

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Cellulose Sheets

2.1.1 Structure of Cellulose Sheets

Cellulose sheet is a layered sheet of interlocking cellulosic fibers held together by hydrogen bonds (Robert, 1996). The cellulosic fibers are highly hydrophilic and are readily wetted and swollen by water. Structure of paper is formed continuously by a pulsed filtration process from an aqueous suspension of cellulosic fibers with possible addition of some polymeric retention aids and inorganic fillers. During the sheet forming process, as water is evaporated, the wet fibers are drawn close by the surface-tension force and ultimately held together by hydrogen bonds between the hydroxyl groups in the opposing fiber surfaces.

2.1.2 The Strength of Cellulose Sheet

The strength properties are extremely important for many applications. Strength is mainly influenced by the type of fiber and the alignment of the fibers in the microstructure of the cellulose. Chemical pulp naturally has greater strength than mechanical pulp. The cellulose has different strength characteristics in the different directions.

2.2 Plant Fibers

2.2.1 Types of Plant Fibers

Fibers obtained from the various parts of the plants are known as plant fibers. Plant fibers include trunk, leaf and seed/fruit fibers. Trunk consists of a wood core surrounded by a stem. Within the stem, there are a number of fiber bundles, each containing individual fiber cells or filaments. For examples of stem fiber is include flax, hemp, jute, kenaf and ramie. Leaf fibers such as banana, sisal, abaca, and henequen. Leaf fibers are coarser than stem fibers. Seed fiber such as cotton. Other examples include coir and oil palm. Other source of lignocellulosics can be from agricultural residues such as rice hulls from a rice processing plant, sun

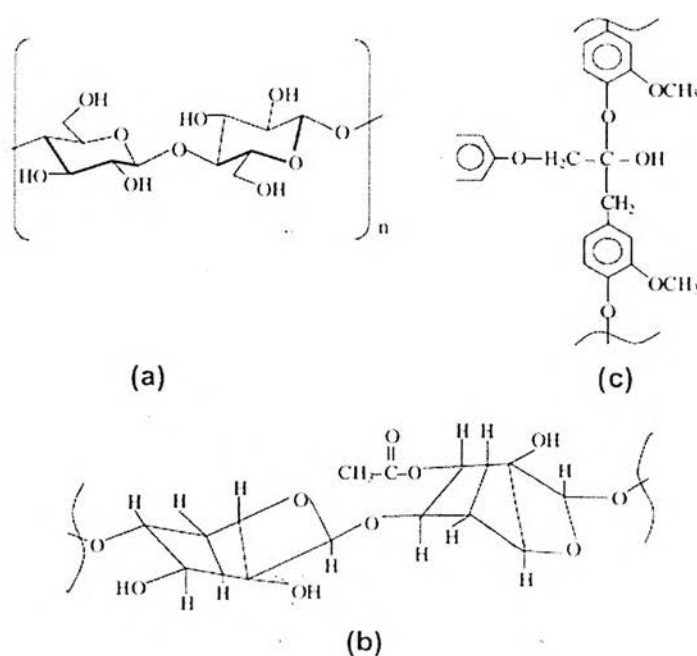
flower seed hulls from an oil processing unit and bagasse from a sugar mill. The properties of natural fibers vary considerably depending on the fiber structure, diameter, degree of polymerization, crystal structure and source, whether the fibers are taken from the plant stem, leaf or seed, and on the growing conditions (Bledzki & Gassan, 1999; Mohanty, Misra & Drzal, 2005; Nevell & Zeronian, 1985).

2.2.2 The Structure of Plant Fibers

Plant based natural fibers are lignocellulosic in nature and are composed of cellulose, hemicellulose, lignin, pectin and waxy substances. The structure compositions of fiber are presented in Table 2.1. Cellulose is the major component of fiber structure. It provides strength, stiffness and structural stability of the fiber. The chemical structure of cellulose (Fig. 2.1a) consists of three hydroxyl groups (OH). Two of them form hydrogen bonds within the cellulose macromolecules (intramolecular) while the other forms hydrogen bond with other cellulose molecules (intermolecular). Hemicellulose occurs mainly in the primary cell wall and has branched polymers containing five and six carbon sugars (Fig. 2.1b) of varied chemical structures. Lignin is amorphous and has an aromatic structure (Fig. 2.1c). Pectin comprises of complex polysaccharides. Their side chains are cross-linked with the calcium ions and arabinose sugars. Additionally, small amounts of organic (extractives) and inorganic (ash) components are present in the fiber structure. Organic extractives are responsible for color, odor and decay resistance while inorganic constituents enhance the abrasive nature of the fiber.

Table 2.1 Structure compositions of natural fibers (Mohanty AK. *et al.*,2000)

Name of the fibers	Cellulose (wt %)	Lignin (wt%)	Hemicellulose (wt%)	Pectin (wt%)	Wax (wt%)	Micro-fibrillar/ spiral angle (°)	Moisture content (wt%)
Bast fibers							
Jute	61-71.5	12-13	13.6-20.4	0.2	0.5	8.0	8.0
Flax	71	2.2	18.6-20.6	2.3	1.7	10.0	10.0
Hemp	70.2-74.4	3.7-5.7	17.9-22.4	0.9	0.8	6.2	6.2
Ramie	68.6-76.2	0.6-0.7	13.1-16.7	1.9	0.3	7.5	7.5
Leaf fibers							
Sisal	67-78	8.0-11.0	10.0-14.2	10.0	2.0	20.0	20.0
PALF	70-82	5-12	-	-	-	14.0	14.0
Seed fibers							
Cotton	82.7	0.7-1.6	5.7	-	0.6	-	-

**Figure 2.1** Chemical structure of (a) cellulose (b) hemicellulose and (c) lignin (Bledzki AK and Gassan J., 1999).

A single or elementary plant fiber is a single cell typically of a length from 1 to 50 mm and a diameter of around 10–50 μm. Plant fibers are like microscopic tubes, for example, cell walls surrounding the central lumen. The lumen contributes to the water uptake behavior of plant fibers (Toumis, 1991). The fiber consists of several cell walls. These cell walls are formed from oriented reinforcing semi-crystalline cellulose microfibrils embedded in a hemicellulose–lignin matrix of varying composition. Such microfibrils have typically a diameter of about 10–30 nm and are made up of 30–100 cellulose molecules in extended chain conformation and provide mechanical strength to the fiber. Figure 2.2 shows the arrangement of fibrils, microfibrils and cellulose in the cell walls of a plant fiber.

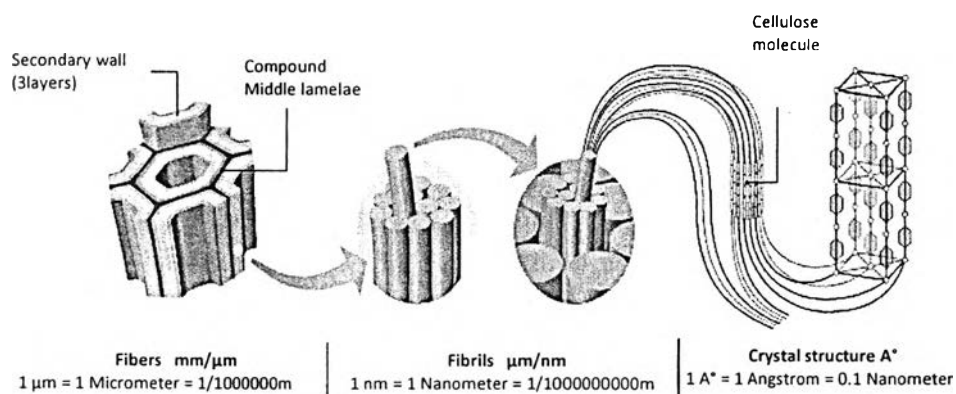


Figure 2.2 Arrangement of microfibrils and cellulose in the plant cell wall. (Zimmermann *et al.*, 2004)

Figure 2.3 shows a schematic structure of a natural fiber and Figure 2.4 presents the model of the structural organization of the three major structural constituents of the fiber cell wall (Madsen B., 2004). In accordance with a specific type of fiber, cellulose microfibrils have their own cell geometry which is a factor effective to the properties of the fiber. Each fiber cell wall consists of primary and secondary layers of cellulose microfibrils. The fiber structure develops in the primary cell wall and is deposited during its growth. The secondary wall consists of three layers and each layer has a long chain of helical cellulose microfibrils. The cellulose content increases steadily from primary to secondary layers and the hemicelluloses

amount are similar in each layer. However, lignin content decreases in this sequence. Hemicellulose molecules are hydrogen bonded with cellulose fibrils and they form cementing materials for the fiber structure. Lignin and pectin are coupled with the cellulose–hemicellulose network and provides an adhesive quality to hold the molecules together. This adhesive quality is the cause for the strength and stiffness properties of the fiber. Secondary thick layer (s2) determines the mechanical properties of the fiber. Generally, fibers with a higher cellulose content and a lower microfibrillar angle (the angle between the fiber axis and cellulose microfibrils) have better strength properties. Mechanical properties of natural fiber over synthetic fiber are presented in Table 2.2. Although natural fibers have relatively lower strength properties compared to the synthetic fibers, the specific modulus and elongation at break signifies the potentiality of these fibers to replace synthetic fibers in engineering polymer composites.

