CHAPTER II

THEORETICAL BACKGROUND

2.1 Tapioca

Cassava is the third most important crop in Thailand. About 18 to 20 million tons of cassava root are produced each year from 1.15 million hectares of planting area. Cassava was unknown to the Old World before the discovery of America. There is archaeological evidence of two major centers of origin for this crop, one in Mexico and Central America and the other in northeastern Brazil. It was dispersed widely by the Portuguese in tropical and subtropical areas of Africa, Asia and the Caribbean (Table 2.1). Export quantity of Thai cassava starch in 1997-2001 is shown in Figure 2.1. Because it grows easily, provides large yields and little affect by diseases and pests, the areas under cassava cultivation are increasing rapidly. The plant is grown for its edible tubers, which serve as a staple food in many tropical countries and are also the source of an important starch. It is now grown widely as a food crop or for industrial purposes. In many regions of the tropics cassava occupies much the same position as white potatoes do in some parts of the temperate zones as the principal carbohydrate of daily diet. The industrial utilization of cassava roots is expanding every year (1-2).

The cassava plant has been classified botanically as *Manihot utilissima Pohl* of the family *Euphorbiaceae*. In recent publications, the name *Manihot esculenta* Crantz is being in creasingly adopted. The plant grows in a bushy form, up to 2.4 m tall, with greenish-yellow flowers. The roots are up to 8 cm thick and 91 cm long. The roots contain from 20 to 32% of starch (Table 2.2). Tapioca easily digested starchy foodstuff extracted from the root of the cassava plant. The term "tapioca" is used to designate products made from cassava like starch, dried chips etc (3).

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Table 2.1 Cassava: Harvested area and production in 1998-2000(1)

Country	Harvested area (1000 rais*)			Production (1000 tons)		
	1998	1999	2000	1998	1999	2000
Total	101,175	104,812	100,619	158,620	169,026	172,737
Nigeria	16,856	19,200	19,200	30,409	32,697	32,697
Brazil	9,913	9,891	10,667	19,809	20,892	22,960
Thailand	6,527	6,659	7,068	15,591	16,507	19,049
Indonesia	7,531	8,500	8,500	14,728	16,347	16,347
Congo	13,750	12,710	6,855	16,500	16,500	15,959
Ghana	3,938	4,063	4,063	7,172	7,845	7,845
India	1,531	4,563	1,563	5,868	5,800	5,800
Tanzania	4,331	4,375	5,301	6,193	7,182	5,758
Uganda	2,138	2,344	2,388	2,285	3,300	4,966
Mozambique	6,344	5,988	5,000	5,639	5,353	4,643
Other	28,316	29,519	30,014	34,426	36,603	36,713

* 1 rai = 0.16 hectares

Source: Thailand, Office of Agricultural Economics, Food and Agriculture Organization of United Nations
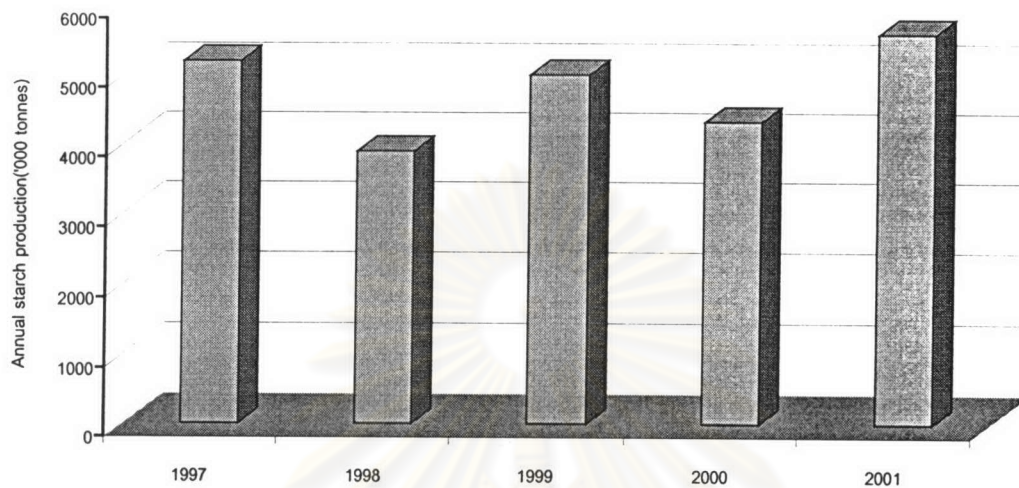
Figure 2.1 Cassava starch production in1997-2001 in Thailand

Source: Office of Agricultural Economics.

