregation of silica template by using CTAB stabilization [8].

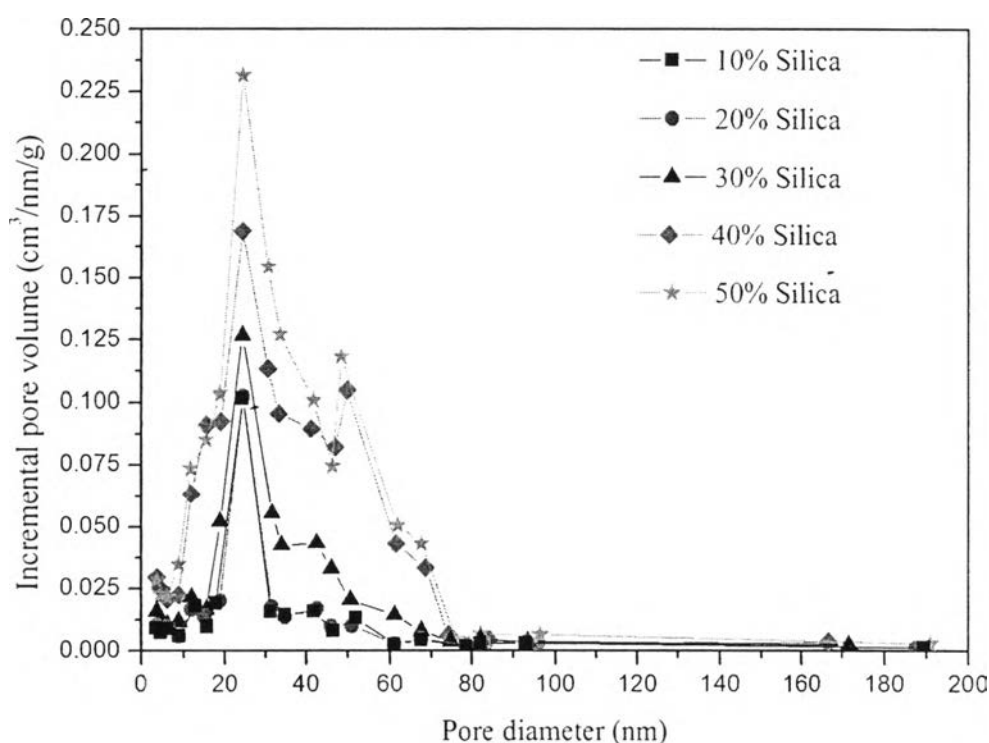


Figure 6.7 Mesopore size distributions of polybenzoxazine-based carbon xerogels obtained after removal of silica nanoparticles.

Mesopore size distribution calculated by the BJH algorithm of all samples [31, 32] is shown in Figure 6.7. All mesoporous carbon xerogels exhibit the narrow pore size distribution of uniform pore with an average pore diameter of 24 nm. However, the mesoporous carbon xerogels obtained from the silica loadings of 40-50% w/w not only exhibited an average pore diameter of 24 nm but also showed some larger pore sizes in the range of 30-70 nm due to the silica nanoparticles aggregations.