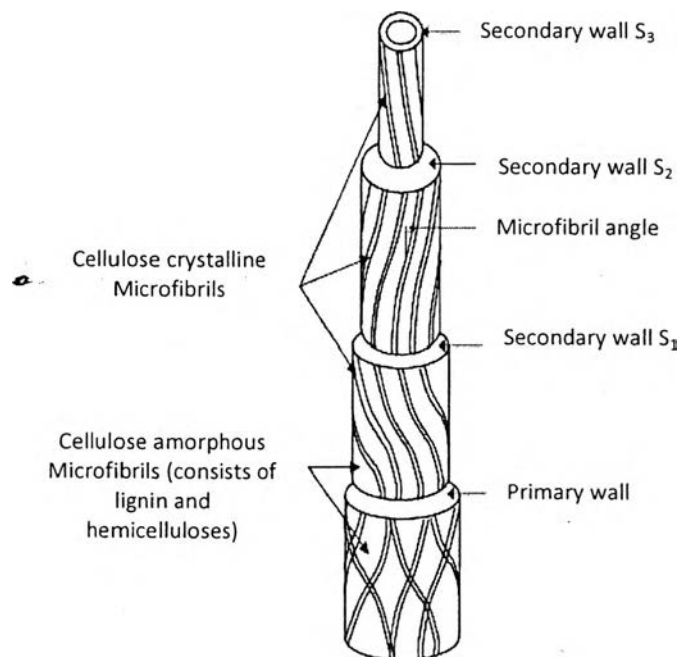


Figure 2.3 Structure of natural fiber.

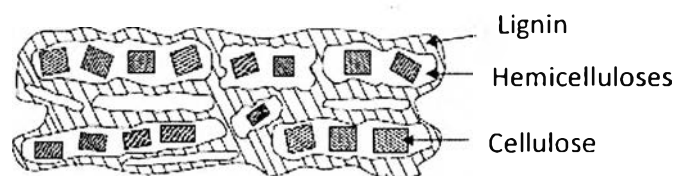


Figure 2.4 Structure organization of the three major constituents in the fiber cell wall.

Table 2.2 Comparative properties of natural fibers with conventional manmade fibers. (Fakirov S. and Bhattacharyya D., 2007)

Name of fibers	Density (g/cm ³)	Tensile Strength (MPa)	Young's modulus (GPa)	Specific strength (GPa/g/cm ³)	Specific modulus	Elongation at break (%)
Jute	1.3-1.4	393-773	13-26.5	0.3-0.5	10-18.3	1.16-1.5
Flax	1.50	345-1100	27.6	0.2-0.7	18.4	2.7-3.2
Hemp	1.14	690	30-60	0.6	26.3-52.6	1.6
Ramie	1.50	400-938	61.4-128	0.3-0.6	40.9-85.3	1.2-3.8
Sisal	1.45	468-640	9.4-22.0	0.3-0.4	6.4-15.2	3-7
PALF	1.52	413-1627	34.5-82.51	0.3-1.1	22.7-54.3	1.6
Cotton	1.5-1.6	287-800	5.5-12.6	0.2-0.5	3.7-7.8	7.0-8.0
E-glass	2.5	2000-3500	70	0.8-1.4	28	2.5
S-glass	2.5	4570	86	1.8	34.4	2.8
Aramid	1.4	3000-3150	63-67	2.1-2.2	45-47.8	3.3-3.7

2.2.3 The Composition of Plant Fibers

The chemical compositions of natural fiber are various, which depends on the type of fiber. Normally, natural fibers consist of cellulose, hemicellulose and lignin. The property of each constituent contributes to the overall properties of the fiber.

2.2.3.1 Cellulose

Cellulose is the basic material of all natural fibers. Cellulose is a linear condensation polymer consisting of D-anhydroglucopyranose connected

together by β -1,4-glycosidic linkages, as shown in Figure 2.5. Therefore, cellulose is a 1,4- β -D-glucan (Nevell & Zeronian, 1985).

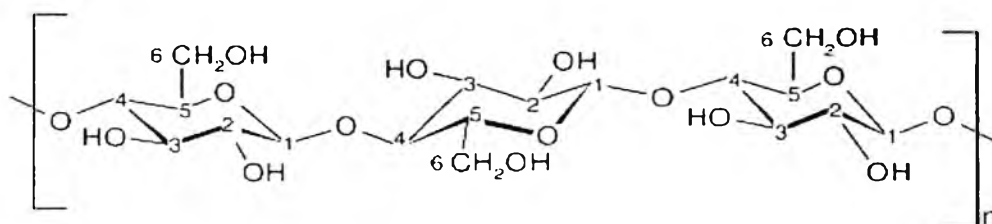


Figure 2.5 The structural unit of cellulose.

The molecular structure of cellulose can be used to determine its chemical and physical properties. In the fully extended molecule, the adjacent chain units are oriented by their mean planes at the angle of 180° to each other. Therefore, the repeating unit in cellulose is the anhydrocellobiose unit, and the number of repeating units per molecule is half the DP. This may be as high as 14,000 in native cellulose.

The cellulose of natural fibers can be affected to the mechanical properties. The mechanical properties are depended on the type of cellulose that each type of cellulose has its own cell geometry. Solid cellulose forms a microcrystalline structure with regions of high order, i.e., crystalline regions, and regions of low order, i.e., amorphous regions. Cellulose is also formed of slender rod like crystalline microfibrils. The crystal nature (monoclinic sphenodic) of naturally occurring cellulose is known as cellulose I. Cellulose is resistant to strong alkali (17.5 wt%) but is easily hydrolyzed by acid to water-soluble sugars. Cellulose is relatively resistant to oxidizing agents.

2.2.3.2 Hemicellulose

Hemicellulose consists of a group of polysaccharides (excluding pectin) that remains associated with the cellulose after lignin has been removed. The hemicellulose is different from cellulose in three things (Nevell & Zeronian, 1985). Firstly, they contain several different sugar units, whereas cellulose contains only 1,4- β -D-glucopyranose units. Secondly, they have a degree of chain branching, whereas cellulose is strictly a linear polymer. Thirdly, the degree of

polymerization of hemicellulose is lower than native cellulose 10–100 times. Unlike cellulose, the constituents of hemicellulose differ from plant to plant (Nevell & Zeronian, 1985; Frollini, Leao & Mattoso, 2000).

2.2.3.3 Lignin

Lignin consists of both aliphatic and aromatic constituents of hydrocarbon polymer (Gassan & Bledzki, 1995 ; Kritschewsky, 1985). The main monomer units are various ring-substituted phenyl propane linked together in the ways that are not fully understood. The mechanical properties of lignin are lower than cellulose. Lignin is totally amorphous and hydrophobic in nature. Its responsibility is gives rigidity to the plants. Lignin is considered to be a thermoplastic polymer that has a glass transition temperature of around 90°C and a melting temperature about 170°C. It is not hydrolyzed by acids, but soluble in hot alkali, readily oxidized and easily condensable with phenol (Sadov *et al.*, 1978).

2.2.3.4 Pectins and Waxes

Pectin is a collective name for heteropolysaccharides, which consist essentially of polygalacturon acid. Pectin is soluble in water only after a partial neutralization with alkali or ammonium hydroxide. It provides flexibility to plants. Waxes make up the last part of fibers and they consist of different types of alcohols, which are insoluble in water as well as in several acids.

2.2.4 Cellulose from Plant Fibers

A single fiber of natural fibers consists of several cells. The cellulose-based crystalline microfibrils are formed to cells. The cellulose-based crystalline microfibrils are connected to a complete layer by amorphous lignin and hemicellulose. One primary and three secondary cell walls of cellulose– lignin– hemicellulose layers stick together to form a multiple layer composite. The fiber strength increases with increasing cellulose content and decreasing spiral angle with respect to fiber axis.

All structures of cellulose do not align in crystalline. However, the ordered regions are extensively distributed throughout the material, and these regions are called crystallites. The threadlike entity, which arises from the linear association of these components, is called the microfibril which is the basic structural unit of the

plant cell wall. These microfibrils are found to be 10–30 nm wide, less than this in width, indefinitely long containing 2–30,000 cellulose molecules in cross section. The predominantly crystalline cellulose core is one of the structure compositions. Individual cellulose nanocrystals (Figure 2.6) are produced by breaking down the cellulose fibers and isolating the crystalline regions (Oke, 2010). These are covered with a sheath of paracrystalline polyglucosan material surrounded by hemicelluloses (Whistler and Richards, 1970).

