CHAPTER II
LITERATURE REVIEW

2.1 Thin film

Thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. The act of applying a thin film to a surface is thin-film deposition, any technique for depositing a thin film of material onto a substrate or onto previously deposited layers. "Thin" is a relative term, but most deposition techniques control layer thickness within a few tens of nanometers. Deposition techniques fall into two broad categories, depending on whether the process is primarily chemical or physical (Advincula and Knoll, 2011).

2.2 Layer-by-layer method

The layer-by-layer (LBL) is a comparatively new method by which thin films particularly of oppositely charged layers are deposited. Thin film layer-by-layer technique can also be utilized for nanoparticles. In general the layer-by-layer is described as sequential adsorption of positive or negative charged species by alternatively dipping into the solutions. The excess or remaining solution after each adsorption step is rinsed with solvent and thus is obtained a thin layer of charged species on the surface ready for next adsorption step.

There are many advantages to the layer-by-layer assembly technique and these include simplicity, universality and thickness control in nanoscale. Further the layer-by-layer assembly process does not require highly pure components and sophisticated hardware. For almost all-aqueous dispersion of even high molecular weight species, it is easy to find an LBL pair that can be useful for building thin layer. Actually, in each adsorption step, we get either a monolayer or a sub monolayer of the species and therefore we can find the number of adsorption steps needed for a particular nanoscale layer.

A variety of species and components are available for layer-by-layer assembly process and this has led to an exceptional growth in the LBL

nanocomposites. Further organic-inorganic composite can act as functional groups and that can improve the performance of the material (http://www.nanotechnology-development.com/research/layer-by-layer-assembled-nanocomposites.html, 4 Dec 2012). Figure 2.1 shows a selection of polyelectrolytes commonly used in LbL systems.
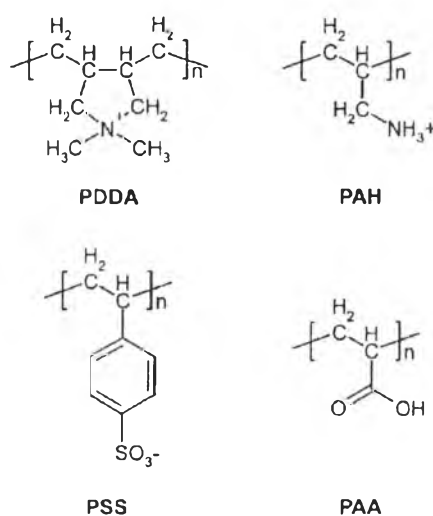

PDDA   **PAH**

PSS   **PAA**

Figure 2.1 A selection of polyelectrolytes commonly used in LbL systems: poly(diallyldimethylammonium chloride) (PDDA), poly(allylaminehydrochloride) (PAH), poly(styrenesulfonate) (PSS) and poly(acrylic acid) (PAA) (Quinn *et al.,* 2006).

The most common form of the LbL method, which is the alternating adsorption of polycations and polyanions is shown in Figure 2.2. Operationally, this method occurs through simple, consecutive exposures of a substrate to polycation and polyanion solutions, with rinsing to remove unadsorbed polymer after each deposition step. Typical polyanions employed for deposition of these films include ionized forms of poly(acrylic acid) (PAA), poly(styrene sulfonic acid) (PSS), and poly(vinyl sulfonic acid), whereas most polycations contain quaternary ammonium functionalities or protonated amines. In addition, early studies showed that LbL methods can also use a much broader range of multiply charged species, including proteins, viruses, nanoparticles, and exfoliated inorganic materials. In some cases, LbL methods also employ other interactions such as hydrogen bonding or covalent linkages.   (http://www.sigmaaldrich.com/technical-documents/articles/material-matters/polyelectrolyte-multilayer-films.html, 6 Dec 2012).
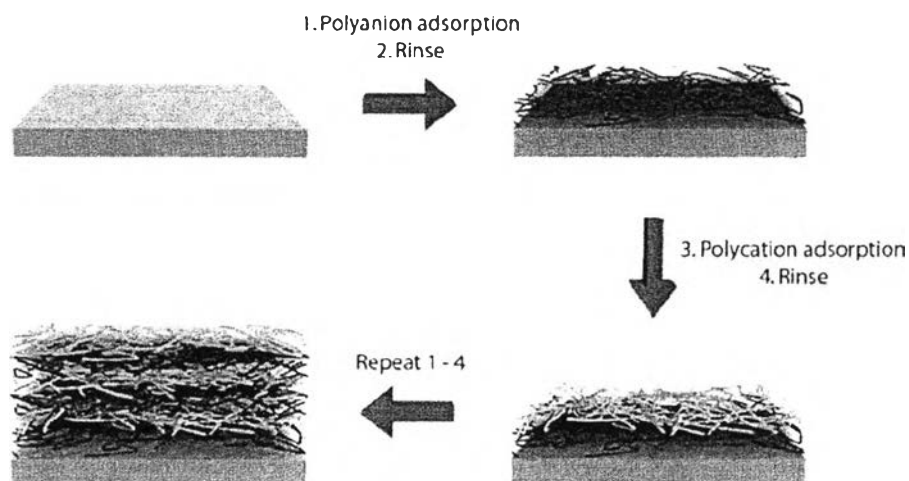
Figure 2.2 Layer-by-layer (LbL) of polyelectrolytes on planar surface. A substrate with inherent charge is first exposed to an oppositely charged polyelectrolyte, followed by careful rinsing. Reversal of the surface charge then facilitates further adsorption steps. The process is continued until the desired layer number (or thickness) is achieved (Quinn *et al.,* 2006).

