# CHAPTER 2: LITERATURE REVIEW

## 2.1 Biopolymers

Biopolymers are organic polymers which are present in, or created by, living organisms (Chandra & Rustgi, 1998) (Kumar, Srivastava, Galaev, & Maltiasson, 2007) (Meyers, Chen, Lin, & Seki, 2008). They are naturally occurring materials formed in nature during the life cycles of green plants, animals, bacteria and fungi. Biopolymers include the polysaccharides such as cellulose, starch, the carbohydrate polymers produced by bacteria and fungi and animal protein based biopolymers such as wool, silk, gelatin and collagen. These polymers are renewable, sustainable and can be carbon neutral. They have the potential to cut carbon emissions and reduce $CO_2$ quantities in the atmosphere because the $CO_2$ released when they degrade can be reabsorbed by crops grown to replace them, making them close to carbon neutral. Biopolymers have the potential to avoid both end-of-life disposal problems and future problems associated with scarcity of fossil origin raw materials. The biopolymers that are currently receiving the most attention for industrial applications are polysaccharides like cellulose and starch. Cellulose is the main component of plant cell walls and starches are carbohydrates stored in plant tissues and both these polysaccharides are made up of a basic unit that is glucose.

Starch is the major carbohydrate reserve in plants tubers, stem and seed endosperm where it occurs in the form of semi-crystalline granules, which vary in size and composition from plant to plant. Variations in granules size (~1-100 μm in diameter), shape (round, lenticular, polygonal), size distribution (uni- or bimodal), association as individual (simple) or granule clusters (compound) and composition (α-glucan, lipid, moisture, protein, and mineral content) reflect the botanical origin of the starches. Starch properties depend on the physical and chemical characteristics such as granule size and size distribution, amylose/amylopectin ratio and mineral content. Starch is hygroscopic because it consists of loose amorphous regions that are interspersed with highly regular crystalline regions, resulting from the formation of hydrogen bonds between the starch molecules. Starch is characterized by two primary polysaccharides, amylose and amylopectin which represent approximately 98-99% of the dry weight, with the remainder comprising small amounts of lipids, minerals and phosphorus in the form of phosphates. The ration of the two polysaccharides varies according to the botanical origin of the starch. Both consist of polymers of glucopyranose molecules, but differ in structure and functional properties. Amylose and amylopectin molecules are complex structures consisting of crystalline and amorphous areas. Starch granules exhibit a so called onion like structure with amorphous and crystalline layers interspersed between each other. The semi crystalline layers consist of ordered regions composed of double helices formed by short amylopectin branches. These are known as the crystalline lamellae. The amorphous regions of the semi crystalline layers and amorphous layers are composed of amylose and branching points of amylopectin (Bullona, Colonna, Planchot, & Ball, 1998) (Jenkin & Donald, 1995) (Liu, Yu, Wang, Li, Chen, & Li, 2010).

Amylose consist of a relatively long, mostly linear α-glucan containing around 99% α-(1,4)- D-glucose residues and has a molecular weight of approximately $1 \times 10^5 - 1 \times 10^6$ (Tester, Karkalas, & Qi, 2004). Figure 2.1 shows the chemical structure of amylose in starch. Amylose is mostly amorphous, soluble in hot water and forms the inner portion of the starch (Briassoulis, 2004) (Liu, Xie, Yu, Chen, & Li, 2009).

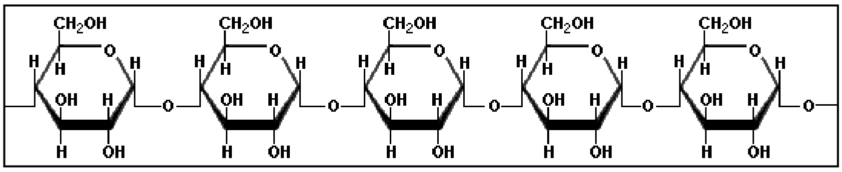

Fig. 2.1 Chemical structure of amylose (Zamora, 2005)

Amylopectin, the major component of starch, is a much larger molecule than amylose with a molecular weight of approximately $1 \times 10^7 - 1 \times 10^9$ and a heavily branched structure built from about 95% of α-(1,4) D-glucose and 5% α-(1,6) D-glucose linkages (Bullona, Colonna, Planchot, & Ball, 1998). Unlike amylose, there is variation with respect to the unit chain lengths and branching patterns. Amylopectin unit chains are short and forms highly branched tree-like structure and are the main crystalline component in granular starch. Figure 2.2 depicts the chemical structure of amylopectin. Amylopectin forms the outer portion of the starch granule and it is insoluble in water.

