



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Silk Sericin Protein

Every year, the silk industries produce several tons of wastes from the removal of a gummy layer of cocoon, which is a necessary step of silk textile processing. Like the components of silk, the waste water composes of two proteins named “fibroin” which are core fibers held together by a glue-like protein called “sericin”. Sericin is usually removed from silk fibroin by a process known as “degumming” because it makes the cocoons difficult to unreel. Sericin can be recovered from the various stages of producing raw silk and textile, in order to reduce the environmental pollution in silk manufacture and to gain economic and social benefits. Nowadays, people modify materials with sericin for various applications including degradable biomaterials, biomedical materials, membranes, fibers, and fabrics (Zhang, 2002).

Table 2.1 Composition of silk in *Bombyx mori* (Mondal *et al.*, 2007)

Component	Per 100 grams of cocoon
Fibroin	70-80
Sericin	20-30
Wax matter	0.4-0.8
Carbohydrates	1.2-1.6
Inorganic matter	0.7
Pigment	0.2

Sericin is a water-soluble globular protein derived from silkworm with molecular weight ranges widely from about 10 to over 310 kDa. The sericin protein is made of 18 amino acids, most of which have strong polar side groups such as hydroxyl, carboxyl, and amino groups. (Sarovart *et al.*, 2003). Sericin is insoluble in

cold water, but it is easily hydrolyzed, i.e. long protein molecules can be broken down to smaller fractions, which are easily dispersed or solubilized in hot water (Mondal *et al.*, 2007). Sericin is especially rich in aspartic acid (~19%) as well as serine (~32%), which has a high content of hydroxyl group (Wu *et al.*, 2007).

On the contrary, Dash *et al.* (2006) reported high molecular weight sericin of 200 kDa extracted from peduncle of *A. mylitta*; non-mulberry tasar silkworm. The amino acid composition of the sericin from peduncle shows a predominance of serine and glycine. In fact serine and threonine amino acids that contain hydroxyl side chains together contribute about 31% of the total amino acids present in this sericin. The acidic amino acid present in sericin is only glutamate and very little amount of bulky amino acids such as tyrosine are present. Most of the residues present in the protein are either hydrophilic or does not have hydrophobic side groups making the sericin a water-soluble protein. A year later, Dash *et al.* reported that about 70 kDa sericin was extracted from tropical tasar silkworm, *Antheraea mylitta*, has a high serine content (19.40%) along with significant amount of glycine (19.20%). while the mole percentages of these two amino acids are different from sericin of mulberry silkworm (*B. mori*).

Sericin protein has several benefits due to its special properties such as antioxidation, antibacteria, UV resistance, and good moisture transfer. According to these beneficial properties, methods to extract the sericin protein were developed. In 2003, Sarovart *et al.* prepared solution by cutting the waste cocoon into pieces and boiling them in distilled water for 1 hour. The cocoon waste was then filtered out to obtain the sericin solution. They found that coating air filters with silk sericin could enhance its properties, which were antimicrobial activities, antioxidant, and antifungus activity.

Lee *et al.* (2004) applied silk sericin as a finishing on synthetic fabrics such as poly(ethylene terephthalate) (PET) and polypropylene (PP). Sericin was fixed on the pre-treated fabric with a crosslinking agent, ethylene glycol diglycidyl ether (EGDE), as a result the moisture adsorption and the antistatic of fabric properties were improved.

Gimens *et al.* (2007) prepared hydrophilic membranes from sericin and poly(vinyl alcohol) (PVA) for applications in alcohol dehydration by pervaporation.

Sericin was extracted from the cocoons of *Bombyx mori* silkworm. The obtained molecular weight of sericin was greater than 35 kDa as measured by SDS-PAGE. Sericin/PVA blend membranes were prepared by blending sericin with poly (vinyl alcohol) or PVA, then followed by chemical crosslinking with dimethylolurea (DMU).

Due to the highly hydrophilic protein of sericin, which is a feature of hydroxyl groups from Ser, Thr, and Tyr, it is difficult to find a nonaqueous solvent for sericin. Teramoto *et al.* (2004) modified the chemical structure of silk sericin by using Lithium Chloride (LiCl)/Dimethyl Sulfoxide (DMSO) as a solvent. They studied the solubility of sericin under nonaqueous condition in some polar aprotic solvents; DMSO; *N,N*-dimethylacetamide (DMAc), which was hardly dissolved sericin at 60°C even in the presence of 1 M LiCl or LiBr; and *N,N*-dimethylformamide (DMF), which showed poorer sericin dissolution than DMSO. However, DMSO alone did not dissolve sericin at 60°C, the solubility rapidly increased with salt concentration especially when LiCl was used because sericin forms strong interchain hydrogen bonds, which was disrupted by Cl⁻ ion. When comparing type of used salt, they found LiCl was more effective than LiBr, probably because of polarizability of anions: the larger anion, Br⁻, being more polarizable, is bound to the solvent more tightly so it was less active to disrupt the interchain hydrogen bonds.

2.2 Polylactide (PLA)

2.2.1 Polymerization of Polylactide

Polylactide (PLA), a hydrolyzable aliphatic polyester has been used for a long time in the medical applications, and is one of the polymers widely accepted to play a major role as future packaging material. Due to its good mechanical properties, which are comparable to today's standard packaging polymer, polystyrene, but more importantly—PLA is produced from lactic acid, which can be prepared by fermentation from nearly any renewable resource such as starch, molasses, whey and sugar. PLA can be recycled after use, either incinerated or landfilled, though it is mainly intended for disposal by composting and in-soil degradation. Thus PLA provides a closed natural cycle, being produced from plants

and crops, polymerized and processed into a packaging product and degraded after used into soil and humus, which is the basic necessity for growth of new plants and crops (Jacobsen *et al.*, 2000).

Sodergard *et al.* (2002) reported the preparation of lactic acid based polymerization method by two different pathways, the step polycondensation of lactic acid and ring-opening polymerization of cyclic diester lactide. The first category of polymerization is traditional polycondensation (PC) which can either be composed of solely one stereoisomer or combinations of D- and L-lactyl units in various ratios. The disadvantages of this method are the high temperature required and long reaction time, besides the obtained polymer has low molecular mass with the poor mechanical properties. Therefore, PC needs some modification including manipulating the equilibrium between lactic acid, water, and poly(lactic acid) in an organic solvent, or using a multifunctional branching agent to be a star-shaped polymer, or polycondensation in the presence of difunctional monomers (e.g. diols or diacids) ending up in telechelic prepolymers. The next category of polymerization known as ring-opening polymerization (ROP) is the most commonly studied way to prepare lactic acid based polymer due to the possibility of an accurate-controlled chemistry and the more controlled properties of polymers. ROP can be achieved through solution polymerization, bulk polymerization, melt polymerization, and suspension polymerization. Their polymerization mechanism involves ionic, coordination, or free-radical type depending on the catalytic system. The used catalysts are transition metal compounds of tin, aluminum, lead, zinc, bismuth, iron, and yttrium (Kaplan *et al.*, 1998).

However, the most frequently used catalyst is Tin(II) 2-ethylhexanoate or stannous octoate, the mechanism of the lactide(LA)/Sn(Oct₂) was proposed by Kowalski *et al.* in 2000. They assumed that Sn(Oct₂) must be converted into tin(II) alkoxide (in order to initiate polymerization) when it met adventitious H₂O, hydroxyl acids, and some other unknown co-initiators, present as impurities in the polymerizing mixture. They suggested that the mechanism involves the polarization of the lactide carbonyl bond by interaction with stannous octoate and a proton with the formation of a carbocation. One of the modifications of PLA after polymerization is grafting. Sodergard *et al.* (2002) considered the graft-copoly-

merization of PLA as a convenient method to obtain a polymer with unique properties. The graft-polymer can be induced with chemical, by plasma discharge or radiation with UV-rays, γ -rays or accelerated electrons. This process has several benefits as highly pure polymer with high conversion was obtained without any use of initiators.

