CHAPTER IV
NOVEL POLYBENZOXAZINE-BASED CARBON AEROGEL ELECTRODE FOR SUPERCAPACITORS

4.1 Abstract

In this study, polybenzoxazine, a new high performance thermosetting resin, was used to prepare carbon aerogels used as an electrode for supercapacitors. Two types of polybenzoxazines, derived from two different amines, aniline and triethylenetetramine, and denoted as BA-a and BA-teta, respectively, were chosen as the reactants for the organic precursor preparation. The surface areas of carbon aerogels from both BA-a and BA-teta were 391 and 368 m^2/g, respectively. The pore size of each carbon aerogel was in the range of 2 to 5 nm which is a suitable pore size for being used as electrodes in electrochemical application. The electrochemical properties of the obtained carbon aerogels showed good performance for supercapacitor applications with specific capacitance of 55.78 and 20.53 F/g for BA-teta and BA-a, respectively. At low voltage scanning, 1 and 5 mV/s, the cyclic voltammogram of the carbon aerogel derived from BA-teta gave better rectangular shape than that of the other carbon aerogel. Impedance spectra of both carbon aerogels confirm the results of the capacitance and the cyclic voltammogram analyses.

Keywords: Cabon Aerogel; Polybenzoxazine; Supercapacitor

4.2 Introduction

Supercacitors, new kind of electrical storage energy devices, can store much more energy than conventional capacitors and offer much higher power density than battery. They are based on carbon materials (activated carbon, carbon black, aerogel particulates, carbon cloth, etc.) and have been attracting much attention because of their high performance, low cost, and evironmentally friendly [1].

Carbon aerogels are highly porous materials, consisting of a continuous rigid solid framework, and opened, continuous network of pores. Due to their attractive properties, such as a high electrical conductivity (25–100 S/cm), controllable pore structure, high porosity (80–98%), and highly useable surface area (up to 1100 m^2/g), carbon aerogels are a promising candidate for application as the supercapacitors [2–8]. Although carbon aerogels have excellent properties, they are cost intensive due to their preparation method, involving the supercritical drying process. Traditionally, carbon aerogel is prepared through the polycondensation of resorcinol and formaldehyde, using acid or base as a catalyst.

Polybenzoxazine, an innovative high performance thermosetting resin, exhibits numerous excellent properties, including low water absorption, low shirnkage up on polymerization, no catalyst required, and high dimentional [9–11]. Due to its molecular design flexibility, the properties of polybenzoxazine can be tailored to accommodate any desired applications. The purposes of this work was thus to reduce the production cost of carbon aerogels by ambient drying process, to prepare carbon aerogels from benzoxazine precursors, and to investigate the electrochemical properties of electrodes prepared from benzoxazine derived carbon aerogels.

4.3 Experimental

4.3.1 Materials

All chemicals were used without further purification. Triethylenetetramine, TETA, was purchased from FACAI Group Limited, Thailand. Aniline (99%) was purchased from Panreac Quimica SA Company. Formaldehyde solution (37% by weight) and sulphuric acid (95–97% H$_2$SO$_4$ analytical grade) were

purchased from Merck, Germany. Paraformaldehyde (95%) was purchased from BDH Laboratory Supplies. Bisphenol-A (commercial grade) was kindly supported by Bayer Thai Co., Ltd. Xylene (98%) was obtained from Carlo Erba Reagenti and 1,4-dioxane (reagent grade) was purchased from Labscan Asia Co., Ltd., Thailand.

4.3.2 Measurements

FT-IR spectra of polybenzoxazine precursor and carbon aerogel were obtained on a Nicolet Nexus 670 FT-IR spectrometer. KBr pellet technique was applied in the preparation of powder samples. TG-DTA curve was collected on a Mettler Toledo TGA/SDTA 851e instrument. The sample was loaded on the platinum pan and heated from ambient temperature to 900°C at a heating rate of 20°C/min under N_2 atmoaphere wih a flow rate of 50 ml/min. Scanning electron microscope (SEM, JEOL/JSM model 5200) was used to observe the surface morphology of polybenzoxazine aerogel and carbon aerogel. The specimens were coated with gold under vacuum before observation. Nuclear magnetic resonance was used to characterize the chemical structure of polybenzoxazine. ^{1}H-NMR spectra were recorded on a Varian Mercury 300 (300 MHz) instrument. Deuterated dimethyl sulfoxide (DMSO-d_6) was used as solvent. DSC analyses were carried out using a Perkin-Elmer DSC 7 instrument. The samples were heated from ambient temperature to 300°C at a heating rate of 10°C/min under $_2$a Natmosphere with a flow rate of 10 ml/min. $_2$N adsorption-desorption isotherms were obtained at 250°C on a Quantachrome Autosorb-1. Samples were degassed at 250°C for 12 hr in a vacuum furnace prior to analysis. Surface areas were calculated using the BET equation. The testing cell for electrochemical measurments was consisted of graphite sheets as current collectors, two carbon aerogels electrodes separated by microporous polyethylene membrane, and 3M H_2SO_4 as electrolyte solution. Before the measurements, The carbon aerogel electrodes were placed in 3M H_2SO_4 for 24 hr to diffuse the electrolyte into the pores of the carbon aerogel electrodes [12, 13]. Electrochemical characterization was succeeded with a computer-controlled potentiostat/galvanostat (Autolab PG-STAT 30 with GPES software). Cyclic voltammetry (CV) was performed between -1V and 1V with scanning rates of 1, 5,

20, and 50 mVs^{-1}. For galvanostatic charge/discharge measurement, the testing cell was charged with current density of 5 mA.cm^{-2} up to 1 V and discharged with 5 mA. cm^{-2} down to 0 V [13]. Electrochemical impedance spectra (EIS) were achieved using an impedance analyzer (Autolab PG-STAT 30 with FRA software) made over the frequency of 10 kHz down to 10 mHz with a sinusoidal signal of 10 mV. All of the electrochemical measurements were performed at room temperature.