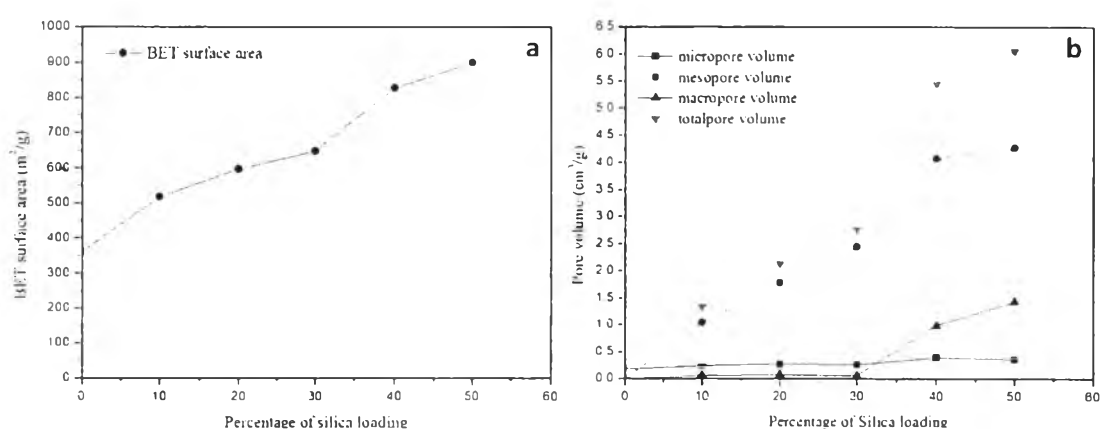


Figure 6.8 The effects of percentage of silica loading on a) specific surface area and b) pore volume of polybenzoxazine-based carbon xerogel obtained after removal of silica nanoparticles.

Figures 6.8a and b show the relationship between the specific surface area and pore volume of all samples with various silica loadings, respectively. The specific surface area increased with the increasing amount of the silica loadings from 362 (or 436 m²/g for C-HF) to 518, 596, 647, 827, and 899 m²/g for the reference carbon xerogel and mesoporous carbon xerogel synthesized at silica loadings of 10%, 20%, 30%, 40%, and 50%, respectively. These results imply that the silica hard templates can be used to improve the specific surface area of carbon xerogel derived from polybenzoxazine. In addition, as shown in Table 6.1 and Figure 6.8b, the amount of meso- and total pore volume were also increased with the increasing amount of silica loadings similar to those of the specific surface area. However, the amount of macropore volume was firstly observed in mesoporous carbon xerogel

synthesized at silica loadings of 40% and continuously increased with increasing silica nanoparticles content due to the appearance of silica nanoparticles aggregation, approximately $0.99 \text{ cm}^3/\text{g}$ and $1.43 \text{ cm}^3/\text{g}$ for silica loading of 40% and 50%, respectively. Moreover, mesoporous carbon xerogel synthesized at the silica loading of 50% shows the largest amount of meso-, macro- and total pore volume – about $4.26 \text{ cm}^3/\text{g}$, $1.43 \text{ cm}^3/\text{g}$, and $6.05 \text{ cm}^3/\text{g}$, respectively. This result is based on the principle that large amount of pore-created material was loaded into polybenzoxazine, resulting in large amount of pore volume after removal of pore-created material. Furthermore, the amounts of meso- and macro pore volume of mesoporous carbon synthesized at silica loading of 50% were nearly the same as those of 40% silica loading. This supports our assumption that the silica loading of 40% was the maximum loading in which silica nanoparticles could be totally encapsulated by polybenzoxazine, corresponding to the TGA results in Figure 6.3 as discussed earlier. The pore characteristics of all samples were summarized in Table 6.1.

6.4.3 Comparison between porous organics/carbons derived from polybenzoxazine and resorcinol-formaldehyde polymer by various synthesis methods

Comparison between porous organics/carbons derived from polybenzoxazine and resorcinol-formaldehyde polymer (RF polymer) by various synthesis methods is tabulated in Table 6.2. Generally, porous carbon derived from RF polymer requires basification agent, like Na_2CO_3 or NaOH [34, 38, 39], to promote the polymerization of RF polymer. By using Na_2CO_3 as basification agent and conventional heating to obtain RF wet gel, Job et al. found that the gelation time of RF polymer was about 10-570 minutes (0.17-9.5 h), depending on both the amount of basification agent and heating temperature used (50-90 °C) [38]. From the results studied by Job et al., it could be concluded that the more amount of basification agent and the higher heating temperature were used, the faster gelation time was observed [38]. Moreover, in 2011, Calvo et al. found that the gelation time