Table 2.2 General properties of cassava starch (4)

Properties	quantity
Chemical composition (% by dry starch)	
- Protein	0.1
- Fats	0.1
- Ash	0.2
- Phosphorus	0.01
- moisture	13
Size of granule (μm)	3-34
Cold paste clarity (%)	40-50
Whiteness (Kett)	81.0-96.0
Amylose (%)	17-23
Size of amylose (DPn)	2000-4600
Solubility (%) at 85 °C	22-42
Swell of power (%) at 85 °C	40-62
Gelatinization temperature (°C)	59-70

Throughout the world, starch plays an important part in the preparation of variety of food products. Corn starch is used in great quantities because of high production and low cost. A pasting history of corn, sorghum and wheat starches with tapioca added for comparison is shown in Figure 2.2. The three cereal starches exhibit a medium paste viscosity and stable paste under heat and shear. During cooling the paste age show a high set-back, forming a stiff gel. In comparison, tapioca starch gives a high viscosity and a paste that is fragile and breaks down quickly under heat and stirring. There is set-back under cooling but the paste is tendered than corn starch. Also, the paste from the cereal starches is short in texture and opaque, whereas tapioca paste is stringy in texture and translucent (5).
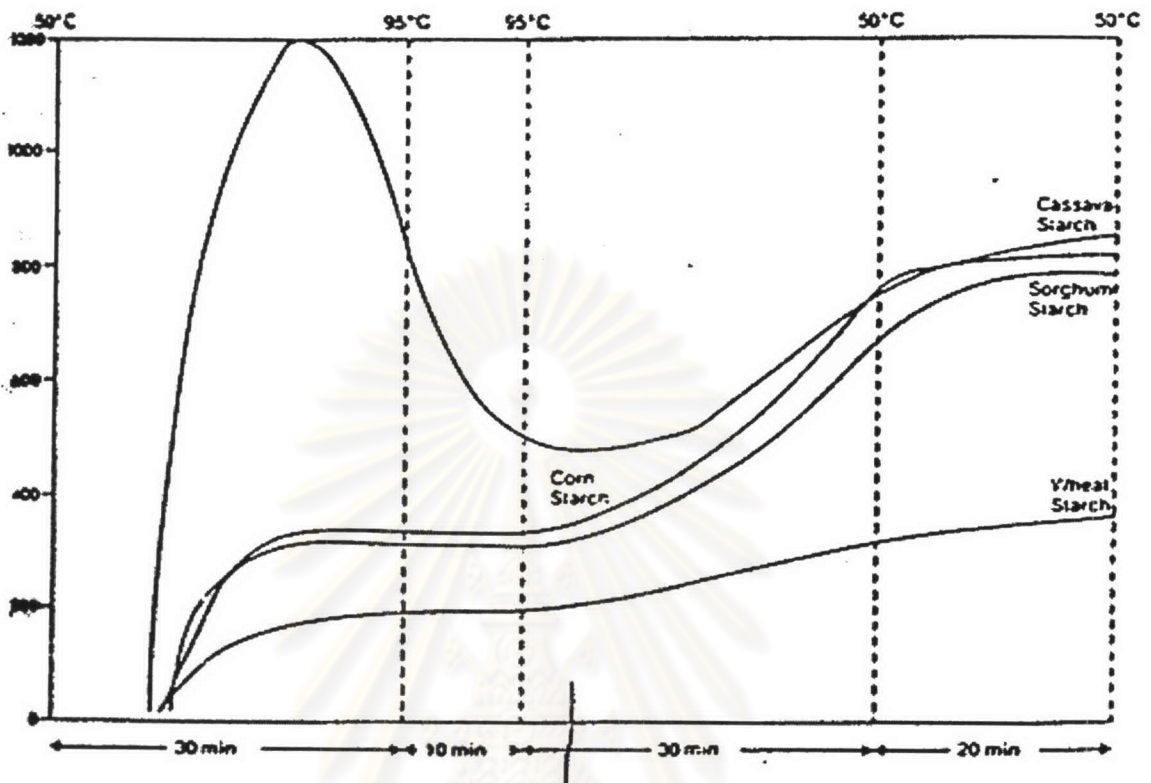
Figure 2.2 Pasting histories of corn, sorghum and wheat starches with tapioca added for comparison (5).