In 1997, Hyon *et al.* synthesized poly (lactic acid) through conventional polycondensation of the lactic acid monomer (condensation polymerization) using stannous octoate as a catalyst produced polylactides with viscosity average molecular weight (M_v) ranging from 2×10^4 to 6.8×10^5 . This ROP study focused on the effect of catalyst concentration, polymerization time, and temperature on the polymer yield and molecular weight. They found that at a catalyst concentration around 0.05 wt%, the maximum of monomer conversion and M_v were achieved. The monomer conversion and M_v increased almost linearly with polymerization time up to a monomer conversion of 80%, but both the conversion and M_v decreased after passing through a maximum point.

In the same year, Bendix produced polylactide and its copolymers by ring-opening polymerization of cyclic monomers suitable for medical application. Figure 2.1 summarizes the reaction sequences. The syntheses of polymers can be achieved by two steps; polycondensation and ring-opening polymerization (ROP). First, the alpha-hydroxy acids can be directly converted into linear polymers by an intermolecular esterification without any catalyst (Figure 2.1, Step 1). This step also has the main side reaction during the polycondensation and it is the main reason why only low-molecular weight products can be formed. Because the reaction conditions to form higher-molecular-weight products by water removal lie in a range, where the unzipping and ring closure reactions become the main reaction. The other method to form higher molecular weights polymers is ROP of the cyclic monomers. Thermolysis catalysts—mainly metals or metal oxides—were significantly used to speed up the polymerization and to minimize pyrolysis by lowering the reaction temperature. For the production of medical polymers, only two tin salts, stannous(II)

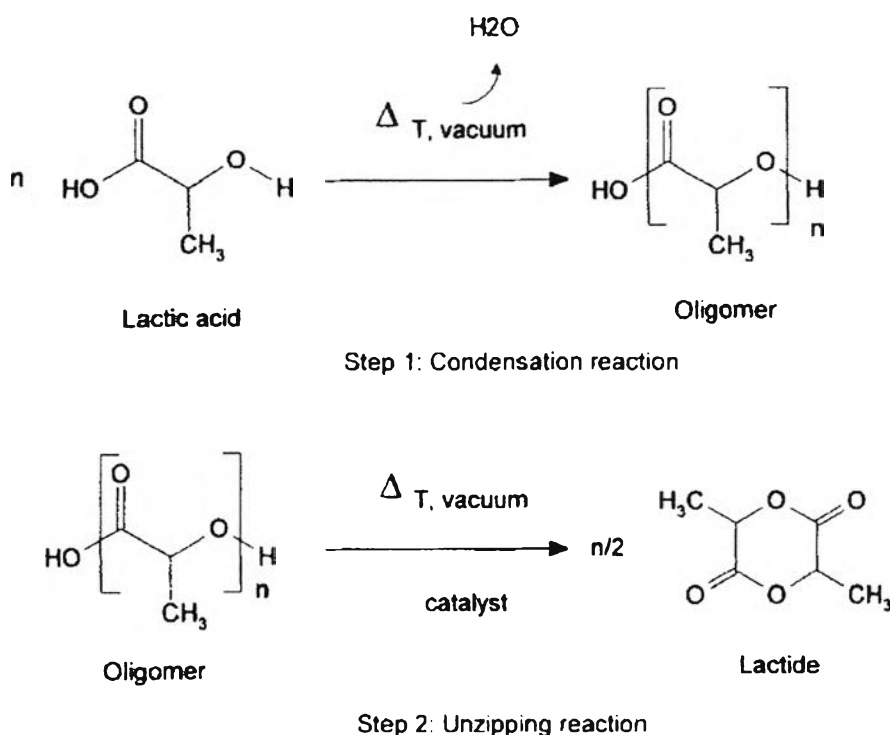


Figure 2.1 Schematic diagram of lactide synthesis (Bendix, 1997).

chloride and stannous(II) 2-ethylhexanoate, are used as catalysts today since both tin salts are approved as food additives. Stannous(II) 2-ethylhexanoate, abbreviated as tin octoate or $\text{Sn}(\text{Oct})_2$, has been proven to be very efficient to prevent racemization during the polymerization of the lactides. To control the reaction rate and regulate the average molecular weight, compounds with free hydroxyl groups are often used, for instance, water, hydroxy acids or esters and various alcohols. And for achieving high molecular weights, the polymerization has to be carried out at low temperatures, low catalyst/moderator concentrations and prolonged reaction times. Therefore, melt polymerization in special reactors, designed to handle highly viscous media, or bulk polymerization are the preferred reaction methods.

Jin *et al.* (1997) synthesized poly (l-lactide-co-serine) and its graft copolymers with poly (ethylene glycol). They began to synthesize monomer—phenylmethyl 2-(6-methyl-2,5-dioxo-3-morpholinyl) ethyl ether—for preparing copolymer with l-lactide monomer and confirmed the result by ^1H NMR. This

monomer can protect the use of amino acid—serine—to form O-benzyl-L-serine form. Next, after polymerization, the resulted poly(L-lactide-co-serine) was protected and then 0.06 wt.% of stannous octoate initiator was added. After deprotected with triethyl silane, triethyl amine, and PdCl₂ the obtained polymer is poly(L-lactide-co-serine) as confirmed by ¹H NMR. The copolymers are expected to be biodegradable and have free hydroxy groups. The latter provide reaction sites to modify the PLA. Flexible diisocyanate-terminated polyethylene glycol was added into the PLA copolymer which increased the amorphous property of the PLA. The free hydroxy groups, pendant to the polymer backbone, will be used to make polymeric-inorganic composites.

In 2000, Jacobsen *et al.* studied the effect of triphenylphosphine P(φ)₃ on the efficiency of tin(II) 2-ethylhexanoate Sn(Oct)₂ as a catalyst for the ring opening polymerization of L,L-lactide into PLA. It was the first time to use a first processing method, a reactive extrusion, to produce PLA. Reactive extrusion was compared to batch polymerization technology on the basis of molecular parameters including conversion rate (c), number average molecular weight (M_n), and molecular weight distribution (MWD). The main processing parameters are screw speed (n), through-put rate (m), and thus a change of extruder head pressure (p) then were compared with the resulting molecular parameter. The conversion would decrease by increasing the mass flow rate and screw speed due to the fact that could be explained by the remaining residence time of material inside the extruder decreases. For the effect on the molecular weight and the molecular weight distribution, the two main causes can be described; first, increasing mass flow rate and screw speed leads to a reduction on the molecular weight and an enhancement of the polydispersity (broader molecular weight distribution) because residence time was reduced and the side reaction or degradation reaction occurred, second, molecular weight would be increased as the extruder head pressure was increased, which is the influence of the die resistance, cause the increasing residence time. However, the polydispersity showed no tendency to change with pressure. They determined the thermal behavior of the resulting polylactide by DSC measurements. Finally, the mechanical behaviors of resulting PLA-polymers were analyzed by means of tensile testing. They exhibited

thermal and mechanical properties sustainable for uses in a wide range of polymer applications.

