

CHAPTER II

LITERATURE REVIEW

2.1 Supercapacitors

Supercapacitors - also called ultracapacitors which are new type of energy storage devices. It is attractive to many researchers because of interesting properties such as high power density and cyclic stability. Normally, supercapacitors consist of two electrodes immersed in an electrolyte with a dielectric separator between the electrodes (Burke 2000). The main advantages of supercapacitors when compared with other energy storage devices are high power density, high energy density, long life cycle, fast charge and discharge rate, and light weight (Rakesh *et al.*, 2009). The performances of supercapacitors exhibit the combination between battery which has high energy density and high power density of conventional capacitor. It is obvious from the data which shown on Table 2.1

Table 2.1 Comparison properties of rechargeable batteries and supercapacitors (Miller and Simon, 2008)

Property	Battery	Supercapacitor
Storage mechanism	Chemical	Physical
Power limitation	Reaction kinetics, mass transport	Electrolyte conductivity
Energy storage	High(bulk)	Limited(surface area)
Charge rate	Kinetically limited	High, same as discharge rate
Cycle life limitaion	Mechanical stability, Chemical reversibility	Side reactions

Supercapacitors mainly divided into two categories by mechanism of storing charge, the electrical double-layer capacitors (EDLCs) and the pseudocapacitors (Prasad *et al.*, 2013).

2.1.1 Electrical Double-layer capacitors (EDLCs)

The mechanism for storing electrical energy of EDLCs is electrostatic or physical separation of charge at the interface between electrode and electrolyte. Cations accumulate inside the pores of negative electrode and anions accumulate inside the pores of positive electrode when charging process take place as shown in Figure 2.1 (Manafet *et al.*, 2013).

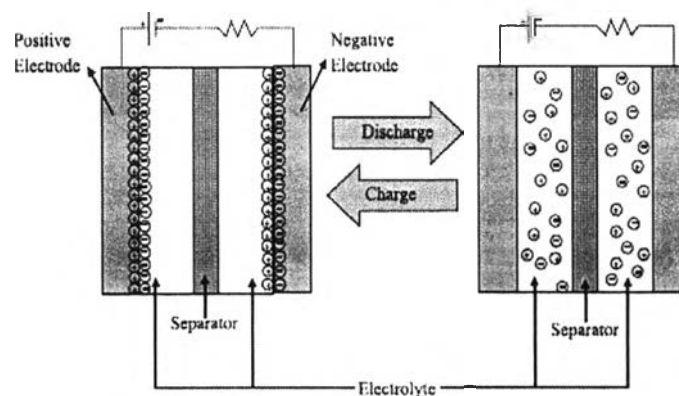


Figure 2.1 Mechanism of charge discharge process of EDLC.

2.1.2 Pseudocapacitors

Mainly mechanisms to store energy of Pseudocapacitors are faradic redox reaction of electroactive materials such as ruthenium oxide (RuO_2), magnetite (Fe_3O_4), and manganese oxide (MnO_2) which is shown in Figure 2.2 and electrosorption. To increase performance of this capacitor, selection of electrode materials is very crucial (Prasad *et al.*, 2013). To enhance specific capacitance by increasing rate of faradaic reaction can be modified by the following:

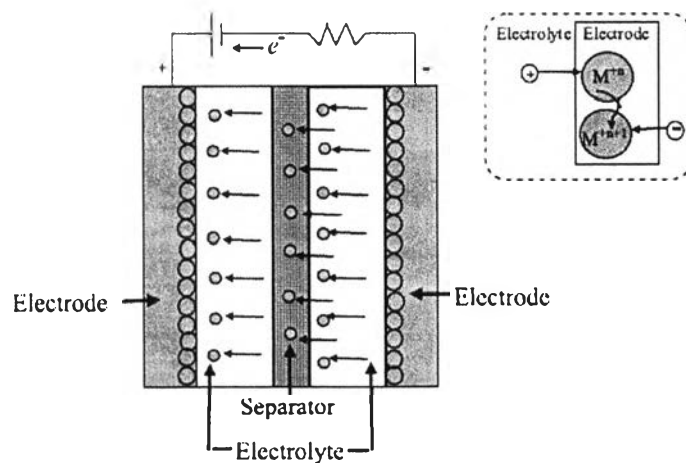


Figure 2.2 Energy storage mechanism for pseudocapacitor.

1) A special oxidation carbon which treated chemical or electrochemical polarization in order to increase surface functionality.

2) The formation of carbon/conducting polymers composites by electropolymerization of a proper monomer on the carbon surface. For example, conductive polymers are used to decrease resistance by coating to the conductive materials. For example, PPy was used as adhesive and charge transfer conductivities between PPy and AC (substrate). Increasing of specific capacitance was observed (Zhang, Kong, *et al.*, 2009).