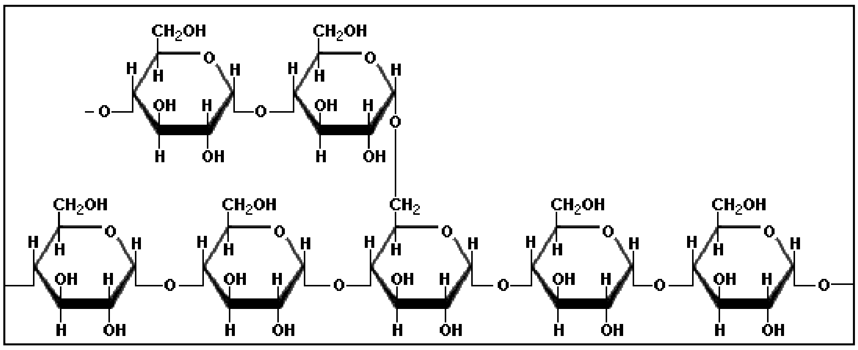

Fig. 2.2 Chemical structure of amylopectin (Zamora, 2005)

## 2.2 Types of Starches

### 2.2.1 Tuber or Roots

Root and tuber crops are grown throughout the world in temperate, hot and humid regions. The root and tubers comprises of the potato, turnip, carrot and onion, with different plants yielding arrowroot, yam and tapioca. The main nourishment of these plants is stored up almost entirely in the form of carbohydrates, chiefly starch. The tuber and roots contain 70-80% water, 16-24% starch and quantities lower than 4% of proteins and lipids (Hoover, 2001). The crops starches are characterized by their low lipid content (1%) which does not have a pronounced effect on the functional properties (Moorthy, 2002).

Most of the tuber and root starches contain significant amounts of mono phosphate esters covalently bound to starch (Hoover, 2001). Mono phosphate esters increase the starch paste clarity and viscosity. The granule size of these crops is variable and ranges from 1 to 110 μm depending on the starch source. Most of the granules are oval, although, round, spherical, polygonal and irregularly shaped granules are also found. The starches consist of simple granules with the exception of cassava and taro starches, which appear to be a mixture of simple and compound granules (BeMiller & Whistler, 2009).

### 2.2.2 Seeds

Seed or cereal crops are grasses that produce edible grains. Wheat, rice, corn, barley and sorghum are a few of the most important cereal crops grown in the world. The starch of the cereal grain is found within the endosperm part of the seed. Starch is laid down as granules in the cereal seed to act as an energy reservoir for the growing seedling. The starch extracted from grain contains about 75% starch, 12% protein, 2% fat and smaller quantities of vitamins and minerals (Eliasson & Tatham, 2001). The granule size of cereal starch ranges from 2 to 100 μm depending on the plant species.

## 2.3 Natural Fibers

Natural fibers are subdivided based on their origins, coming from plants, animals and minerals. Plant fibers are composed of cellulose fibrils embedded in lignin, hemicellulose and pectin matrix while animal fibers consist of proteins. During the last decade, researches have been done involving the usage of natural plant fibers as load bearing constituents in composite materials. Below is a list of the advantages and disadvantages of using plant fiber as part of a composite:

Advantages:

1. Biodegradability
2. Low cost
3. Low density
4. No abrasion to processing equipment
5. High degree of flexibility
6. Good thermal properties
7. Carbon dioxide neutral when burned

Disadvantages:

1. Hygroscopic
2. Strong polar character which creates incompatibility with most polymer matrices
3. Low impact resistance
4. Limited processing temperature to about 200°C
5. Low dimensional stability (shrinkage and swelling)
6. Low microbial resistance (susceptibility to rotting)

In order to eliminate or improve the natural disadvantages aspects of using plant fibers as reinforcement in the composite and to understand the mechanical properties and durability of the fibers, properties of the individual chemical components and history of the fiber must be known. The characteristics properties of the plant fibers that makes it efficient does not only depend on cellulose content and low microfibrillar angle but also on the quality of plant location, the age of the plant, and the preconditioning processing methods adopted for the extraction of the fibers.

Natural plant fibers can be considered a good competitor against conventional reinforcing fibers such as glass or carbon because in the long run the usage of natural fiber benefits humankind.