In the same year, they developed a new method to polymerize PLA via ring-opening polymerization at 180°C, based on a new catalytic system (using equimolar complex of $\text{Sn}(\text{Oct})_2 \cdot \text{P}(\phi)_3$ as catalyst and ULTRANOX 626—Bis (2,4-di-*t*-butylphenyl) Pentaerythritol Diphosphite—as a stabilizer, a reactive extrusion polymerization process, which can produce PLA continuously in larger quantities and at lower costs than before. This extrusion polymerization process has been developed and tested with laboratory scale machines and the possibilities to extend this polymerisation process to lactide based blockcopolymers have been investigated. Poly (L-lactide) or PLLA, which produced in glass ampoules using bulk batch polymerisation technology and in single-stage continuous reactive extrusion polymerisation, were compared on the basis of molecular parameters. Although the starting polymerisation used same conditions, the comparison of two polymers was very difficult because they were polymerised under different conditions. The resulting conversions; 98.5%, for bulk batch polymerization; and 99%, for reactive extrusion, show that in both cases the polymerisation reaction has been finished, though for the bulk batch polymerisation in a glass ampoule, the time required to reach this conversion was approximately 40 min, compared with only 7–8 min in the reactive extrusion process. The low molecular weight distribution (MWD) values smaller than 2 in both cases show that intermolecular transesterification reactions had been very limited, which was due to the use of a co-catalyst and a stabilising agent.

2.2.2 Polylactide Graft Copolymer

The copolymerisation of two or more monomers provide the possibility to incorporate pre-oligomerised, hydroxy-terminated blocks as starting molecules to a second type of monomer(as shown in Figure 2.2). Thus the homopolymerisation of this second monomer will start at both ends of the oligomers and will be incorporated them as blocks of predefined size into the polymer. Using this technique, one could generate a blockcopolymer of defined composition and with defined blocklength of the second monomer by using a large amount of prepolymers and $\text{Sn}(\text{Oct})_2$ as a catalyst.

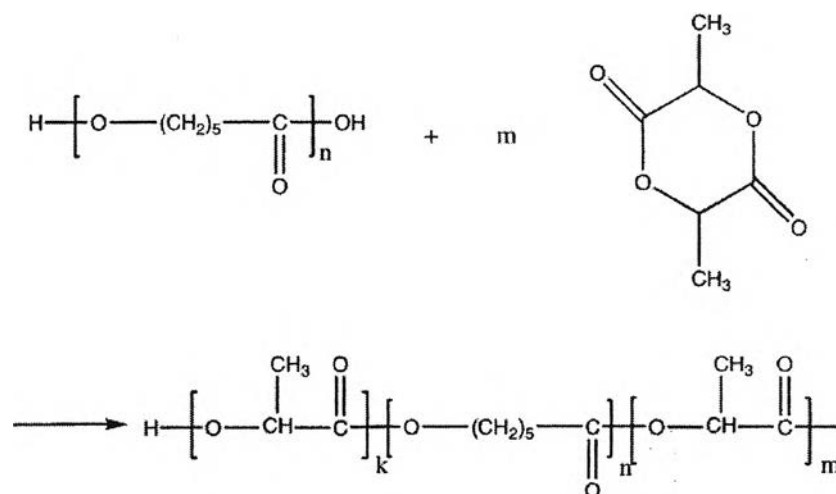


Figure 2.2 Schematic diagram of a synthesis reaction for blockcopolymerisation: using pre-oligomerised blocks of one monomer (ϵ -caprolactone) and a second monomer (lactide) (Jacobsen *et al.*, 2000).

Janata *et al.* (2003) attempted to synthesize the polystyrene and polystyrene-block-poly(methyl methacrylate) grafted with poly(ϵ -caprolactone) or poly(DL-lactide) by “grafting from” method. The graft copolymers synthesis began with low-molecular-weight polystyrene (PS), as starting materials, were functionalized by introducing the 1-hydroxyethyl functionality into the benzene rings of PS to be a multifunctional initiators. Then, the ring-opening polymerization (ROP) of ϵ -caprolactone or DL-lactide initiated with the hydroxy group and stannous octoate was used as co-initiator/catalyst in toluene at 90°C for 24 h. as shown in Figure 2.3. They synthesized polystyrene ring-substituted with 1-hydroxyethyl group by a two-step procedures consisting of acetylation of PS with acetyl chloride followed by reduction of acetyl groups to secondary hydroxy groups with LiAlH_4 . Successful grafting of ϵ -caprolactone or DL-lactide from this hydroxylated PS was confirmed by SEC and NMR.

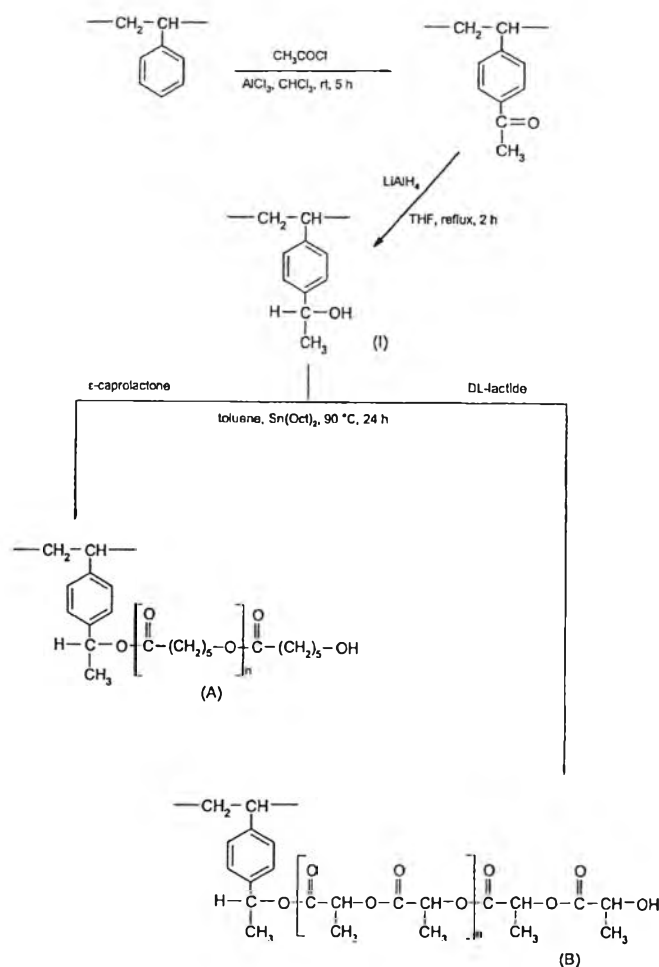


Figure 2.3 Schematic diagram of the synthesis polystyrene grafted with poly (ϵ -caprolactone) or poly (DL-lactide) by a “grafting form” method (Janata *et al.*, 2003).

Starch and dextran are the two examples of polysaccharides which are natural biodegradable hydrophilic polymer, while PLA is a hydrophobic biopolymer. Therefore, the lactide polymerization initiated directly by the hydroxyl groups of dextran was usually unsuccessful, because polysaccharides are insoluble in common organic solvents or in melted lactide to give a homogeneous reaction. In 2003, Cai *et al.* tried to improve the mechanical properties of the blend of PLA with dextran by preparing brush-like biodegradable polylactide-grafted dextran copolymer (PLA-g-dextran) via a bulk polymerization reaction using a trimethylsilyl-protected (TMS) dextran as macroinitiator—to protect dextran initiating lactide polymerization, in the presence of stannous octoate as a catalyst at 140°C for 18 h. The PLA-g-dextran

copolymers were characterized by ^1H NMR, GPC and intrinsic viscosity measurements. As a result, this copolymer had an amphiphilic structure that the hydrophobic PLA branches were attached to hydrophilic dextran backbones. It could be used as a compatilizer in PLA/dextran blend to enhance the compatibility between PLA and dextran, and to reduce the phase separation between the two components. Consequently, the mechanical properties of the PLA/dextran blends were improved by introducing of PLA-g-dextran copolymer, and thus the blends had enough mechanical strength to be made into three-dimensional scaffolds.