3) Insertion of transition metal oxides which act as electroactive materials to increase specific capacitance by the redox reaction on the surface of the electrodes of capacitors.

2.2 Electrode Material Properties

Materials that are interested for using as electrode materials in the present would be inevitable carbon materials due to it can reach to equilibrium point in the industrial fields. Electrode materials should have the following qualifications: good conductivity, high thermal stability, inertness, and high surface area. Moreover, it should be environmental friendly and relatively low cost (Pandolfo and Hollenkamp, 2006). From the following qualifications, carbon can perform in that way.

The majority of commercial carbon materials are derived from organic rich precursors. After heat treat the organic rich precursors under inert atmospheres or

carbonization, carbon materials are obtained. There are many factors that affects to the properties of carbon. For example, types of carbon precursors, processing conditions (Marsh and Radovic, 2002).

2.2.1 Carbon Forms

There are various types of carbons that used in commercial supercapacitrs. But each types of carbon will perform differently and cost of productions also different.

2.2.1.1 *Carbon Blacks*

Carbon blacks are produced by the partial combustion or thermal decomposition of hydrocarbon such as gases, or oils in gas phase (Casperson and Hann, 1986). The main properties of carbon blacks are fineness, high porosity so it normally filled in batteries to perform as conductive fillers. The conductivity of carbon black is in the range of 10^{-1} to 10^2 (Ωcm)⁻¹ (Donnet *et al.*, 1993).

2.2.1.2 *Glassy Carbons*

Production process of glassy carbons are thermal degraded the chosen polymer resin. Typically are phenolic resins. Firstly, carbon precursors are cured to form network structure and then slowly carbonized. After that they are heated to higher temperatures. There are reported that carbonized at around 1800 °C will obtain desirable properties (Marsh *et al.*, 1997).

2.2.1.3 *Carbon Nanostructures*

Carbon nanotubes are produced by the catalytic decomposition of certain hydrocarbons. There are interested in the application of electrode materials for supercapacitor because the combination between low electrical resistivity and high porosity. But it has some limitations. For example, carbon nanotubes are very inert so surface activation is required in order to can be mixed with another components. Although there are a good candidate EDLC electrode which may offer power capabilities well above 8 kWkg⁻¹(An *et al.*, 2001), the efficiency in the application of them are dependent on their method of preparation and generally below than conventional carbon. Moreover, the production cost still really high when compare to commercial carbon.

2.2.1.4 Carbon Aerogels

Carbon aerogels are synthesized by the poly-condensation of resorcinol and formaldehyde via a sol-gel process and follow by pyrolysis. Carbon aerogels are highly porous materials. Moreover, the pore size and shape are flexible to design by varying the conditions of sol-gel process (Pröbstle *et al.*, 2003). Carbon aerogels normally provide higher electrical conductivity higher than most activated carbon due to the interconnected colloidal of carbon particles. For the electrical properties on carbon aerogels have been reported that carbon aerogels with pore diameters in the range 3-13 nm exhibited stable capacitive behavior and the highest capacitances.

From many previous works in order to reach the goal for using carbon materials as electrode of supercapacitors, carbon in form of aerogel or xerogels is the most suitable because of flexibility on morphology design and possibility to scale up in industry field. But the properties of carbon aerogels depend on carbon precursors and process of synthesis.

2.2.2 Electrical Conductivity of Amorphous Carbons

Carbon xerogels or carbon aerogels which derived from organic precursors normally are amorphous carbons. Although in some cases provides high surface areas but applying in electrode applications electrical conductivity also requires to concern.

Kumari and Subramyam (2009) synthesized amorphous carbon from carbon-sulfur composite films (a-C:S) by vapour phase pyrolysis of maleic anhydride and sulfur. In this work pyrolysis temperature and sulfur content was varied. They found that the electrical conductivity of carbon composite increased after incorporated of medium amount of sulfur and pyrolysis at 900 °C. If the amount of sulfur was too much it would induce the crystal defects that will obstruct the mobility of carrier. The highest electrical conductivity was 300 S/cm.

Naoyuki *et al.* (2014) used reactive magnetron sputtering technique to prepared hydrogen-free amorphous carbon nitride (a-CN_x) films. In this study, they also vary the deposition temperature in order to observe the effect of process temperature to electrical conductivity of materials. The results show that the

conductivity increased with rising deposition temperature because of the predominant sp^2 C-C bonding sites. In contrast, nitrogen incorporation induced structure change to disorder and led to an increase in the sp^3 C-C bonding fraction in the film and as the result the conductivity was lower. At 900 °C, a-CN_x showed the highest conductivity about 10^{-2} ($\Omega^{-1} \text{ cm}^{-1}$) which still lower than amorphous carbon film without nitrogen incorporation ($10^2 \Omega^{-1} \text{ cm}^{-1}$).