### 2.3.1 Classification of Plant Fibers

#### 2.3.1.1 Bast and Core Fibers

Natural plant fibers can be categorized into several divisions such as bast plant fibers (kenaf, roselle, ramie, jute, hemp, and papyrus), hard fibers (sisal, abaca, and raffia), grass fibers (bamboo, bagasse, banana stalk, and Napier grass), straw fibers (rice, corn, and wheat), fruit fibers (coconut) and etc. Bast fibers are obtained from fibrous plant stems. They are found in the inner part of the stem and typically account for less than 30% of the stem depending on the species of the bast plant (Xanthos, 2000). All bast fibers are cellulosic fiber because the main component is cellulose. Structural and chemical differences between these bast fiber plants results from the different chemical contents. Apart from cellulose, hemicellulose, lignin and pectin are also the basic chemical component in bast fibers. The lignin, hemicelluloses, and pectins collectively function as matrix and adhesive, helping to hold together the cellulosic framework structure of the natural plant fiber. These hydroxyl containing polymers are distributed throughout the bast fibers. Figure 2.3 depicts the cross section view of the bast and core fiber plant stem.

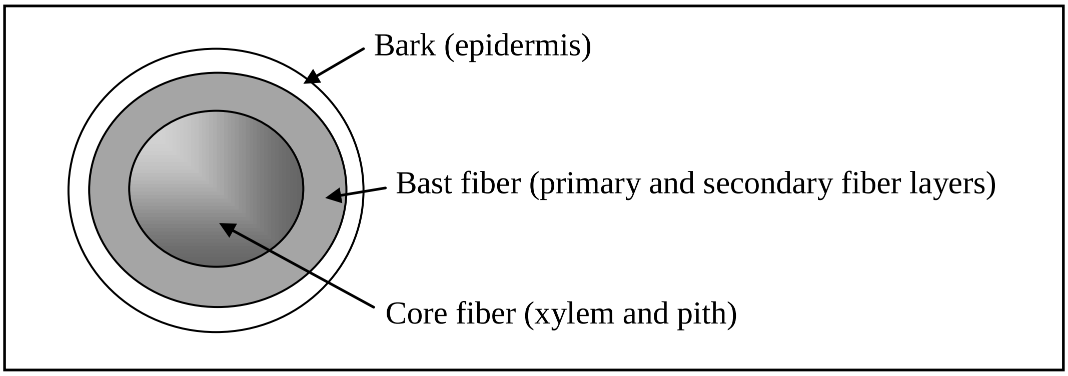

Fig. 2.3 Cross section view of bast and core fiber plant stem.

A fiber plant stem consist of a bark layer, a bast layer and a stem core. The bark layer or the epidermis is a thin skin that holds the bast fiber bundles and protects the whole plant stem. The bast layer is made up of three distinct layers, the secondary layer being by far the thickest and the most important in determining the mechanical properties of the fiber (Prasad, 1989). The stem core fiber consists of two parts that is the xylem and pith (Chen & Liu, 2010). The core fiber is mainly composed of short fibers and is a highly porous material. Bast fiber have a better physical structure than core fibers because of the high aspect ratio and this also makes bast fiber less processable than the core fiber. The bast layer is important in determining the mechanical properties of the fibers because it consists of a series of helically wound cellular microfibrils formed from long chains of cellulose molecules. These long chains of crystalline cellulose molecules are embedded in an amorphous matrix of lignin, hemicellulose and pectin. Natural bast plant fibers also contain lesser amount of additional components including low molecular weight components such as waxes and oils and inorganic matter (ash). Bast fibers are long, continuous fibers that support the main structural framework of the plant.

Most of the bast fibers obtained from commercially grown natural plant are processed for use in making carpets as in carpet yarn, in geotextile (netting and matting), hessian and burlap, paper, sacks, etc. These fibers are also used in composite boards as furniture materials, automobile door panels and headliners.

#### 2.3.1.2 Grass Fibers

Grasses come in a vast range of sizes and types, ranging from lawn grass to corn, sugarcane, rice, bamboo, Napier and etc. The fibers obtained from grasses are strong and fibrous but because of limited availability or processing difficulties, most of these fibers (except sugarcane bagasse) have not been widely used as commercial fibers for industrial use. Naturally, grass stem, called culms, grow up from the base of the plant and are mostly hollow, cylindrical, except at the nodes or joint where the stem segments join together (Metcalfe, 1960) (TAPPI (Technical Association of the Pulp and Paper Industry) T 259, 2009). The stem of grasses is built up essentially from the parenchymatous tissue with the vascular bundles embedded in it. In grass stem, the parenchyma tissue contains the fiber strands. All fiber cells in the stem are axially oriented within the length parallel with the stem. There are no cells for radial support like the fiber in bast plants. The vascular bundles situated in the middle of the stem run from root to the leaves and their function is to transport water and food and to give rigidity to the plant. The outermost layer of the stem is built up of the epidermis (Pfaffli, 1995). Grass fibers contain the same chemical components such as cellulose, hemicellulose, lignin and pectin as bast fiber but in different quantities depending on the plant species. Fiber from grasses like bamboo and pandan are processed and weave into baskets, containers, mats, and decorative items.