Generally, the polymerization process of PLA often occurs in the organic solvent but in 2006, Gong *et al.* prepared the in situ polymerization of cornstarch with lactic acid in aqueous media. The graft copolymerization proceeded under vacuum (<1 mm Hg) for drawing water out and using stannous octoate, $\text{Sn}(\text{Oct})_2$, as a catalyat at 90°C . HPLC analysis was conducted ,in order to validate the polymerization, showed that small amounts of lactide were included in the reaction system.

Liu *et al.* (2004) synthesized a kind of novel graft copolymer by “grafting-onto” method with the natural polysaccharide chitosan as the main chain and the artificial biopolymer poly (DL)-lactide as the side chains using triethylaluminum (Et_3Al) as the catalyst in toluene at 70°C for 24 h. FTIR spectroscopy, ^1H NMR, DSC scanning, and wide-angle X-ray scattering, respectively, were used to characterize these branch copolymers. It was found that a greater lactide content in the feeding ratio results in a higher grafting percentage. This indicates that the higher the concentration of the lactide in toluene, the higher the opportunity for the lactide to react with chitosan reactive centers. In 2005, Wu *et al.* successfully synthesized amphiphilic chitosan-PLA graft copolymer with the grafting-onto method like Liu *et al.* (2004), as shown in Figure 2.4, but they carried out with the different polymerization conditions, which were used dimethyl sulfoxide as a solvent in the presence of triethylamine as catalyst at 80°C for 12 h. They confirmed the graft copolymer with IR spectra, ^1H NMR, X-ray diffraction spectrometry, and thermogrammetry.

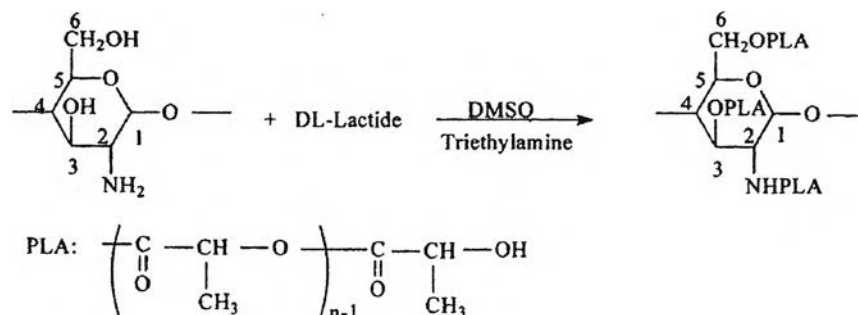


Figure 2.4 Schematic of graft copolymerization of DL-lactide onto chitosan (Wu *et al.*, 2005).

This copolymer can form polymeric micelles with a unimodal size distribution. Since chitosan-PLA polymeric micelles have a hydrophobic core, they can be used as a promising delivery carrier for the entrapment and controlled releasing of hydrophobic drugs.

Elizabeth *et al.* (2006) synthesized the graft copolymerization of L-lactide (LLA) onto chitosan (CS), as shown in Figure 2.5, which was carried out by ring opening polymerisation in a number of solvents and catalysts and at various temperatures to identify the most effective ring opening catalyst and to optimize the conditions of grafting. The results showed that a substantially good amount of grafting was observed in DMF, DMA, and DMSO. But, no significant grafting was observed in pyridine.

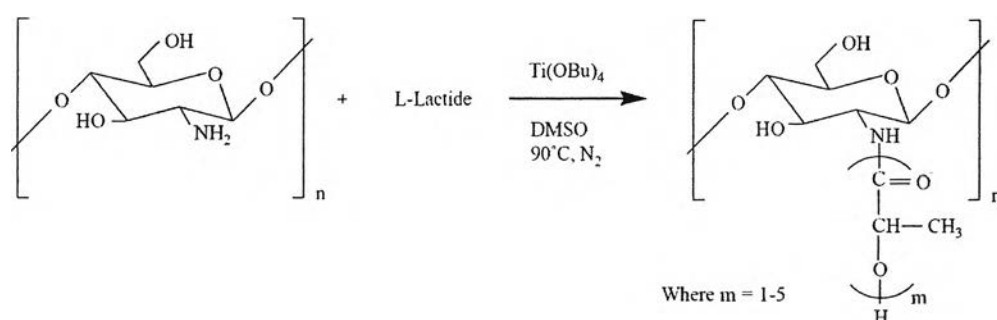


Figure 2.5 Schematic representation of the synthesis of chitosan-g-poly(lactide) copolymer (Elizabeth *et al.*, 2006).

Among the different catalysts studied for the grafting reaction, metal alkoxides are found to be better catalysts than Lewis acids. Because it involved in a co-ordination insertion mechanism with the presence of $-OH$ and $-NH_2$ groups of chitosan will act as cocatalysts for the lactide ring opening polymerization. It was observed that the percentage grafting was quite low and the product was in brown colour when using above $100^\circ C$. A maximum grafting of 99.50% was observed in system, which used $Ti(OBu)_4$ as catalyst in DMSO at $90^\circ C$ in nitrogen atmosphere for 24 h. Grafting studies indicated that the higher the concentration of lactide, bring the higher grafting percentage, which means the higher the reactivity of lactide with chitosan. The graft copolymers were characterized by FTIR, 1H NMR, WAXD, TGA and DSC.

In 2007, Patcharakamon *et al* synthesized a graft copolymer of polylactide (PLA)/poly(ethylene-co-vinyl alcohol) (EVOH) by a continuous single-step catalytic reactive extrusion using 2-ethylhexanoic acid tin(II) salt, $Sn(Oct)_2$, as a catalyst. From their results, the optimum condition consisted of; concentration of catalyst of 0.1 wt%; LA to EVOH ratio at 60/40 wt%; and the screw speed of 40 rpm, which provided the graft copolymer with superior mechanical properties, particularly elongation at break and Young's modulus.

Cellulosic graft copolymers have recently received increasing interests according to the concept of green chemistry and sustainable development. Dong *et al.* (2008) synthesized a new biodegradable copolymer comprised of hydrophobic poly(l-lactide) (PLLA) segments and hydrophilic cellulose segment (cellulose-g-PLLA) with addition of $Sn(Oct)_2$ 0.1 wt% at $130^\circ C$ for 8 h. The copolymer can self-assemble into micelles in aqueous media with the cores as hydrophobic PLLA segments and the outer shells as hydrophilic cellulose segments, which showed the potential application as drug carrier in the aqueous media in the nanoscale.

2.3 Polybenzoxazine (PBZ)

Polybenzoxazine(PBZ) is a newly developed thermosetting resin in the type of addition-cure phenolic system. PBZ has gained several interests because it has the capability to exhibit the thermal and flame retardance properties of phenolics along with mechanical performance and molecular design flexibility. Benzoxazine(BZ)

monomers are typically synthesized using phenol, formaldehyde and amine (aliphatic or aromatic) as starting materials either by employing solution or solventless methods. The molecular structure of PBZ 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, namely (i) near-zero volumetric change upon curing, (ii) low water absorption, (iii) for some polybenzoxazine based materials T_g much higher than cure temperature, (iv) high char yield, (v) no strong acid catalysts required for curing, and (vi) release of no by-products (even nontoxic) during curing (N.N. Ghosh *et al.*, 2007).

The BZ ring polymerized via a thermally ring-opening preferentially with the free ortho positions of a phenolic compound and forms a Mannich bridge ($-\text{CH}_2-\text{NR}-\text{CH}_2-$), as shown in Figure 2.6.