4.3.3 Methodology

4.3.3.1 Synthesis of Polybenzoxazine based Aerogels

In this research, we used two types of polybenzoxazine precursors for carbon aerogel preparation. The precursors were synthesized using two different amines, aniline and triethylenetetramine, as the reactant.

The synthesis of benzoxazine precursor (abbreviated as BA-teta), as shown in scheme 1, from bisphennol-A, formaldehyde and TETA was carried out using "quasi-solventless method", our first recovery, unlike the traditional method requiring solvent and long reaction, as first described by Takeichi *et al.* [11]. Dioxane was used in our method to only help the mixing of all reactants to consequently produce benzoxazine precursor. The ratio of all reactants used was 1:4:1. The synthesis was started by firstly dissolving bisphenol A (4.52 g) in dioxane (20 ml) in a glass bottle and stirring until the clear solution was obtained. Formaldehyde solution (6.48 g) was then added to bisphenol A solution. The temperature was kept under 10°C by using an ice bath. TETA was then added dropwise into the mixture and stirred continuously for approximately 1 hr until transparent yellow viscous liquid precursor was obtained. The precursor was placed in an oven at 80°C for 72 hr in a closed system, yielding benzoxazine aerogel. Finally, benzoxazine aerogel was cut into a disk shape and placed in an oven set the temperature at 160°, 180°C for 3 hr at each temperature, and 200°C for 2 hr in order to polymerize benzoxazine aerogel. The structural characteristics of BA-teta-based aerogel was investigated using FTIR and ^{1}H-NMR. The thermal properties were measured using DSC and TG/DTA. The morphology was also observed by SEM.
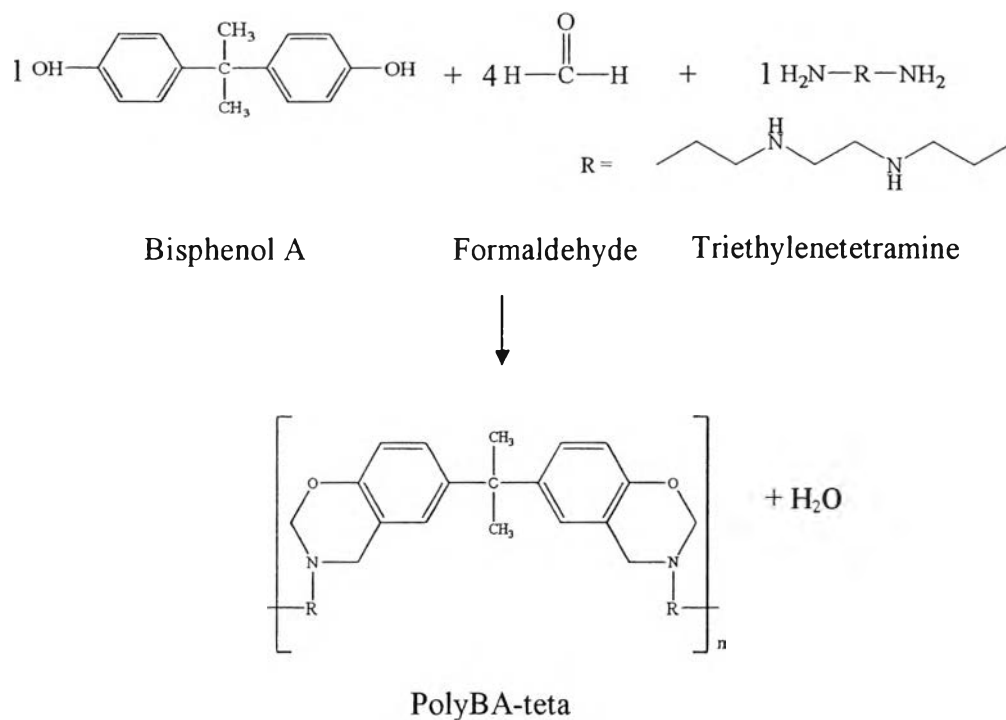
Scheme 4.1. Preparation of Poly BA-teta

Another benzoxazine precursor used in this study, denoted as BA-a, was synthesized via solventless process proposed by Ishida *et al* [9]. Bisphenol A (22.8g), aniline (18.6g), and paraformaldehyde (12g) with the mole ratio of 1:2:4 (scheme 2) were mixed together and heated at 110°C for an hour until transparent light yellow viscous liquid was obtained.
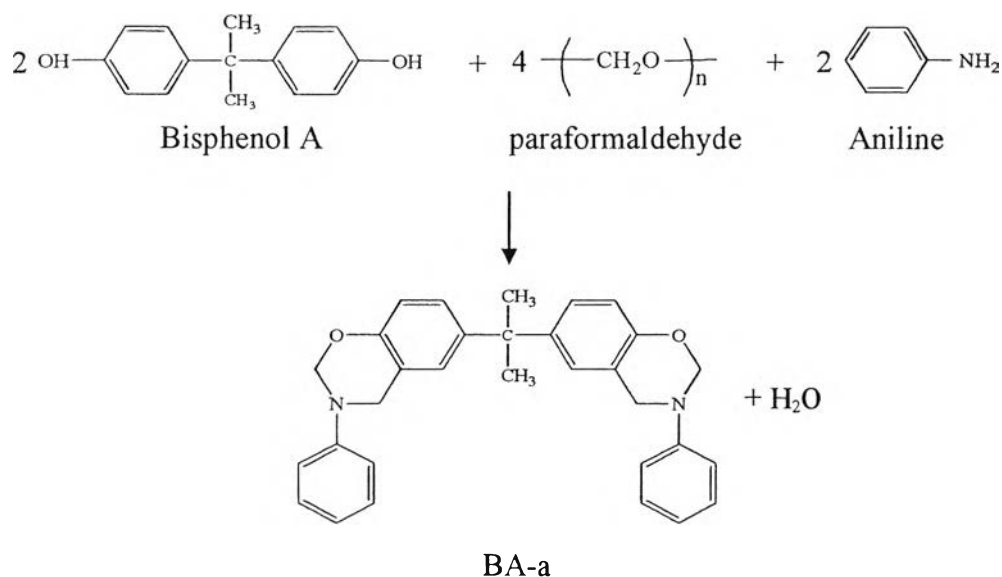
Scheme 4.2. Preparation of BA-a monomer.