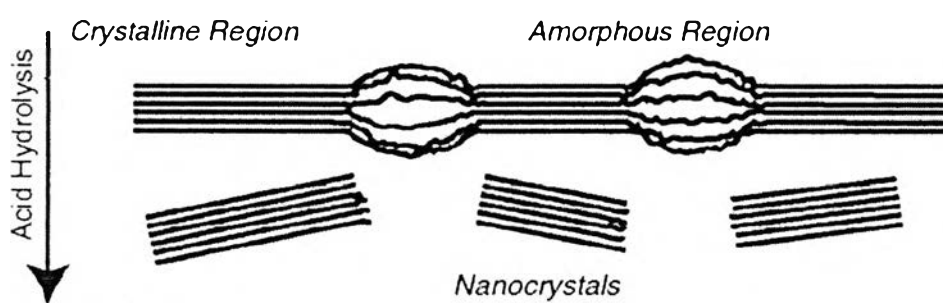


Figure 2.6 Acid hydrolysis breaks down disordered (amorphous) regions and isolates nanocrystals (Oke, 2010).

2.2.5 Factors Affecting the Composite Properties

2.2.5.1 *Thermal Stability of Fibers*

The degradation of natural fiber starts at about 240 °C. Structural compositions of the fiber (cellulose, hemicelluloses, lignin, etc.) are sensitive with different range of temperatures. Lignin starts degrading at a temperature around 200°C, hemicelluloses and cellulosic degrading at higher temperatures (Joseph PV et al., 2003). Thermal stability of the fiber can be enhanced by removing hemicelluloses and lignin constituents by different chemical treatments. This properties is an important issue in both manufacturing (curing, extrusion or injection molding) and materials in service (Sgriccia N. *et al.*, 2008).

2.2.5.2 *Structure of Plant Fibers*

The cellulose structures of the fiber consist of crystalline and amorphous regions. The strength in intra-molecular hydrogen bonds is formed in the crystalline region. This creates cellulose block and makes it difficult for other

chemical penetrations. Dyes and resins are absorbed easily by the amorphous region. In this region has hydrophilic hydroxyl groups are combined with water molecules from the atmosphere. Hemicellulose, lignin, pectin and waxy substances do normally hold these water molecules. All of these make character of fiber is hydrophilic and polar which lower the compatibility with the non-polar/hydrophobic matrix. Therefore, necessary to eliminate the hydrophilic hydroxyl groups and to remove surface impurities, natural fiber requires chemically treatment.

2.2.5.3 The Length of Fibers, Loading and Orientation

The mechanical properties of the natural fibers are depended on several factors such as fiber length, loading, the direction and orientation of fiber and the compatibility between fiber–matrix interfaces. There are three types of fiber orientation at the matrix. Firstly, longitudinally aligned fiber composites generally have higher tensile strength but lower compressive strength (due to fiber buckling). Secondly, transversely directed fibers undergo very low tensile strength. Finally, randomly orientated short fiber composites have different mechanical properties. This is due to the complexities of load distribution at different direction along the interfaces. The properties can be enhanced by controlling factors such as the aspect ratio, the dispersion and orientation of fibers (Fakirov S. and Bhattacharyya D., 2007).

2.2.5.4 Moisture Absorption of Fibers

The lignocellulosic fibers are hydrophilic and absorb moisture. When moisture from the atmosphere contacts with the fiber, the hydrogen bond breaks and hydroxyl groups form new hydrogen bonds with water molecules. The cross section of the fiber becomes the main access of water penetration. The interaction between hydrophilic fiber and hydrophobic matrix causes fiber swelling within in the matrix. This results in weakening the bonding strength at the interface, which leads to dimensional instability, matrix cracking and poor mechanical properties of the composites (Zakaria S. *et al.*, 2002).

2.2.5.5 The Void of Fibers

Between the insertion of fiber and the matrix, air or other volatile substances may be trapped inside the composites. After the curing process micro-voids are formed. If there are a lot of voids, they cause sudden failure of the

composites and show poor mechanical properties. The curing and cooling rate of the composites are also responsible for the void formation (Joseph PV. *et al.*, 2003).

2.2.6 Surface Modification of Natural Fibers

The interface of fiber-matrix is play importance role in mechanical properties of the composites. The poor mechanical properties occur due to the poor adhesion across the phase boundary that relatively weak dispersion of force. For reinforcement of natural fiber into the matrix, several problem occur because the presence of hydrophilic hydroxyl groups. The pectin and waxy substances are over the reactive functional groups of the fiber and act as a barrier to interlock with the matrix. Modifications of fiber surface by chemical treatment, reactive additives and coupling agents are necessary due to improve the effectiveness of interfacial bonding. Chemical treatment method can create more reactive groups on the fiber surface, so it is more react with the matrix. As a result in better mechanical properties of composites can be enhanced.

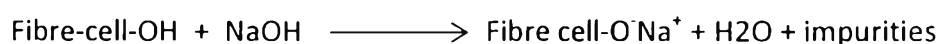
2.2.6.1 *Chemical Methods*

The major problem of natural fiber composites originate from the hydrophilic nature of the fiber and hydrophobic nature of the matrix. Therefore, they are incompatibility and result in weakening bonding at the interface. The hydrophilicity of nature fiber can be reduced by chemical treatment.

2.2.6.1.1 *Alkaline Treatment*

Sodium hydroxide (NaOH) is widely used to modify the cellulose molecular structure. It changes the orientation of highly packed crystalline cellulose and forming amorphous region that provides more access to penetrate chemicals. In the amorphous region, cellulose micromolecules are separated and the spaces are filled by water molecules. Alkali sensitive to hydroxyl (OH) group are broken down, which then react with water molecules (H-OH) and move out from the structure of fiber. The remaining of reactive molecules from fiber-cell-O-Na groups between the cellulose molecule chains. Due to this, hydroxyl groups are reduced and fiber moisture resistance property is increase. Alkaline treatment can also remove hemicellulose, lignin, pectin, wax and oil covering materials. In other words, the fiber surface becomes more uniform due to elimination

of microvoids and thus the stress transfer capacity between the ultimate cells improves. In addition to this, it reduces fiber diameter and increase aspect ratio (length/diameter). This increases effective fiber surface area for good adhesion with the matrix. If the alkali concentration is higher than the optimum condition, the fiber will weakening or damaging. The chemical reaction of the fiber-cell and NaOH is represented in Scheme 2.1. Figure 2.7 presents the schematic view of the cellulose fiber structure, before and after an alkali treatment.



Scheme 2.1 The chemical reaction of the fiber-cell and NaOH.

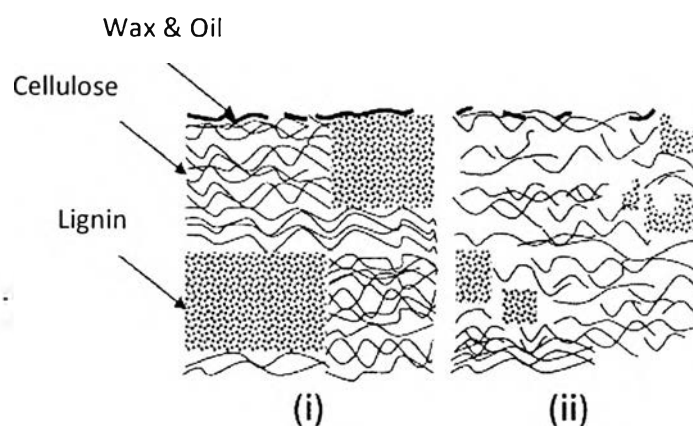
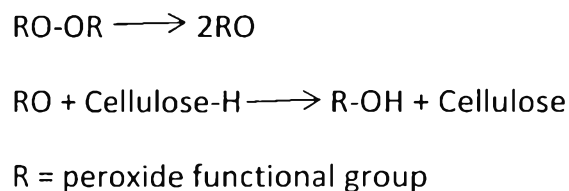


Figure 2.7 Typical structure of (i) untreated and (ii) alkalinized cellulose fiber (Leonard YM and Martin PA, 2002).

2.2.6.1.2 Peroxide Treatment

The peroxide-induced grafting of polyethylene adheres onto the fiber surface. In addition, peroxide initiated free radicals react with the hydroxyl group of the fiber and with the matrix. As a result, they obtain good adhesion between fiber and matrix at the interface. This treatment can also reduce moisture absorption and improve thermal stability (Wang B. *et al.*, 2007). The decomposition of peroxide can be improved by heating the solution at higher

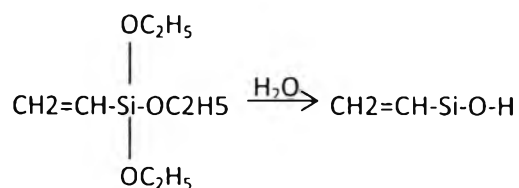
temperature. The reaction between the cellulosic –OH group of the fiber and decomposition of the peroxides is shown in Scheme 2.2 (Sreekala MS *et al.*, 2000).