### 2.3.2 Main component of natural fibers

#### 2.3.2.1 Cellulose

Cellulose is the most common organic compound on Earth. About 30% of all plant matter is cellulose. Cellulose is the major framework component that provides strength, stiffness, and structural stability for plant fibers. It differs in some respect from other polysaccharides produced by plants because its molecular chain is linear and long, consisting of only one repeating unit, cellobiose, and occurs in a crystalline state. The basic unit, cellobiose, is composed of two molecules of glucose (Park, Baker, Himmel, Parilla, & Johnson, 2010). Figure 2.4 shows the chemical structure of cellulose.

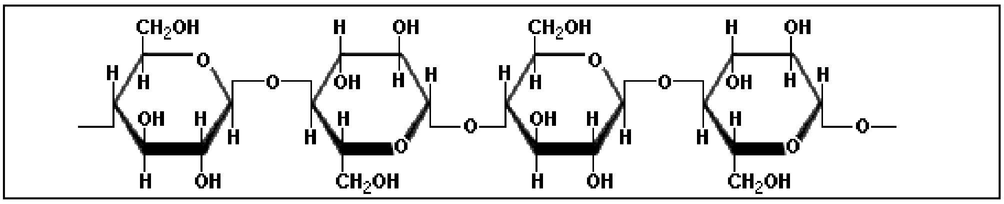

Fig. 2.4 Chemical structure of cellulose (Zamora, 2005)

Cellulose is a high molecular weight polymer consisting of D-anhydroglucose ($C_6H_{11}O_5$) repeating units joined by 1,4-β-D-glucosidic linkages. The degree of polymerization of cellulose is around 10,000 (John & Thomas, 2008). Each repeating unit of cellulose contains three hydroxyl groups. These hydroxyl groups and their ability to form intra- and intermolecular hydrogen bond play a major role in directing the crystalline packing. Cellulose is a highly crystalline polymer because unlike starch, no coiling or branching of molecule occurs, so the cellulose molecule adopts an extended and rather stiff-like conformation. Several types of crystalline structure of cellulose are listed in Table 2.1.

Table 2.1. Crystalline structure of cellulose (French & Johnson, 2007)

| | |
|---|---|
| Cellulose I (cellulose $I_\alpha$) | Produced by bacteria and algae |
| Cellulose I (cellulose $I_\beta$) | Produced by plants and wood |
| Cellulose II | Produced by swelling of cellulose I with alkali<br>(mercerization) |
| Cellulose III | Produced by immersing cellulose I and II in liquid ammonia at -78°C |
| Cellulose IV | Produced by annealing cellulose III at high temperature (260°C) |

The formation of strong hydrogen bonds in cellulose which is responsible for its crystallinity, makes it not soluble or swellable in water and relatively resistant to most solvents and oxidizing agents (Park, Park, & Ruckenstein, 2001). Cellulose is strongly polarized and resistant to strong alkali but is easily hydrolyzed by acid. Cellulose is mainly used to produce paper and paperboard and it is also converted into a wide variety of derivative products such as cellophane and rayon (Kaplan, 1998).

#### 2.3.2.2 Hemicellulose

Hemicelluloses are embedded in the cell wall of plants, sometimes in chains that they bind with pectin and form a matrix for the cellulose. The combination of hemicelluloses and pectin acts as a link between the fibrous cellulose and amorphous lignin. Hemicelluloses are branched polymers composed of a combination of five- and six-carbon sugars of varied chemical structure. The different types of carbon sugars are xylose, mannose, galactose, rhamnose, and arabinose (Xiao, Sun, & Sun, 2001). Figure 2.5 depicts the chemical structure of different carbon sugars in hemicellulose.

