



CHAPTER II

LITERATURE SURVEY

Plastic wastes derived from petrochemical source became a serious problem in Thailand because of their use over a long period of time for degradation. Nowadays, the plastic wastes are annually increasing. Moreover, plastic packagings such as plastic bag and food packaging are one of the major plastic wastes in Thailand. As see in Figure 2.1, about 42 % of all plastic industry in Thailand produced plastic packaging. The plastic packaging made from synthetic polymers such as PE, PP, PVC which is non renewable source have been popular for many years because they are relatively cheap to produce, waterproof, and durable. However, they are not biodegradable and are almost indelible; so that, these products produce a large amount of green house effect. There is currently a wide revival of interest in use of biodegradable plastic for reducing the plastic wastes.

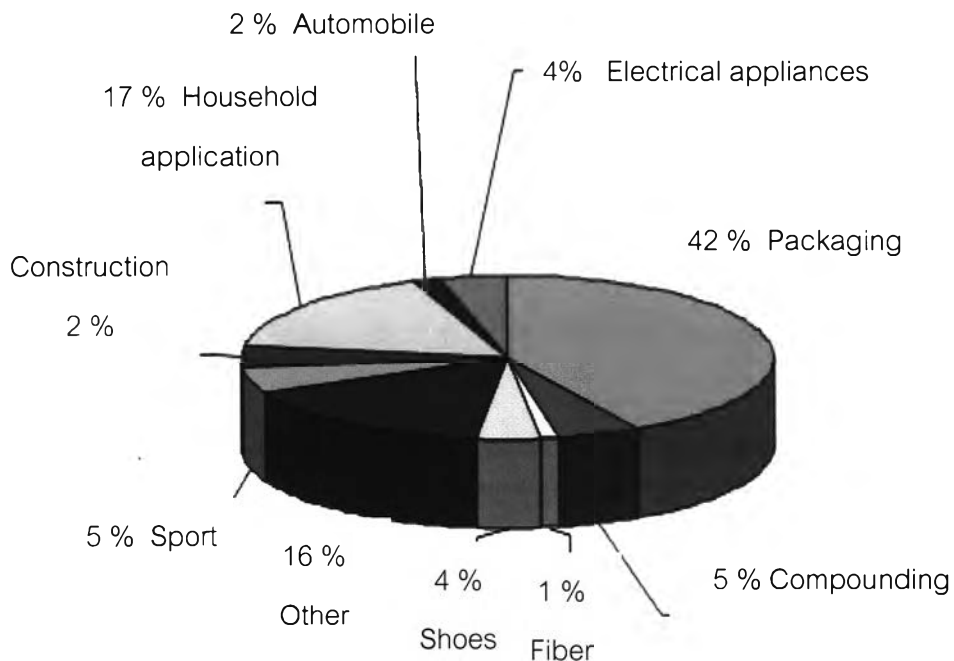


Figure 2.1 Proportion of plastic industry in Thailand [1]

2.1 Degradable Plastic

The American Society for Testing of Materials (ASTM) and the International Standards Organization (ISO) define degradable polymer or degradable plastic as those which undergo a significant change in chemical structure under specific environmental conditions. These changes result in a loss of physical and mechanical properties, as measured by standard methods. So the degradable plastic was grouped by ASTM D20.96 as [2]

1. Photodegradable or light-induced degradation plastic is a degradable plastic in which the degradation results from the action of natural daylight.

2. Oxidatively degradable plastic is a degradable plastic in which the degradation result from the oxidation.

3. Hydrolytically degradable plastic is a degradable plastic in which degradation result from hydrolysis.

4. Biodegradable plastic is a degradable of plastic in which the degradation result from the action of naturally occurring are two classes of microorganisms such as bacteria, fungi, and algae.

However, according to the definition of degradable plastic in categories, 1 to 3. Additional input such as light (UV) or oxygen is required for degradation, the biodegradation plastic in number 4 offers only products which are naturally degradable.

2.2 Biodegradable Polymer

When considering biodegradable plastic, there biodegradable plastic which material scientists are currently focusing. Moreover, these polymer materials are usually referred to in the general class of plastics by consumers and industry [3].

1. The first class of biodegradable plastic under consideration is partially degradable. The product of this class usually includes a conventional (petroleum base)

matrix and is filled the biodegradable material in matrix. It is designed with the goal of more rapid degradation than the conventional plastic. When it is disposed, microorganisms are able to consume the biodegradable material within the conventional plastic matrix. This leaven cause a weakened material, with rough, open edges. Further degradation is occurred. This group of materials usually has an impenetrable petroleum based matrix such as starch filled polyethylene film.

2. The second class of biodegradable plastic is compostable polymer. It is currently attracting a lot of attention from researchers and industry because of its design to be completely biodegradable. The product in this class includes only the biodegradable polymer material such as biocomposite that matrix is derived from natural sources, i.e. starch or microbially grown polymers, and the fiber reinforcements are produced from common crops such as flax or hemp. Microorganisms are able to consume these materials in their entirety eventually leaving carbon dioxide and water as by-products.

In recent years, there has been increased interest in biodegradable material for packaging application. The belief is that biodegradable polymer will reduce the need for synthetic polymer production and reduce pollution. Moreover, it is producing a positive effect on both environmentally and economically. Figure 2.2 shows carbondioxide sequestration reused by renewable resource. Therefore, much effort has been made in recent years to develop the biodegradable material and renewable resource. Furthermore, Biodegradable polymers are growing into mainstream use, and the polymers that are biopolymer or based on renewable feedstock may soon be competing with commodity plastics

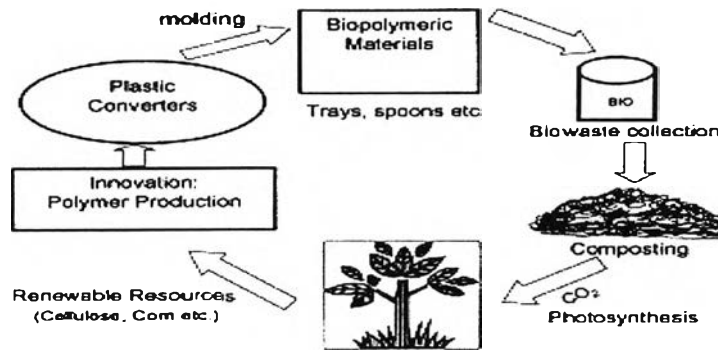


Figure 2.2 Carbondioxide was reused by renewable resource [4]

Biodegradable polymer was categorized into four families based on source as shown in Figure 2.3 [4]

1. Agro-polymers obtained from biomass by fraction such as starch, cellulose, protein, lipid.
2. Polyester obtained by fermentation of biomass or from genetically modified plants such as polyhydroxyalkanoate: PHA, poly(hydroxybutyrate): PHB.
3. Polyester synthesis from monomer obtained from biomass such as polylactide, polylactic acid: PLA.
4. Polyester totally synthesized by the petrochemical process such as polycaprolactone: PCL, polyesteramide: PEA, aliphatic or aromatic copolyesters.

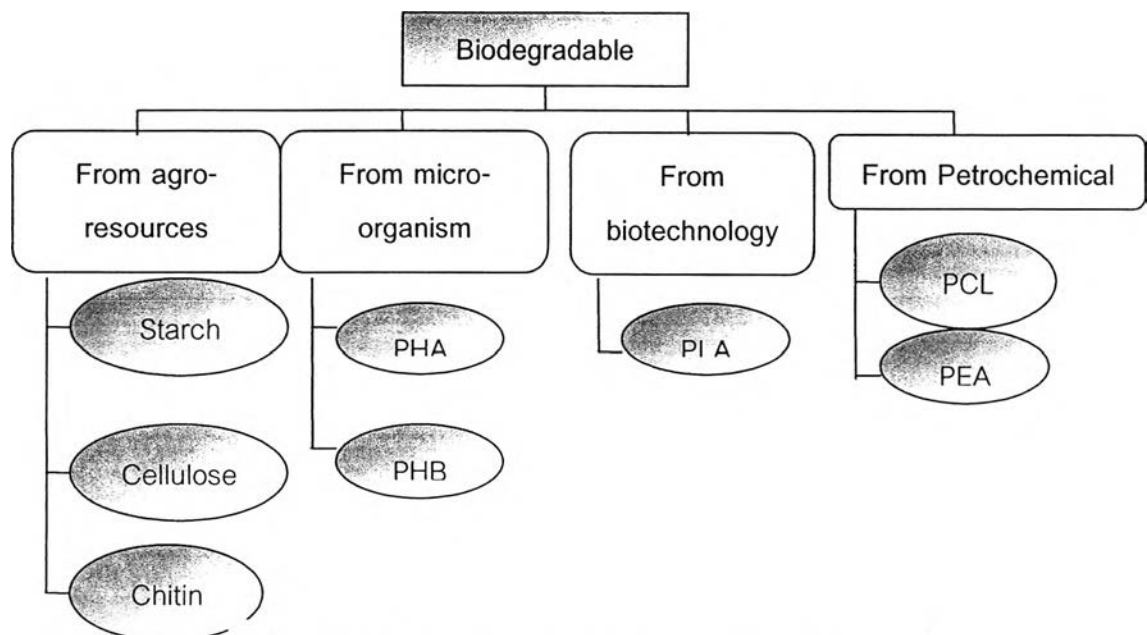


Figure 2.3 Classification of biodegradable polymer [4]