The key feature in the deposition of polyelectrolyte multilayers (PEMs) is charge overcompensation. The initial layer adsorbs onto the substrate by electrostatic or hydrophobic interactions and either creates a charged surface or reverses the substrate surface charge. Adsorption of subsequent layers again overcompensates the charge on the surface to reverse the substrate's charge and allow adsorption of the next layer. In many cases, the thickness of multilayer polyelectrolyte films increases linearly with the number of adsorbed layers. This suggests that the extent of charge overcompensation does not vary greatly with the number of adsorbed layers, so the amount of polyelectrolyte deposited in each step is approximately constant. However, for some polyelectrolyte systems, film thickness increases exponentially with the number of layers when one of the polyelectrolytes diffuses into the entire film during deposition. Upon addition of the oppositely charged polyelectrolyte, the previously adsorbed polyelectrolyte diffuses out of the whole film to form a very thick polyanion-polycation complex at the surface. Because one of the polyelectrolytes, usually one with low charge density and high swelling in water,

diffuses into the entire film, the thickness of each adsorbed layer increases with the number of layers.

In addition to the polyelectrolyte selected for deposition, a number of adsorption parameters such as supporting electrolyte concentration and composition, pH of the polyelectrolyte solutions, adsorption time, and temperature also influence the amount of polyelectrolyte deposited in LbL methods. Many studies show a dramatic effect of supporting electrolyte concentration on the thickness of PEMs. In the absence of added salt, polyelectrolytes are highly extended to maximize the distance between charged repeat units of the polymer. Under these conditions, adsorbed layers are thin and overcompensate the surface charge only slightly as shown in Figure 2.3. For example, the thickness of a 10-bilayer PSS/Poly(diallyl dimethyl ammonium chloride) film prepared without addition of salt is about 6 nm. Thus, the average thickness per layer is only 0.3 nm. However, when deposited from solutions containing 2 M salt, the thickness of the corresponding 10-bilayer film is more than 300 nm. Of course the film structure and composition also vary greatly with deposition conditions.
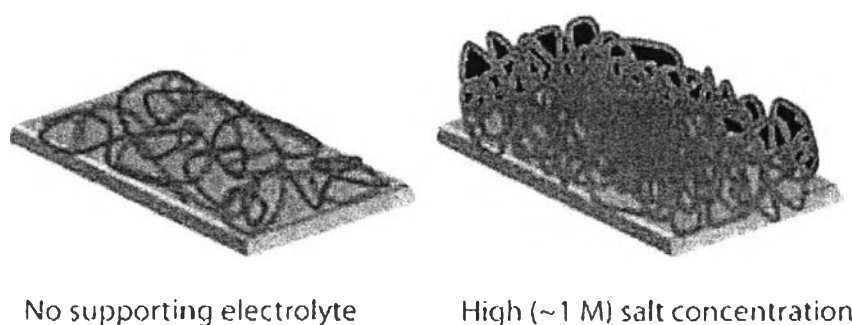

No supporting electrolyte   High (~1 M) salt concentration

Figure 2.3 Schematic drawing of polyanion/polycation bilayers prepared without (left) and with (right) supporting salt (http://www.sigmaaldrich.com/technical-documents/articles/material-matters/polyelectrolyte-multilayer-films.html, 6 Dec 2012).

2.3 Copper removal

Water pollution is the contamination of water bodies such as lakes, rivers, oceans, and groundwater caused by human activities, which can be harmful to organisms and plants which live in these water bodies. Water pollution by toxic heavy metals through the discharge of industrial waste is a worldwide environmental problem. The presence of heavy metals in streams, lakes, and groundwater reservoirs has been responsible for several health problems with plants, animals, and human beings. Heavy metal contamination exists in aqueous waste stream from many industries such as metal plating, mining, tanneries, painting, car radiator manufacturing, as well as agricultural sources where fertilizers and fungicidal spray are intensively used.

Since copper is a widely used material, there are many actual or potential sources of copper pollution. Although a limit of 2 mg/L was proposed by the World Health Organization as the provisional guideline value for copper content of drinking water, intake of excessively large doses of copper by man leads to severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage and central nervous system irritation followed by depression. Severe gastrointestinal irritation and possible necrotic changes in the liver and kidney could occur.