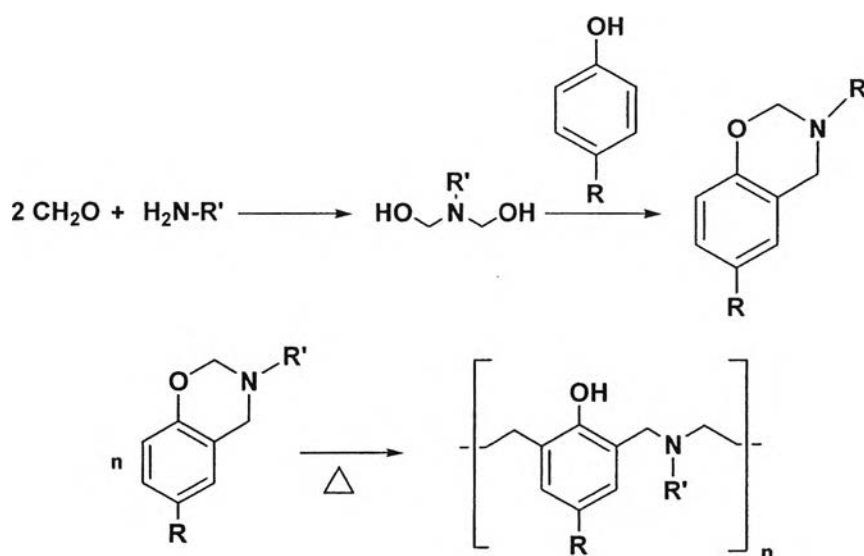


Figure 2.6 Schematic diagram of synthesis(top) and thermal induced ring-opening polymerization of PBZ to form Mannich bridge (N.N. Ghosh *et al.*, 2007).

The synthetic procedure of the Mannich condensation for BZ synthesis in a solvent proceeds by first addition of amine to formaldehyde at lower temperatures 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 elevated temperature to form the oxazine ring

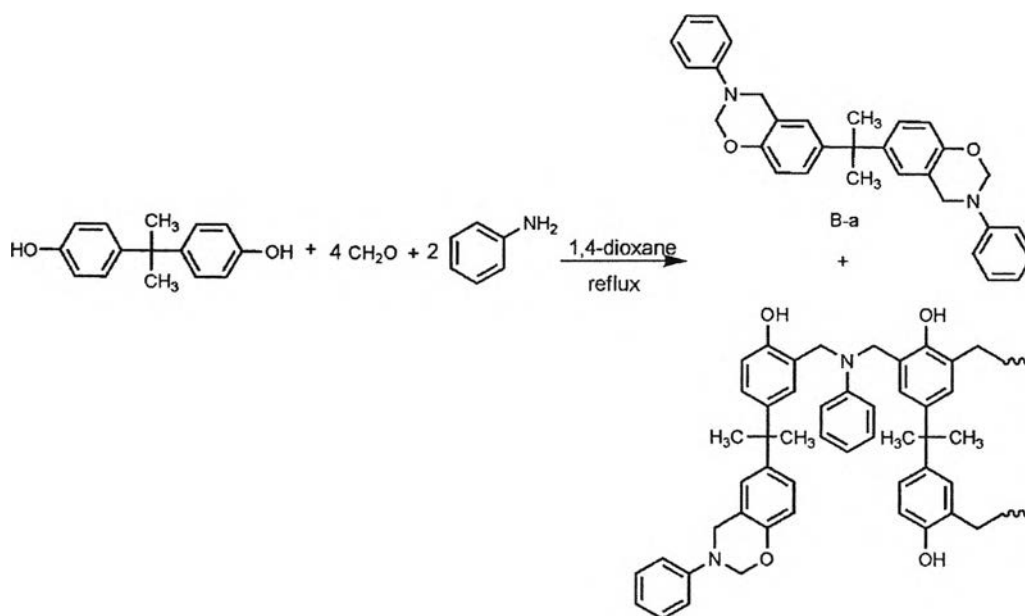


Figure 2.7 Schematic diagram of synthesis difunctional benzoxazine (B-a) monomer based on bisphenol-A and aniline (N.N. Ghosh *et al.*, 2007).

Ishida and coworkers have developed a new class of difunctional or multifunctional BZ monomers to conquer the limit of product resulted from mono-functional benzoxazines with phenol which gave only oligomeric structure; an average molecular weight around 1000 Da. The difunctional or multifunction BZ precursor was synthesized using bisphenol-A, formaldehyde and methylamine in different solvents referred to as B-m structure (as a reference to two of its original ingredients: bisphenol-A and methylamine). The similar type of difunctional benzoxazine was prepared using aniline instead of methylamine and the pure monomer was referred to as B-a (as a reference of bisphenol-A and aniline, as shown in Figure 2.7).

According to the work done by Ishida *et al.* (2001), BZ monomer and polycaprolactone (PCL) were melt blended in the range of 0-15 wt% of PCL, which had a number average molecular weight in the range of 35,000–40,000, then

polymerized without adding any catalyst or initiator to study the hydrogen bonding and thermal properties.

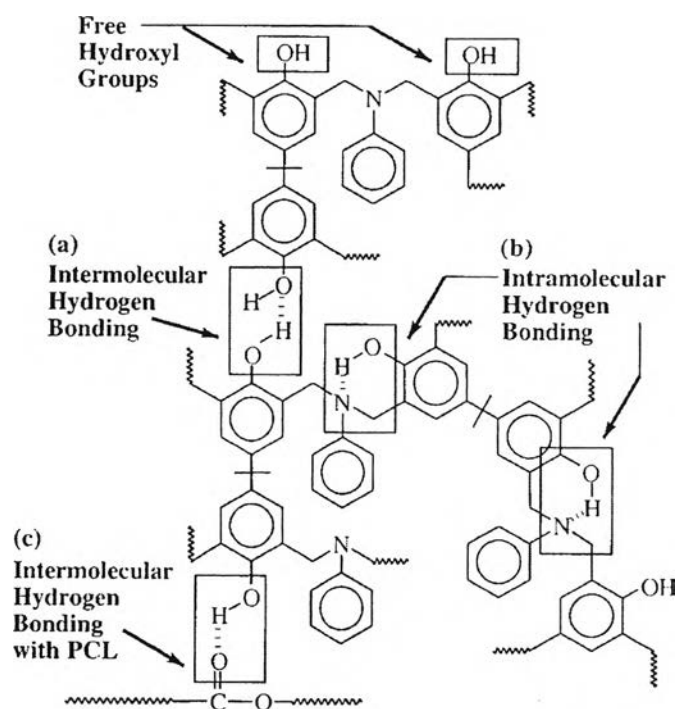


Figure 2.8 Three types of hydrogen bonding that could possibly occur in the PCL-PBZ blend: (a) intermolecular hydrogen bonding between two hydroxyl groups of PBZ, (b) intramolecular hydrogen bonding between hydroxyl groups and nitrogen atoms on the Mannich bridge, and (c) intermolecular hydrogen bonding between the carbonyl groups of PCL and hydroxyl groups of PBZ (Ishida *et al.*, 2001).

The problem of polymer-polymer blends were immiscibility or unmixing at the molecular level. However, PCL was chosen to blend with PBZ resin because the intermolecular hydrogen bonding, which was expected to result on physical and mechanical properties of polybenzoxazine, could occur between the hydroxyl groups of the PBZ main chain and the carbonyl groups of PCL. BZ monomers were synthesized through Mannich reaction via a solventless method with the stoichiometric amounts (1:2:4) of bisphenol-A, aniline, and paraformaldehyde at 110°C. The ring-opening reaction and subsequent polymerization reaction of the benzoxazine were facilitated significantly by the presence of a PCL modifier.