2.3 Native starch

In recent years, many researchers have focused on developing plastic packagings that are degradable and while retaining properties to conventional plastics. One of the most studied and promising raw materials for production of biodegradable plastic is starch such as corn, wheat, rice, and cassava starch. Therefore, starch-based plastics have generated much interest recently because it is abundant, inexpensive, and degradability.

Starch is a biological material and naturally. It is the major carbohydrate reserved in plant tubers and seed endosperm where it is found as granules. The size and shape of starch granules are varied in diameter from 2 to 130 microns and depend upon the source as shown in Figure 2.4. The size of starch granules is exemplified in Table 2.1.

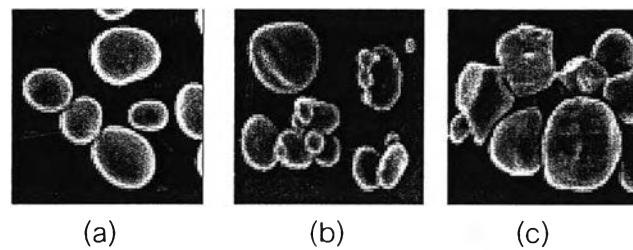


Figure 2.4 Micrographs of (a) potato (b) cassava and (c) corn starch granule [5]

Table 2.1 Granule size distribution of various starch [5]

Starch	Granule Size Range (μm)	Average size (μm)
Waxy Rice	2 – 13	5.5
Corn	5 – 25	14.3
Cassava	3 – 28	14
Wheat	3 – 34	6.5, 19.5
Potato	10 – 70	36

Starch is a polysaccharide. The empirical formula of cassava starch is $C_6H_{12}O_5$. It is made up of glucose units linked together to form long chains. The glucose unit in starch is anhydroglucopyranose. Starch consists of two major components which are amylose, a linear polymer and amylopectin, a branched polymer. Amylose and amylopectin are inherently incompatible molecules; amylose has lower molecular weight with a relatively extended shape; whereas, amylopectin has large but compact molecules. The ratio of these components varies with the source of starch, normally amylose and amylopectin present about 20-30% and 70-85% of total mass of starch, respectively. Most of their structure consists of α -1,4-D-glucose units.

2.3.1 Amylose

Amylose molecule is a linear component. It makes up of α -1,4-D-glucosidic linkage. The Chemical structure of amylose and partial structure of amylose are shown in Figure 2.5 and 2.6. The ratio of amylose component is dependent upon source of starch. The degree of polymerization of amylose ranges from 500 to 600 giving a molecular weight range of 10^5 - 10^6 Da. Amylose can form an extended shape but generally tends to wind up into a rather stiff left-handed single helix or form even stiffer parallel left-handed double helical junction zone as seen in Figure 2.7. The helical structure consists of six glucose units per turn. The single helical amylose has hydrogen-bonding at oxygen atom in position 2 and 6 on outside surface of the helix with only the ring oxygen pointing inwards. Hydrogen bonding between aligned chains present extensive inter- and intra-strand hydrogen bonding, resulting in a fairly hydrophobic structure of low solubility [5]

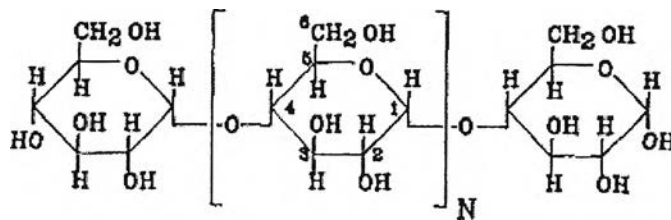


Figure 2.5 Chemical structure of amylose molecule [5]

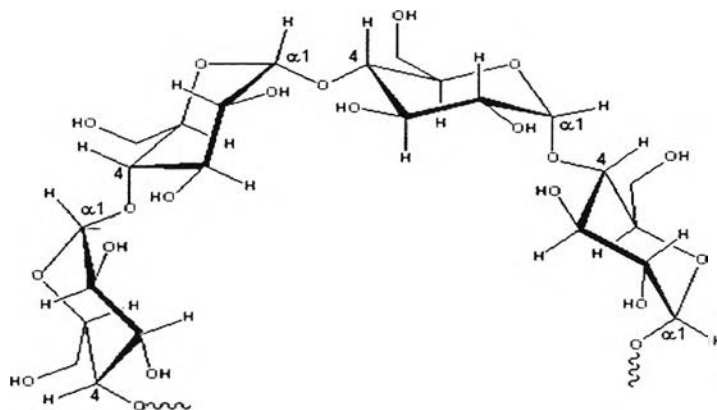


Figure 2.6. Representative partial structure of amylose [6]

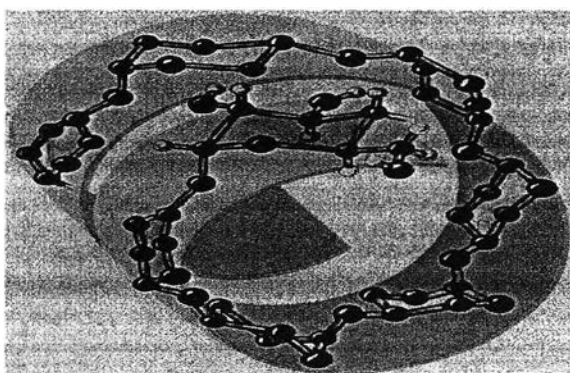


Figure 2.7 helical structure of amylose [7]

2.3.2 Amylopectin

Amylopectin molecule is a highly branched polymer. It has an average molecular weight ranging from 10^7 to 5×10^8 g/mol and DP of 2×10^6 . It consists of glucose residues linked together mainly by α -1,4- glucosidic linkages and by α -1,6- glucosidic linkages at branched points, as presented in Figure 2.8 and 2.9. The unbranched unit sections are approximately 20-25 glucose unit in length. In fact, the structure of amylopectin has been controversy for many years so the exact structure of the amylopectin molecule is not known. However, a cluster model is the most generally accepted [8]. Each amylopectin molecule consists of main chain called the C chain, which carries the one reducing end group and numerous branches, in termed A chains

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In addition, each amylopectin molecule contains the two million glucose residues in a compact structure. The molecules are oriented radially in the starch granule while the radius increases made up the number of branches required to fill up the space so that they made the consequent formation of amorphous and crystalline structure in the starch granule. The structure of the amorphous and crystalline regions of amylopectin contribute to the "Growth rings" that are visible by light microscopy as shown in Figure 2.11. Moreover, the double helix structure of linear component in amylopectin gives rise to the extensive degree of crystallinity in granule.