Copper has been known as one of the most common toxic metals, which finds its way to the water stream from industries like electroplating, mining, electrical and electronics, iron and steel production, the non-ferrous metal industry, the printing and photographic industries and metalworking and finishing processes. Copper as a metal provides limited scope for environmental pollution, but the waste generated by copper-based industries with various toxic elements can pollute the environment. Copper mining, smelting, and refining activities are often associated with the generation of a large quantity of wastes. Overburden, mine tailings, sediment from concentrator plants and scrap, slag, dross, slime, flue dust, mill scales, and sludge from the process are the major sources of pollution unless handled and treated suitably.

Studies proved that metals such as copper, lead, zinc, nickel, chromium, and mercury which have been considered as hazardous heavy metals are very toxic

elements and they are commonly found in water and wastewater. So, the removal of these metals from wastewater is necessary. In wastewater treatment technology, various methods have been used to remove heavy metals from aqueous solutions. Traditional methods for the removal and recovery of heavy metals from industrial waste streams are precipitation, ion exchange, electrolysis, adsorption on activated carbon, etc. Most of these methods are extremely expensive or inefficient, especially for a large amount of solution at relatively low concentrations. Among the various water-treatment techniques described, adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness.

Recently, there has been an increasing emphasis on the adsorbent with low cost for the heavy metal ions removal. Most cases have also confirmed that the use of large quantities of such kind of wastes for the treatment of polluted water is an attractive and promising option with a double benefit for the environment (Nadaroglu and Kalkan, 2010).

2.4 Humic Acid

Humic substances are commonly described as heterogeneous compounds containing both a large proportion of oxygen containing functional group (essentially carboxylic and phenolic) that make them and segregated aromatic and aliphatic moieties that give them surface active and hydrophobic-binding properties. The structures, molar masses and functional groups of humic acid vary depending on origin and age. The structure of the humic acid is presented in Figure 2.4 (Rahman *et al.*, 2010).
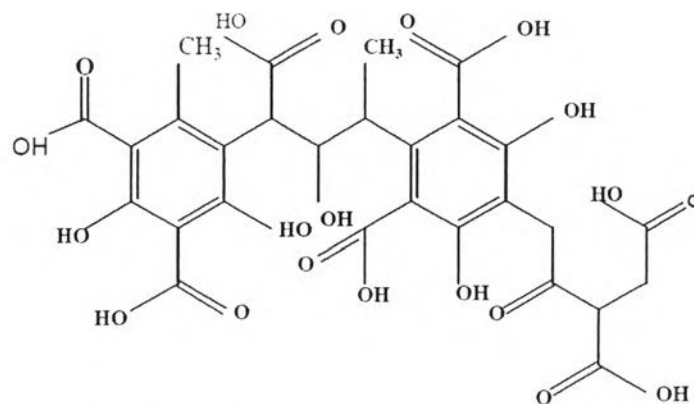
Figure 2.4 Structure of humic acid.

In soils, humic acid acts as a plant growth promoter, nutrient carrier, soil conditioner, and perfoliating beneficial soil organism. In water, humic acid kills harmful bacteria, act as an ion exchange resin, and removing heavy metals that are harmful to aquatic life and human health (Saied *et al.,* 2005).

Humic substances have been documented to interact in some manner with over 50 elements from the periodic table. These include nutrients, toxic metals, radionuclide (including the transuranium series) and the halogens. Furthermore, humic substances contain long-lived (almost stable populations) of free radicals, which are capable of reducing inorganic species such as Fe(III), Cd(II), Hg(II), Cr(VI), and Pu(VI) to name a few. High concentration of iron in the river water made scaling in the boiler of water purification system. Cadmium is not only heavy metal but also toxic in nature. It is one of the most harmful elemental pollutants and is of particular concern because of its toxicities to humans. Pollutant cadmium in water may arise from industrial discharges and mining wastes. The iron and cadmium complexes would be deposited in the bottom of the river. This iron and cadmium free surface water can be used for the municipal water supply system. Therefore, the study of the interaction of Fe (III) and Cd (II) with humic acid is very much important (Rahman *et al.,* 2010).

The observations from Saied and coworkers experiments reveal that humic acid can chelate heavy metals effectively and have potential to be used in wastewater treatment for heavy metal removal. It is found that humic acid-metal interaction is pH dependent, therefore, particular pH was set for each of the metal. The Cu^{2+}, Fe^{2+}