(at 85 °C) was significantly decreased from 120 minutes (2 h) for conventional heating to 24 minutes (0.4 h) when using microwave heating, suggesting that microwave heating was an effective method to decrease the gelation time of RF polymer resulting in the reduction of synthesis time [39]. However, when polybenzoxazine was used as carbon precursor in our study, without the need of catalyst, the gelation time was around 720 minutes (12 h) at room temperature. Moreover, benzoxazine interestingly quickly solidified within 10 minutes when heated by conventional heating at 80 °C, which was faster than those of most cases of RF polymer [38, 39], as shown in Table 6.2. These phenomena can be explained by the use of highly reactive di-functional amine (triethylenetetramine) and di-functional phenol (bisphenol-A) as starting materials to synthesize benzoxazine, resulting in fast reaction rate. In general, various types of phenols and amines could be used as starting materials due to the excellent molecular design flexibility of the benzoxazine chemistry (Figure 6.1) [14, 19], which could affect the gelation time and tailor the pore structure of PBZ-based organic xerogel and carbon xerogel after carbonization [15-19]. The more reactive starting materials are used, the faster reaction time is obtained.

In general, supercritical CO₂ drying is a classical-appropriate drying method used to remove the solvent from RF-based organic wet gels with the least structural damage since few capillary force, usually-greatly occurring during evaporative drying, and no volume change of liquid to solid, usually-considerably occurring in freeze drying, are generated [34, 40, 41]. In addition, mesoporous carbon could also be produced by using organic cryogels, obtained from freeze drying, as precursor [34]. Despite the fact that RF-based carbon aerogel/cryogel – obtained via supercritical CO₂ drying and freeze drying – exhibited larger surface area compared to that of PBZ-based carbon xerogel obtained through silica templating method, the mesopore volume of RF-based carbon aerogel/cryogel [34] was lower than that of PBZ-based carbon xerogel about 2-3 times, as shown in Table 6.2. In addition, either a supercritical CO₂ drying or a freeze drying also requires the solvent exchange step before drying, the severe condition to operate the process, the coolants for a freeze drying, and liquid CO₂ for a supercritical CO₂ drying. Those

lead to considerable amount of time and energy consumption, resulting in low production rate and significant cost. The total synthesis time of RF-based organic cryogel and aerogel is approximately 265 h and 296 h [34], respectively, as shown in Table 6.2, which is longer than that of PBZ-based organic xerogel obtained through silica templating method – about 151 h. Moreover, after carbonization and silica removal process, PBZ-based carbon xerogel possess the overall synthesis time of 160 h, which is still shorter than that of RF-based organic cryogel/aerogel [34]. However, in our work, the use of silica nanoparticles and the need of etching process with HF might limit the flexibility of silica templating method to be applied in industrial scale since silica nanoparticle and HF were expensive and dangerous, respectively, resulting in considerable cost and health concern.

In 2006, Job et al. simplified the drying method, using convective air-drying [38]. They found that the drying duration could be done within 8 h [38] shorter than those of freeze and supercritical CO₂ drying [34], and the total synthesis time of RF-based organic xerogels – maximum 24 to 48 h depending on the process – is shorter than that of PBZ-based organic xerogels obtained through silica templating method (~151 h). In 2011, microwave-assisted method was used to prepared mesoporous carbon xerogels by Calvo et al. [39]. They found that, as shown in Table 6.2, the total synthesis time of RF-based organic xerogels could drastically be decreased from hundred hours for conventional method to approximately 5 h for microwave-assisted method [39], and was much shorter than that of PBZ-based organic xerogel obtained through silica templating method (~151 h). However, although the synthesis time of RF-based carbon xerogel could be shortened by microwave technique [39, 42], the porous properties of RF-based carbon xerogel derived from microwave-assisted method were lower than those of PBZ-based carbon xerogels synthesized through silica templating method (Table 6.2), such as specific surface area of 637 and 899 m²/g and mesopore volume of 0.91 and 4.26 cm³/g, respectively [39]. In addition, as described in section 3.2, the specific surface area, mesopore volume, and mesopore diameter could precisely be controlled by changing silica loading content and particle size of silica nanoparticle.