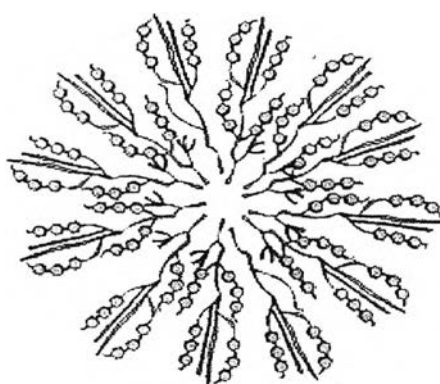


Figure 2.11 Structure of amylopectin contribute to the " Growth rings" [9]

2.3.3 Gelatinization starch

The first step in starch utilization generally is one of that disrupts the granular structure leading to granule swelling, hydration, and solubilization of starch molecules. These events referred to collectively as starch gelatinization. It is an important characteristic of starch properties. Starch gelatinization is a process as the melting of starch crystallite that breaks down the intramolecular bonds of starch molecules in the presence of water and temperature. This situation allows the hydrogen bonding sites which of the hydroxyl hydrogen and oxygen to engage more water then penetration of water increases randomness in the general structure and decreases the number and size of crystalline regions. In fact, crystalline regions do not allow water entry in cold water but heat and stirring cause such regions to be diffused, so that the chains begin to separate into an amorphous form. When the temperature reach to

"gelatinization temperature" that is 60-70 °C, starch becomes to gel form. When primary consideration is being given to this appearance of gelatinization, solvents other than water such as liquid ammonia, formamide, and formic acid also effect gelatinization by disrupting hydrogen bonding within the granule or by forming soluble complexes with the starch. Furthermore, alkali and salts are examples of chemicals that decrease or increase starch gelatinization temperature. Under alkali conditions, starch gelatinizes at a lower temperature. Salt, such as sodium chlorite and sodium sulfate, are used to rise the gelatinization temperature of starch. However, Garcia and co-wok [10] suggest a relationship between initial gelatinization temperature, water activity, the volume fraction of water in starch granules, the rupture of hydrogen bonding in starch molecule.

When consideration of starch structure, the starch molecule is classified as either linear (amylose) or branched (amylopectin). Its monomer unit contains three hydroxyl groups so it can absorb moisture when immersed in water, but retain their basic structure due to crystalline and hydrogen bonded structure within the granules. Amylose molecules contribute to gel formation. This is because the linear chains can orient parallel to each other, moving close enough together to bond. Probably due to the ease with which they can slip pass each other in the cooked paste ; however, they do not contribute significantly to viscosity. The branched amylopectin molecules give viscosity to the cooked paste. This is partially due to the role it serves in maintaining the swollen granule. The effect of side chains and bulky shape keep them from orienting closely enough to bond together, so they do not usually contribute to gel formation. The gel network of starch was shown in Figure 2.12. Different starches have different relative amounts of amylose and amylopectin within the starch granule which give each starch different in its characteristic properties in cooking and gel formation. In addition, dry granules show polarization crosses reflecting crystalline organization when examine microscopically under polarized light that it is called birefringence properties. However, the granular structure is ruptured by heating in water or treating with aqueous solutions that disrupt crystalline areas and hydrogen bonding within the granules then gelatinization of starch was occurred after heated above a critical temperature, which is 60-70 °C. This events cause losing of birefringence occurs at the time of initial rapid

gelatinization; so that, loss of birefringence is a good indicator of the initial gelatinization temperature that means crystalline area in granules were disrupted.

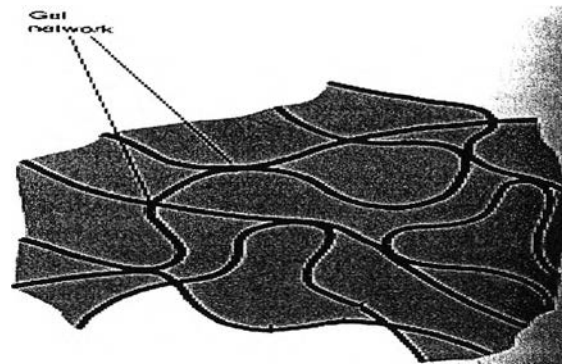


Figure 2.12 Gel network of starch[5]

2.3.4 Cassava starch

Cassava (*Manihot esculenta* Crantz) has many names which depend on the continents. The English word is cassava, but in South America where it is in the area around Brazil. It is called mandioca and it is called manioc in Africa where French is spoken. In Asia, it is called tapioca [11]

Cassava can grow well in the tropical countries such as Indonesia, India, and Thailand. Cassava is one of the most important commercial crops in Thailand. It is currently planted in approximately seven million rai of land in 48 provinces in Thailand, which annually produces over 20 million tons of cassava roots. Moreover, Thailand is currently the largest producer and exporter of tapioca flour in the world. Fifty percent of cassava root is used as raw material for the production of cassava starch. Cassava starch is widely used as materials to produce biodegradable film because of it is a cheap renewable source and contains a high concentration of starch (dry-matter basis) that can equal or surpass the properties offered by other starches such as maize, wheat, sweetpotato, and rice. Moreover, the most important characteristic of cassava starch film is excellent thickening characteristics and clarity appearance than other

starches as seen in Figure 2.13 The chemical composition of cassava starch is shown in Table 2.2

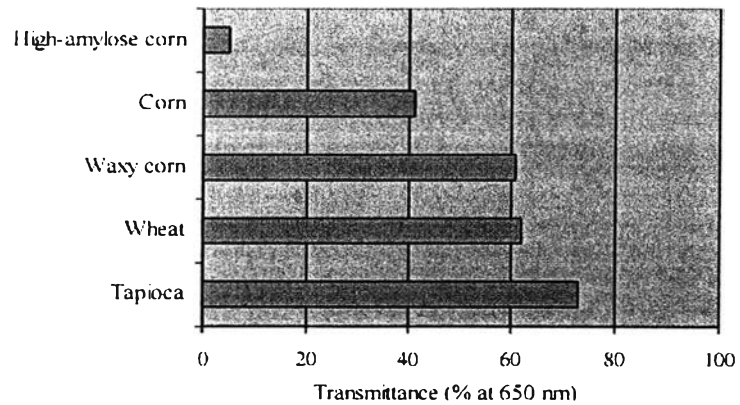


Figure 2.13 Film clarity as indicated by % light transmittance at 650 nm of difference starch sources [12]

Table 2.2 Chemical composition of cassava starch [12]

Composition %	Cassava starch
Moisture	13
Ash	0.2
Protein	0.1
Lipid	0.1
Phosphorus	0.01
Amylose	17

2.4 Starch-based film

Starch is a well known polymer with some advantage of biodegradable and renewable characters. However, starch is non-plastic material so it is difficult to fabricate because of its higher glass transition temperature (T_g) than its decomposition temperature (T_d). This higher T_d is attributed to its regularly structure and hydrogen bonding in the molecule due to dense packing of its molecule and high crystallinity. In order to making native starch into plastic, it is important to decrease T_g of starch. The

addition of plasticizer is one of the methods to resolve this problem. When the starch is modified into plastic that it is called thermoplastic starch. After adding plasticizer, Tg of starch is decreased and film flexibility is increased because polymer chain can easily move; hence, internal hydrogen bonding between polymer chain is reduced while molecular space is increased. In addition, the most effective plasticizer is generally resemble most closely to the structure of the polymer that it plasticizes; thus, the most commonly plasticizer used in starch based films is substance with hydroxyl group such as water, sorbitol, and glycerol [13]. In addition, plasticized starch can be fabricated by various techniques such as extrusion, compression molding, and casting.

Many researches have been interested in fabrication starch film via casting technique because it is easy processing and can produce the large sheet. In addition, glycerol is familiarly used as a plasticizer. A lot of researches have been studied on properties of glycerol plasticized starch film by casting technique

For example, in 2005, Mali et al [13] studied the effects of plasticizers (glycerol, sorbitol, and 1:1 mixture of glycerol and sorbitol) on moisture sorption characteristics of cassava starch films at three levels of plasticizer concentration (0, 20, and 40 g/100g starch). The combined effects of relative humidity and plasticizer on mechanical properties of starch films were also examined. Water affinities of cassava starch films were affected by hydrophilicity of the plasticizer and its concentration. Films plasticized with glycerol, under all RH conditions, adsorbed more moisture with higher initial adsorption rate, and films with higher plasticizers contents exhibited higher equilibrium moisture contents. Mechanical properties were affected by plasticizing effect, including the water adsorbed, resulting in higher strain and Young's modulus values and, in all cases, glycerol exerted a more effective plasticization.

Later on in 2006, Sirikhajornnam and Danwanichakul [14] studied the optimum conditions to prepare films from corn and tapioca starch by casting technique. Glycerol was used as a plasticizer. They reported that the suitable condition for obtaining gelatinized starch solutions was at a temperature around 80-85 °C then film was dried at

100 °C for 24 hours. This condition made films from both corn and tapioca starches appeared homogeneous and suitable for utilization. The effects of glycerol on the properties of the films for both types of starch, showed that when increasing the amount of glycerol, both tensile strength and water vapor permeability of the films were decreased while film flexibility and water absorbability were increased.