and Zn^{2+} showed the maximum interaction at pH= 5.5, whereas the other metals showed the high affinity at pH range 6.5 to 7.5 as shown in Figure 2.5.
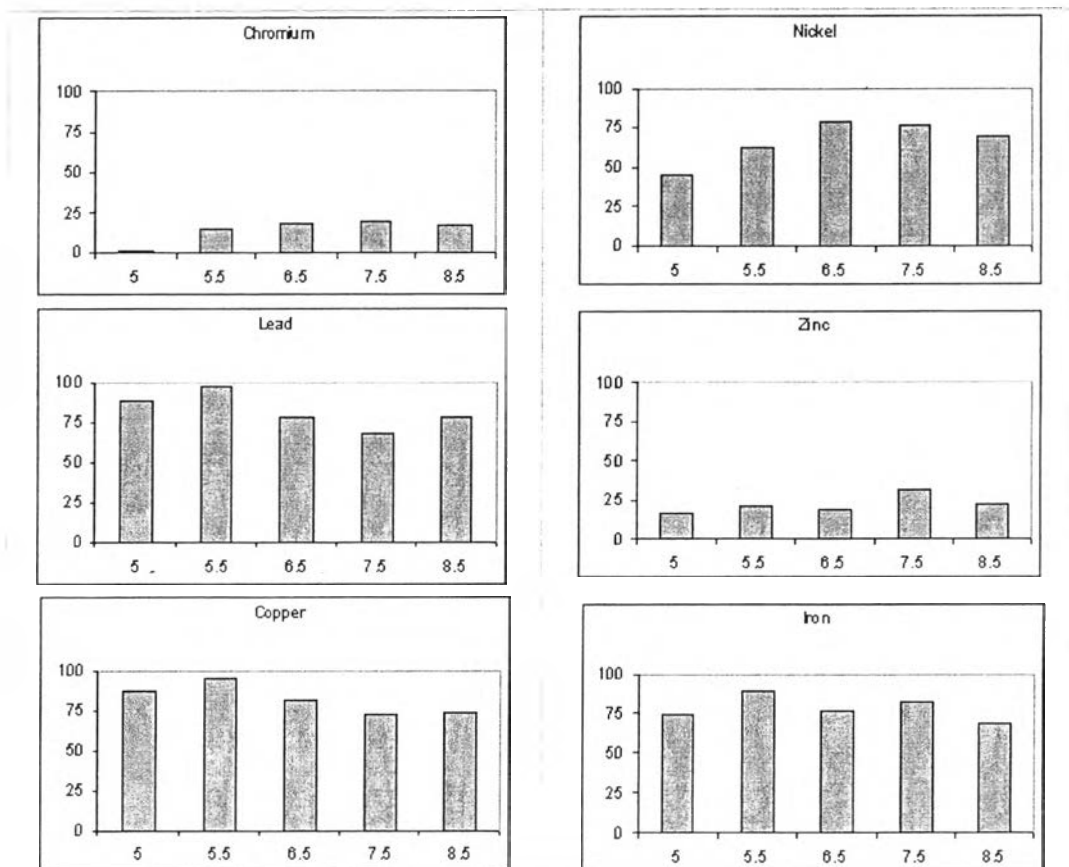

Figure 2.5 Relative % of complexed species of each metal (Y-axis) at different pH (X-axis).

The study also confirmed that humic acid chelates more strongly with metals in +2 oxidation state as it is evident in case of Cr^{3+} except in case of Zn^{2+} both were chelated only up to 30% of the total metal concentration. Present study reveals the reactivity order for metal-humic acid chelation is as follows: $Pb^{2+} > Cu^{2+} > Fe^{2+} > Ni^{2+} > Zn^{2+} > Cr^{3+}$. This study leads to the conclusion that humic acid can be used in leaching out a metal ion from its aqueous solution.

In 2006, Hankins and coworkers studied to remove heavy metal ions bound to humic acid. The enhanced removal of heavy metal ions from solution, such as Pb^{2+} and Zn^{2+}, was studied by binding the ions to humic acid (HA) and then coagulating–flocculating with the cationic polyelectrolyte polydiallyldimethylammonium chloride (PDADMAC). The effect of the dosage of PDADMAC, the pH level and the

concentrations of HA and metal ions were studied. Ultrafiltration was used to separate bound metal ions from free ions in solution. The removal of bound metal ions was found to increase with the extent of coagulation–flocculation of the HA by PDADMAC. The pH affects the removal efficiency of bound (complexed) metal, in so much as it affects the binding strength of metal ions to the HA. The removal efficiency of metal also increases with the initial concentration of HA. The effective coagulation–flocculation region of the HA by PDADMAC is affected by the initial concentration of the metal ions; an increase in the concentration leads to a decrease in the amount of PDADMAC required. Humic substances have the advantage of being naturally occurring, and the results indicate that such a complexation–flocculation process is of potential interest for the removal of heavy metals during water treatment.

In 2008, humic acid (HA) coated Fe_3O_4 nanoparticles (Fe_3O_4/HA) were developed for the removal of toxic Hg(II), Pb(II), Cd(II), and Cu(II) from water by Liu and coworkers. Fe_3O_4/HA were prepared by a coprecipitation procedure with cheap and environmentally friendly iron salts and HA. Sorption of the heavy metals to Fe_3O_4/HA reached equilibrium in less than 15 min. The Fe_3O_4/HA was stable in tap water, natural waters, and acidic/basic solutions ranging from 0.1 M HCl to 2 M NaOH with low leaching of Fe ($\leq 3.7\%$) and HA ($\leq 5.3\%$). The Fe_3O_4/HA was able to remove over 99% of Hg(II) and Pb(II) and over 95% of Cu(II) and Cd(II) in natural and tap water at optimized pH. Leaching back of the Fe_3O_4/HA sorbed heavy metals in water was found to be negligible.