Table 6.2 Comparison between porous organics/carbons derived from polybenzoxazine and resorcinol-formaldehyde polymer by various synthesis methods

Starting material	Total synthesis time of organic xerogels (h)	Basification agent	Gelation time (min)	Synthesis method	Solvent removal process	Template	S _{BET} (m ² /g)	V _{meso} (cm ³ /g)	APD (nm)
Resorcinol(R)-Formaldehyde(F)									
1. Job et al.'s work [38]	Maximum 24-48 ^a								
1.1 X-500-50-24 ^b		Na ₂ CO ₃	275 at 50 °C	Conventional	Convective air-drying at 70 °C	-	110 ^Y	0.19 ^Y	14 ^Y
1.2 X-500-90-24 ^b		Na ₂ CO ₃	10 at 90 °C	Conventional	Convective air-drying at 70 °C	-	300 ^Y	0.83 ^Y	24 ^Y
1.3 X-2000-50-24 ^c		Na ₂ CO ₃	570 at 50 °C	Conventional	Convective air-drying at 70 °C	-	75 ^Y	0.66 ^Y	180 ^Y
1.4 X-2000-90-24 ^c		Na ₂ CO ₃	22 at 90 °C	Conventional	Convective air-drying at 70 °C	-	195 ^Y	0.64 ^Y	60-80 ^Y
2. Calvo et al.'s work [39]									
2.1 CX-5.8-C1 ^d	101	NaOH	120 at 85 °C	Conventional	Evaporation at 85 °C	-	694 ^Z	0.57 ^Z	13 ^Z
2.2 CX-5.8-MW ^d	4.7	NaOH	24 at 85 °C	Microwave-assisted	Microwave heating at 700 W	-	637 ^Z	0.91 ^Z	45 ^Z
2.3 CX-3.1-MW ^e	~5	NaOH	42.2 at 85 °C	Microwave-assisted	Microwave heating at 700 W	-	N/A	0.13 ^Z	~70 ^Z
3. Han and Hyeon's work [7] ^f	~168 ^X	-	N/A (85 °C)	Template-assisted	Evaporation	Silica beads (Ø 12 nm)	1238 ^Z	4.7 ^Z	
4. Gorka and Jaroniec's work [9]									
4.1 C ^g	~40 ^X	-	N/A	Template-assisted	Ambient drying and Evaporation at 100 °C	Silica beads	1434 ^Z	3.02 ^Z	14.3 ^Z
4.2 C ^g	~40 ^X	-	N/A	Template-assisted	Ambient drying and Evaporation at 100 °C	(Ø 20 and 50 nm), TEOS, and triblock copolymer	1577 ^Z	3.60 ^Z	14.3 ^Z
5. Tamon et al.'s work [34]									
5.1 B2 (Carbon cryogel)	~265	Na ₂ CO ₃	N/A (90 °C)	Conventional	Freeze drying	-	908 ^{Z1}	1.39 ^{Z1}	5.5 ^{Z1}
5.2 B2 (Carbon aerogel)	~296	Na ₂ CO ₃	N/A (90 °C)	Conventional	Supercritical CO ₂ drying	-	1215 ^{Z2}	2.44 ^{Z2}	6.2 ^{Z2}
Polybenzoxazine (this work) (at 50 wt.% of silica beads)	151 ^{X1}	-	720 at RT 10 at 80 °C	Template-assisted	Soxhlet and Evaporation at 90 °C	Silica beads (Ø 24 nm)	899 ^Z	4.26 ^Z	24 ^Z