Benzoxazine monomer was prepared by using xylene as a solvent. The monomer concentration was 40 wt%. After that, the mixtures were moved into vials and then sealed. The temperature was gradually raised up to 130°C for 96 hr in an oven. The attained products were partially cured benzoxazine hydrogels. The hydrogels were dried at ambient temperature for 2 days to remove the xylene from their matrixes yielding organic aerogels which were then subjected to step-curing in an oven at 160°, 180°C for an hour at each temperature, and 200°C for 2 hr, respectively.

4.3.3.2 Preapation of Carbon Aerogel Electrodes

The fully cured organic aerogels of BA-teta and BA-a were cut into a disk shape by using diamond saw and then pyrolyzed under a nitrogen flow rate of 500 cm³/min using the following ramp cycle: 30° to 250°C in 60 min, 250° to 600°C in 300 min, 600° to 800°C in 60 min, and holding at 800°C for 60 min. The carbon aerogel electrodes were then obtained.

4.3.3.3 Characterization of Carbon Aerogel Electrodes

Surface areas of the carbon aerogel electrodes were calculated from N_2 adsorption isotherm at -196°C (77K). Galvanostatic

charge/discharge, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to determined electrical properties.

4.4 Results and Discussion

4.4.1 Chemical Structure of Polybenzoxazine Precursors

The chemical structure of BA-teta precursor was confirmed by ^{1}H-NMR and FT-IR, as shown in Figures 4.1 and 4.2. The aromatic protons appeared at 6.62—6.96 ppm. The peaks at 4.76 (O-CH$_2$-N) and 3.89 (Ar-CH$_2$-N) ppm were assigned to the methylene bridge of oxazine ring. The methylene group of opened oxazine ring was observed at 3.68 ppm. The methyl groups of bisphenol A appeared at 1.53 and the proton of aliphatic amine was observed around 2.51—2.71 ppm. The ^{1}H-NMR spectrum indicates that the precursor was in a partially cured state which means that benzoxazine precursor contained both ring-opened and ring-closed benzoxazine functional groups in the structure similar to the one prepared by conventional method reported by Takeichi et al. [11]
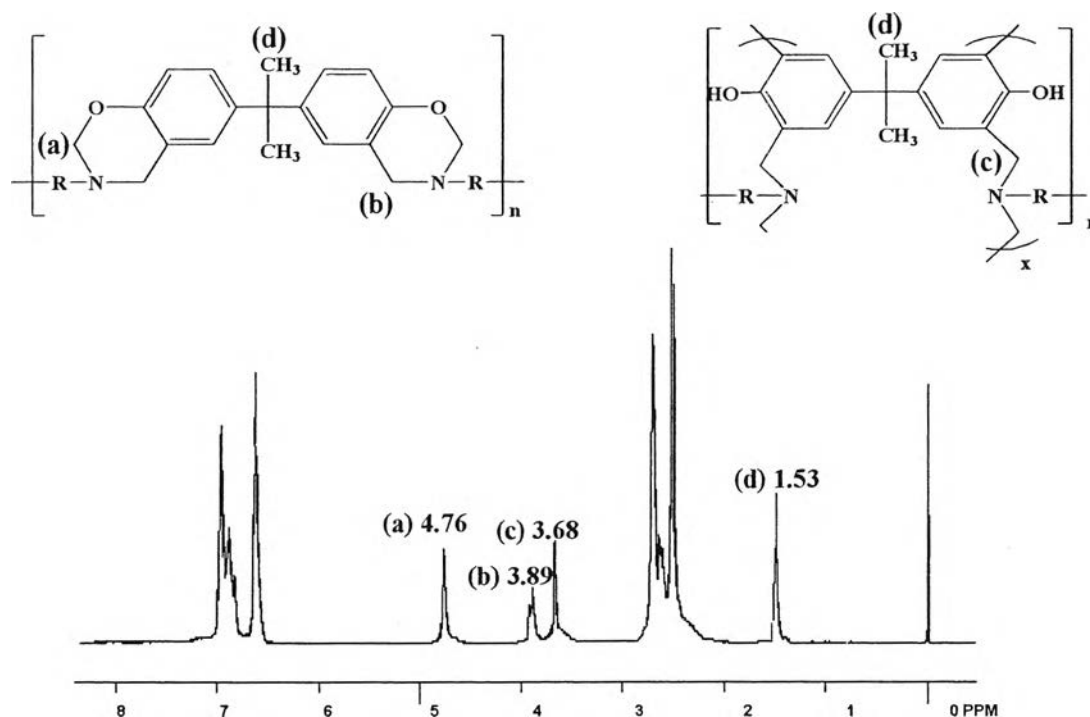

Figure 4.1 ^{1}H-NMR spectrum of BA-teta precursor.