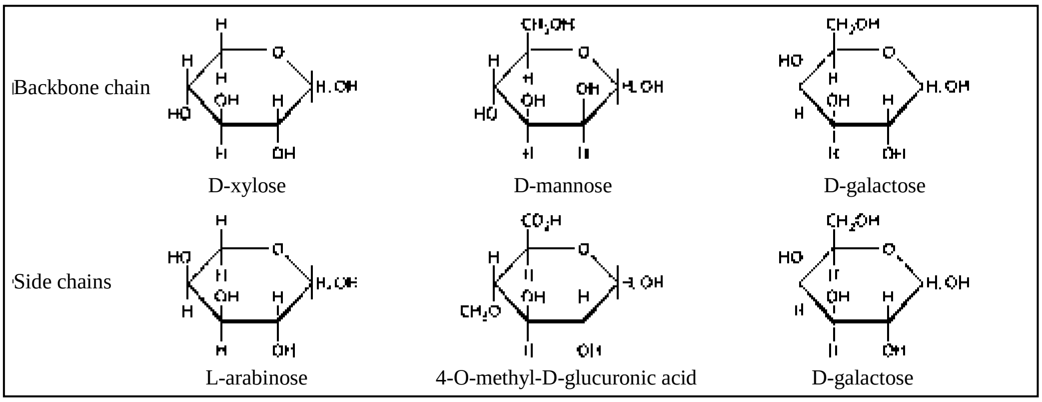

Fig. 2.5 Chemical structure of different carbon sugars in hemicellulose
(Gropper, Smith, & Groff, 2009)

Hemicellulosic polymers are branched, fully amorphous, and have a significantly lower molecular weight than cellulose. Hemicellulose is very hydrophilic, soluble in alkali and can be easily hydrolyzed by acids due to its open structure containing many hydroxyl and acetyl groups (Li, Tabil, & Panigrahi, 2007).

### 2.3.2.3 Lignin

Lignin is a complex biopolymer of aliphatic and aromatic constituents that acts as a cementation agent in the cellulose/hemicellulose matrix. Lignin is the compound that gives rigidity to the plants and it also plays a crucial part in conducting water in plant stems (Sarkanen & Ludwig, 1971). They are totally amorphous, hydrophobic and mainly consist of aromatic units such as guaiacyl, syringyl, and phenylpropane. Figure 2.6 shows the chemical structure of lignin.

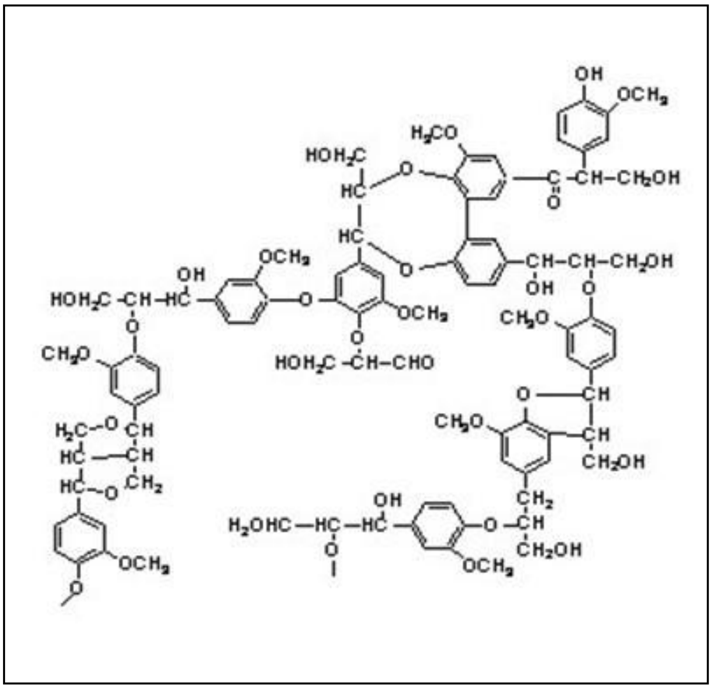

Fig. 2.6 Chemical structure of lignin (Hatakeyama & Hatakeyama, 2004)

Lignin is insoluble in most solvents, cannot be hydrolyzed by acids, but partly soluble in hot alkali.

### 2.3.2.4 Pectin

Pectin is a structural heteropolysaccharide that can be considered as a binder in the primary wall of plants. The amount, chemical composition, and structure of pectin differ between plants, within a plant over time, and in different parts of a plant. Pectin's backbone is usually an unbranched chain of $\alpha$-1, 4-linked D-galacturonic acid units. Additional sugars such as rhamnose, arabinose, xylose, fucose and galactose are usually found attached as side chains to the backbone (Lilholt & Lawther, 2000). Figure 2.7 shows the chemical structure of pectin.