Focusing on electrical conductivity of amorphous carbons, it was obvious that conductivity was very low when compared to commercial carbon or crystalline carbon such as graphene which has conductivity around 1.00×10^8 S/cm (University of Maryland, 2008) or graphite which has conductivity about 3.30×10^2 S/cm (Pierson O.H., 1993). In order to obtain such high conductivity, changing structure of carbon to more order or close to graphene like structure is very important. And the process condition usually acute. In some cases, very high temperature and pressure are required. Xu *et al.* (2014) prepare graphene nanosheets by pyrolysis of coal-tar pitch with the presence of aluminum. Pyrolysis at 1700 °C with slow heating rate and apply pressure around 100 Pa.

Due to the limitation of amorphous carbon which provide such a low conductivity even if some types of its give high surface area that suitable for using in electrode applications. In order to obtain graphene-like carbon have to synthesize under critical conditions which is difficult to process. Focus on electrical conductivity, graphene is a good candidate for apply due to a great properties such as high surface area and great high of electrical conductivity.

2.3 Graphene

In 1986, graphene was first proposed as the name for an isolated single two-dimensional sheet of carbon atoms, take place in a graphite intercalation compound. The schematically of graphene started from a two-dimensional carbon layer has neighboring intercalated layers and then isolated from other carbon layers as shown in Figure 2.3 (Inagaki *et al.*, 2014). Graphene was defined as an isolated single layer of carbon hexagons consisting of sp^2 -hybridized C-C bonding with π -electron clouds.

2D graphene crystals exhibited many interesting properties, like room temperature quantum Hall effect (Novoselov *et al.*, 2007), availability of charge carriers that behave as massless relativistic quasiparticles like Dirac fermions (Novoselov *et al.*, 2005), long-range ballistic transport at room temperature with around ten times higher electron mobility than silicon (Berger *et al.*, 2006), and ultimate sensitivity of adsorption of individual gas molecules (Schedin *et al.*, 2007). Moreover, graphene also shown large specific surface area, also provided great electrical, mechanical, and thermal properties (Novoselov *et al.*, 2004, Geim, 2009). Form the engineering point of view, the interesting structural and physical characteristics of graphene can display potential applications in technological fields.

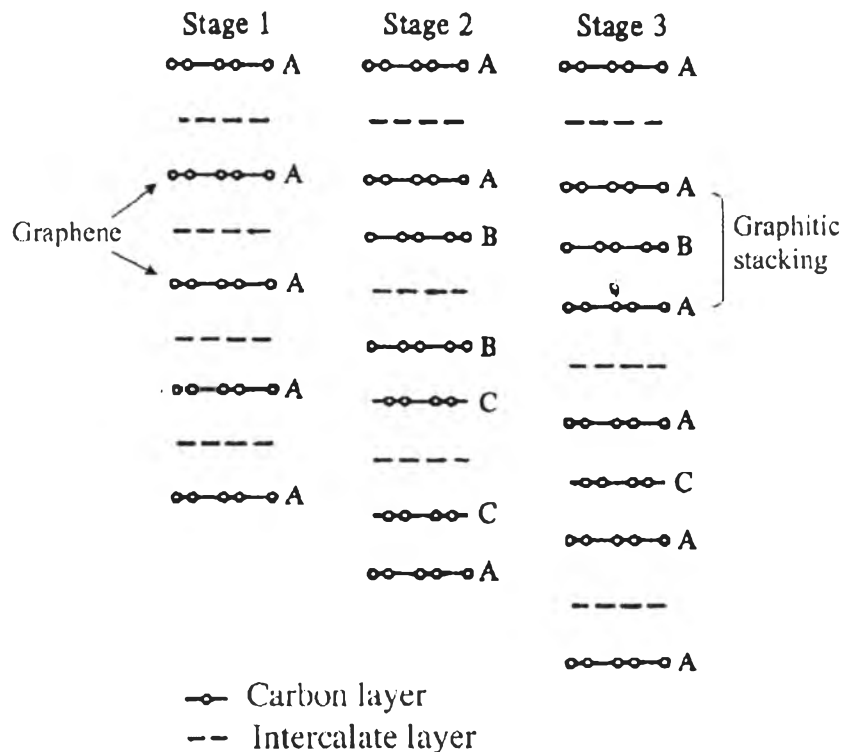


Figure 2.3 Graphite intercalation compounds in stage structure.