The BA-teta precursor was analyzed by FT-IR to confirm the chemical structure. The asymmetric stretching of C–O–C (1230 cm^{-1}), C–N–C (1185 cm^{-1}), and CH$_2$ wagging of oxazine (1325–1328cm^{-1}) were detected [11]. The progress of polymerization and derivation from the precursor to carbon aerogel were monitored at the bands of 936 and 1498 cm^{-1} which are attributed to the CH- out of plane bending of oxazine ring and trisubstituted benzene ring, respectively. After polymerization, the intensity of these peaks was decreased due to the ring-opening of oxazine ring. These results are in agreement with Takeichi *et al.* [11]. Furthermore, all of the peaks of polybenzoxazine disappeared after pyrolysis, indicating that all organic residues were removed.
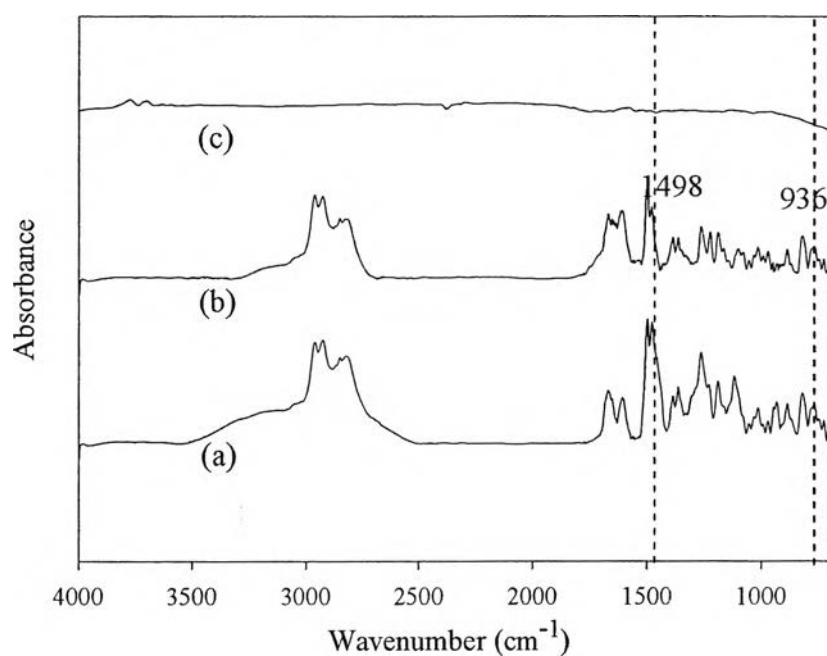

Figure 4.2 FT-IR spectra of of BA-teta (a), polymerized BA-teta at 200°C (b), and pyrolyzed BA-teta at 800°C (c).

4.4.2 Thermal Properties of Polybenzoxazine Precursor

Thermal properties of polybenzoxazine were observed by DSC and TGA, as shown in Figures 4.3 and 4.4, respectively. DSC thermogram (a) shows a broad exothermal peak centered at 245°C, representing the ring-opening polymerization of the precursor. The onset of the polymerization was observed

around 180°C, which implies that the benzoxazine precursor is partially-cured. In fully-cured stage (b), the exothermal peak disappears, suggesting that the benzoxazine precursor was completely polymerized. This DSC result is in agreement with the study of Takeichi *et al.* [11], who showed the polymerization progress of polybenzoxazine precursor from bisphenol-A, paraformaldehyde and methylenedianiline (B-mda). The exotherm decreased when increasing temperature and the exotherm peak disappeared after 240°C, representing completely opening oxazine ring.
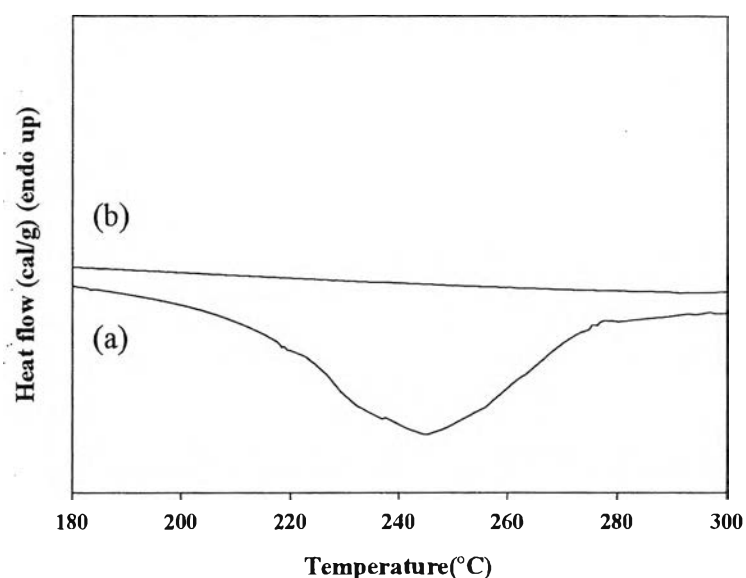
Figure 4.3 DSC thermograms of BA-teta benzoxazine precursor (a) and polybenzoxazine in fully cured stage (b).
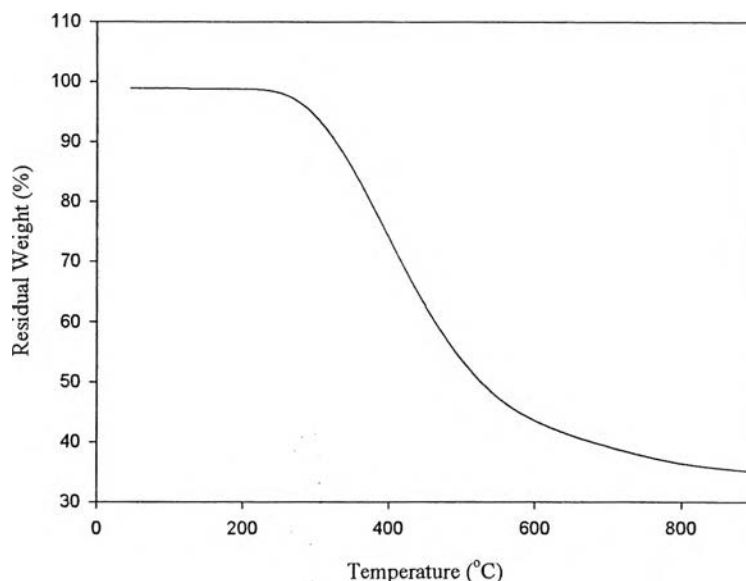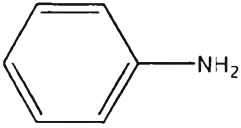
Figure 4.4 TGA thermogram of BA-teta benzoxazine precursor.

From Figure 4.4, Ba-teta started to decompose around 250°C. The weight was rapidly decreased in the range of 250°-600°C. After 800°C, the weight of BA-teta approached steady state. Kansinee *et al.* [14] also identified the decomposition of polybenzoxazines through TGA-GC-MS technique, and found that the decomposed compounds were from the degradation of polybenzoxazine or recombination of evaluated compounds during degradation.