Hydrogen-bond formation between the hydroxyl groups of PBZ and the carbonyl groups of PCL was evident from the FTIR spectra. The glass transition temperature (T_g) value of the PCL/benzoxazine monomer blend from DSC analysis appeared to be higher than T_g of pure PCL (approximately -62°C) and the neat PBZ resin (163°C) as a function of a greater amount of PCL (from 0 to 33 wt%), which could imply an increasing extent of polymerization on the addition of PCL. The blend results showed improved thermal stability and mechanical properties, including higher crosslink densities, rubbery plateau moduli, and flexural strengths compared to pure PBZ. They also concluded that intramolecular hydrogen bonding contributed to the stiffness of the chain and led to favorable properties including low water uptake and near-zero shrinkage on polymerization.

The advantage of the rich molecular design opportunities of benzoxazines helps to develop a matrix material with an inherently flexible molecular structure to be less brittle than typical benzoxazines. In 2006, Allen and Ishida studied the effect of aliphatic diamine chain length on the physical and mechanical properties of the flexible PBZ resin. The synthesis composed of phenol, paraformaldehyde, and a series of linear aliphatic diamine with the stoichiometric as 2:4:1 via a thermally activated cationic reaction of the oxazine ring, and thus no external initiators or catalysts were required to produce PBZ from the aliphatic diamine-based series of monomers (solventless method). Polymerized PBZ samples were prepared for dynamic mechanical analysis (DMA), flexural analysis, thermogravimetric analysis (TGA), and polymer density measurement from gas pycnometry. Properties including room temperature modulus, glass transition temperature, crosslink density, thermal degradation temperature, and char yield of the PBZ were investigated as a function of the chain length. The results showed that density of these PBZ was shown to decrease as a function of aliphatic diamine chain length. Meanwhile, dynamic mechanical analysis exhibited the values of glass transition temperature, which could be determined from the peak maximum of the loss modulus, and storage modulus of each PBZ material were decrease as the increasing of amine chain length. Those aliphatic amine-based PBZ were found to be much more flexible than the bisphenol-type PBZ.

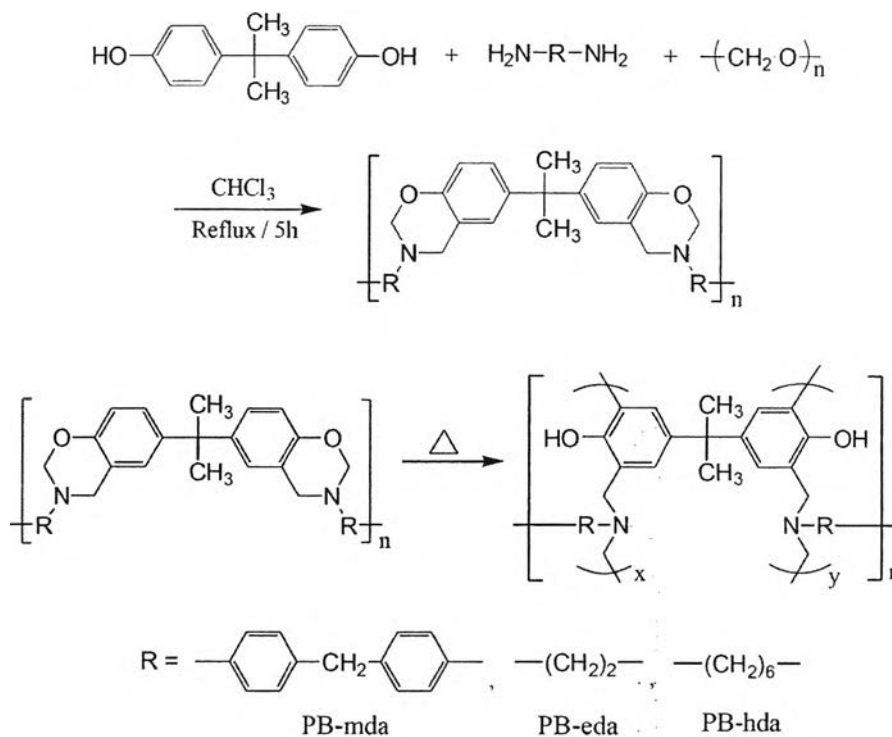


Figure 2.9 Schematic diagram of preparation and thermal induced polymerization of PBZ precursors, which synthesized from bisphenol-A, formaldehyde, and diamine (mda = methylenedianiline, eda = ethylenediamine, and hda = hexamethylenediamine) and the possible structure of PBZ (Takeichi *et al.*, 2005).

Takeichi *et al.*, 2005 synthesized high molecular weight PBZ precursors from paraformaldehyde, aromatic or aliphatic diamine and bisphenol-A at the molar ratio of 4:1:1, as shown in Figure 2.9. The precursor solution was cast on glass plate—giving transparent and self-standing precursor films—which was thermally cured up to 240 °C to give brown transparent PBZ films. The toughness of the crosslinked PBZ films from the high molecular weight precursors was greatly enhanced compared with the cured film from the typical low molecular weight monomer. Tensile measurement of the PBZ films revealed that PBZ from aromatic diamine exhibited the highest strength and modulus. While, PBZ from longer aliphatic diamine had higher elongation at break. The viscoelastic analysis showed that the glass transition temperature of the PBZ derived from the high molecular

weight precursors were as high as 238–260°C. Additionally, high molecular weight PBZ thermosets showed improved toughness and excellent thermal stability.

In 2005, Huang and Yang studied the miscibility and thermal behavior of polybenzoxazine/poly(ϵ -caprolactone) blends using DSC, DMA, FTIR, and solid state ^{13}C NMR. Polymer blends were prepared by solution blending of PCL polymer and benzoxazine monomer (B-m), which was synthesized from bisphenol-A, formaldehyde, and methylamine with dioxane as a solvent, followed by thermal curing of B-m. The FTIR spectra indicated that hydrogen bonding interactions occurred between the carbonyl groups of PCL and the hydroxyl groups of PBZ upon curing. The DSC results indicated that both the melting temperature and degree of crystallinity of the PCL component in the blend decreased upon increasing the PBZ content and the PBZ/PCL blend system had a single glass transition temperature over the entire range of compositions that they investigated. The DMA results indicated that the values of T_g of the PBZ/PCL blends were higher than those of the pure polymers. In addition, at higher PCL concentrations, they observed two glass transitions for the PBZ/PCL blends. The one at the temperature region belonged to the PCL component and the other, at the higher temperature region, to the PBZ component. This finding indicated that PCL and PBZ are partially miscible in the amorphous phase. The most pronounced effect of the addition of PCL was to broaden the glass transition region, judging from the E'' peaks and the decrease in the value of the loss tangent ($\tan \delta$) in the transition region upon increasing the PCL content. They had also studied the ^1H spin-lattice relaxation times with the result strongly suggested that PBZ and PCL were immiscible on the scale of the spin-diffusion path length.

Su *et al.* (2005) developed nanoporous materials derived from BZ-terminated poly(ϵ -caprolactone)/polybenzoxazine co-polymers which had low dielectric constant and acted as the labile and stable constituents. They used PCL as co-polymers because of their biodegradability and polymer blend compatibility. In addition, PBZ contained a high density of hydroxyl groups that interacted with the carbonyl groups of PCL through hydrogen bonding. To prepare a microporous material, it was essential to prepare a well-dispersed microphase-separated labile constituent within a stable matrix. Hence, they modified the PCL's end group to

decrease the degree of phase separation. They synthesized BZ monomer (pa-OH) from formaldehyde, aniline, and 4-Hydroxybenzyl alcohol with the stoichiometric as 2:1:1 in dioxane solvent at 100°C. Next step was the synthesis of pa-OH terminated PCL(pa-PCL) which hydroxyl groups acted as initiators for the polymerization of ϵ -CL polymerization in the presence of Sn(Oct)₂ as a catalyst. The ring opening polymerization of PCL was performed at 120°C over 24 h as shown in Figure 2.10.