With in the same year, Talja et al [15] investigated the effects of plasticizer (glycerol, xylitol, and sorbitol) and relative humidity on physical and mechanical properties of potato starch-based edible films. Films were obtained from solutions containing gelatinized starch, polyol, and water by casting and evaporating water at 35 °C. Water content of films increased with increasing relative humidity and plasticizer content. Water vapor permeability of films increased with increasing plasticizer content and storage relative humidity. Young's modulus decreased with increasing polyol content with a concurrent increase in elasticity of films. Both increased polyol and water content increased elongation at break with a decreased tensile strength. Glass transition temperatures decreased as a result of plasticization as polyol and/or water content increased. Effects of plasticizers on physical and mechanical properties of films were largest for glycerol and smallest for sorbitol. High contents of xylitol and sorbitol resulted in changes in physical and mechanical properties of films probably due to phase separation and crystallization.

Recently in 2007, Alves et al[16] investigated the effects of different amylose quantities (6.3,15.6, and 25.0 g/100g of starch) and glycerol contents (20.0, 32.5, and 45.0 g/100g of starch) on filmogenic solution by casting technique. They reported that mechanical properties of cassava starch films were influenced by glycerol and amylose contents. The enrichment of filmogenic solutions with amylose solution originates stronger and more permeable films. Glycerol behaved as a typical plasticizer in starch film; with increasing glycerol concentration, water vapor permeability, strain at break, and puncture deformation increased, and stress at break, Young's modulus, and puncture strength decreased.

Later, Bergo et al [17] investigated physical and mechanical properties of cassava starch films containing glycerol. Films were prepared from casting. Film-forming-solution with 2 g of cassava starch per 100 g water plus 0, 15, 30, and 45 g of glycerol per 100 g starch. The results showed that the resistance values of the films decreased while those of elasticity increase with the increase of the glycerol concentration. Moreover T_g of films prepared decreased with the glycerol content. According to the XRD diffractograms, films with 0 and 15 g glycerol per 100 g starch presented an amorphous character, but some tendency to show crystalline peaks was observed for films with 30 and 45 glycerol per 100 g starch.

However, plasticized starch has two main disadvantages when compared to common plastic currently in use, i.e. it is mostly water-soluble and has poor mechanical properties. The researchers have been using many methods to improve plasticized starch film such as coating, blending, or preparing composite starch film. The details are as follows

In 2006, Bangyekan et al [18] prepared chitosan-coated cassava starch films. Chitosan coating solutions varying from 1 to 4 wt% were coated on to the free starch films containing 2, 3, 4, 5, and 6 wt% glycerol as a plasticizer. They found that chitosan and starch molecules, resulting in their good adhesion. Coating of chitosan solutions led to an improvement in several film properties including mechanical and physical properties. The results of mechanical properties evaluation showed that an increase in chitosan coating concentration resulted in a significant increase in tensile stress at maximum load and tensile modulus, and a decrease in percent elongation at break. Film strength along coating direction was higher than that of transverse direction as a result of force applied during coating process. Concerning physical properties, a remarkable decrease in water uptake was observed due to the contribution of hydrophobicity of chitosan coating layer. The hydrophobic acetyl groups of chitosan caused a notable reduction of wettability as well as water vapour permeability which are preferable for packaging film application.

Later on, Godbole et al [19] prepared biodegradable poly-3-hydroxybutyrate–starch blend films and examined the thermal and mechanical properties of the blended films. The results shown the compatibility of PHB with starch as evidenced by a single glass transition temperature for all the proportions of PHB:starch tested. Moreover, the results indicated that blending of thermoplastic starch with PHB in a ratio of 30:70 could be advantageous for cost reduction and made the maximum tensile strength and Young's modulus than the virgin PHB.

Beside coating and blending, preparation of starch biocomposite film is another approach of interest for improving the physical and mechanical properties of plasticized starch. Furthermore, composite can improve the excellent mechanical properties because composite products usually present the good properties from each component [20]. Therefore, composite is a popular method for improving plasticized starch. For example, In year 2006, Wilhelm et al [21] prepared a mineral clay reinforced glycerol-plasticized Cará starch films order to improve the mechanical properties of this films. The dynamic mechanical analyses showed that the composite films give rise to three relaxation processes, attributable to a transition of the glassy state of the glycerol-rich phase, to water loss including the interlayer water from the clay structure, and to the starch-rich phase. A film obtained with 30% in w/w of clay showed an increase of more than 70% in the Young modulus compared to non-reinforced plasticized starch

Composite is a heterogeneous material. It is consisted of two or more distinct compositions or phases, generally, a matrix or continuous phase and disperse phase. The disperse phase may consist of additive such as reinforcement and filler. The matrix phase can be a thermoplastic or thermoset. Furthermore, each component in composite dose not loss their component and they do not dissolve into each other. Regularly, a human made composite would consist of reinforcement or filler phase which is stiff and strong material. Frequently, its shape is found in fibrous, particle, and flake that is embedded in a continuous matrix phase. Normally, the matrix phase is often weaker and more compliance than the reinforcement. Two of the main functions of the matrix are to transmit externally applied loads, via shear stresses at the interface, to the reinforcement

and to protect the latter from environmental and mechanical damage [20]. The advantage of a such connection is that the high strength and stiffness of the reinforcement is to support the external applied load which is transmitted from matrix. Therefore, a third part of composite is the interface between disperse phase and matrix. The interface determines the reinforcement efficiency of a composite since strong bonding between matrix and disperse phase is essential. In particular, the strong interface adhesion will aid the transmittal externally applied load from matrix to reinforcement. The matching polarity of the matrix and disperse phases will assist interfacial adhesion, but specific interactions or chemical bonding will be preferable. From the literature have been presented various types of fillers or reinforcement were added in plasticized starch such as Clay[22], Silica [22], Chitosan whisker [23], short-fiber [24] and micro or nanocrystalline cellulose. Micro or nano crystalline cellulose is famous filler or reinforcement with in plasticized starch to prepare the biocomposite film. Moreover, the advantage of crystalline cellulose is high strength, low cost and degradability.

2.5 Natural fibers

Crystalline cellulose made from cellulose which is found in plants or natural fibers. The source of natural fibers can be classified into four categories [25]

1. Wood fibers such as soft and hard wood (many species)
2. Vegetable fibers such as cotton, hemp, jute, ramie, kenaf. etc.
3. Animal fibers such as wool, silk, spider, feather, down. etc.
4. Mineral fibers such as asbestos, in organic whisker. etc.

The cellulose can be found in plant cell wall. Each layer of plant cell wall is composed of cellulose embedded in a matrix of hemicellulose and lignin. The structure and contents of cell wall depend on type, species, and different parts of the plants. The primary (outer) cell wall is usually very thin. The microfibrils are formed in the secondary cell wall. Furthermore, microfibrils are contained of cellulose molecules. The microfibrils run fairly pararell and arrange their molecules into helix around the cell. In addition, the

microfibrils are composed of crystalline regions and amorphous regions. Usually, the crystalline is found along the axis in the microfibrils; therefore, the cellulose molecules pass through several crystallites along the axis [26]. This model structure of crystalline is called a fringed micelle structure. Although this structure model is classical and may become old-fashioned but it is still believed because it is reasonable. Figure 2.14 presents the fringed micelle model of cellulose structure.