2.5 Porous Materials

Classically porous materials are organic materials, polymeric foams. A large number of inorganic porous materials have been developed, e.g. for insulation, cushioning, impact protection, catalysis, membranes, construction materials.
- Materials with different pore sizes (from nanometer to millimeter)
- Ordered or irregular arrangement of pores
- Various chemical compositions (metal, oxide)
- Different preparative approaches.

Pore size is important for applications. According to IUPAC classification, three pore size regimes, associated with transport mechanisms:

• Microporous, smaller than 2 nm: pore size comparable to the molecules. Activated transport dominates.

• Mesoporous, between 2 and 50 nm: same order or smaller than the mean free path length. Knudsen diffusion and surface diffusion. Multilayer adsorption and capillary condensation ay contribute.

• Macroporous, larger than 50 nm: larger than typical mean free path length of typical fluid. Bulk diffusion and viscous flow.

Micropores and mesopores are especially important in the context of adsorption. Nowadays, micro- and mesoporous materials are generally called "nanoporous materials". Particularly, mesoporous materials are remarkably very suitable for catalysis applications, whereas the pores of microporous materials may become easily plugged during catalyst preparation is high loading is sought.

2.6 Polybenzoxazines

Benzoxazines are a unique non-halogen thermoset resin compounds which can be synthesized from phenols, formaldehyde, and amines with no halogen based precursors. Benzoxazines can homopolymerize to form a polybenzoxazine thermoset networks. The advantages of benzoxazines include of potential low cost high performance thermoset, high purity resin system, high glass transition temperature, low shrinkage, low coefficient of thermal expansion, better moisture resistance, better flammability resistance than epoxies and other thermosets, and excellent electrical properties (Roger *et al.*).

The structure of polybenzoxazine from polymerization of bisphenol-A benzoxazines as shown in Figure 2.6 below:
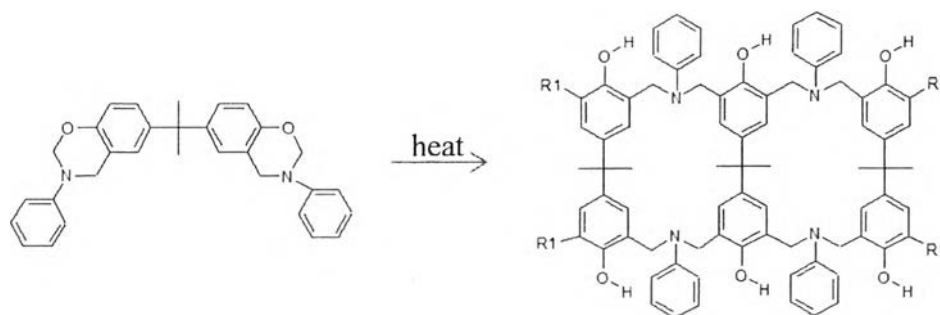
Figure 2.6 Polybenzoxazine polymerization from bisphenol-A benzoxazine monomers.

Polybenzoxazine as a novel phenolic type thermoset has been developed to overcome the shortcomings associated with the use of the traditional phenolics. It can be prepared from cyclic benzoxazines via thermally induced ring-opening polymerization. Various benzoxazine monomers can be synthesized from mono-or diamines and mono-or bisphenols with formaldehyde. Polybenzoxazines have not only the advantageous properties of conventional phenolic resins such as high thermal properties, but also other interesting advantages that are not found in the traditional phenolic resins such as excellent dimensional stability. The disadvantages of the typical polybenzoxazines are the high temperature needed for complete cure and the brittleness of the cured materials (Takeichi *et al.*, 2005). Polybenzoxazines have been developed to be more useful over conventional resins. The molecular structure of polybenzoxazines offers enormous design flexibility, which allows the properties of the cured materials to be tailored for a wide range of applications. These newly developed resins possess unique features such as near-zero volumetric change upon curing, low water absorption, for some polybenzoxazine based materials Tg much higher than cure temperature, high char yield, no strong acid catalysts required for curing, release of no by-products (even nontoxic) during curing, good mechanical properties, excellent electrical properties, and low melt viscosity (Low *et al.*, 1998).