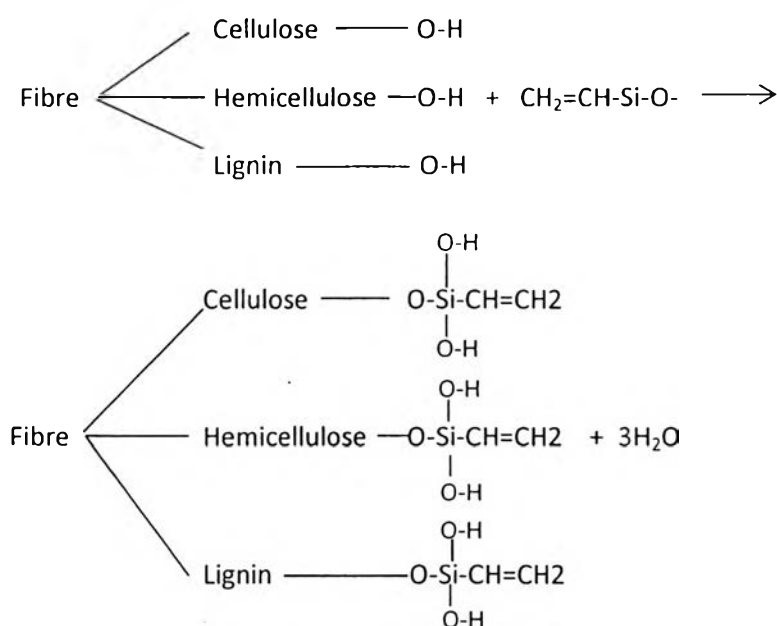
Scheme 2.2 The reaction between the cellulosic –OH group and decomposition of the peroxides.

2.2.6.1.3 Silane Treatment

Silane is used as a coupling agent to modify fiber surface. The silane will form a chemical link between the fiber and the matrix through a siloxane bridge. Silanols form by the presence of moisture and hydrolysable alkoxy groups (hydrolysis, Scheme 2.3a (Sreekala MS *et al.*, 2000)). During condensation process, one end of silanol reacts with the cellulose hydroxyl group (Si–O–cellulose, Scheme 2.3b) and other end reacts with the matrix (Si–Matrix) functional group. It also provides the hydrocarbon chain that gives the fiber swelling into the matrix. As a result, improving the adhesion of fiber matrix and stabilizing the composite properties.



Scheme 2.3a The formation of silanol.



Scheme 2.3b Silanol reacts with the cellulose hydroxyl group.

2.2.7 Literature Reviews on Natural Fiber

In 2007, Bilba K. et al. studied four natural fibers from banana leaves (BL), banana core (BC), coconut husk (CH) and coconut leaves (CF). The results showed that the chemical and botanical compositions depend on 1) localization of fibers in the tree 2) the type of tree where they come from such as green wood or not. They found that the banana core contain the highest cellulose content.

In 2009, Elanthikkal S. et al. studied the effect of alkaline, bleaching agent and acid hydrolysis on treated the cellulose microfibrils. The treatment can remove hemicellulose and lignin. When the concentration of sulphuric acid was increased, the size of particles were reduced. Significant size reductions were obtained when banana fibers of initially smaller dimensions were used.

In 2010, Khampan et al. prepared pineapple leaf papers from pineapple plantation waste for using as wet media in the evaporation cooling system by improving wet mechanical property (tensile strength) without compromising

water absorption property. Handsheets of pineapple leaf paper (PALP) were formed using pulp obtained from soda pulping process. Dry and wet strengths of PALP were improved by modifying with Polyamideamine-epichlorohydrin resin (PAE) and carboxymethylcellulose (CMC). They found that PAE and CMC ratio of 80:20 showed the optimum wet and dry tensile index values, which were higher than those of the commercial cooling pad (CCP). Compared with CCP, PALP itself and all the PAE/CMC modified PALP possessed better water absorption. As a result, treated PALP showed a potential for evaporative cooling application.

In 2012, Anamaria et al. modified unbleached and bleached Kraft cellulose pulp fibers that used as reinforcements in low density polyethylene (LDPE) with oleic acid in cold plasma conditions in order to enhance the interfacial adhesion between cellulose and matrix and to increase the dispersability. Before plasma treatment, fibers were impregnated with solutions of fatty acid, i.e. oleic acid (OA) (20% solution, in acetone). Then they treated the unbleached (UBP) and bleached (BP) Kraft cellulose pulp fibers in plasma at a P = 300 W, frequency of 13.56 MHz, pressure = 0.3–0.5 mm Hg, for 5 or 10 min. Composites containing up to 10 wt.% of untreated and modified cellulose pulp fibers with LDPE were prepared by melt mixing. The samples were characterized by processing behavior, mechanical and rheological properties, SEM, contact angle measurements, TGA and DSC. They found that when the modified pulp fibers were incorporated into composites matrix, the physical properties and thermal stability have been improved.

In 2013, Benitez A.N. et al. investigated the effect of physical and chemical treatments on the suitability of fiber from the Canary banana tree for used as reinforcement for polymers in injection molding processes. The fiber must be treated to improve their adherence to plastic matrices. This research sodium hydroxide and maleic anhydride were used to treat the fiber under different conditions of pressure and temperature. Treatment with maleic anhydride used for modify the surface of fiber via an esterification reaction with the surface OH groups, to yield ester functional groups, which were less polar than OH groups (maleic anhydride help to modify the hydrophilic character of fiber to make it compatible with the hydrophobic of the polymeric matrix. Treatment with alkali use for removed hemicellulose and lignin from the surface of natural fiber. In addition, treatment

under pressure efficiently eliminated the non-cellulosic substances. If NaOH and maleic anhydride were combined, it can both increase thermal stability and improve adhesion to polymer. From TGA result that the degradation temperature increased with increasing concentration of NaOH but when using 4 N NaOH has less improvement in degradation temperature than its drawbacks. The mechanical properties, the alkaline treatment influenced the mechanical behavior in negative manner. The conclusion, the best treatment to improve thermal stability and no significant decrease in mechanical properties was combination of 1 N NaOH and saturation pressure.

2.3 Conductive polymers

2.3.1 The History of Conductive Polymers

Conductive polymers were produced several decades ago, until now there are over 25 conductive polymer systems (Ateh DD *et al*, 2006). You can see them from the table 2.3 (Balint R., *et al.*, 2014). They collect the good properties of metals and conventional polymers the ability to conduct charge, great electrical and optical properties with flexibility in processing and ease of synthesis (Ateh DD *et al*, 2006). The conductivity can increase by “doping”.

Table 2.3 A list of conductive polymers and their abbreviations.

Polymer	Abbreviations
Polypyrrole	PPy
Polyaniline	PANI
Poly (3,4-ethylenedioxythiophene)	PEDT, PEDOT
Polythiophene	PTh
Polythiophene-vinylene	PTh-V
Poly(2,5-thienylenevinylene)	PTV
Poly(3-alkylthiophene)	PAT
Poly(p-phenylene)	PPP
Poly(p-phenylene-sulphide)	PPS
Poly(p-phenylenevinylene)	PPV
Poly(p-phenylene-terephthalamide)	PPTA
Polyacetylene	PAC
Poly(isothianaphthene)	PITN
Poly(α -naphthylamine)	PNA
Polyazulene	PAZ
Polyfuran	PFu
Polyisoprene	PIP
Polybutadiene	PBD
Poly(3-octylthiophene-3-methylthiophene)	POTMT
Poly(p-phenylene-terephthalamide)	PPTA

2.3.2 Doping

The doping is the process that introduces the charge carriers (polarons and bipolarons). The doping can happen into two ways 1) p-doping, where the polymer is oxidized and will have a positive charge 2) n-doping, where the polymer is reduced and will possess a negative charge. The amount of dopant and the type of dopant are related to the conductivity of polymer. Moreover, the type of dopant will affect the surface and bulk structure properties of polymer. The doping is reversible, so it can switch between conductive and insulating redox state (Balint R. *et al.*, 2014).

2.3.3 The Source of Their Conductivity

Conductive polymers can conduct charge due to the ease with which electrons jump within and between the chains of the polymer (Ghasemi Mobarakeh L. *et al.*, 2011). The polymers possess a conjugated backbone (Figure 2.8). Single and double bonds both contain a chemically strong, localized σ -bond, while double bonds contain a less strongly localized π -bond (Ravichandran R. *et al.*, 2010). The

p-orbitals in the π -bonds overlap each other, allowing the electrons to be more easily delocalized and move freely between the atoms. The other source of conductivity is the dopant. The polymer is synthesized in its oxidized, conducting form, and only in the presence of the dopant molecule (a negative charge) is the backbone stabilized and the charge neutralized (Wallace G. *et al.*, 2007). The dopant introduces a charge carrier into this system by removing or adding electrons from/ to the polymer chain and relocalizing them as polarons or bipolarons. When electrical potential is applied, the dopant starts to move in or out of the polymer, disrupting the stable backbone and allowing charge to pass through a polymer in the form of polarons and bipolarons (Figure 2.9) (Balint R. *et al.*, 2014). From figure 2.9, it can easily explain in steps that start from (A) The dopant removes or adds an electron from/to the polymer chain, creating a delocalized charge. (B) It is energetically favourable to localize this charge and surround it with a local distortion of the crystal lattice. (C) A charge surrounded by a distortion is known as a polaron (a radical ion associated with a lattice distortion). (D) The polaron can travel along the polymer chain, allowing it to conduct electricity.