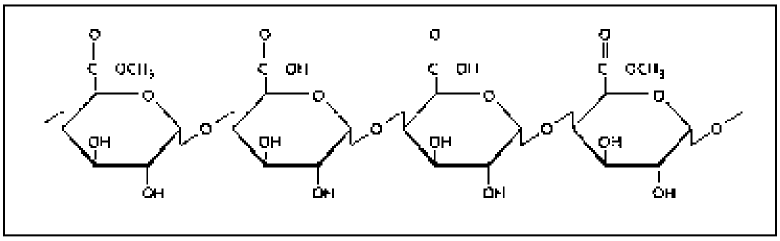

Fig. 2.7 Chemical structure of pectin (Gropper, Smith, & Groff, 2009)

Pectin provides the structural support to the cell wall whilst giving plants flexibility.

### 2.3.3 Surface treatment of natural fibers

#### 2.3.3.1 Bleaching

Bleaching with hydrogen peroxide is one of the chemical treatments widely used in providing surface modifications to the fibers. Hydrogen peroxide is one of the most important future bleaching chemical. It is a strong oxidizing agent that can replace other bleaching agents such as chlorine and chlorine dioxide. Hydrogen peroxide acts by creating active oxygen and it reacts very willingly with many chemical substances but creates no harmful by-products. The advantage of using hydrogen peroxide is that it is environmentally friendly. When used in the bleaching of chemical pulps, it produces a less coloured effluent, reduces pollution load on the effluent treatment system, and improves product quality in strength, brightness, and brightness stability (Tutus & Usta, 2004).

The purpose of bleaching is to remove lignin, waxes, oils and other impurities to improve the physical and chemical properties of the fiber. Hydrogen peroxide is especially used in bleaching cellulose materials because the oxidative damage to the material is usually minimal. In alkali solution, the addition of hydrogen peroxide to natural fiber promotes the bleaching action as follows (Trotman, 1970) (Modibbo, Aliyu, & Nkafamiya, 2009):

$$H_2O_2 \xrightarrow{NaOH} H^+ + HOO^-$$

$$HO_2 \longrightarrow OH^- + [O]$$

$$[O] + I \longrightarrow I\,O$$

where I = impurities

In an alkaline condition, the hydroxyl ion ($OH^-$) produced by the perhydroxyl ion $HOO^-$, hydrolyzes the hydrogen ion ($H^+$), thereby promoting the liberation of more perhydroxyl ions.

$$H^+ + OH^- \longrightarrow H_2O$$

The perhydroxyl anion ($HOO^-$) is the principal active species in peroxide bleaching. The reactions of lignin which constitutes of aldehydes and ketones with peroxide are not reversible and lead to the permanent removal of these groups present in the lignin molecule (Presley & Hill, 1996).

During bleaching, the physical and chemical changes to the fibers are:

- The length of the fiber did not change but due to yield loss the linear density of the fiber is reduced.
- The pliability and flexibility of the fiber increases due to the removal of lignin.
- The hydrophillicity of the fibers decreased.
- The brightness/whiteness of the bleached fibers increases.

The physical result of the bleaching process can be seen by the changes in the colour of the fibers and this indicates that the expected modifications such as removal of wax, fatty substances, oils, and lignin have been achieved.

#### 2.3.3.2 Alkali Treatment or Mercerization

Alkali treatment or mercerization is a versatile, inexpensive and effective treatment for chemical modification of surface fibers. According to ASTM D1695, this is the "process of subjecting a vegetable fiber to the action of a fairly concentrated aqueous solution of a strong base so as to produce great swelling with resultant changes in fine structure, dimensions, morphology and mechanical properties" (ASTM D1695-07, 2007). It is the most widely used chemical treatment to produce high quality fibers when used to reinforce thermoplastics and thermosets to produce composites. Chemical treatment like mercerization provides the right surface modification of natural fibers that are needed to facilitate fiber dispersion and induce bond formation between fiber and polymer matrix when used in composite materials. Addition of liquid sodium hydroxide (NaOH) to the natural fiber promotes the formation of hydroxyl group (Bogoeva-Gaceva, et al., 2007):

$$\text{Fiber-(OH)} + \text{NaOH (liquid)} \rightarrow \text{Fiber} - \text{O} - \text{Na}^{+} + \text{H}_2\text{O}$$

Alkali treatment modifies the structure of natural fibers and the effects of the modification are listed below:

- By removing the natural and artificial impurities such as hemicellulose, lignin, pectin, wax and oils, the natural fiber bundles are broken down and split into finer filament and thus increasing the effective area available for contact with the polymer matrix (Cao, Shibata, & Fukumoto, 2006).
- Removal of the impurities also disrupts the hydrogen bonding in the network structure of the fiber walls and this leaves a major number of hydroxyl groups accessible to the polymer matrix to develop links and results in better mechanical interlocking between fiber and matrix.
- The steady and gradual removal of sensitive alkali material in the fiber reduces the density and fiber diameter and this leads to the enhancement of the fiber aspect ratio and this can provide a better matrix interface adhesion and an increase in the mechanical properties of the composites.
- The treatment destroys and collapses the cellular structure due to the removal of the cementing materials such as hemicellulose, pectin and lignin. This makes the interfibrillar region less dense and rigid and thereby makes the cellulose fibrils more capable to rearrange themselves and leads to better packing of the cellulose chains. A more compact packing of the cellulose chains leads to higher fiber strength (Bledzki & Gassan, 1999).
- The solubilization of hemicellulose, pectin and lignin exposes a higher amount of short cellulose crystallites on the fiber surface and this directly increases the number of possible reaction sites and provides additional sites for mechanical interlocking between fiber and matrix.

- The treatment changes the structural unit cell of natural cellulose, cellulose I, to allotropic modified cellulose I structure with different dimensions that is cellulose II. Basically, when aqueous sodium hydroxide is added to natural fiber, sodium cellulose II is formed. Upon rinsing and drying to remove the alkali, sodium cellulose II adopts a different crystalline state called cellulose II (Revol, Dietrich, & Goring, 1987).
- The alkali treatment is also able to remove any volatile component that might be responsible for giving bad odours to the natural fiber strands.

One of the disadvantages of modifying surface fibers using alkali treatment is that cellulose can be partially degraded if the concentration of soda is high. To avoid degradation by this method, the removal of non-cellulosic material must be carefully controlled. The alkali treatment must only hydrolyze the surface material of the fibers. The strong base sodium hydroxide changes the crystal structure of cellulose but must not cause any significant changes in the mechanical properties of the fibers. High concentration of sodium hydroxide will trigger a reaction called the ‘peeling’ phenomenon. This reaction is not random and will occur at the reducing end of the cellulose chain where the glucose derivatives will be eliminated one by one. The loss of the glucose units does not cause any significant changes in the mechanical properties of the fiber but too strong of an alkaline solution will cause major degradation to the cellulose and this will lower the mechanical properties of the fibers drastically (Vilaseca, et al., 2007).

## 2.4 Studies and application of polymer/starch/fiber composites

The durability, toughness and flexibility are the properties that make synthetic petroleum derived plastics ideal for many applications such as packaging, commodities and building materials, as well as in hygiene products, but can lead to waste disposal and landfill problems because these materials are not biodegradable and they resist microbial degradation, so they accumulate in the environment. These fact and combining with a marked increase in oil prices these recent times have helped in stimulating interest in biodegradable polymers as alternatives for non-degradable. Biodegradable polymers were first commercially introduced in 1980s (Vroman & Tighzert, 2009). Since the 1960s continuous researches have been done to produce biodegradable polymers that can overtake the usage of synthetic plastics in every part of our lives. In the early 2000s, research that was done on the synthetic biodegradable polymer matrix polyvinyl alcohol as reported by Siddaramaiah et. al. They did an initial study on structural, mechanical and biodegradation properties of the corn starch filled polyvinyl alcohol films. In the findings it was observed that there was only a slight improvement in the tensile strength and elongation at break for the composition of corn starch/PVA compared to that of plain PVA film. The study also shows that with the addition of starch to the composite, the crystal region of PVA as the polymer matrix was not affected. For the biodegradation test, its shows that the rate of biodegradation increases with increasing starch content in the PVA matrix (Siddaramaiah, Raj, & Somashekar, 2004). In the same year, Jayasekara et. al analyzed the preparation, surface modification, and characterization of solution cast starch/PVA blended films. The blends were prepared using different percentages of PVA, starch, and glycerol and were modified by treatment with chitosan. When the starch was blended with

PVA, it was noted that there was no new bond formation formed between the composite and chitosan because there was no evidence in the FTIR and CMR analysis. From the analysis done, PVA and starch form a flexible and homogeneous film with individual component present but did not show any evidence of any new functionality (Jayasekara, Harding, Bowater, Christie, & Lonergan, 2004).

In 2006, Guohua et. al investigated the mechanical properties, water resistance, and biodegradability of methylated corn starch (MCS) and polyvinyl alcohol. The mechanical properties of the MCS/PVA were better than the native corn starch/PVA blends but lower than those of the matrix PVA films. It was also reported that water resistance of the MCS/PVA blends were higher than the native corn starch/PVA blends but the increase of methylated corn starch proportion in the blends deteriorated both the tensile strength and elongation at break of the composite (Guohua, Ya, Cuilan, Min, Caiqiong, & Zongdao, 2006).