Table 4.1 shows 5% weight loss temperatures and the char yields of BA-a and BA-teta. BA-a has higher thermal stability than BA-teta because of the presence of aromatic groups. However, the char yield of BA-teta is higher because of higher crosslink density due to the H-bonding of the secondary amines in the chain.

Table 4.1 Thermal properties of polybenzoxazine precursors

Precursor	Type of amine	T$_{-5\%}$ (°C)	Char yield (%)
PolyBA-a[15]		330	25
PolyBA-teta		293	37

4.4.3 Surface Area of Polybenzoxazine-based Carbon Aerogel Electrodes

Table 4.2 summarizes physical properties of polybenzaxazine-based carbon aerogel electrodes using BET method. With the data of the pore volume and the surface area, specific capacitance of carbon aerogels can be estimated [16]. The pore size of each carbon aerogels are in the range of 2 to 5 nm which is a suitable pore size for electrodes in electrochemical application [17]. Moreover, the result indicates that carbon aerogel electrodes derived from BA-teta benzoxazine precursor contain larger amount of mesopores, comparing with micropores, suitable for efficient ion motion into the porous electrode materials [18].

Table 4.2 Texture characteristics of carbon aerogel electrodes derived from BA-teta (CA(BA-teta)) and BA-a (CA(BA-a)) polybenzoxazine precursor

Parameter	CA(BA-teta)	CA(BA-a) [15]
BET surface area (m^2/g)	368	391
Total pore volume (cm^2/g)	0.34	0.21
Average pore size (nm)	3.67	2.20
Micropore volume (cm^3/g)	0.13	0.17
Mesopore volume (cm^3/g)	0.21	0.05
*Mesoporosity (%)	62	23

*Mesoporosity (%) = (Mesopore volume/ Total pore volume) x100

4.4.4 Morphology of Organic Aerogel and Carbon Aerogel

Figure 4.5 shows SEM micrographs of organic aerogel and carbon aerogel. The porous structure was obtained from the removal of the solvent. According to the structure of the organic aerogel, the solid phase presents a smooth continuous polymer network incorporated with open macropores. However, in the case of the carbon aerogel, the denser porous structure of three dimension carbon network containing contigous open macropores was obtained.
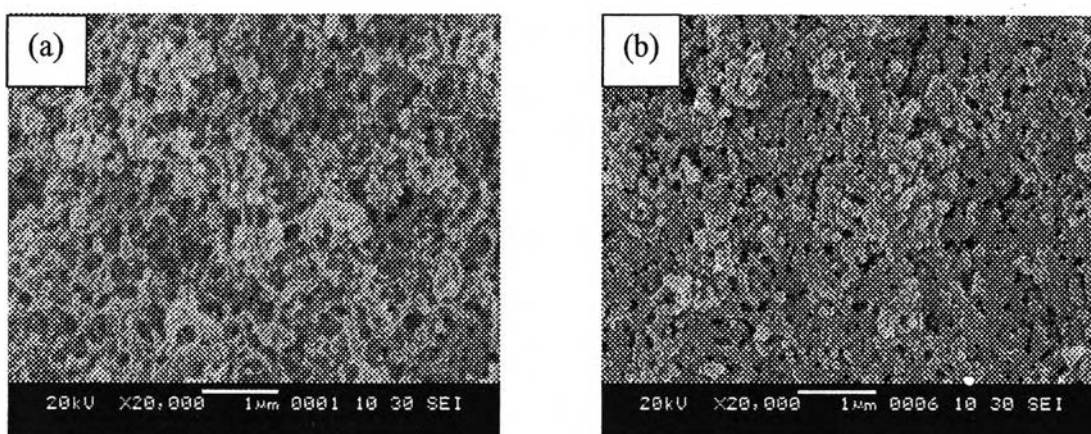

Figure 4.5 SEM micrograph of organic aerogel (a) and carbon aerogel (b).

Kim *et al.* [21] reported that the pore distribution of the resorcinol/formaldehyde resin aerogel was broadly spread with diameters ranging from nanopores to macropores. In our case, TEM observation indicates that carbon aerogels have a three-dimensional nano-network, and the pore size was less than 10 nm, as shown in Figure 4.6.
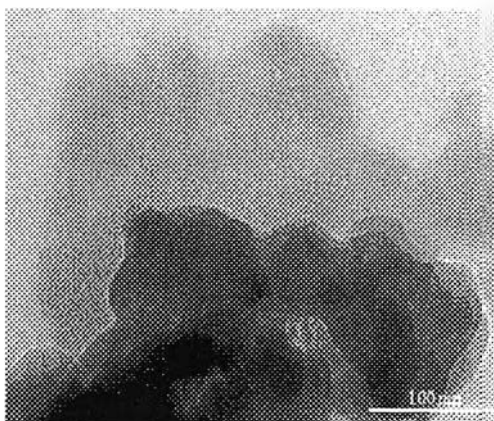
Figure 4.6 TEM photograph of the carbon aerogel.