2.3.1 Preparation of Graphene

Process for preparing graphene can be categorized into five routes: (1) mechanical cleavage of graphite crystals, (2) exfoliation of graphite through its intercalation compound, (3) chemical vapor deposition (CVD) on different substrate crystals, (4) organic synthesis processes, and (5) other processes (Inagaki, Kang *et al.*, 2014).

Graphene can be prepared through graphite oxide (GO). Graphite oxide which is a covalent-type intercalation compound has been used on a large scale in industry to prepare flexible graphite sheets. The main process for synthesized GO is strong oxidation, exfoliation at high temperature, and forming into thin sheets via compressing and rolling. Try to prepare graphene from GO have been reported since 1962. The method for preparing flexible graphite sheets and thin graphene-like flakes are compared as shown in Figure 2.4. Both of thermal and chemical exfoliation is involved for graphene preparation. In addition, reduction process is crucial in order to have high electrical conductivity.

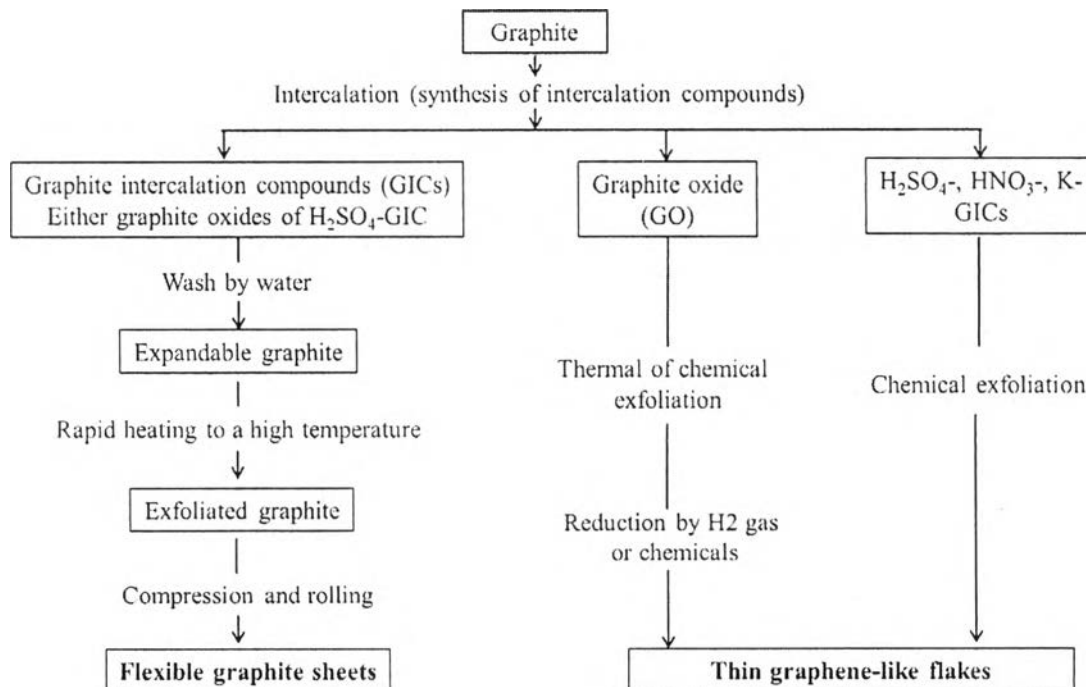


Figure 2.4 Comparison the process for preparing of flexible graphite sheet and graphene via intercalation compounds.

GO was firstly prepared by Oxford chemist Benjamin C. Brodie in 1859, by adding potassium chlorate and fuming nitric acid into graphite (Brodie, 1859). Due to the hazard chemicals that have been used in process, Hummer and Offeman improve the method which was safer, quicker, and more effective process called The Hummers' Method (Hummers and Offeman, 1958). This method used sulfuric acid, sodium nitrate, and potassium permanganate in the process that is still used in the present. Roughly, the process will start with production of intercalated graphite by treated graphite with sulfuric acid/nitric acid mixture. Then the intercalated graphite was given a thermal shock at 800 °C for minute, exfoliated graphite was obtained as the resulted. After that oxidation step was occurred by using KMnO₄ and H₂O₂, the brown colored exfoliated graphene oxide was obtained. And to success in preparing single-layer graphene, reduction of graphene oxide was involved by disperse in dimethylformamide with hydrazine hydrate (Park *et al.*, 2009).

Meng and Park (2012) prepared reduced graphene nanosheets from pre-exfoliated graphite flakes. In this work start with exfoliated pristine graphite flakes to graphite nanoplatelets in the presence of acetic acid. Then treat graphite nanoplatelets by using Hammer's method to produce graphite oxide sheets. Finally, exfoliation to graphene nanosheets by ultrasonication and reduction processes.