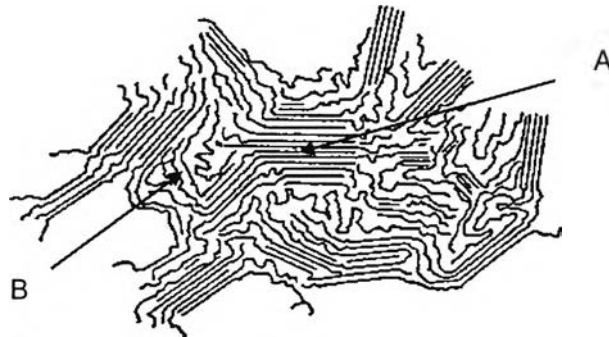


Figure 2.14 Fringed micelle theory of cellulose showing (A) ordered regions (crystallites) embedded in (B) inordered regions (amorphous) matrix [32]

2.5.1 Cellulose

Cellulose is the essential component of all plant-fibers. It is a linear chain. Cellulose is derived from D-glucose units, which condense through α -1,4-glycosidic linkage. The chemical structure of cellulose is presented in Figure 2.15. Native cellulose is a straight chain polymer that is aligned to form fiber with high crystallinity owing to its has the extensive intra and intermolecular hydrogen bonding through the chain that makes it completely insoluble in water and normal aqueous solutions; thus, it is presented hydrophobic properties. Many properties of cellulose depend on its degree of polymerization or chain length. In addition, cellulose from wood pulp has typical chain lengths between 300 and 1700 units such as cotton and other plant fibers as well as bacterial celluloses have chain lengths ranging from 800 to 10,000 units.

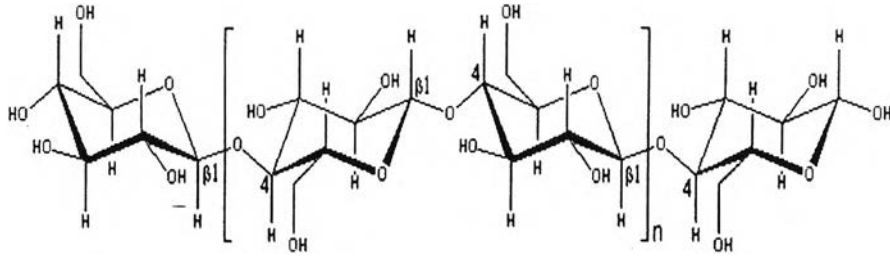


Figure 2.15 Chemical structure of cellulose [26]

Comparing of cellulose and starch, cellulose contains beta glucose in the monomer unit. As a result of the bond angles in the beta acetal linkage, cellulose is mostly a linear chain. In contrast, starch contains alpha glucose in the monomer unit . As a result of the bond angles in the alpha acetal linkage, starch-amylose actually forms a spiral much like a coiled spring. From different structure, they have different properties such as crystalline starch can convert to amorphous transition when heated beyond 60-70 °C in water as in cooking; whereas, cellulose requires a temperature of 320 °C and pressure of 25 MPa to become amorphous in water because cellulose has much more crystalline structure. Furthermore, the difference in acetal linkages results in a major difference in digestibility in humans. Humans are unable to digest cellulose because the suitable enzymes to breakdown the beta acetal linkages are lacking but humans are able to digest starch. However, the advantage of undigestible cellulose is the fiber which aids in the smooth working of the intestinal tract for human. Figure 2.16 presents the dissimilar conformation between starch and cellulose.

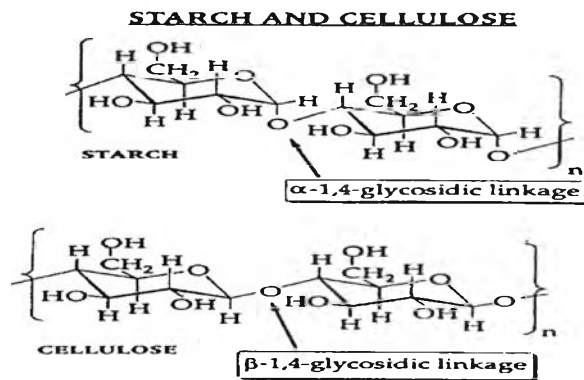


Figure 2.16 Chemical structure of starch and cellulose[27]

2.5.2 Other compositions

- Hemicellulose

Hemicellulose is derived from several sugars in addition to glucose, including especially xylose but also mannose, galactose, rhamnose, and arabinose. Hemicellulose consists of shorter chains - around 200 sugar units as opposed to 7,000 - 15,000 glucose molecules in the average cellulose polymer. Furthermore, hemicellulose is branched, whereas cellulose is unbranched [28].

- Lignin

Lignin fills the spaces in the cell wall between cellulose, hemicellulose and pectin components. Lignin is formed by removal of water from sugars to create crosslink structures. Furthermore, the structure of lignin is very complex. The lignin molecule consists of various types of substructures such as aliphatic and aromatic which appear to repeat in a random manner. Usually, Lignin has masses in excess of 10,000 Da. However, the degree of polymerization in nature is difficult to measure, since it is fragmented during extraction. The types and proportions of monomers of lignin depend on the source in nature. Function of lignin is that it makes vegetables firm and crunchy because of its reinforcing cell walls and keeping them from collapsing. Lignin resists attack by most microorganisms owing to an anaerobic processes tend not to attack the aromatic rings at all. However, aerobic breakdown of lignin is slow and may take many days. For lignin removing, some pulping processes are able to remove a much lignin.

- Pectin

Pectin is formed complex in the nature. In the middle lamella between plant cells, pectin helps to bind cells together and regulates water in the plant. The amount, structure and chemical composition of the pectin differ between plants and

parts of a plant. The chemical structure of pectin is a linear chain of α -(1-4)-linked D-galacturonic acid that forms the pectin-backbone, a homogalacturonan. Into this backbone, there are regions where galacturonic acid is replaced by 1,2-linked L-rhamnose. The neutral sugars are mainly D-galactose, L-arabinose, and D-xylose; the types and proportions of neutral sugars vary with the origin of pectin. Isolated pectin has a molecular weight of typically 60 - 130 000 g/mol, varying with origin and extraction conditions.

2.5.3 Polymorphism of cellulose

Cellulose displays six different polymorphs, namely I, II, III, IV with the possibility of conversion from one form to another. The natural crystal from the native cellulose is made up from metastable. This cellulose I or natural cellulose contains two coexisting phases cellulose I_{α} , which is triclinic, and cellulose I_{β} , which is monoclinic in varying proportions dependent on its origin; I_{α} generally was found more in algae and bacteria; while, I_{β} is the major form in higher plants. Moreover, the I_{α} phase is a metastable form which can be converted to the more stable I_{β} form by annealing in a different medium. The unit of cellulose I consists of four D-glucose residues. In the chain direction (c), the repeating unit is a cellobiose residue, and every glucose residue is accordingly displaced 180° with respect to its neighbors, giving cellulose a 2-fold screw axis. It has been largely accepted that all chains in native cellulose microfibrils are parallel and present their chain oriented in the same direction as shown in Figure 2.16. The chain from layer in the a-c crystallographic plane where they are held together by hydrogen bonds from O(3) in one chain to O(6)H in the other. There are no hydrogen bonds in cellulose I between these layers, only weak van der Waals forces in the direction of the b-axis.

Regenerated cellulose or cellulose II such as rayon and viscose has antiparallel chains as shown in Figure 2.17. The hydrogen bonds within the chains and between the chain in the a-c plane are the same in the cellulose I. Cellulose II is formed whenever the lattice of cellulose I is destroyed, for example on swelling with strong alkaline or on the

dissolution of cellulose. Since the strongly hydrogen bonded cellulose II is thermodynamically more stable than cellulose I. It cannot convert into the latter. Figure 2.18 shows projection of the plane in cellulose I.

Cellulose III and cellulose IV are produced when cellulose I and II are subjected to certain chemical treatments and heating. The morphology of microfibrils has two regions which are amorphous and crystalline regions which are disorder and ordered. In addition, the proportions of ordered and disordered regions of cellulose vary considerably depend on the origin of sample such as cotton cellulose is more crystalline than cellulose in wood [29]

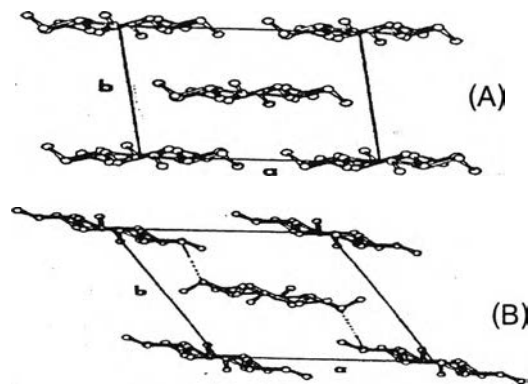


Figure 2.17 Axial projection of the structure of (A) native cellulose (cellulose I) and (B) regenerated cellulose II [27].