Notes : S_{BET} : BET surface area; V_{meso} : mesopore volume; APD: average pore diameter; C*: sample was prepared using 50 wt.% of the silica beads with 20 nm in diameter; C#: sample was prepared using 50 wt.% of the silica beads with 50 nm in diameter; B2: the condition is R/F=0.5, R/W=0.25, and R/C=200; X: the total synthesis time of dried organic-silica composite excluding the etching time of silica removal process; X1: the total synthesis time of organic xerogels is a combination between the total synthesis time of dried organic-silica composite and the time required for removing silica templates from the composite; Y: value belonging to organic xerogel; Z: value belonging to carbon xerogel; Z1: value belonging to carbon cryogel; Z2: value belonging to carbon aerogel; N/A: data not reported; RT: room temperature

^a total synthesis time of organic xerogel depending on the process used such as gelation temperatures (50, 70, and 90 °C), aging times (0, 24, 48, and 72 h), and R/C ratios (500, 1,000, and 2,000)

^b the condition is R/F=0.5, D=5.7, and R/C=500

^c the condition is R/F=0.5, D=5.7, and R/C=2,000

^d the condition is R/F=0.5, D=5.7, and pH=5.8

^e the condition is R/F=0.5, D=5.7, and pH=3.1

^f the condition is 1R:2F:7.5SiO₂:86H₂O and pH=8

In 1999, Han and Hyeon synthesized high surface area porous carbon using silica-templates method and found that the specific surface area and mesopore volume were $1,238 \text{ m}^2/\text{g}$ and $4.7 \text{ cm}^3/\text{g}$, respectively [7], which were higher than those of our work, as seen in Table 6.2. In 2011, hierarchically porous RF-based carbons were synthesized by Gorka and Jaroniec using block copolymer-colloidal silica templating and TEOS under acidic condition and post-synthesis activation for 3-5 h with carbon dioxide and water vapor [9]. In their work, the amount of silica template was fixed at 50% w/w with respect to the resin concentration [9]. Depending on the conditions used, their porous carbon showed the larger specific surface area of about $844\text{-}2,793 \text{ m}^2/\text{g}$ and the comparable mesopore volume of about $0.89\text{-}5.46 \text{ cm}^3/\text{g}$ [9], comparing to those of PBZ-based carbon xerogels obtained through silica templating method. Moreover, micropore volume of $0.06\text{-}0.22 \text{ cm}^3/\text{g}$ was also found in the hierarchically porous RF-based carbons [9]. According to the study by Gorka and Jaroniec, it was concluded that cylindrical/spherical mesopores could be created by using soft template (surfactant) and silica hard template, respectively, whereas the fine pore could be both created and increased by using TEOS-based silica as a hard template or by using post activation in steam or carbon dioxide, which lead to improvement of specific surface area comparing to that of porous carbon without post activation process [9]. Because of the prominently rapid gas transportation, the hierarchical pore system in carbon structure is suitable for some applications such as gas adsorption or gas separation [20]. Although the good porous properties were obtained from hierarchically porous carbon derived from RF polymer, the various kinds of activation processes and templates were required during the synthesis step, such as activation with water vapor or carbon dioxide, TEOS-based silica template, silica beads, and surfactant, leading to considerable cost.

Depending on the targeted applications, the optimization between the desired textural properties of carbon xerogels – such as specific surface area or pore volume – and the synthesis method used is required so that the optimum synthesis method and carbon precursor can be selected and used to synthesize carbon xerogels with desirable textural properties within the shortest preparation time, resulting in reduction of time and energy consumption leading to low cost.