Some important characteristic properties of polybenzoxazines compiled by Roger *et al.* are revealed in Table 1 below:

Table 2.1 Characteristic properties of polybenzoxazines

Properties	
Visual appearance	Yellow chunks
Melting point, °C	80-85
Viscosity @ 125°C, cps	185
Volatile, %	~2
Curing cycle	2hr/180°C + 2hr/200°C
Flex properties dry at RT	
Modulus, ksi, MPa	667, 4602
Strength, ksi, MPa	19.1, 132
Tensile properties dry at RT	
Modulus, ksi, MPa	773, 5334
Strength, ksi, MPa	4.5, 31
Elongation, %	1.2
Compression properties dry at RT	
Modulus, ksi, MPa	508, 3505
Strength, ksi, MPa	33, 228
Elongation, %	8.3

Aromatic oxazines were first synthesized in 1944 by Holly and Cope through Mannich reaction from phenols and formaldehyde, and amines. According to the reported procedure, this reaction was performed in a solvent in two-steps (Ghosh *et al.*, 2007).

In 1950s to 1960s, Burke and coworkers found that the benzoxazine ring reacts preferentially with the free ortho positions of a phenolic compound and Mannich Bridge is generated. Later, benzoxazine were also produced as the intermediate in the synthesis of novalac resins. The heat cured polymers derived from benzoxazine were first achieved by Schreiber (Yildirim *et al.*, 2006).

Reiss and his co-workers worked on the polymerization of monofunctional benzoxazines in present or absent of phenol as an initiator. This procedure was lead to produce linear polymers under 4000 molecular weight (Shen *et al.*).

Recently, the development of the benzoxazine-based phenolic resins has attracted significant attention. This attention causes to the synthesis of polybenzoxazines with quite good thermal and mechanical properties. They not only have the characteristics of traditional phenolic resins such as good flame retardancy and chemical resistance, but also unique characteristics that are not found in the traditional phenolic resins such as low moisture absorption, low shrinkage during polymerization, low dielectric constant and melt viscosity, no need for harsh catalysts, high thermal stability, good mechanical properties, excellent electrical properties and molecular design flexibility. These characteristics make this type of polymers as high performance polymers (Hemvichian *et al.*, 2002).

Ishida and his colleagues studied on thermal degradation of a series of polybenzoxazines based on bisphenol-A and various aliphatic amines. They used Thermo Gravimetric Analysis Fourier Transform Infrared (TGA-FTIR) and Gas Chromatography Mass spectrometry (GC-MS) techniques. Ishida proposed that the Mannich base in polybenzoxazines plays an important role in the thermal degradation of polybenzoxazines. He worked on effect of hydrogen bonding on the degradation mechanism of benzoxazines. In addition, in 1997 he also studied on the aniline based polybenzoxazines under both inert and oxidative environments.

Takeichi and Agag added proparyl and allyl groups to benzoxazines to obtain higher glass transition temperature and higher thermal stability. In 2005, Liu and his coworker researched on furfurylamine as a raw material to form Mannich bridge networks in the polymerizations of polybenzoxazines which increased the crosslinking densities and thermal stability. They also exhibited high glass transition temperatures above 300°C, high char yields, and low flammability with limited oxygen index values of 31 (Liu *et al.*, 2005).

Recently, 2007, Calo *et al.* synthesized a novel cardanol based, a well known renewable organic resource, benzoxazine as a pre-polymer which is used to produce bio-composites containing high percentage of renewable materials.

It has been shown that glass transition temperature (Tg) of PB-a (6,6-(1-methylethyliden)-bis-(3,4-dihydro-3-phenyl-2H-1,3-benzoxazine) are 150 °C which is not high enough for the use in a harsh condition. The thermal properties of polybenzoxazines can be improved mainly by two ways. One is the modification of

the monomer structure and the other is the preparation of alloys with highly thermally stable materials, such as polyimide (Ghosh *et al.*, 2007). In fact, these new materials combine the thermal properties and the mechanical performance of advanced composites. For this reason, the polybenzoxazines show better physical and mechanical properties compared to those of the conventional phenolic and epoxy resins.

Although polybenzoxazines were classified as high performance polymers, there are some disadvantages on their use in practical application. For instance the monomers are usually powder so processing into thin films is difficult. Additionally, because of the low molecular weight of the network structure the formed polymers are brittle. To overcome these problems benzoxazine structures can be combined with conventional polymers (Shen *et al.*). Yagci and coworkers suggested a macromonomer method generating polybenzoxazines with polymer segments and good mechanical properties by using Atom Transfer Radical Polymerization (ATRP) and Ring Opening Polymerization (ROP) methods (Kiskan *et al.*).

Synthesis and reactions

Benzoxazine monomers are typically synthesized using phenol, formaldehyde and amine (aliphatic or aromatic) as starting materials either by employing solution or solventless methods. Various types of benzoxazine monomer can be synthesized using various phenols and amines with different substitution groups attached. These substituting groups can provide additional polymerizable sites and also affect the curing process. Consequently, polymeric materials with desired properties may be obtained by tailoring the benzoxazine monomer (Ghosh *et al.*, 2007).

Researchers have recognized that, in order to obtain thermal stability, the presence of aromatic and heterocyclic ring structures in the polymer main chain is necessary. It was shown that the thermal stability increases as the number of aromatic rings increases (Low *et al.*, 1999). Benzoxazines are readily synthesized, either in solution or by a meltstate reaction using a combination of a phenolic derivative, formaldehyde, and a primary amine (Ghosh *et al.*, 2007).