During the middle of the 2000s also, Imam et. al characterized and investigated the properties of blends of polyvinyl alcohol with corn starch and orange fibers. The blends were evaluated for their thermal stability, water permeability and biodegradation process. The blends showed a slightly higher thermal stability compared to that of pure PVA. It was also detected that although the PVA, starch and orange fiber were hydrophilic in nature, the water permeability and soil burial tests suggests that the blends will allow water to permeate easily and maintain the moisture content of the soil. The presence of the starch and orange fibers also stimulated PVA degradation in the soil because of higher degradation was detected in the PVA/starch/orange fiber blends compared to the starch/orange fiber blends (Imam, Cinelli, Gordon, & Chiellini, 2005). Cinelli et. al then investigated the effect of different fibers such as sugar cane bagasse, apple and orange waste when they're incorporated in the corn starch/PVA composite. Glycerol was used as a plasticizing agent. The mechanical properties observed of the prepared composites were dependent from fiber types and plasticizer content. The blends prepared from apple and sugar cane bagasse have higher tensile strength and Young Modulus value compared to blends composed of starch, PVA and orange fibers. The biodegradation rate between apple, orange and sugar cane bagasse composites were the same (Cinelli, Chiellini, & Imam, 2008). In 2008, Lu et. al reported on the preparation, thermal and mechanical properties of the microfibrillated cellulose and polyvinyl alcohol composite. Microfibrillated cellulose (MFC) was prepared by a mechanical process and used as reinforcement in polyvinyl alcohol matrix. In the preparation process of the composite, there was a good dispersion of the MFC in the PVA matrix due to stability of MFC in water and solubility of PVA. With increasing MFC content, there was no significant effect on the crystallization of PVA but there was an overall increase in mechanical strength of the composite. As summarized, the web-like structure of the MFC could render better toughness compared to discrete microfibrils when incorporated into polymer matrices (Lu, Wang, & Drzal, 2008). Rosa et. al then reported an investigation on surface chemical treatments effects on the mechanical properties of fiber incorporated in starch/ethylene vinyl alcohol copolymers (EVOH)/coir composites. The chemical treatments used are washing with water, alkali treatment (mercerization) and bleaching. Different treated fibers were blended in the composites. All the surface treatments done on the fiber produced surface modifications that improved the thermal stability of the fibers and consequently the composite. From all the treatments done on the fibers, alkali treatment produced the best mechanical testing result of the composite. The strength of the composites were increased by 53% compared to the composite with untreated fibers, and about 33% compared to the composite with only starch and EVOH (Rosa, et al., 2009). Recently, Phattaraporn et. al analyzed and reported on the thermal and mechanical properties of rice starch films reinforced with palm pressed fibers (PPF). It was found that, with increased content of palm pressed fibers, the tensile strength and water permeability properties of the rice starch/PPF composites improved and the thermal stability and glass transition temperature ($T_g$) shifted to higher temperatures (Phattaraporn, Waranyou, Fazilah, & Thawien, 2010).

The need to reduce and substitute synthetic polymers that has different functions in our daily lives escalates because of the enormous pressure exerted to rectify the ecological imbalance of the environment. All synthetic plastics form potential candidates for substitution by biodegradable polymers in the future. Applications for biodegradable polymers come in many forms and are listed below:

- In the medical field:
  - starch based degradable bone cements (Boesel, Mano, & Reis, 2004)
  - starch based biodegradable polymers in the form of microsphere or hydrogels, suitable for drug delivery
  - Biodegradable screws, sutures and pins
  - hospital applications such as vomit bowls inserts, bedpan, biohazard and pathology sample bags, hospital laundry bags which are “washed away” allowing sanitary laundering of soiled laundry.
  - non-resterilizable, single use medical devices and catheter bags

- In the food industry:
  - soluble wrappings for sweets or chocolate
  - disposable food service items such as trays, cutlery, and plates
  - edible food wrappers

- In agriculture:
  - dissolvable ground bait and fertilizer bags
  - the covering for a greenhouse
  - mulch film
  - fertilizer release controlled materials (Kumbar, Kulkarni, Dave, & Animabha, 2001)
  - biodegradable plant pots
  - disposable fertilizer, composting, chemical containers and storage bags

- Others:
  - Soluble bottle caps, closures and labels
  - Industrial protective films and wrappings
  - Garbage bags
  - Dissolvable single-use sachets such as detergent bags and premeasured consumer pouches
  - Reinforcement materials in plastic parts of automobiles and commercial vehicles (for the interior part)
  - Loose-fill packaging materials
  - Packaging boxes and films such as egg boxes