Normally, graphite oxide itself is nonconducting, restoring the graphitic network by thermal annealing or through treatment with chemical reduction agents. Ruoff's group provided detail the use of hydrazine hydrate to eliminate oxidation through the formation and removal of epoxide complexes (Stankovich *et al.*, 2007). The process was done by adding hydrazine directly to aqueous dispersions of GO. As the reported the product was used as an additive for polystyrene-based composites which help to increase the conductivity and strength of the matrix.

It was obvious that in the process for preparing GO and reduce graphene oxide have to use hazard chemicals such as anhydrous hydrazine which required great care because it is both highly toxic and potentially explosive (Schiessl, 2000). So preparing carbon graphene like structure by using other materials is interested.

2.4 Carbon Gel

Important materials that have been used as electrode for supercapacitors are materials that provide the suitable properties such as high porosity and controllable pore structure, and high conductivity. These properties also appear in carbon gel, so carbon gel is a good candidate to challenge to apply as electrode materials. In addition carbon gel also performs excellent properties that proper for electrode such as light weight, high surface area, high porosity, and high electrical conductivity. Carbon gel can be classified into three types; carbon aerogel, carbon cryogel, and carbon xerogel. Generally carbon gel can form pore structures, classified into two types; micropore (<2 nm) which is located on the carbon particle and meso-macropore (2-50 nm and >50 nm) formed by inter-connection between carbon particles (Rouquerol *et.al.*, 1994).

From the beginning of carbon gel, carbon aerogel was prepared by Pekala (1989). The method that was used is polycondensation of resorcinol and formaldehyde in alkaline condition, the step to obtain aerogel normally compose of 4 steps; sol-gel formation, solvent exchange, a supercritical drying, and pyrolysis which shown in Figure 2.5. But this method also has drawbacks which are long period of time to prepared and high cost in step of drying. In the present, another raw material have been used to preparing carbon aerogels which is less toxic than past and try to develop the method of production to reduce cost and time.

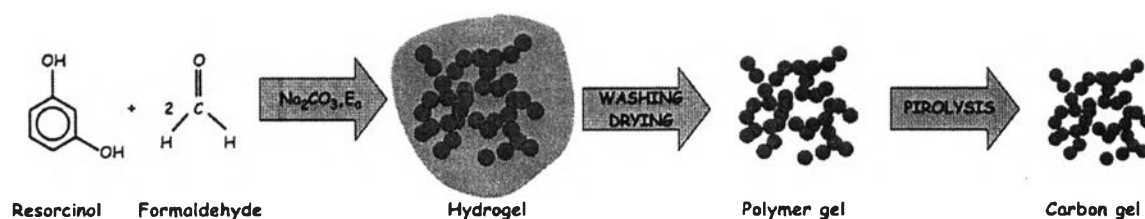


Figure 2.5 Preparation steps of carbon aerogel; resorcinol with formaldehyde (Czakkel 2010).

2.4.1 Soft Template Method

Ordered mesoporous carbons are mainly prepared by the nanocasting method using mesoporous silica materials as hard templates. But the problems of preparing mesoporous carbons from hard method are multistep and high cost which is difficult to produce for the large scale manufacturing of OMCs. That is the reason why soft template method is more interesting than the old one. In order to obtain various types of porous structure, there are many factors that needed to concern such as solvent, types of surfactant, and mixing ratio. In Figure 2.6 shown the preparation of porous carbon by using soft-template method which shown that after the final process, shape of carbon still remain.

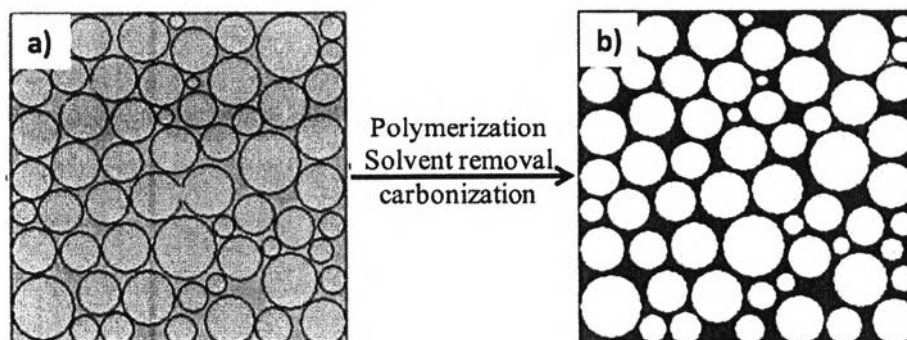


Figure 2.6 Preparation of porous carbon by using soft-template method (Aled et al., 2014).