4.4.5 Electrochemical Characterization

Figure 4.7 shows the cyclic voltammograms (CV curve) of the carbon aerogel electrodes obtained at 1 and 5 mV/s. The rectangular shape of the CV curves were observed at a low scanning rate, implying that the electrodes derived from polybenzoxazine-based carbon aerogels show good capacitor performance because the rectangular shape of the CV curves represent electrochemical double layer, corresponding to the mechanism of energy storage at the interface of electrolyte and the carbon aerogel electrodes, also suggesting that ions occupy some of pores to form the electrochemical double layer [20]. Moreover, the CV curves of CA(BA-teta) were closer to rectangular shape than those of CA(BA-a), indicating that the CA(BA-teta), having larger amount of mesopoes (as shown in Table 4.2), has lower resistance [20]. However, the CV curves were deviated from the rectangular shape when the scanning rate was increased, as shown in Figure 4.8 because the ions of electrolyte could not transport easily into the pore of electrodes at the shorter time, and may be due to electrolyte trapped in the micropores of the carbon aerogels [21].
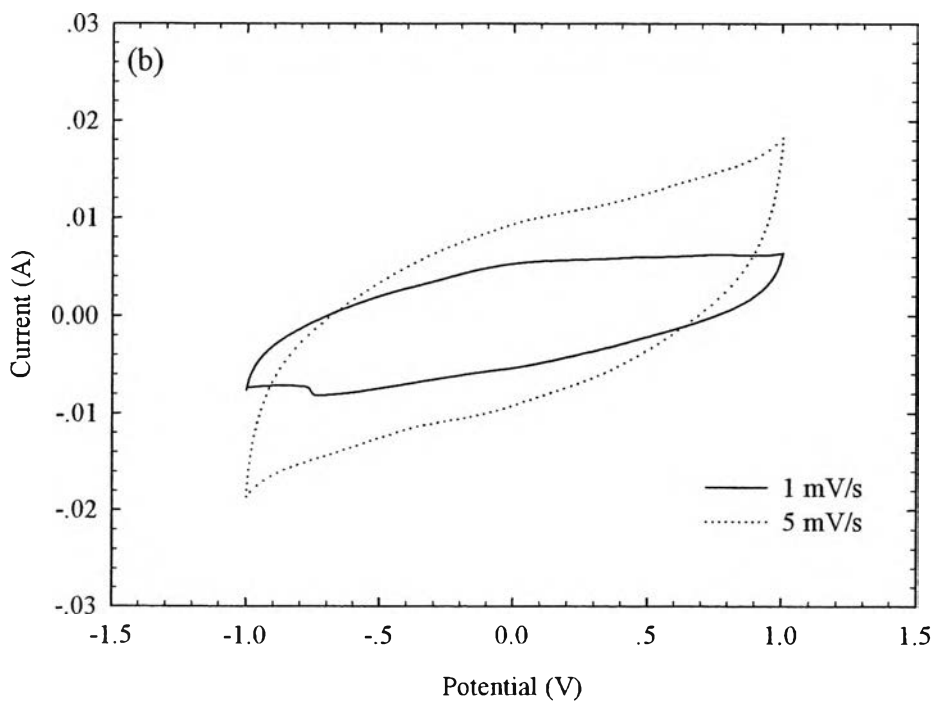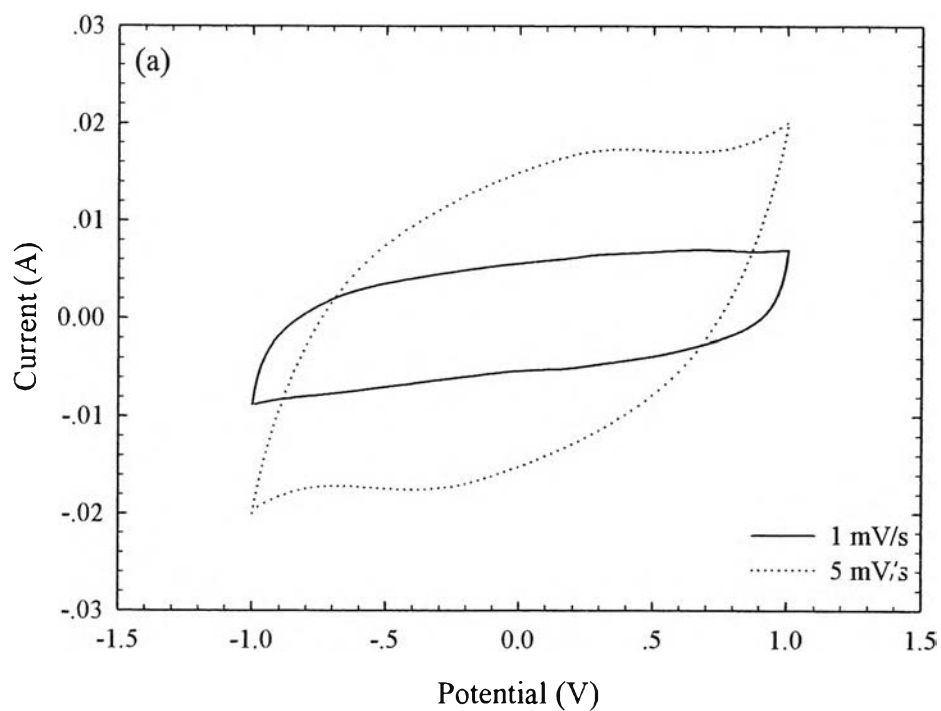
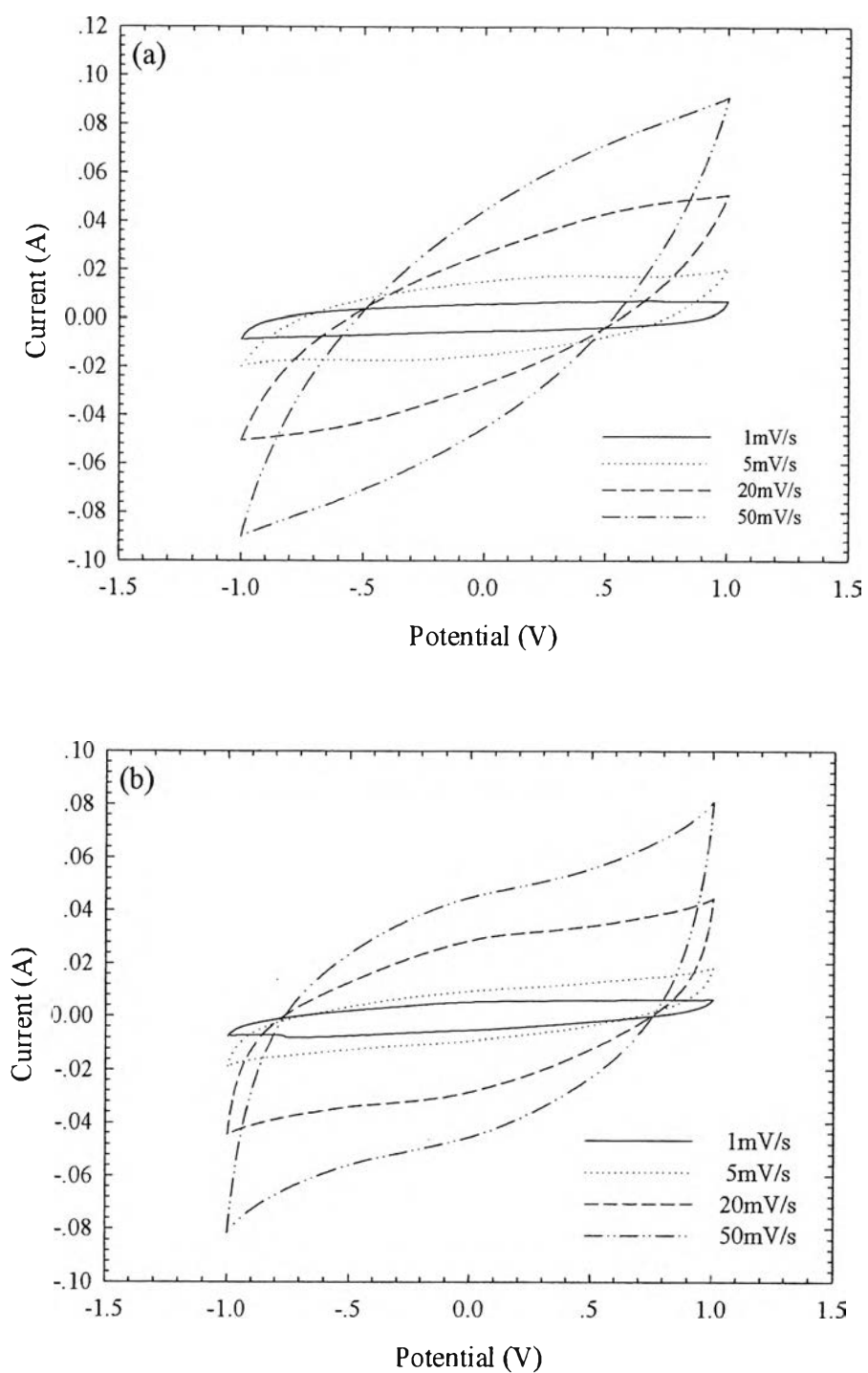**Figure 4.7** Cyclic voltammograms of CA(BA-teta) (a) and CA(BA-a) (b) with scan rate: 1 and 5 mV/s .