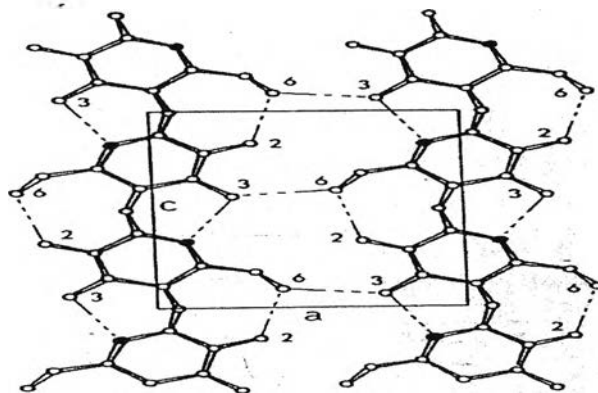


Figure 2.18 Projection of the plane in cellulose I, showing the hydrogen bonding network and the numbering of the atoms. Each glucose residue forms intermolecular hydrogen in the structure [27].

2.6 Crystalline cellulose preparation

Crystalline cellulose has been widely used especially in food, cosmetic, medical, and biocomposite film as a water-retainer, a suspension stabilizer, a flow characteristics controller in the systems used for final products, and as a reinforcing agent for plasticized starch film. The basic step for preparing crystalline cellulose from native plant has generally three steps that is delignification, bleaching and hydrolysis. The step of delignification and bleaching is remove lignin and other composition in microfibrils to produce cellulose microfibrils. Moreover, lignin and other composition effects on hydrolysis reaction in cellulose microfils because they are obstructive to the hydrolysis reaction. So they are must be remove as much possible

2.6.1 Hydrolysis

Crystalline cellulose is prepare from removing of amorphous regions in cellulose microfibrils. Under controlled conditions, this transformation consists of the disruption of amorphous regions surrounding and embedded within cellulose microfibrils that is occurred on β -1,4- glycosidic linkage, while leaving the micro or nanocrystalline segments intact. However, size and shape of crystalline depend on type and nature of plants. Figure 2.19 shows the mechanism of mild and drastic hydrolysis conditions to prepare crystalline cellulose [30].

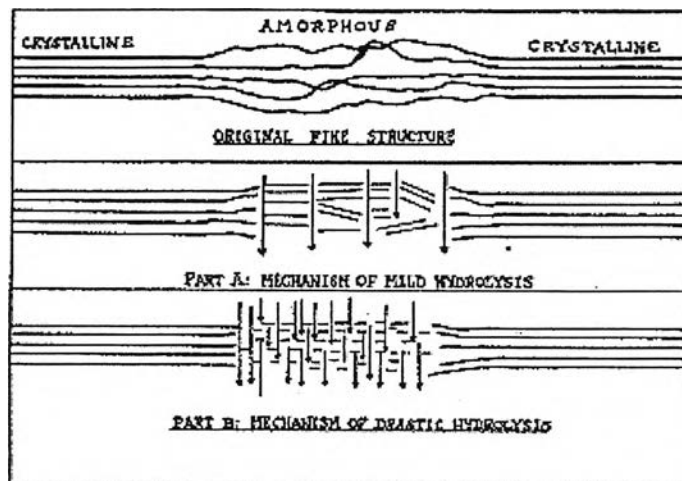


Figure 2.19 Schematic representation of mild and drastic hydrolysis of cellulose [31]

- Enzyme hydrolysis process is the mild condition. This process is depolymerization of cellulose via chemical reaction catalyzed by enzymes which are synthesized by microorganisms such as cellulase which is isolated from bacteria and fungi. The reaction of enzyme hydrolysis depends on the reaction condition such as temperature, pH and pressure. The advantage of enzyme hydrolysis is the mild condition and has very specific action. Furthermore, the product from this process is high purification. However, this process is not well-known for industries owing to the enzyme hydrolysis is a slow reaction and high cost.

- The acid hydrolysis of cellulose is strong condition. The reaction of acid hydrolysis depends on type of acid, temperature, and time. The great advantage of this process is simple and economical. Furthermore, acid hydrolysis is quite rapid reaction and low cost. On the other hand, the advantage of acid hydrolysis is not specific reaction and the product is not purification. However, the acid hydrolysis is well-known process for industry because it is viable commercially and simple. In fact, concentrated acids give quantitative yields of hydrolysis of micro-crystalline cellulose powder (MCP). However, in native cellulose it is difficult to hydrolyse because it is presented as a highly ordered crystalline structure, and lignin accompanying the cellulose fibre inhibits hydrolysis. In addition, treatment with alkali could remove lignin as well as some hemicellulose from the native cellulose and thus make cellulose more accessible to hydrolytic attack. Alkali treatment also makes the cellulose structure amorphous and may render it more prone to hydrolysis [31]

From the several advantages of acid hydrolysis, many researches have been studied crystalline cellulose prepared from acid hydrolysis process. Their researches have been focused on physical and chemical properties and size of crystalline cellulose.

Since 1988, Paralikar and Bhatawdekar [32] prepared microcrystalline cellulose from bagasse pulp. The pulp was bleached with sodium chlorite and then hydrolyzed for 15 min by 2 N HCl at a boiling temperature. The microcrystalline cellulose consist of

cellulose 98%, moisture 3.7 %, and ash 0.05 %. The weight loss during hydrolysis was about 18%. The particle length measured by light microscopy was in the range of 30 μm to 40 μm . The MCC prepared from bleached bagasse pulp was also subjected to the dispersion test in water, and it formed a uniform dispersion. These results showed that bagasse pulp can be a source for the preparation of microcrystalline cellulose.

Later on in 2000, Uesu et al [33] prepared microcrystalline from soybean husk. The soybean husk was delignified with sodium hydroxide solution then hydrolyzed with 2 N HCl at a boiling temperature. After that, it was characterized through various techniques such as scanning electron microscopy (SEM), thermogravimetry analysis (TGA), and compared with a commercial MCC. The results obtained show that the prepared sample has similar crystallinity and lower particle size than the commercial MCC. The shape of both microcrystalline commercial and soybean husk are the typical elongated shape of microcrystalline crystals and a nearly narrow particle size distribution. Although the prepared microcrystalline shows a little lower particle size. The thermal decomposition temperature of commercial MCC is higher than that of microcrystalline from soybean husk which are near 270 °C and 250 °C, respectively.

Afterwards, in 2006, Zhao et al [34] prepared microcrystalline from hydrolyzed cotton linters with dilute 1 M sulfuric acid for 10 min. The results show that the crystalline region in cellulose is composed of microfibril bundles instead of separated microfibrils. These microfibril bundles in the macrofibrils were exposed by removing amorphous cellulose on and near the surface of the macrofibrils as hydrolyzed rapidly as directly observed in SEM. From XRD result it was suggested that cellulose apparent crystallinity was not altered by hydrolysis. These facts suggest that amorphous cellulose in the bulk (not on the surface) is not accessible to hydrolysis and that microfibril bundles are hydrolyzed through a surface reaction process. The observed agglomeration of macrofibers could be the result of higher surface potential from the remaining microfibrils or acid catalyzed intermolecular surface dehydration between macrofibrils.

In 2007, Nitin A. Bhimte and Pralhad T. Tayade [35] prepared the microcrystalline cellulose from sisal fiber. The fiber was treated with 2% sodium hydroxide solution for 3 hours after that bleached with sodium chlorite. The bleached pulp was hydrolyzed with 2 N HCl, keeping the solid:liquor ratio of 1:20 and refluxing at 105 °C for 15 minutes. The particle size of sisal microcrystalline cellulose and Avicel microcrystalline cellulose was compared. They reported that the average particle size of sisal microcrystalline cellulose is smaller than that of Avicel microcrystalline cellulose. From SEM result, the particle of Avicel-102 appeared as small and plate shape. The particle size of sisal microcrystalline cellulose appeared as long thread-like fibers. There are no comparable difference in the X-ray diffraction pattern of all cellulose samples. The crystallinity index showed to be around 60%.