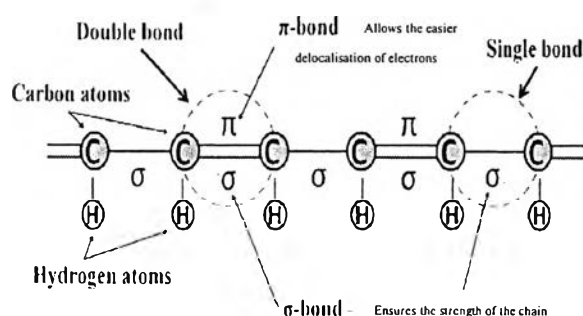


Figure 2.8 A simplified schematic of a conjugated backbone: a chain containing alternating single and double bonds.

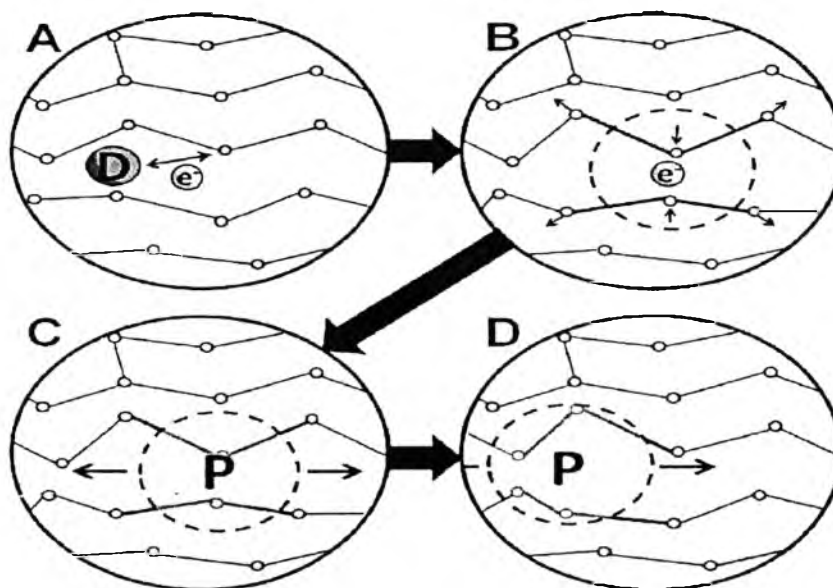


Figure 2.9 A simplified explanation of the electrical conductivity of conducting polymers.

2.3.4 Polyaniline (PANI)

Polyaniline (PANI) has become one of the most fascinating conductive polymer due to high stability, low cost and easy methods of synthesis. PANI has many applications such as sensor, anticorrosive coatings, batteries, artificial muscles, fuel cells, supercapacitors and electrocatalysts. It exists in various forms depend on its oxidation level: the fully oxidized pernigraniline base, half-oxidized emeraldine base and fully reduced leucoemeraldine base (Balint R. *et al.*, 2014) as shown in Figure 2.10. Only intermediate oxidation state, the protonated emeraldine form is conductive. The fully reduced leucoemeraldine and fully oxidized pernigraniline are insulating materials (Li *et al.*, 2009).

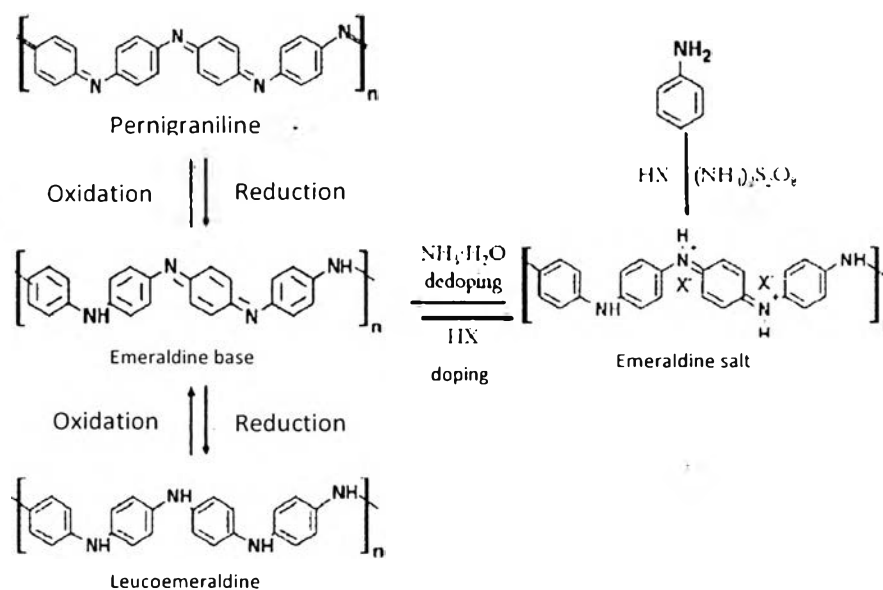


Figure 2.10 Diagram showing the chemical structure, synthesis, reversible acid/ base doping/ dedoping, and redox chemistry of PANI.

PANI in emeraldine base form has lower conductivity than salt form that created by modifying the base's oxidative state (Bettinger CJ. *et al.*, 2009). The conductivity increase from base to salt form because the polymer's molecular structure (Ghasemi-Mobarakeh L *et al.*, 2009); in its base state the polymer chains are coiled, when it becomes salt form the additional positive charges in the polymer repel each other extending the chains. The extended chain form electrons are easier to delocalize, so the conductivity increase.

2.3.5 Literature Reviews on Conductive Polymers

In 2012, Kunzo P. *et al.* studied palladium-free hydrogen sensor by using oxygen-plasma-treated polyaniline thin film. They used oxygen-plasma for treatment, which enhanced the sensitivity to hydrogen and shortened the sensor response and recovery times. Moreover, the sensor that treated with this method can use at several room temperature application.

In 2012, Shao D. *et al.* modified polyaniline on multiwalled carbon nanotube (MWCNTs) magnetic composites for removal of Pb(II) by using plasma

induced polymerization technique. This modify enhanced MWCNT absorption capacity because the amine and imine functional group of polyaniline had strong affinity with Pb(II) ions. After MWCNT-treated with polyaniline the surface was rougher than MWCNT (Figure 2.11), so it was better attach with other functional groups.

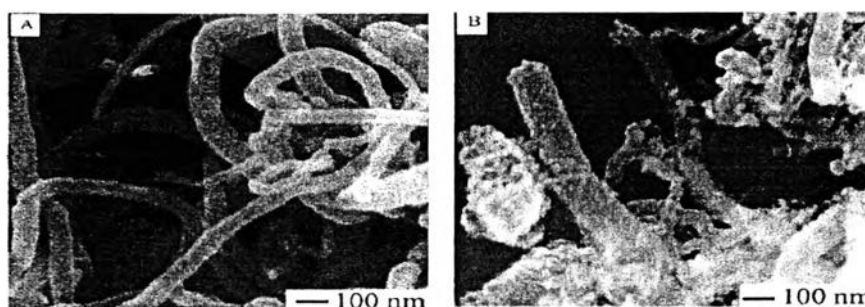


Figure 2.11 SEM images of MWCNTs (A) and PANI/MWCNTs (B).

In 2013, Lin Y.C. *et al.* enhanced conductivity and thermal stability of conductive polyaniline/graphene composite synthesized by in situ chemical oxidative polymerization with sodium dodecyl sulfate (SDS). They varied concentrations of SDS solution. They found that the conductivities of PANI/graphene composites are strongly dependent on the content of SDS. The SDS act as a dopant that can be incorporated to affect the π - π^* transition of the PANI structure. Therefore, SDS can improve the conductivity of PANI/graphene composites.

In 2014, Bober P. *et al.* prepared polyaniline-silver by 2 ways: (1) by the oxidation of aniline with silver ions (2) by the reduction of silver ions with polyaniline. When the content of silver increasing, the conductivity also increasing. This research reported that the conversion of conducting polyaniline salt to a non-conducting polyaniline base may be associated with an increase of composite conductivity.

2.3.6 Polymerization of Aniline

2.3.6.1 Oxidative Polymerization

Oxidative polymerization can be used for synthesis various class of monomer. The monomers used in oxidative polymerization should have electron donor properties and high oxidation tendency such as aromatic, amines, phenols, thiophenols, aromatic hydrocarbon and heterocycles (Higashimura and Kobayashi, 2004). Oxidation of monomer occurs under applied potential or the action of inorganic (or organic) oxidizing agent. The initiation of polymer growth takes place when the cation or cation radical sites are formed in monomer (polymer) molecule. There are many types of linkage between monomer units such as head-to-head, tail-to-tail and head-to-tail.