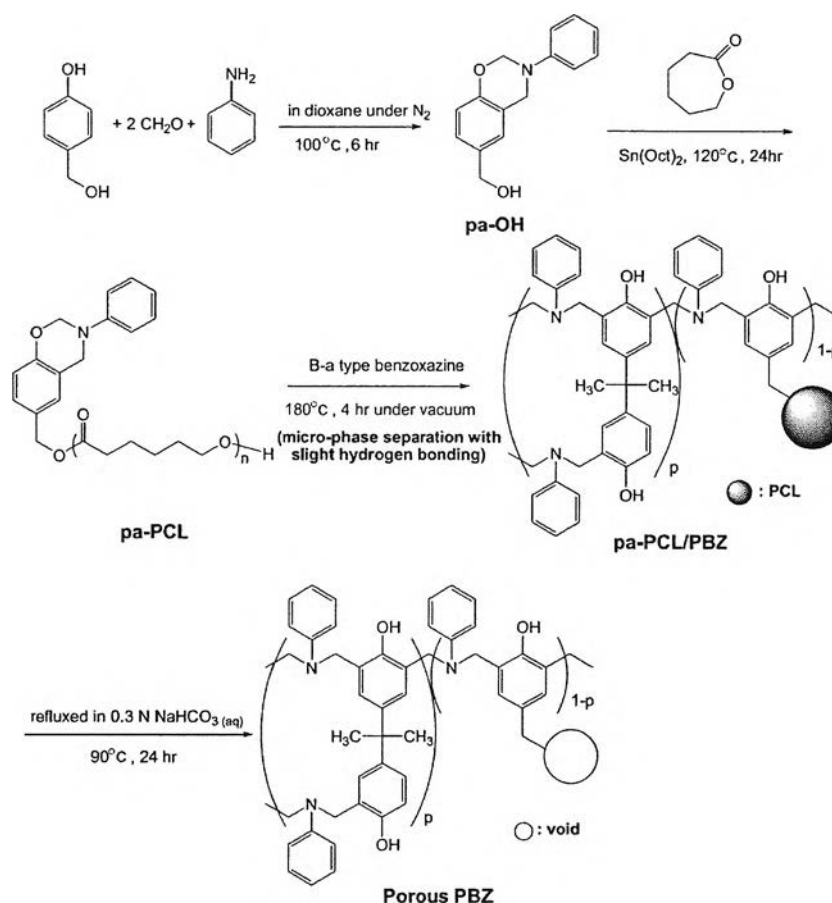


Figure 2.10 Schematic diagram of the synthesis of pa-OH, pa-PCL, pa-PCL/PBZ and the generation of nanoporous PBZ films from phase-separated copolymers (Su *et al.*, 2005).

Mixtures of pa-PCL (25 wt%) and B-a type benzoxazine (75 wt%) having several different molecular weights were prepared by solution blending. The mixture was dissolved by stirring in THF and then cured at 180°C to ensure total curing of the

copolybenzoxazine(co-PBZ). The cured sample was stirred and refluxed in 0.3 N aqueous NaHCO_3 to remove the ester group of the labile constituent (PCL). The porous structures were obtained after drying under vacuum in an oven.

Kiskan and Yagci (2005) synthesized naphthoxazine functional PCL. For this purpose, first hydroxyl functional naphthoxazine was prepared by the reaction of 2-naphthol, ethanolamine and paraformaldehyde either in bulk or in dioxane as a solvent at 110°C . Subsequently, naphthoxazine(end with OH group) was used as the coinitiator for the stannous-2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) catalyzed living ring-opening polymerization of ϵ -caprolactone. Upon curing in the presence of BZ monomer, thermosettings of PBZ with covalently bonded PCL segments can be formed. The GPC, IR, ^1H NMR, UV, and fluorescence spectroscopic studies revealed that low-polydispersity PCL with naphthoxazine functionality at the end of the chain was obtained. The resulting PCL macromonomer underwent thermal curing in the presence of low molar mass BZ at various temperatures with the formation of thermosets having PCL segments which may significantly influence physical and mechanical properties.

However, there are some disadvantages of the cured PBZ, namely its brittleness and relatively high curing temperature(such about 200°C). Recently, to enhance the mechanical performance of PBZ and lower the polymerization temperature, various approaches have been proposed. One approach was the modification of monomer by introducing another crosslinkable functional unit to it; this method was found to be very effective in improving the thermal properties. Another approach is to make polymer alloys of PBZ with high performance polymers or with elastomers resulting a tough film with high performance. The third approach is to make a hybrid PBZ with inorganic material, such as layered clay and metal oxide nanoparticles, which is also successful in making PBZ with improved properties.

In 1999, Wang and Ishida performed a comprehensive survey of initiators and/or catalysts for the polymerization of BZ monomer and search for the effective compounds to reduce the curing temperature and time of these novel BZ resins. They used a bisphenol-A/aniline based benzoxazine monomer designated as BA-a. With certain cationic initiators, benzoxazine rings could be opened and polymerized at

room temperature. The examination of the polymerization of BA-a with 5 mol% of a variety of cationic initiators, an anionic initiator and a free radical initiator was carried out with either 1,2-dichloroethane, chloroform, or 1,2-dichlorobenzene as the tentative solvent at a desired temperature for 20 h. Fourier transform infrared spectroscopy, ^1H and ^{13}C nuclear magnetic resonance spectroscopy, size exclusion chromatography, differential scanning calorimetry, and thermogravimetric analysis have been used to monitor the polymerization process and to characterize the obtained polymers. Various initiators were studied for the polymerization of BA-a benzoxazine resin. Several initiators, PCl_5 , PCl_3 , POCl_3 , TiCl_4 , AlCl_3 , and MeOTf , were found to be effective for the ring-opening polymerization of BZ resins at moderate temperatures. Several attractive polymers with high T_g and high char yield under nitrogen environment were produced from these initiating systems.

Agag and Takeichi (2007) developed novel high-molecular-weight PBZ precursors—namely AB-type benzoxazine precursors. They were synthesized from aminophenols such as, tyramine or p-aminophenol, and formaldehyde in a molar ratio of 1:2. Both ^1H NMR and IR of the precursors confirmed the presence of a cyclic benzoxazine structure in the backbone of the precursors. The weight average molecular weight was estimated by SEC in the range of 1300–4500. The precursors gave self-standing thin films and upon a gradual thermally cured up to 250°C , reddish-brown, transparent PBZ had been obtained. The viscoelastic analyses showed that the glass transition temperatures of the PBZ films as high as $260\text{--}300^\circ\text{C}$. Thermogravimetric analysis indicated that the onset of decomposition and the char yield of the thermosets derived from these AB-type precursors were higher than those of traditional PBZ. This enhancement in the thermal properties could be attributed to the increase in the crosslinking density and hence suggested that the use of AB precursors was an effective approach for obtaining a novel polybenzoxazine matrix with excellent thermomechanical properties as well as high thermal stability.

2.4 Marl Filler

Marl or marly limestone—which is known in Thai as “din-so-pong”—is the white soil contained a main composition, calcium carbonate, about 80–97% and

another such as SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , CaO and MgCO_3 . In Thailand, at Lopburi, Saraburi, Kanchanaburi, Nakornsawan, Phetchabun, Tak, Lampang, Chaingmai, Ratchaburi, and Krabi provinces were the original resources of marl. It has several benefits in Thai medical treatment as a cool powder to be used as an anti-sweat, an anti-infection, and skin diseases reduction. Due to its advantages, marl, similar to use calcium carbonate or clay, is chosen to use as a filler to improve the mechanical properties with can lower a price of product at the same time.