Later on, with in the same years, El-Sakhawy et al [36] prepared microcrystalline cellulose from local agricultural residues, namely, rice straw and cotton stalks bleached pulps. Hydrolysis of bleached pulps was carried out using 2 N hydrochloric or sulfuric acid to study the effect of the acid used on the properties of the produced microcrystalline cellulose such as morphology and particle size. They reported that microcrystalline is rod-like shape. All prepared microcrystalline cellulose sample had slightly lower particle size than the Avicell microcrystalline cellulose but with wider particle size distribution. The average particle size of cotton stalk is larger than rice straw at each kind of acid used. Furthermore, the effect of different acid used was shown that cotton stalk and rice straw microcrystalline cellulose samples with larger particle size was obtained in case of using H₂SO₄ in the hydrolysis process. The average particle size of cotton stalk and rice straw with hydrochloric and sulfuric acid are 3.66, 4.06 and 4.07, 5.49 μm, respectively. The average particle size of Avicell microcrystalline cellulose is 5.53 μm.

Apart from that, Hafraoui and co-work [37] studied the shape and size distribution of crystalline nanoparticles resulting from the sulfuric acid hydrolysis of cellulose from cotton, Avicel, and tunicate by transmission electron microscopy(TEM) and atomic force microscopy(AFM). Images of TEM specimens showed that the majority

of cellulose particles were flat objects. Particle from cotton and Avicel have a length between 100 and 300 nm. Whereas those from tunicin are several micrometers long and have a whisker like morphology. Moreover, tunicin whiskers were described as twisted ribbons with an estimated pitch of 2.4-3.2 μm .

Recently in 2008, Ejikeme et al [38] prepared microcrystalline cellulose from agricultural waste, namely, orange mesocarp. After removal of the epicarp and the endocarp from oranges, orange mesocarp was dried, pulverized and digested with 2% w/v sodium hydroxide at 80 °C for 3 hours. Alpha and microcrystalline cellulose were extracted from the pulp using 17.5% w/v and 2.5 N hydrochloric acid, respectively. The physiochemical of microcrystalline cellulose was evaluated. They reported that microcrystalline cellulose obtained from orange mesocarp was almost white in colour and odorless. Yield of α -cellulose from the orange mesocarp was 62.5% and that of microcrystalline cellulose was 25.3%. The particle size is varied from 53 -1200 μm . In addition, 24.49 gram or 62.4% of the 40 gram sample has particle size less than 600 μm .

2.7 Degree of polymerization (DP)

The degree of polymerization, or DP, is the number of repeat units in an average polymer chain. It is a measure of molecular weight. Natural polymer such as cellulose has high molecular weight and supramolecular structure. However, it has lower molecular weight after chemical reaction. The degree of polymerization of cellulose can be lowered by acid hydrolysis under heterogeneous conditions. When pulp is subjected to acid hydrolysis, glucosidic linkages of the cellulose are broken and the degree of polymerization decreases. In the initial stage of reaction a strong decrease of DP is observed as degradation takes place in the amorphous region. The degree of polymerization decreases rapidly until it reaches that so-called 'levelling-off' or 'limiting degree of polymerization (LODP)'. The LODP depends on the origin and pre-treatment of cellulose. The LODP is relationship with size of hydrolyzed crystalline cellulose. The viscosity measurement of cellulose is one of the methods to determined the LODP. Thus,

there are many researchers investigated the effects of acid hydrolysis by studying the viscosity measurement of cellulose.

In 1950, Batissta [31] studied the effects of time on weight loss and degree of polymerization of four cellulose samples using mild (5.0 N hydrochloric acid) at 5, 18 and 40 °C) and drastic (2.5 N or 5.0 N hydrochloric acid at 105 °C) hydrolysis conditions. The samples were purified cotton, bleached cotton linters, textile rayon, and wood pulp. The percent crystallinity as measured by acid hydrolysis (based on weight of residue) and the leveling-off degree of polymerization was shown to be dependent on whether mild, drastic, or mild plus drastic conditions of hydrolysis. The result shown that mild hydrolysis condition are used for long period of time, much smaller losses in weight are found than when drastic conditions of hydrolysis are used for short periods of time, eventhough the average degree of polymerization approaches the same leveling-off values in each case. The use of 2.5 N hydrochloric acid at 105 °C for 15 minutes is recommended as optimum conditions for measuring weight loss and leveling-off degree of polymerization. The degradation of sample was occurred in 5.0 N hydrochloric acid at 105 °C. Moreover, the effect of crystallization on hydrolysis was found to be pronounced for regenerated cellulose than for native cellulose.

In 2005, Helena Hakansson and Per Ahlgren [39] studied LODP microcrystalline cellulose with dilute acid hydrolysis of pulps by following the decrease in intrinsic viscosity. The decrease in intrinsic viscosity and the loss of weight during hydrolysis at reaction temperatures of 60 and 80 °C were investigated, using acid concentrations from 0.5 to 4 M with two different acids (HCl and H₂SO₄). The same levelling-off degree of polymerization (LODP) was reached under all hydrolysis conditions, but a longer time was needed under milder conditions. An appropriate method of determining the intrinsic viscosity at LODP was established and used in this investigation. The greatest difference in LODP was found between a birch prehydrolysed kraft pulp and a mixed hardwood prehydrolysed kraft pulp; the intrinsic viscosities at LODP being 178 and 72 dm³/kg, respectively. The effect of the intrinsic viscosity of a given starting material was

also investigated, but only a small difference 10% in the LODP was found for pulp samples with very different initial intrinsic viscosities.

2.8 Starch biocomposite film

Biocomposites are composite materials comprising one or more phase(s) derived from a biological origin. In terms of reinforcement, this could include plant fibers such as cotton, flax, hemp, and products from nature plants. Matrix may be polymers from renewable sources such as vegetable oils or starches [40].

There are a few numbers of researchers working on starch biocomposite film reinforced crystalline cellulose. For example, in 2005, Orts and co-workers [41] prepared biocomposite film from potato starch reinforcing cellulose microfibrils obtained by the acid hydrolysis of cotton. These were added at low concentrations (2-10% w/w) to polymer gels and films as reinforcing agents. Significant changes in mechanical properties, especially maximum load and tensile strength, were obtained for fibrils derived from several cellulosic sources, including cotton, softwood, and bacterial cellulose. The addition of cotton-derived microfibrils at 10.3% (w/w) concentration increased Young's modulus by 5-fold relative to a control sample with no cellulose reinforcement that has a Young's modulus of 12.49 GPa.

In 2006, Lu et al. [42] prepared biocomposite film from plasticized starch (PS) reinforcing nanocrystalline cellulose from ramie (RN) fiber from 0–40 wt%. The ramie cellulose nanocrystalites, having lengths of 538.5 to 125.3 nm and diameters of 85.4 to 5.3 nm on average, were prepared from ramie fibers by acid hydrolysis. The results indicate that the synergistic interactions between fillers and PS matrix play a key role in reinforcing the composites. The PS/RN composites, conditioned at 50% relative humidity, increase, respectively, in both tensile strength and Young's modulus from 2.8 MPa for PS film to 6.9 MPa and from 56 MPa for PS film to 80 MPa with increasing RN content from 0 to 40 wt%. Further, incorporating RN fillers into PS matrix also leads to a decrease in water sensitivity for the PS based biocomposites.

2.9 Agricultural waste

Using agricultural waste as raw material provides a renewable source as well as generating a non-food source of economic development from farming and rural area. The utilisation of agricultural waste in biocomposite film which is raw material for producing microcrystalline cellulose has been increased due to the many advantages such as low cost, abundant, and biodegradable properties. The examples of agricultural waste that has been used for producing microcrystalline are rice husk, cotton stalk, rice straw, bagasse, and banana stem.

2.9.1 Bagasse

Sugarcane is one of the most important crops in the tropics, with global production now estimated at 1,250 million tons a year. The production yield of sugarcane in Thailand is about 50 million tons per year. Sugarcane contains 73–76 g liquid/100 g and the remaining 18–25 g/100 g is fiber. Granular sugar is produced from sugarcane liquid with bagasse being the main byproduct generated during this process. Normally, bagasse is used in cattle and chicken feed, papermaking, and insulating boards. The chemical constituents of bagasse are shown in Table 2.4 . Many commercially available products are made from bagasse such as cellulose and purified hemicellulose, fuel, and chemical. Bagasse is also used in health foods for its dietary fiber. The high cellulose content and abundant in Thailand is encouraging this research focus on preparation of microcrystalline cellulose from bagasse.