2.3.6.1.1 The Mechanism of Aniline Polymerization

The polymerization of aniline can do by electrochemical and chemical method. There are two ways for chain formation. The first, the recombination of cation radical oxidation sites. This growth process is classed as polycondensation. The second, the electrophilic substitution; in the case of aniline, oxidized nitrogen in the structure attacks another aniline molecule of phenyl ring and substitutes one proton of the ring (Figure 2.12 and 2.13). The ring and nitrogen in aniline structure lose one proton, so monomer units bind each other and become longer chain.

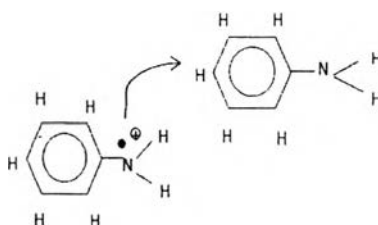


Figure 2.12 Electrophilic substitution reaction.

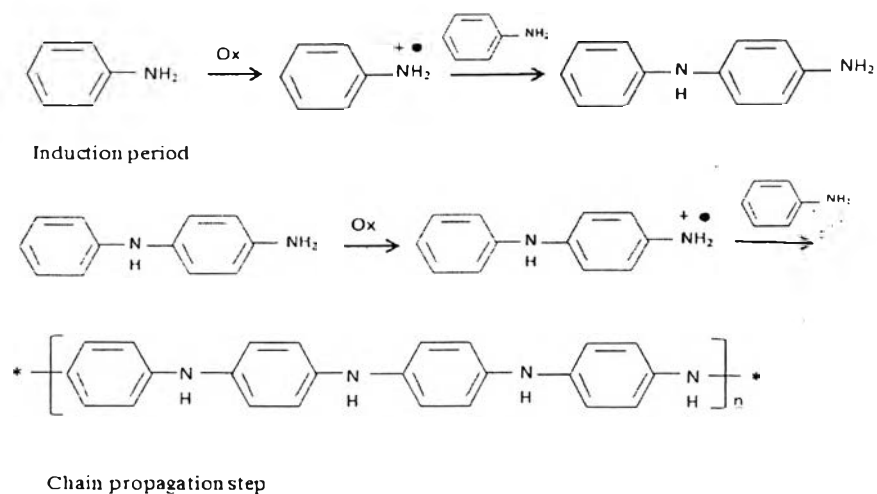


Figure 2.13 Aniline oxidative polymerization.

2.3.6.1.2 The Active Site of Polymerization

The active site formed at the end of chain attacks the monomer molecule. The attack occurs at a hydrogen atom in the aromatic ring and results in replacing hydrogen by a polymeric fragment. Addition of new monomer units lead to chain propagates (Sapurina I.Y. and Shishov M.A., 2012).

2.4 Plasma

2.4.1 Basic Principle of Plasma

There are four states of plasma that referred to the state of matter: solid, liquid, gas and plasma (Lieberman *et al.*, 2005). Plasma is ionized gas. The components of plasma are positive and negative ions, electrons, as well as free radicals. The degree of ionization can vary from fully ionized gas (100%) to partially ionized gas (low value). The free charge particles in plasma system move in random directions, on the average, electrically neutral ($n_e \approx n_i$) (see Figure 2.14).

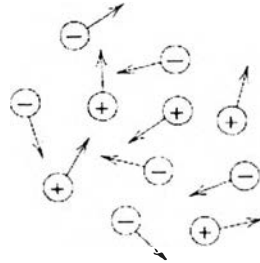


Figure 2.14 The movement of free charge particles in plasma system.

Plasma can take place in nature. The most common natural plasma is lightning and auroras borealis (Fridman and Kennedy, 2004). However, plasmas can be generated artificially at laboratory levels for practical applications. It is required a continuous source of energy to generate and sustain a state of matter. The electrical energy usually used for operating and sustaining artificial plasmas and is often referred to as ‘discharges’. Figure 2.15 shows a simple discharge. It consists of a voltage source that drives current through a low-pressure gas between two parallel conducting plates or electrodes. The gas “breaks down” to form plasma, usually weakly ionized which is the plasma density only a small fraction of the neutral gas density (Lieberman and Lichtenberg, 2005).

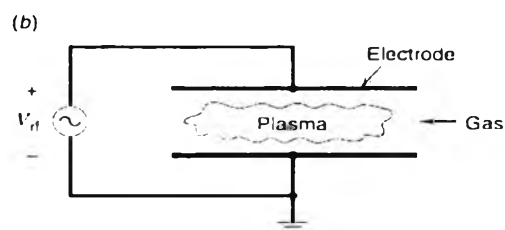
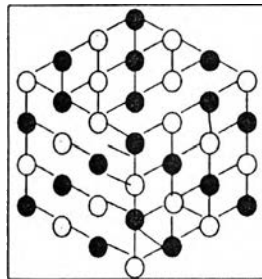


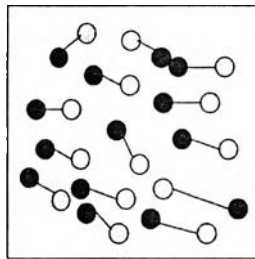
Figure 2.15 A simple discharge.

The plasma forming has four states (Lieberman, and Lichtenberg, 2005).

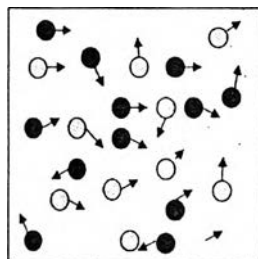
1. Solid state: At very low temperature, matter is in solid state with the atoms arranged in well-organized.



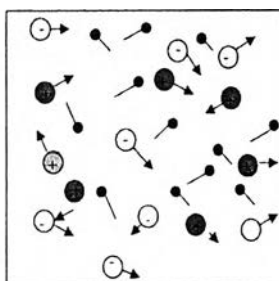
2. Liquid state: At above critical value temperature, solids will melt and become a liquid. The grid of atom is broken, but molecular bonds are maintained.



3. Gas state: A liquid is heated above a second critical temperature and become gas. The molecules in the gas decompose to form a gas of atoms that move freely in random directions.



4. Plasma state: If the temperature is continue increased, then the atoms can change into freely moving charged particles (electrons and positive ions), and the substance enters the plasma state.



Normally, electrons are generated from plasma that can make the gas conductive. These electrons obtain energy from the electric field and further ionize, excite, and dissociate gas molecules via energy transfer during collisions. This makes plasmas very reactive. The plasma process has higher temperatures and energy densities in comparison with other chemical processes, that make it is interesting for many applications. The plasma process can be operated at a wide range of pressures with different electron temperatures and densities.

2.4.2 Solution Plasma Process (SPP)

Solution plasma process (SPP) is a liquid-phase plasma which widely utilized in nanomaterial synthesis, surface modification, water treatment, sterilization, recycling of rare metals and decomposition of organic compound. The variety of plasmas can be generated choosing the combinations of solvents and solutes in solutions. SPP can be used supercritical fluids aqueous, liquid nitrogen and non-aqueous solutions etc. This process can produce various kinds of active species during discharge in aqueous solution such as active radical (H^{\cdot} , O^{\cdot} , OH^{\cdot} , HO_2^{\cdot} , etc.), high energy electrons as well as visible light. The different active species are specifically used as the source of many kinds of reaction. For example, H^{\cdot} is subjected to be an initiator for the reduction process demonstrated in the nanoparticles synthesis. O^{\cdot} and OH^{\cdot} are the dominated radicals for oxidation process

in the decomposition of organic compounds. There are many parameters that effect on process efficiency such as solution conductivity, the type of electrodes and the distance of electrode. SPP can be operated in a high reaction rate under lower-temperature with greater chemical reaction. The molecular in liquid phase is higher than gas phase.(Takai, 2008)

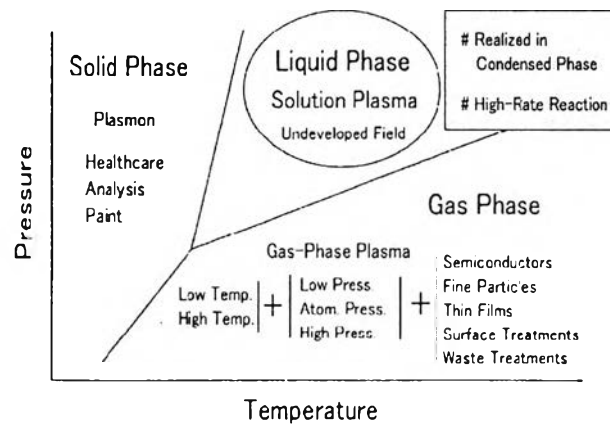


Figure 2.16 Three categories of plasma corresponding to the pressure–temperature relationship of three phases.

The structure of the solution plasma is described in Figure 2.17, which the plasma is generate in the center and surround by the gas phase, the liquid phase also cover the gas phase. So, there are two interfaces: plasma/gas and gas/liquid.