Wang et al., (2008) studied the effect of phenols reactivity with formaldehyde on the formation of ordered mesoporous carbon. To prepare ordered mesoporous carbon, soft template method has to use in this work by using Pluronic block copolymer, F127 as a soft template. To speed up the polymerization of phenolic resins, strongly acidic condition was needed. In this work they also varied the concentration of HCl to the study the effect of acidic concentration to morphology of mesoporous. The results demonstrate that the cooperative self-assembly of F127 and resorcinol-formaldehyde affords a simple and highly reproducible synthesis of a highly ordered mesoporous carbon.

Tian et al., (2013) prepared Fe-containing mesoporous carbon with highly surface areas and pore volumes by a soft-template method. Phenolic resin was used as a carbon precursor, template agent was triblock copolymer F127, TEOS as a silica precursor (1, 2, 3 g), and hydrated iron nitrate as an iron source. Moreover, to the effect of carbonization temperature to pore volume and pore sizes, carbonization temperature was varied, 600, 700, and 850 °C. As the results, magnetic Fe-containing mesoporous carbons (Fe/OMCs) from multi-component cooperative assembly process exhibited uniformly distribution of iron nanoparticle in the OMCs. Carbonization temperature and amount of TEOS affected to the structure parameters of Fe/OMCs. They found that the specific surface area and the total pore volumes

increased when the carbonization temperature was increased from 600 to 850 °C, and increasing of TEOS loading.

2.4.2 Properties and Electrochemical Application of Carbon Aerogels

Carbon aerogels is a good candidate to apply as electrode of supercapacitors because of special properties that discussed from the above. Moreover, size of particles carbon aerogels are about 4-9 nm and interconnected between particles lead to form interparticle mesopores (Inagaki *et al.*, 2010)

Wei *et al.* (2005) prepared carbon aerogel from resorcinol and formaldehyde and then activated surface with CO₂ and modified surface with a surfactant, sodium oleate. They found that surface area increase highly after activated. Surface modification improved wettability that led to decrease internal resistance of capacitor which affected to increase specific capacitance.

Li *et al.* (2006) reported that carbon aerogel from resorcinol, formaldehyde, and Na₂CO₃ as catalyst via sol-gel process which dried in ambient condition is an amorphous material with a pearly network structure. Specific capacitance of carbon aerogel electrode in 6M KOH electrolyte was nearly 110.06 Fg⁻¹. And after used this carbon aerogel as active electrode material for supercapacitor they found that capacitance was up to 28 Fg⁻¹ and good reversibility. Qu and Shi (1998) found that activated carbon which has large pores size can deliver high energy at high rate so it suitable for high power supercapacitors but it can store less charge.

Ritter *et al.* (1999) investigated the effects of pyrolysis temperature and gel type by comparing between two types of carbon gel which prepared from resorcinol and formaldehyde; carbon aerogel and carbon xerogels. The difference between carbon aerogels and carbon xerogels is drying step, for carbon xerogels supercritical drying is no needed. The experiment showed that final temperature of pyrolysis affect the pore structure of carbon aerogels and xerogels.

Katanyoota *et al.* (2010) prepared benzoxazine derived carbon aerogel electrode of supercapacitors for studied electrochemical properties. They summarized that surface area of carbon aerogel from BA-a and BA-teta was 391 and 368 m²/g, respectively. Moreover, the average pore size from benzoxazine aerogel

was in the range of 2-5 nm, which fit pore size for use as electrodes. The obtained carbon aerogels showed good electrical properties and carbon aerogel from BA-teta showed higher specific capacitance than the other one because contained more mesopores.

Hongsumreong (2011) studied electrochemical properties and morphology of electrode of supercapacitor which prepared from benzoxazine (BisphenolA and Teta) carbon xerogel impregnated iron oxide. Heat treatment at 300 °C was required to improve wettability of xerogel. A specific capacitance of heat-treated carbon xerogel electrode was investigated. Found that it was 108F/g in 6M KOH at current density 5mA/cm². After heat-treated carbon xerogel was impregnated with 3 wt.% Fe₃O₄, specific capacitance was increase to 120 F/g because of the pseudocapacitive properties of iron oxide.