Table 2.3 Chemical constituents of bagasse [43]

Chemical component	% Dry Weight
Holocellulose	71.41
Alpha cellulose	51.04
Lignin	21.09
Ash	3.85

2.9.2. Banana stem

Banana is grown extensively in tropical regions. It is important crop in the world because it is the principal food resources. Banana is economic crop of this region generating vast agricultural waste after harvest. The agro-waste including dried leaves and pseudostem after harvest. The banana stem called the pseudostem is a juicy material rich in fiber. The chemical component of banana stem is shown in table 2.5. The stem though highly edible and nutritious forms a major waste material in large-scale banana plantations. Extracting good quality fiber from these stems is gaining popularity in Thailand. The fiber from the banana stems is as strong as any other plant yarn. Many units engaged in extracting banana fiber for making a wide range of products such as rope, clothes, shoes. These many advantages of banana stem, such as high cellulose content and low cost, have stimulated researcher in using banana stem to prepare microcrystalline cellulose.

Table 2.4 Chemical constituents of banana stem [43]

Chemical component	As % Dry Weight
Holocellulose	55.50
Alpha cellulose	47.37
Lignin	19.43
Ash	15.34

2.10. Tensile properties

Tensile properties are most widely used for defining the quality of production of polymeric material. Tensile properties indicate how the material will react to forces being applied in tension. A tensile test is a fundamental mechanical test where a carefully prepared specimen is loaded in a very controlled manner while measuring the applied load and the elongation of the specimen over some distance. The stress-strain curve relates the applied stress to the resulting strain and each material has its own unique stress-strain curve. Figure 2.20 shows stress-strain behavior of polymer material.

- The term stress (s) is used to express the loading in terms of force applied to a certain cross-sectional area of an object. From the perspective of loading, stress is the applied force or system of forces that tends to deform a body. From the perspective of what is happening within a material, stress is the internal distribution of forces within a body that balance and react to the loads applied to it.

- Strain is the response of a system to an applied stress. When a material is loaded with a force, it produces a stress, which then causes a material to deform. Engineering strain is defined as the amount of deformation in the direction of the applied force divided by the initial length of the material.

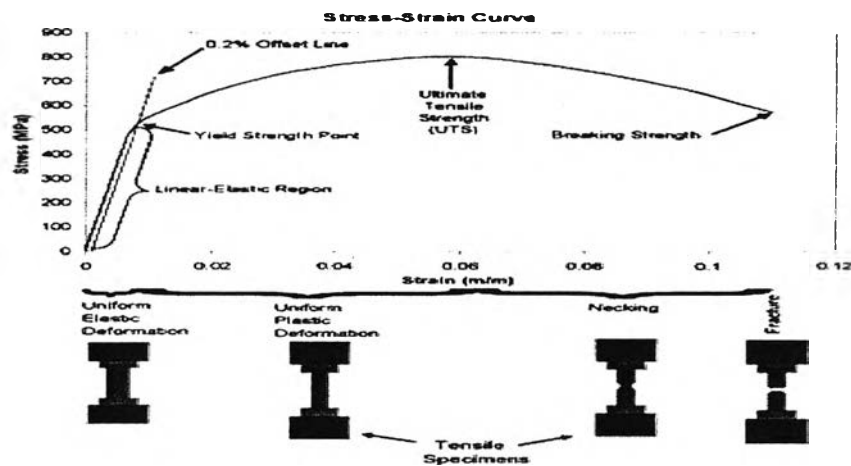


Figure 2.20 Stress-strain behavior of polymer material[44]

- Tensile tests are used to determine the Young's modulus, elongation, proportional limit, tensile strength, yield point, yield strength, and other tensile properties.

- Modulus of elasticity or Young's modulus (E) defines the properties of a material as it undergoes stress, deforms, and then returns to its original shape after the stress is removed. It is a measure of the stiffness of a given material. To compute the modulus of elastic, simply divide the stress by the strain in the material. Since strain

is unitless, the modulus will have the same units as the stress, such as GPa or MPa. The modulus of elasticity applies specifically to the situation of a component being stretched with a tensile force.

- Yield point deviates from the straight-line relationship of stress-strain curve. To determine the yield strength using this offset, the point is found on the strain axis (x-axis) of 0.002, and then a line parallel to the stress-strain line is drawn. This line will intersect the stress-strain line slightly after it begins to curve, and that intersection is defined as the yield strength with a 0.2% offset.
- Yield strength is the stress required to produce a small-specified amount of plastic deformation. The yield strength obtained by an offset method is commonly used for engineering purposes because it avoids the practical difficulties of measuring the elastic limit or proportional limit.
- Proportional limit is the highest stress at which stress is directly proportional to strain. It is obtained by observing the deviation from the straight-line portion of the stress-strain curve.
- The ultimate tensile strength (UTS) or, more simply, the tensile strength, is the maximum engineering stress level reached in a tension test. The strength of a material is its ability to withstand external forces without breaking. In brittle materials, the UTS will be at the end of the linear-elastic portion of the stress-strain curve or close to the elastic limit. In ductile materials, the UTS will be well outside of the elastic portion into the plastic portion of the stress-strain curve.

2.11. Biodegradation

Biodegradation is the natural process. The biodegradable process is organic substances are attacked by living organisms. The Organic material can be degraded

aerobically, with oxygen, or anaerobically, without oxygen and it is converted into small molecule such as H_2O and CO_2 . The change in the chemical structure of biodegradable plastics under specific environmental conditions results in a loss of some properties including physical and mechanical properties. The biodegradation processes are usually followed by monitoring the changes in these properties using standard test methods appropriate to the plastic. Today's plastics are designed with little consideration for their ultimate disposability. This has resulted in mounting worldwide concerns over the environmental consequences of such materials because they were entered to the waste stream after their uses especially in single use and disposal plastic applications. Polymer waste management requires sound complementary practices of conservation, recycling, incineration and biodegradation. Since biodegradation is potentially the most environmentally friendly of all these practices, there is activity in the area of biodegradable polymers as packaging materials. Generally, starch removal does occur when the starch-based films are exposed to microbial. The first mechanism of degradation is the production of enzyme amylase by microbial [45].

Generally, there are several ways to test the biodegradability of plastics. The methods for testing biodegradability are highlighted as following:

2.11.1 Environmental Chamber Method

Environmental chambers employ high humidity (>90%) situation to encourage microbial growth. Test material are hung in the chamber, sprayed with a standard mixed in columns of known fungi in the absence of additional nutrients and incubated for 28 to 56 day at constant temperature. A visual assessment is subsequently made and a rating given based on the amount of growth on the material. This test is particularly stringent and was designed to simulate the effects of high humidity condition on electronic components and electrical equipment. Growth of fungi across a printed circuit board can result in a gross systems failure in a computer system or military equipment.

2.11.2 Soil Burial tests

The material is buried in soil beds prepared in the laboratory. The soil beds containing the samples are incubated at a constant temperature for between 28 days and 12 months. The soil beds are normally conditioned for up to 4 weeks prior to use and may be supplemented with organic fertilizer to encourage an active microbial. The microbial activity is tested using a cotton textile strip, which should lose 90% of its tensile strength within 10 days of exposure to the soil. The moisture content is normally set at 20-30%. Samples are removed for assessment of changes in their properties such as weight loss, mechanical properties, or morphology that is surface damage. However, the soil burial tests are that a 3 to 6 month test is sufficient to demonstrate the environmental resistance of polymer materials [46].

2.11.3 Specific Microorganism or Enzyme degradation

Biodegradation is an event which takes place through the action of enzymes associated with living organisms (bacteria, fungi, etc). Generally, microorganisms produce enzymes involving in the chemical mode of degradation and attack natural polymer. The attack is specific with respect to both the enzyme and biopolymer couple. All enzymes are protein, even small changes in temperature or pH can result in changes in the enzyme activity. The accessibility of a polymer to be degradatively attacked by living organisms has no direct relation to its origin and not all biopolymers are truly biodegradable. This test method is also appropriate for the evaluation of degradable plastic that have undergone specific chemical, thermal, or photo degradation or combination.

2.11.4 Activative sludge Waste water treatment

This method is the simulation studies range from laboratory designed equipment, which replicates aerobic sewage treatment anaerobic sludge digestion, through the exposure trials and where material is submerged in activated sludge environment. Exposure trials require that the samples be securely held on some form of

racking for aqueous environments. The racks, normally made of stainless steel, are submerged in the test situation and samples periodically removed. This test method is designed to be applicable to all plastic materials that are not inhibitory to the bacterial present in the activated sludge.