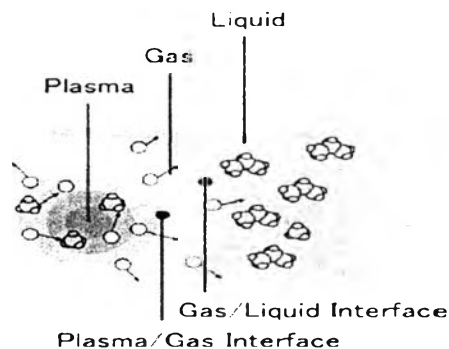


Figure 2.17 The reaction model of solution plasma.

2.4.2.1 Solution Plasma Set Up

Figure 2.18 shows the setting of solution plasma system. The pulsed electric discharge was generated between two electrodes, made of tungsten, using a high frequency bipolar pulsed DC power supply. The two electrodes, of which the distance is 0.5 mm, are set inside a glass reactor where polymer solution is filled. Once the power is applied, the plasma was generated.

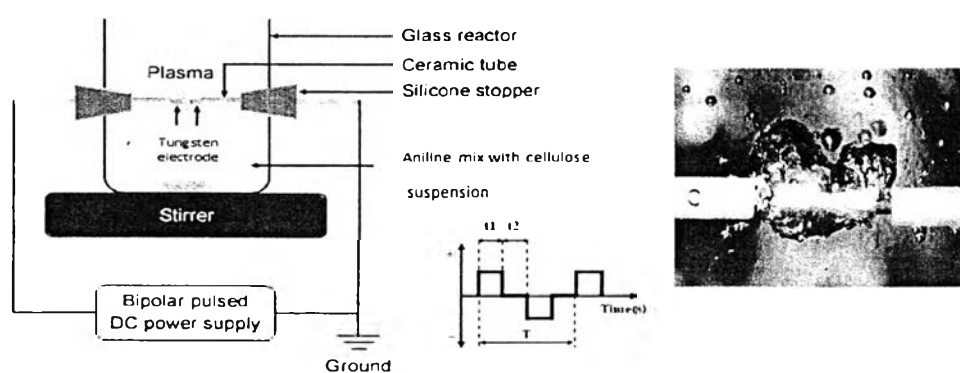


Figure 2.18 Solution plasma experimental set up (Kang J. *et al.* (2013)).

2.4.3 Literature Reviews on Polyaniline by Oxidative Polymerization

In 2009, Lee C.W. *et al.* investigated the effect of initiator dosage and molecular oxygen on synthesis and properties of nanostructured polyaniline. The results showed that polymerization yield of PANI can be improved without any detrimental effect on molecular weight by increasing the APS/aniline feed ratio.

In 2011, Kulkarni S.B. *et al.* prepared nanostructure polyaniline thin film by oxidative chemical polymerization onto glass and stainless steel substrates (Figure 2.19). In addition, the study of physico-chemical characteristics with XRD, FTIR, SEM, surface wettability, optical and electrical techniques confirmed preparation of amorphous, nanostructure, wide optical band gap and low resistivity of p-type hydrophilic PANI thin film.

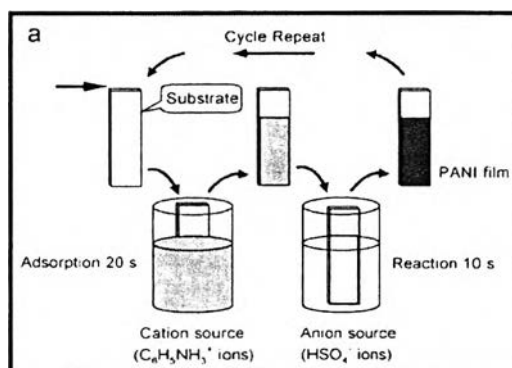


Figure 2.19 The schematic of SILAR method for deposition of PANI on the substrate.

In 2012, Lee B.H. *et al.* polymerized bacterial cellulose/polyaniline nanocomposite films by chemical oxidative polymerization. They found that bacterial cellulose was completely encapsulated with polyaniline spherical spheres as shown in the figure 2.20. The oxidant and dopant also had effect on the electrical conductivity and thermal stability of the films.

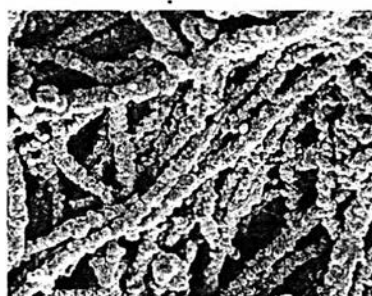


Figure 2.20 FE-SEM images of BC/PANI.

In 2012, Ragupathy D. *et al.* synthesized electrically conductive polyaniline nanostructure (PANI-NS) by oxidative polymerization method. In this study, they used cetyl trimethyl ammonium bromide (CTAB) as surfactant to improve the properties of PANI with respect to the yield, stability solubility and processability. The conductivity of PANI-NS was higher than pristine PANI due to

large aspect ratio, surface to volume and good dispersion of 1D nanostructured PANI.

In 2012, Wang H. *et al.* synthesized bacterial cellulose nanofiber-supported polyaniline nanocomposites with flake shaped morphology as supercapacitor electrodes via in situ polymerization. They can achieved outstanding electrical conductivity as high as 5.1 S/cm with well-controlled composite morphologies.

In 2013, Guo B. *et al.* prepared polyaniline nanofiber by high gravity chemical oxidative polymerization (HGCOP) in a rotating packed bed (RPB). When it increased of APS/aniline ratio, the products became shorter and thicker. The conductivity and yield of PANI dramatically increased with the ratio of APS/aniline at first, but an inflection point showed up at the ratio being 0.5. The conductivities of PANI decreased when the molar ratios of APS/aniline were too high and too low.

In 2013, Liu X. *et al.* researched on the detoxification by convert from highly toxic Cr(VI) to less toxic Cr(III) using polyaniline/cellulose fiber composite. The preparation of polyaniline/cellulose fiber composite: after adding hydrogen chloride solution fibers, under continuous stirring, aniline and ammonium persulfate were added. The in situ polymerization reaction was stopped after a given time, and the mixture was filtered. Then it washed by tap water. They found that reaction temperature, ammonium persulfate/aniline ratio, hydrogen chloride concentration, reaction time and aniline dosage had effect to the efficiency of detoxification.

In 2013, U.M. Casado *et al.* prepared and characterized the conductive nanostructured particles based on polyaniline and cellulose nanofiber. They used the sonochemical method to synthesis PANI fibers. Aniline was doubly distilled. A 0.2 mol/L ANI solution in HCl (1 mol/L) were prepared in a beaker and sonicated. Then 0.2 mol of APS were dissolved in 100 ml HCl (1 mol/L) and dropwise added to ANI containing beaker (25 °C, 4 h). After that, the acid suspension was dialyzed using the membrane until the dialyzed water become colorless. PANI was doped in HCl solution, then washed with distilled water and freeze-dried to yield a green powder. The synthesis of PANI coated nanocellulose (PANI-NC) fibers, the nanocellulose fiber suspension (1g/L) was previously

dispersed in ANI solution. The result from FTIR spectra, the most peak of nanocellulose could not be observed in PANI-NC because large amount of PANI that was deposited on the cellulose sheet. The TGA showed that the onset decomposition temperature of first step was slightly increase in PANI-NC due to increasing in crystallinity and also confirmed with XRD. The electrical conductivity of PANI-NC was higher than PANI. The electrical conductivity of the longer fibers will be higher than that of particles are aggregate.

2.4.4 Literature reviews on plasma

In 1997, Cruz G.J. *et al.* synthesized polyaniline film by using radio frequency (RF) glow discharges with stainless-steel electrodes. There were two parts, the first part was synthesis of PANI alone, the second part was synthesis PANI with I₂ as the dopant. The thin film formed on the internal surfaces of the reactor.

In 2008, Tiwari A. and Singh V. used microwave-induced synthesis of electrical conducting gum acacia-graft-polyaniline. At high microwave power can generate more monomer and macro radicals the result in high %grafting. When increased the HCl concentration, %grafting also increased. Because more protonation of the aniline monomer which accelerated the generation of PANI ion radicals.

In 2011, Pootawang P. *et al.* used solution plasma for template removal in mesoporous silica by vary pH of discharge solution (pH3, pH7 and pH11) and discharge time (1-15 min). The various pHs led to the change of solution conductivity, at pH3 and pH11 solutions can generated higher current density and number of the active species. The conductivity tended to be increased as the increase in discharge time resulting from the molecule dissociation and ionization. The transmission electron microscope (TEM) images showed that the adjustment of pH and discharge time did not change the structural morphology of the mesopore structure.

In 2012, Pootawang P. *et al.* studied the rapid synthesis of ordered hexagonal mesoporous silica and their incorporation with Ag nanoparticles (AgNPs) by solution plasma (SPP). When compare between SPP method and conventional sol-gel method, SPP provided the new advanced benefit to synthesize mesoporous silica with higher surface area and pore diameter as short time process. In addition,

the increased in Ag loading resulted in decrease in surface area with insignificant variation in the pore diameter of mesoporous silica.