Figure 4.8 Cyclic voltammograms of CA(BA-teta) (a) and CA(BA-a) (b) with scan rate: 1, 5, 25 and 50 mV/s.

The specific capacitance (C) of the carbon aerogels was calculated from the discharge curve (Figure 4.9), using the following equation [20]:

$$C = \frac{it}{m\Delta V} \tag{1}$$

Where i is the discharge current (A), t is the discharge time (s), m is the mass of the carbon aerogel electrode (g), and ΔV is the potential difference during the discharge (V).

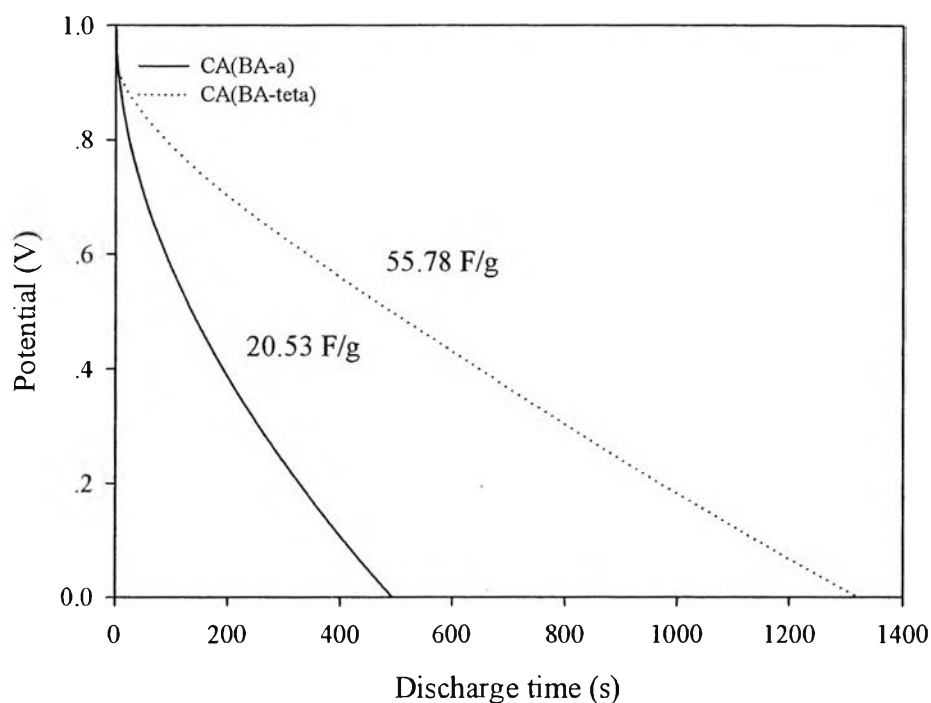**Figure 4.9** Discharge curves of polybenzoxazine-based cabon aerogel electrode at current discharge ($5mA/cm^2$).

The electrodes derived from CA(BA-teta) showed better specific capacitance than the one derived from CA(BA-a). As given above that CA(BA-teta) has about twice higher mesoporosity than CA(BA-a) and has lower resistance, as indicated in the cyclic voltammogram results, this can thus be concluded that the mesoporosity of the carbon aerogel electrodes indeed has influence on the electrochemical properties of supercapacitors, as proposed by Lv *et al.* [18].