Benzoxazines are bicyclic heterocycles. These monomers contain oxazine ring which opens during thermal polymerization and form a phenolic structure in acidic medium as shown in Figure 2.7. During the polymerization, benzoxazines are produced by thermally activated ring-opening reaction to form a Mannich base bridge (Choi *et al.*, 2006).
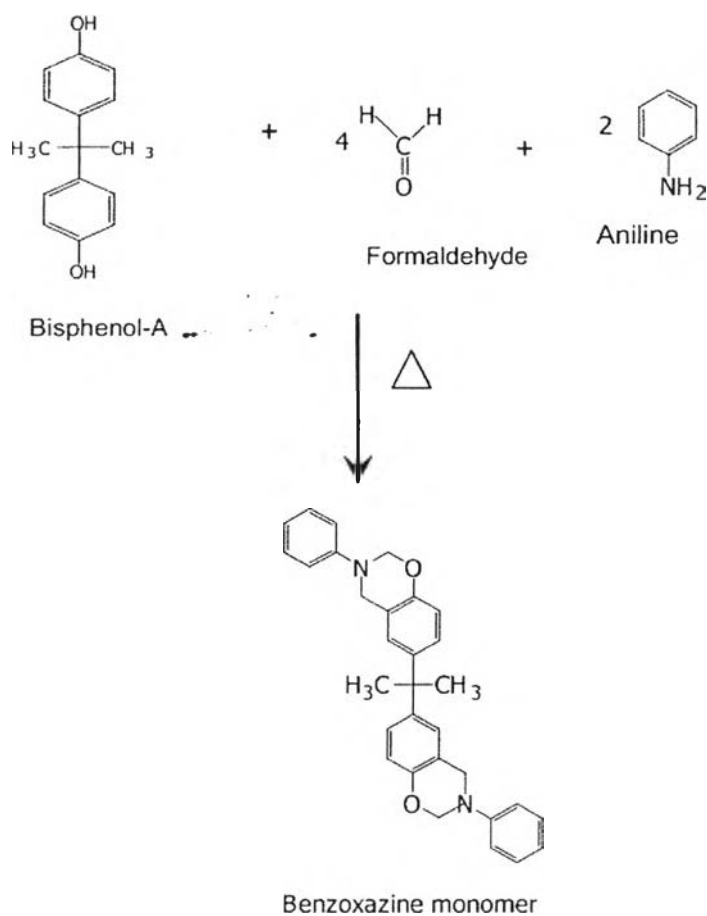

Benzoxazine monomer

Figure 2.7 Synthesis method of benzoxazine monomer.

Polymerization takes place through the ring opening of the cyclic monomers as shown in Figure 2.8 by heat treatment in the absence of a catalyst and without producing harmful byproducts during the cure process (Jubsilp *et al.*, 2007). The presence of different functional groups in the structure makes polybenzoxazines more suitable for many applications.
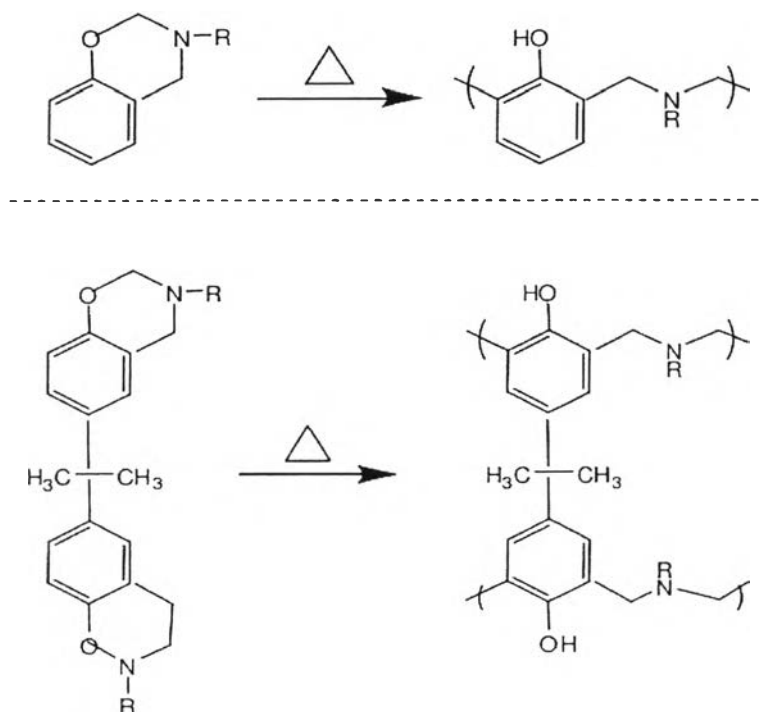
Figure 2.8 Synthesis of polybenzoxazines by ring opening reaction.