In 2013, Bratescu M.A. *et al.* synthesized the gold bimetallic nanoparticles with various metal composites (3d, 4d, sp divalent or trivalent categories) by using solution plasma process (SPP). SPP is environmental friendly because SPP is not use gold precursor or chemical reducing agents.

In 2013, Hu *et al.* fabricated the PtAu alloy clusters using solution plasma sputtering and supporting on carbon. Solution plasma sputtering synthesis nanoparticles in solution by the rapid energetic radicals bombardment under atmospheric pressure. The composition and size of the alloyed nanoparticles were dependent on the discharge conditions such as discharge voltage/ discharge current, pulse frequency, pulse width, the surrounding solvent and solvent temperature.

In 2013, Kang J. *et al.* studied synthesis of structure-controlled carbon nano spheres (CNSs) by solution plasma process using benzene as a carbon precursor. They found that average diameters of CNSs increased from 20 to 100 nm when the pulse frequency of bipolar power supply adjusted from 25 to 65 kHz. From TEM images showed that CNSs synthesized at 25-50 kHz consisted of amorphous carbon and at 65 kHz were composed of continuous short range graphite with turbostratic structure.

In 2013, Kang J. *et al.* synthesized noble nanoparticles (NPs) support on carbon nanoballs (CNBs) using one-step solution plasma process (SPP) at atmospheric pressure. CNBs are formed using benzene as a carbon precursor and gold (Au) or platinum (Pt) nanoparticles are generated via sputtering from metal electrodes. CNBs are in form of spherical with uniform sizes and excellent pore structure.

In 2013, Prasertsung I. *et al.* found that ethanol can provide more free radical than water in solution plasma process. In addition, when the concentration of ethanol increased, the hydroxyl radicals also increase.

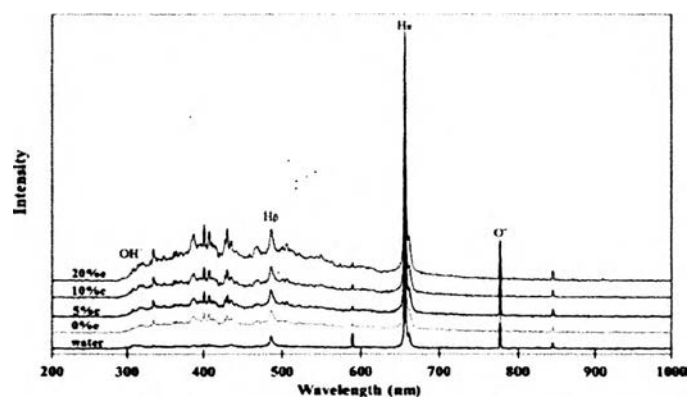


Figure 2.21 OES spectrum of pure water and plasma-treated gelatin solutions containing various concentrations of ethanol after treated for 1 min.

In 2014, Saito G. *et al.* synthesized ZnO nanoflowers using solution plasma. The temperature and agitation effected on product morphology (ZnO nanoflowers, amorphous ZnO nanospheres and metallic Zn particles) and composition. ZnO nanoflowers were synthesized at a high electrolyte temperature and no agitation (Figure 2.22a). In the case of without agitation, the produced particles partially melted or vaporized. The ZnO then ionized to form $\text{Zn}(\text{OH})_4^{2-}$, and ZnO nanoflowers grew by precipitation from the ions. On the other hand, both amorphous ZnO nanospheres and spherical metallic zinc particles occurred by agitation (Figure 2.22b). The thickness of the hydrothermal area decreased. The produced particles were immediately cooled, without melting or ionization, to form Zn particles and amorphous ZnO. The 700 °C annealed ZnO nanoflowers had higher photocatalytic activity than the others due to their highly crystalline structure and high surface area.

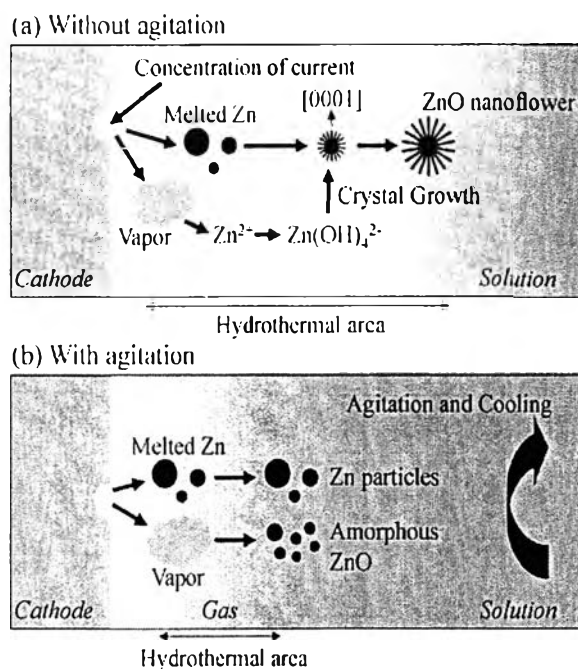


Figure 2.22 Formation mechanisms of the products (a) Without agitation (b) With agitation.

2.5 Metals

In recent time the metal particles such as silver, gold, copper, zinc and lead have interesting properties in many applications. Silver often naturally occurs in sulphide deposits along with copper, lead and zinc. Silver is a precious metal, also used in jewelry, currency coins, solar panels, water filtration. In addition, silver can be used in industries in electrical conductors and in catalysis of chemical reactions. On the other hand, the dilute silver nitrate solutions and other silver compounds can be added to wound-dressings, bandages and medical instruments.

Table 2.4 Electrical conductivity of metals

(<http://metals.about.com/od/properties/a/Electrical-Conductivity-In-Metals.htm>)

Metals	Electrical conductivity (S/m)
Silver	6.30×10^7
Copper	5.98×10^7
Gold	4.52×10^7
Copper	5.80×10^7
Zinc	1.682×10^7
Lead	4.87×10^6

2.5.1 Literature Reviews on Silver Particles

In 2005, Khanna P.K. *et al.* synthesized silver/polyaniline nanocomposite by an in situ photo-redox mechanism. The UV lamp used as radiation source (long wavelength (365 nm) and short wavelength (254)). The wavelength 254 nm made the reaction complete faster than wavelength 365 nm. Thermogravimetric analysis (TGA) showed that the silver/polyaniline nanocomposites have higher degradation temperature than only polyaniline.

In 2008, Ma P.C. *et al.* studied the effect of carbon nanotube (CNT) with silver nanoparticles (Ag-NPs) in order to increase the electrical conductivity of carbon nanotube. Silver decorated carbon nanotubes (Ag@CNTs) can be used as effective conducting filler in epoxy resin to form the electrically conductive polymer composites. The results found that composites of silver decorated carbon nanotubes have electrical conductivity more than four orders of carbon nanotubes.

In 2009, Choudhury A. prepared polyaniline/silver nanocomposites by in situ oxidative polymerization with difference concentrations of silver nanoparticles. From the TEM images showed that the size of particles increase when the silver concentration increase as shown in figure 2.23. In addition, the AC conductivity of polyaniline/silver nanocomposite is in the range $1.12-1.83 \times 10^{-2} \text{ S cm}^{-1}$, which is dramatically higher than pure polyaniline ($10^{-4} \text{ S cm}^{-1}$).

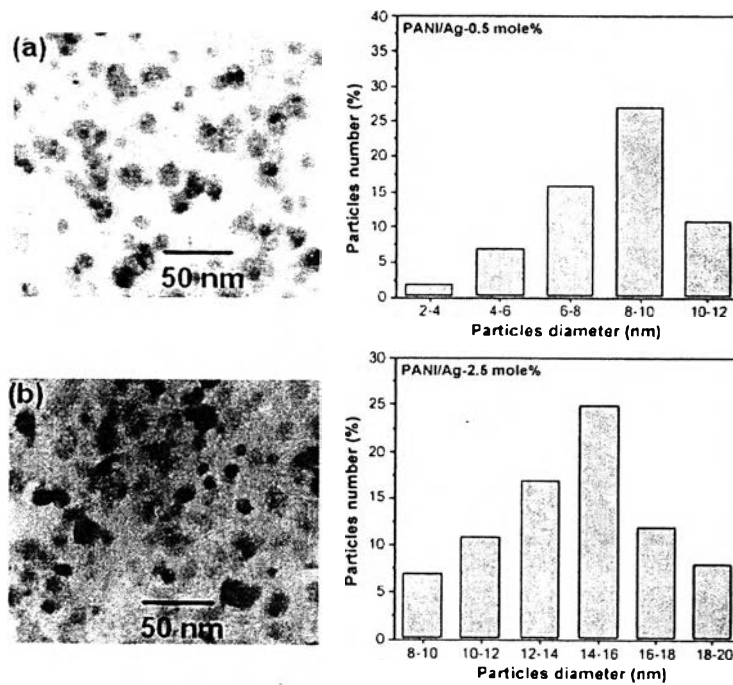


Figure 2.23 TEM images and particles size histograms of silver nanoparticles with concentration a) 0.5 mol% and b) 2.5 mol%.