2.5 Polybenzoxazines

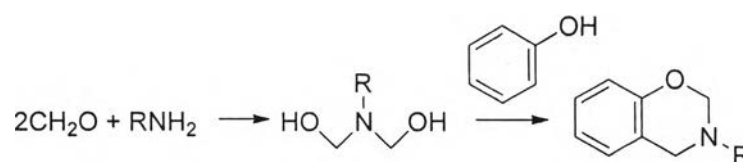
Since polybenzoxazine was found, it became an attractive candidate to replace traditional phenolic resin because in the process of synthesis, polybenzoxazine eliminated byproducts during the curing reactions and no needed strong acid as catalyst or any toxic raw materials. Due to the wide range of mechanical and physical properties of benzoxazine resins which could meet to demand such as easy processibility, good thermal properties, near low shrinkage after polymerization, and molecular design flexibility (Ishida *et al.*, 1996). New applications of benzoxazines have been developed due to outstanding properties, especially low shrinkage, high char yield, good electrical property, and low water uptake (Ishida and Agag, 2011). Owing to high performance of benzoxazine resins, make them become choice for aerospace applications, electronic packing materials, adhesives, and interior decoration.

2.5.1 Chemical Methodologies for Synthesis of Benzoxazine Monomers

2.5.1.1 *Mono-functional Benzoxazine Monomers*

Since 60 years ago, Benzoxazine monomer was firstly found by Holly and Cope (1944). The preparation of benzoxazine monomer took place via

condensation polymerization between primary amine, formaldehyde, and substituted phenols. The reaction was performed in a solvent in two steps. After that Burke *et al.* (1965) demonstrated that benzoxazine ring prefer to react with ortho positions of a phenolic compound and forms a Mannich bridge. The process to synthesize benzoxazine in a solvent via Mannich condensation firstly by added amine to formaldehyde at lower temp to form an N,N-dihydroxymethylamine derivative, which then reacts with the labile hydrogen of the hydroxyl group and ortho position of the phenol at the risen temperature to form oxazine ring. The reaction was shown in Scheme 2.1.



Scheme 2.1 Synthesis of 3,4-dihydro-2H-1,3-benzoxazines.

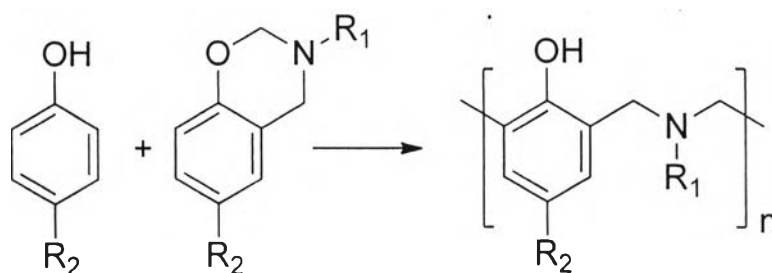
Nevertheless, this method exposed many disadvantages such as slow rate of reaction. Moreover, large amount of solvent was consumed and it leads to a big problem if the precursors were low solubility. The use of organic solvent also raises the cost of products and effects to the environmental. In addition, the residue solvent inside precursors could cause problems during the processing of the benzoxazine resins. To eliminate this problem, the solventless synthesis method was introduced by Ishida (1996).

Liu (1995) proposed reaction mechanism and kinetics of the solventless benzoxazine precursor synthesis. In a typical synthesis, the reactants such as aldehyde, amine, and phenolic precursor are mixed physically. After that heated to their melting temperature and held until the reactants interact with each other and produced the desired benzoxazine. It could indicate that formaldehyde is not suitable to use because of easy to evaporate and fast to lose stoichiometry. So paraformaldehyde is replaced formaldehyde. Selection of phenols and amines provide the flexibility in designing monomer structure which effects to the properties

of polybenzoxazine polymer. The main advantages of solventless synthetic method are decrease the reaction time and reduce intermediate by-products.

2.5.1.2 Di-functional and Multifunctional Benzoxazine Monomers

The downside of monofunctional benzoxazine monomer is cannot form high molecular weight, only obtained oligomers which has molecular weight around 1000Da. Moreover, reactivity of the reaction is decreased because of hydrogen bonding formation. Ishida and coworker tried to overcome this limitation by developed difunctional and multifunction benzoxazine monomer. Ring opening polymerization occurred during the curing process, dimers and higher oligomers acted as initiator. Benzoxazine precursor of bisphenolA, methylamine, and diaxane as solvent took place via ring opening reaction mechanism which shown in Scheme 2.2. The results exhibited that main products was monomer with difunctional benzoxazine ring structures at both ends of the bisphenolA. The residue components were mixture of dimers and oligomers, with both benzoxazine ring and phenol structures, as detected by NMR, FTIR and SEC (Ning and Ishida, 1994; Wang and Ishida, 2002).