Electrochemical impedance measurement was made over the frequency range of 10 kHz to 10 mHz and the voltage between the two electrodes was kept at 0 V during the measurement. Nyquist plots of the electrodes derived from both carbon aerogels are shown in Figure 4.10. A small semicircle at the high frequency range was corresponded to the double layer charging at the electrodes. The intercept on real axis (Z') at high frequency side corresponded to the electrolyte resistance (R_s) and the diameter of semicircle represented charge transfer resistance (R_{ct}), which represents the charge transfer process at the interface of the electrode and electrolyte [22]. The electrolyte was identical in all samples so the diameter of the semicircle indicates the R_{ct} of the carbon aerogel electrodes. R_{ct} of the CA(BAteta) was lower, suggesting that ions of electrolyte can adsorb at the interface of CA(BA-teta) electrode easier than those of CA(BA-a). A straight line along imaginary axis (Z'') in the Nyquist plots with slope of about 45° in the low frequency range represented the porous structure of the electrodes which contributes to the diffusion resistance of electrolyte into the pores [21, 23]. The slope was also related to the dispersed capacitance C and resistance R, derived from various porous structures of the carbon aerogels [23]. This phenomenon can be stated that our system contains variety of pore structures; giving variety of R and C values, as can be explained by a transmission line model reported by Levie (Figure 4.11) [24].
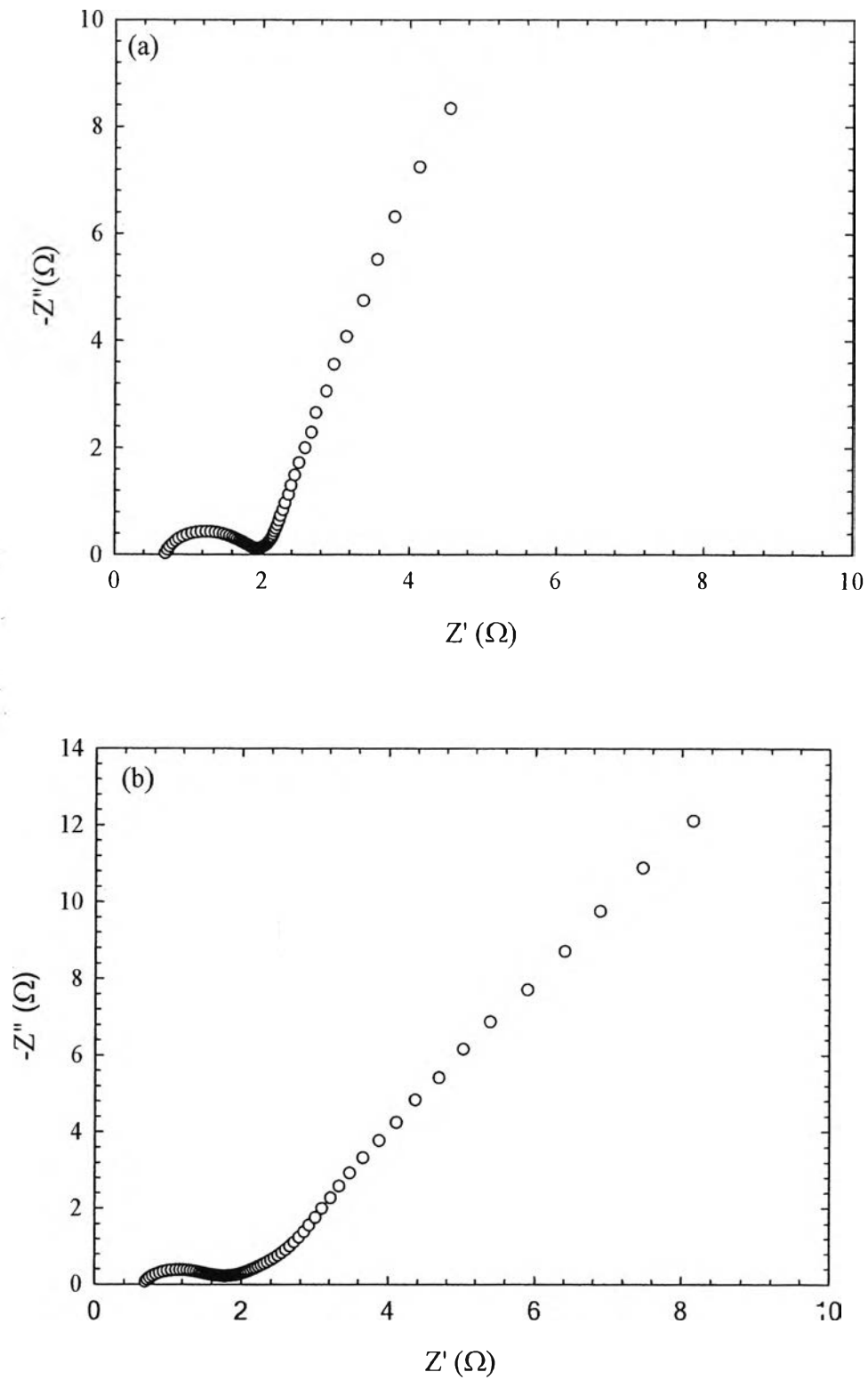
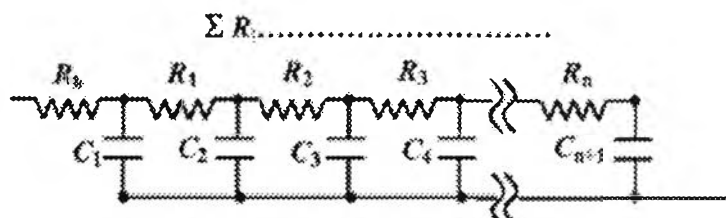**Figure 4.10** Nyquist plots for CA(BA-a) (a) and CA(BA-teta) (b).

Figure 4.11 The equivalent circuit of carbon aerogel electrodes [25].

Conclusions

Polybenzoxazine was successfully used as organic precursors to prepare carbon aerogel with a suitable pore size for electrodes in the electrochemical application. The carbon aerogels derived from bisphenol-A and teta showed higher specific capacitance than that derived from bisphenol-A and aniline due to larger amount of mesopores.

Acknowledgements

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