6.5 Conclusions

Carbon xerogel was successfully synthesized using polybenzoxazine as a carbon precursor. The shorter preparation time with fewer steps was required when polybenzoxazine was used as a precursor for preparation of carbon xerogel. By using silica nanoparticles as a hard template, the mesoporous carbon xerogel derived from polybenzoxazine with good distribution of uniform pore was successfully synthesized by an easy synthesis method. TGA, EDX, and FE-SEM techniques were used to confirm the successful incorporation of silica nanoparticles into polybenzoxazine xerogel structure before carbonizing and etching as mesoporous carbon xerogel. When silica nanoparticles with diameter of 24 nm was used as hard templates, after the removal of silica template, the specific surface area of carbon xerogel was increased from 362 m²/g for reference carbon xerogel (or 436 m²/g for C-HF) to 518-899 m²/g, depending on the amounts of silica loadings. Moreover, the amounts of pore volume were also significantly increased to 1.04-4.26 cm³/g for mesopore volume, 0.06-1.43 cm³/g for macropore volume, and 1.34-6.05 cm³/g for total pore volume, depending on the content of silica loadings. However, at the silica loading exceeding 40%, the mesopore volume were nearly the same regardless of the silica content. Furthermore, the micropore volume was independent of the silica content. An average mesopore diameter of all mesoporous carbon xerogel was identical with an average diameter of silica nanoparticles – about 24 nm. Therefore, silica nanoparticles were the easy-suitable method for improving the specific surface area, meso- and total pore volume, and mesopore diameter of polybenzoxazine-based carbon xerogel.

6.6 Acknowledgements

This work has been financially supported by the Petroleum and Petrochemical College, and the Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University. In addition, the authors also would like to express their deep appreciation to the Ratchadaphiseksomphot Endowment Fund of Chulalongkorn University (RES560530021-CC), for its financial support on this project. -

6.7 References

- [1] F. Su, J. Zeng, X. Bao, Y. Yu, J.Y. Lee, X.S. Zhao, *Chem. Mater.* 17, 3960 (2005)
- [2] H. Chang, S.H. Joo, C. Pak, *J. Mater. Chem.* 17, 3078 (2007)
- [3] A.B. Fuertes, G. Lota, T.A. Centeno, E.E. Frackowiak, *Electrochim. Acta* 50, 2799 (2005)
- [4] T.J. Levario, M. Dai, W. Yuan, B.D. Vogt, D.R. Nielsen, *Micropor. Mesopor. Mater.* 148, 107 (2012)
- [5] M. Kaneda, T. Tsubakiyama, A. Carlsson, Y. Sakamoto, T. Ohsuna, O. Terasaki, *J. Phys. Chem. B* 106, 1256 (2002)
- [6] P. Karandikar, K.R. Patil, A. Mitra, B. Kakade, A.J. Chandwadkar, *Micropor. Mesopor. Mater.* 98, 189 (2007)
- [7] S. Han, T. Hyeon, *Carbon* 37, 1645 (1999)
- [8] S. Han, T. Hyeon, *Chem. Commun.* 19, 1955 (1999)
- [9] J. Gorka, M. Jaroniec, *Carbon* 49, 154 (2011)
- [10] X. Ning, H. Ishida, *J. Polym. Sci., Part A: Polym. Chem.* 32, 1121 (1994)
- [11] N.N. Ghosh, B. Kiskan, Y. Yagci, *Prog. Polym. Sci.* 32, 1344 (2007)
- [12] H. Ishida, D.J. Allen, *Polymer* 37, 4487 (1996)
- [13] T. Agag, T. Takeichi, *J. Polym. Sci., Part A: Polym. Chem.* 45, 1878 (2007)
- [14] H. Ishida, Overview and historical background of polybenzoxazine research in "Handbook of Benzoxazine Resins", Eds. by H. Ishida and T. Agag (Elsevier, Amsterdam, 2011), pp. 3-81
- [15] P.-Katanyoota, T. Chaisuwan, A. Wongchaisuwat, S. Wongkasemjit, *Mater. Sci. Eng., B* 167, 36 (2010)
- [16] T. Chaisuwan, T. Komalwanich, S. Luangsukrer, S. Wongkasemjit, *Desalination* 256, 108 (2010)
- [17] U. Thubsuang, H. Ishida, S. Wongkasemjit, T. Chaisuwan, *Micropor. Mesopor. Mater.* 156, 7 (2012)
- [18] P. Lorjai, T. Chaisuwan, S. Wongkasemjit, *J. Sol-Gel Sci. Technol.* 52, 56 (2009)