Although PLA exhibits high tensile strength and modulus, but it has very low strain-at-break and toughness. Incorporating organically modified layered silicates (OMLS) into a PLA matrix has been studied extensively for improvements of PLA properties. Jiang *et al.* (2007) reported the comparison of the reinforcing effects and the toughening mechanisms of polylactide/nano-sized calcium carbonate (NPCC) and polylactide/montmorillonite (MMT) composites by melt compounding using a twin-screw extruder and injection molded into test specimens. They compared the reinforcing and toughening effects of the MMT with those of NPCC, for better understanding, which possesses significantly different geometric structures and surface characteristics. The nano-sized calcium carbonate particles, which are in cubic shape with an average primary particle size of ca. 40 nm., were coated with stearic acid for better dispersion, while montmorillonite clay was modified with methyl dihydroxyethyl hydrogenated tallow ammonium. MMT and NPCC showed significantly different effects on the strength, modulus and elongation of the PLA nanocomposites. The strain-at-break of PLA increased with NPCC concentration ranging from 0 to 7.5 wt%, whereas it only increased with MMT concentration up to 2.5 wt% and decreased at higher concentrations. The tensile strength of PLA nanocomposites decreased with NPCC, whereas it increased with MMT up to 5 wt%. The different reinforcing effects of these two nanoparticles could be mainly attributed to the differences in microstructures and interactions between the nanoparticles and PLA in the respective nanocomposites, which were evidenced by SEM and TEM.

In 2001, Phiriyawirut *et al.* prepared immiscible polymer-clay nanocomposite by dispersing layers of organically modified, with 5 types of modifying agents which done via ion exchange reaction, montmorillonite (OMOM) in a polybenzoxazine matrix by solution mixing and melt mixing. From WAXD results

revealed that the silicate layer expansion of all polybenzoxazine OMOM nanocomposites prepared from either melt or solution methods were similar and it depended on size of modifying agent. While TEM results showing the aggregation of silicate layers indicating that all prepared OMOM were immiscible with the polymer matrix, which could be classified as intercalated incompatible nanocomposite. They suggested that the compatibility between amine modifying agents and benzoxazine played the most important role for the characteristics of the nanocomposite.

Calcium carbonate is one of the most widely used fillers either for thermoplastics or composite materials. Nevertheless, the polar nature of it often requires surface treatment before incorporation into a non-polar plastic matrix in order to modify filler-filler and filler-polymer interactions, and to facilitate dispersion in the polymer matrix. To improve the compatibility results in high mechanical properties of composites, different coupling agents, for example silanes and titanates, can be applied depending on the chemical character of the participating components. In 1979, Nakatsuka *et al.* modified calcium carbonate with silane, γ -methacryloxypropyltrimethoxysilane and γ -mercaptopropyltrimethoxysilane, and synthesized the graft copolymer of styrene on the treated surface calcium carbonate. They added silane with calcium carbonate and used an aqueous methanolic solution (methanol+H₂O) as a solvent, after that dried calcium carbonate at 80°C for 3 h. They confirmed the graft copolymer with FTIR and GPC.

Various silane coupling agents are commercially available, but for phenolic and epoxy resins, they often used amino-functional silane. Ishida *et al.* (1998) used silane coupling agents to promote the adhesion between glass fiber and polymeric resin by 2 synthesizing routes; first entailed synthesizing a benzoxazine with an allyl group of allyl-terminated phenol, as used *tert*-butyl amine; the second method was the direct synthesis of the benzoxazine functional silane by using amino-functional silane, γ -aminopropyltriethoxysilane, as the primary amine for benzoxazine synthesis. However, one occurred problem was that the water molecules, which were by-produced of the benzoxazine synthesis, could hydrolyze the alkoxy portion of the amino-silane. Consequently the stoichiometry was disturbed, and gelation of the reaction mixture may occur as silane oligomers were formed. They used FTIR, SEC, HPLC, and ¹H NMR to confirm the structure of silane functional polybenzoxazine.

Moreover, they prepared benzoxazine-glass fiber, treated with silane coupling agents, reinforced composites by hydrolyzing amino functional silane— γ -aminopropyltrimethoxysilane(γ -APS)—with deionized and distilled water, then immersing glass fiber in the silane solution and molding composite with the synthesized polybenzoxazine as the matrix by using a 30-ton compression molder. They used interlaminar short-beam shear (ILSS) to assess the overall adhesion properties of fiber-reinforced composites. The silane coupling agent had been shown to improve the LISS strength of the glass-fiber-reinforced polybenzoxazine.

Leong *et al.* (2005) studied the effects of filler treatments on the properties of calcium carbonate filled polypropylene hybrid composites. The surface treatment with 3-aminopropyltriethoxy silane and neoalkoxy titanate (Lical2) was performed in an aqueous alcohol solution. The silane/ ethanol solution was left for 5 min to pre-hydrolyze the silane to activate the silane group. Once it was activated (hydrolyzed), the resultant silanol groups condensed with other silanols or with reactive groups on the surface of the filler, as shown in Figure 2.11.

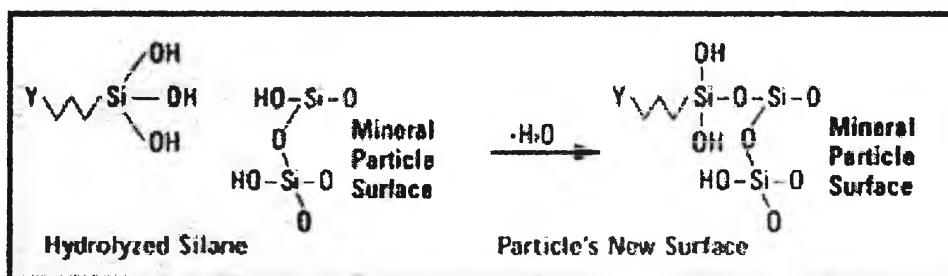


Figure 2.11 Schematic diagram of the condensation of silanol (hydrolyzed silane) with reactive groups on the filler surface (Leong *et al.*, 2005).

After the treatment, the fillers were then dried in an oven at 110°C for 24 h. The dried fillers were rinsed again with ethanol to drive away any residual silane before the fillers were dried again at the same temperature and for the same period.

However, calcium carbonate has very few hydroxyl groups on its surface for reacting with hydrolyzed silane, which may lead to the less responsive to silane. On the other hand, the much cheaper nonreactive coupling agents such as fatty acids

have been successfully applied in polymer composites. Stearic acid is one of the earliest and the most often used fatty acids. Nonreactive coupling takes place in composites where the filler and the polymer are bonded by secondary forces through the alkyl chain of stearic acid: and with the carboxylic group at the other end the stearic acid is able to form covalent bonds at the filler surface. In 2003, Wang *et al.* studied the interfacial interaction of surface modification in calcium carbonate–polypropylene composites. Calcium carbonate (CaCO_3) was modified with two types of coupling agents based on fatty acid and titanate. The treatment of calcium carbonate with stearic acid was followed; dried calcium carbonate (110°C , 24 h) was loaded into a stirrer of stearic acid solution (toluene used as a solvent) and stirred for 24 h, and then the filler was separated and dried. The completely modified CaCO_3 , exhibited a surface of little polarity, evident by an infrared analysis, i.e. stearic acid reacted extensively with the filler surface to produce chemically bound organic salt compound, in addition to the increase in peak intensity due to the methylene vibration of the alkyl chain.