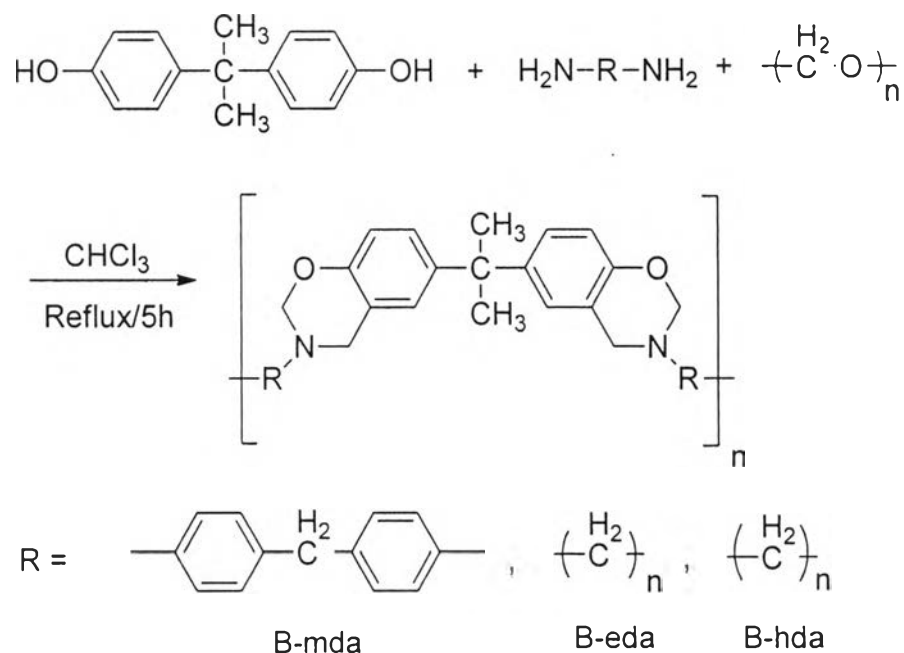


Scheme 2.2 Ring opening reaction of monofunctional benzoxazine initiated by a para-substituted phenol (Ning 1994).

2.5.2 Preparation of High Molecular Weight of Benzoxazine Precursors

High molecular weight of polybenzoxazine precursors have been synthesized from aromatic or aliphatic amine and bisphenolA, with paraformaldehyde. Amines that used to prepare polybenzoxazine precursor were

ethylenediamine (eda), hexamethylenediamine (had), and methylenedianiline (MDA). Preparation of polybenzoxazine precursors was shown in Scheme 2.3.

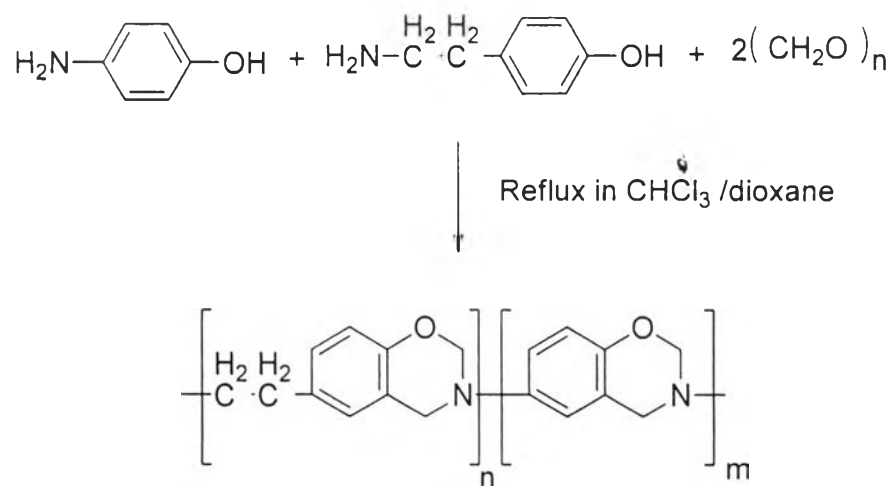


Scheme 2.3 Preparation of polybenzoxazine precursors.

Mechanical properties of polybenzoxazine from various types of amines were observed. They found that polybenzoxazine from aromatic diamine exhibited the highest strength and modulus. On the other hand, highest elongation at break was exhibited in polybenzoxazine from longer aliphatic diamine (Takeishi *et al*, 2005).

Agag and Takeichi (2006) prepared high molecular weight of polybenzoxazine precursors name was AB-type benzoxazine precursor as shown in Scheme 2.4, which was synthesized from amino phenol and formaldehyde. Curing temperature was 250 °C. Data from characterization of NMR and IR proposed that cyclic benzoxazine structure was in the backbone of precursors. Moreover, the result from thermogravimetric analysis indicated that thermoset derived from AB-type benzoxazine precursor has higher char yield than traditional polybenzoxazines which means higher thermal stability. They suggested that the use of AB precursors is an

effective method for receiving polybenzoxazine matrix with excellent thermomechanical properties.



Scheme 2.4 Preparation of AB-PAP-co-Tyr as a polybenzoxazine prepolymer.