Recent researchers have developed a new class of difunctional or multifunctional benzoxazine monomers yielding the ring opening reactions during curing to produce phenolic materials which initiated by dimers and higher oligomers in the resin composition as shown in Figure 2.9:
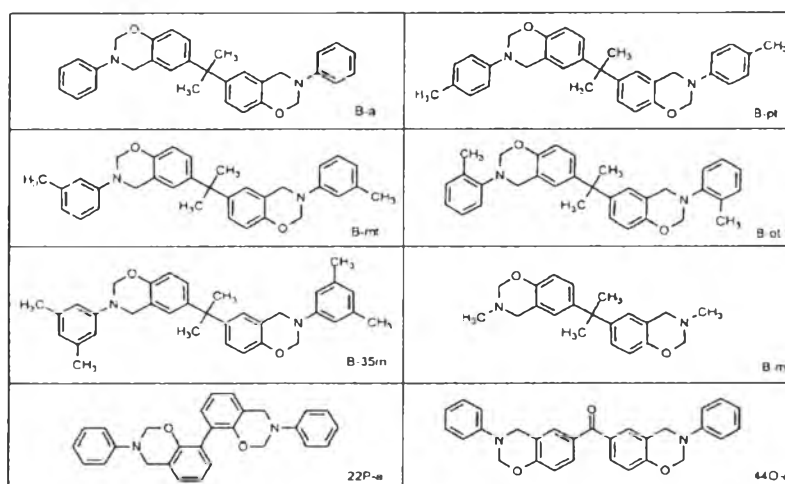

Figure 2.9 Chemical structure of multifunctional benzoxazine monomers.

The knowledge of mechanisms of curing and thermal degradation of polybenzoxazines and the effect of functional groups are very important for determination of the application areas and the strategies for modifications of the monomers and polymers.

Bagherifam *et al.,* (2009) studied benzoxazines which are prepared by reactions of phenol or bisphenol-A and methylamine or aniline and formaldehyde. The monomers based on phenol and methyl amine, Ph-m, based on phenol and aniline, Ph-a, based on bisphenol-A and methylamine, BA-m and based on bisphenol-A and aniline BA-a and the corresponding polybenzoxazines were synthesized and characterized by Dr. Tamer Uyar. The procedure followed to synthesize the benzoxazine monomers and polymers were explained in detail in the literature. The mechanism of formation of benzoxazine monomers is shown in Figure 2.7.

The benzoxazine monomers were cured by applying a stepwise curing program to obtain polybenzoxazines. The curing programs and types of polymer produced during the curing and the proposed polymerization mechanisms are shown in Table 2.2 and Table 2.3, respectively.

Table 2.2 Curing temperature program of polybenzoxazine monomers

Benzoxazine sample	Curing Temperature Programs
Bisphenol A + Aniline	0.5 hr at 160, 180, and 200 °C and 1.5 hr at 210°C
Phenol +Aniline	0.5 hr at 160, 170, and 180 °C and 1.5 hr at 190°C
Bisphenol A + Methylamine	0.5 hr at 160, 180, and 200 °C and 1.5 hr at 210°C
Phenol + Methylamine	0.5 hr at 160, 180, and 200 °C and 1.5 hr at 210°C

Table 2.3 Types of polymers produced during curing of benzoxazine monomers

Name	Polymer
PPh1-m	Polybenzoxazine based on phenol and methylamine, type 1
PPh1-a	Polybenzoxazine based on phenol and aniline, type 1
PBA1-m	Polybenzoxazine based on bisphenol-A and methylamine, type 1
PBA1-a	Polybenzoxazine based on bisphenol-A and aniline, type 1
PPh2-m	Polybenzoxazine based on phenol and methylamine, type 2
PPh2-a	Polybenzoxazine based on phenol and aniline, type 2
PBA2-m	Polybenzoxazine based on bisphenol-A and methylamine, type 2
PBA2-a	Polybenzoxazine based on bisphenol-A and aniline, type 2
PPh3-m	Polybenzoxazine based on phenol and methylamine, type 3
PPh4-a	Polybenzoxazine based on phenol and aniline, type 4
PBA4-a	Polybenzoxazine based on bisphenol-A and aniline, type 4

2.7 Thermal degradation

Thermal degradation of polymeric materials is an important issue from both the academic and the industrial viewpoints. Organic polymers are more suitable to thermal degradation than inorganic materials. Organic polymers can cleave by thermal, oxidative or radical means. Thermal degradation process is affected by various parameters such as environment of degradation, types of additives and the structure of the polymer. The structure of the polymer can be affected by the molecular weight, degree of crosslinking, the structures of the end groups and the substituents (Low *et al.*, 1998).

The chemical reactions involved in thermal degradation lead to changes in physical and optical properties relative to the initially specified properties. Thermal degradation generally involves changes of the molecular weight and molecular

weight distribution. The thermal degradation study of polymers may be difficult since the polymers fragment to a large number of decomposition products during pyrolysis (Hemvichian *et al.*, 2002).