- [19] T. Chaisuwan, Porous materials from polybenzoxazine in "Handbook of Benzoxazine Resins", Eds. by H. Ishida and T. Agag (Elsevier, Amsterdam, 2011), pp. 457-468
- [20] G.P. Hao, W.C. Li, D. Qian, G.H. Wang, W.P. Zhang, T. Zhang, A.Q. Wang, F. Schuth, H.J. Bongard, A.H. Lu, *J. Am. Chem. Soc.* 133, 11378 (2011)
- [21] D.A. Rubenstein, H.B. Lu, S.S. Mahadik, N. Leventis, W. Yin, *J. Biomater. Sci. Polym. Ed.* 23, 1171 (2012)
- [22] Y. Si, T. Ren, B. Ding, J.Y. Yu, G. Sun, *J. Mater. Chem.* 22, 4619 (2012)
- [23] M. Sevilla, A.B. Fuertes, *Carbon* 56, 155 (2013)
- [24] D.C. Guo, J. Mi, G.P. Hao, W. Dong, G. Xiong, W.C. Li, A.H. Lu, *Energy Environ. Sci.* 6, 652 (2013)
- [25] F. Cheng, S. Wang, A.H. Lu, W.C. Li, *J. Power Sources* 229, 249 (2013)
- [26] H. Ishida, Process for preparation of benzoxazine compounds in solventless systems, US Patent 5543516, (1996)
- [27] T. Takeichi, T. Kano, T. Agag, *Polymer* 46, 12172 (2005)
- [28] J. Kim, J. Lee, T. Hyeon, *Carbon* 42, 2711 (2004)
- [29] S. Brunauer, P.H. Emmett, E. Teller, *J. Am. Chem. Soc.* 60, 309 (1938)
- [30] B.C. Lippens, J.H. Boer de, *J. Catal.* 4, 319 (1965)
- [31] E.P. Barrett, L.G. Joyner, P.P. Halenda, *J. Am. Chem. Soc.* 73, 373 (1951)
- [32] L.G. Joyner, E.P. Barrett, R. Skold, *J. Am. Chem. Soc.* 73, 3155 (1951)
- [33] D. Wu, R. Fu, M.S. Dresselhaus, G. Dresselhaus, *Carbon* 44, 675 (2006)
- [34] H. Tamon, H. Ishizaka, T. Yamamoto, T. Suzuki, *Carbon* 37, 2049 (1999)
- [35] J. Wang, X. Yang, D. Wu, R. Fu, M.S. Dresselhaus, G. Dresselhaus, *J. Power Sources* 185, 589 (2008)
- [36] D. Wu, R. Fu, S. Zhang, M.S. Dresselhaus, G. Dresselhaus, *Carbon* 42, 2033 (2004)
- [37] F. Rouquerol, J. Rouquerol, K.W.S. Sing, *Adsorption by Powders and Porous Solids, Principles, Methodology and Applications* (Academic press, London, 1999)
- [38] N. Job, F. Panariello, J. Marien, M. Crine, J.-P. Pirard, A. Leonard, *J. Non-Cryst. Solids* 352, 24 (2006)
- [39] E.G. Calvo, E.J. Juarez-Perez, J.A. Menendez, A. Arenillas, *J. Colloid Interface Sci.* 357, 541 (2011)

- [40] H. Tamon, H. Ishizaka, T. Araki, M. Okazaki, *Carbon* 36, 1257 (1998)
- [41] N. Job, A. They, R. Pirard, J. Marien, L. Kocon, J.-N. Rouzaud, F. Beguin, J.-P. Pirard, *Carbon* 43, 2481 (2005)
- [42] L. Zubizarreta, A. Arenillas, J.A. Menendez, J.J. Pis, J.-P. Pirard, N. Job, *J. Non-Cryst. Solids* 354, 4024 (2008)