Tapioca starch has been applied as the raw material in 6 main industries in Thailand, which are paper industry, textile industry, food, and beverage industry, plywood industry, glue industry and alcohol industry. The tapioca starch will be used in three stages of production process in paper industry; Beater Sizing or Wet-end, Surface Sizing or Size-press and Surface Coating. In textile industry, the tapioca starch has an important role in three stages of production of textiles; mixing, printing and finishing. In addition, the tapioca starch is applied to increase its density, in order to decrease the cost and give a sticky consistency in the food and beverage industry. Tapioca starch is used for making glue, which is and important raw material of the plywood industry. The strength and the quality of plywood depend on the quality of glue. A total of 1,182,940 kilograms of tapioca starch is fed to the plywood industry annually. As for glue industry, tapioca starch becomes sticky when it is mixed with water or certain chemicals. It stays

sticky over a very long period of times. Alcohol derived from tapioca starch in alcohol industry, especially extraction of the ethanol to use as fuel is drawing more attending from developing countries (6).

In Thailand, tapioca starch is produced in five different forms: flour, pellets, chips, meal and waste. Approximately 80% of the total productions are pellets destined for European markets, about 15% are flour for Japan and the United States of America and the rest is in chips, meal and waste.

2.2 Starch

Starch is the major reserve polysaccharide of higher plants where it occurs in storage organs such as seeds, tubers or roots and also in smaller quantities on stems and leaves. It exists as water insoluble roughly spherical granules whose shape, size and size distribution are characteristic of the particular plant species. The starch is described by its plant source as corn starch, rice or glutinous, potato starch, tapioca starch, *etc*. Since the conditions of growth are different in each plant, the starch from each plant source will vary somewhat in appearance, composition and properties.

2.2.1 Characteristics of Starch Granules

Starch is the only one universally produced in small individual packet called granules. The size and shape of starch granules vary from plant to plant, each different and recognizable as to plant source when examined under the microscope. Granules of rice starch are polygonal in shape and mostly run about 3 to 8 μm in diameter. They tend to aggregate in clusters. Corn or maize starch have polygonal and some round granules which range from about 5 to 25 μm in diameter, with about a 15 μm average. Tapioca starch granules usually have round shapes, which are truncated at one end. They average about 20 μm in diameter, but many range from 5 to 35 μm in diameter. Wheat starch has flat, round or elliptical granules, which tend to cluster in two size ranges: 2 to 10 μm and 20 to 35 μm. Potato starch has the largest granules of any commercial starch. They are

oval or egg-shaped and range from 15 to 100 μm. Potato has the largest granules and rice the smallest of the commercial starches (7).

Large starch granules tend to build higher viscosity, but the viscosity is delicated because the physical size of the granule makes it more sensitive to share. In spite of such difference, the more compact structure of a smaller molecule does not always mean a significant difference in gelatinization. However, the gelatinization properties of the large and small granules do not show significant performance differences (8).

2.2.2 Chemical Structure of Starch

Starch is a polymeric carbohydrate consisting of anhydroglucose unit linked together primarily through $\alpha-D-(1 \rightarrow 4)$ glucosidic bonds. Starch is a heterogeneous material consisting at the extremes of two major types of polymers: amylose, an essential linear structure and amylopectin, a highly branched polymer. It contains varied ratio of amylose and amylopectin in defferent plants, resulting in different properties of plant starch (Table 2.3).

Table 2.3 Percent of amylose and amylopectin in reserve plant starch (9)

Starch	Amylose (%)	Amylopectin (%)
Rice	18.5	81.5
Waxy rice	0	100
Wheat	28	72
Barley	22	78
Waxy barley	0	100
Oat	27	73
Maize	28	72
Waxy maize	0.8	99.2
Tapioca*	16.7	83.3
Potato	20	80
Sweet potato	17.8	82.2
Smooth pea	35	65
Wrinkled pea	66	34

Normal starches contain roughly 25% amylose. Mutant varieties of corn, called high-amylose corn, produce starch with amylose contents ranging up to 85%, although commercial varieties usually have a maximum of 65% amylose. As expected, these starches are difficult to gelatinize some requiring temperatures in excess of 100°C. At the other extreme, some starches consist only of amylopectin. These are waxy corn, waxy barley and waxy rice or glutinous rice. They usually produce clear pastes, somewhat resembling pastes of root tuber starches. With no amylose to retrograde, these starch pastes are fairly stable.

Amylose is essentially a linear polymer in which the anhydroglucose units are predominantly linked through α-D- (1$\rightarrow$4) glucosidic bonds. Its molecular size varies depending upon the plant source and processing conditions employed in extracting the

starch. It may contain anywhere from about 200 to 2000 anhydroglucose units (Figure 2.3). The abundance of hydroxyls imparts hydrophilic properties to the polymers, giving it and affinity for moisture and dispersibility in water. However, because of their linearity, mobility and hydroxyl groups, amylose polymers have a tendency to orient themselves in a parallel fashion and approach each other closely enough to permit hydrogen bonding between hydroxyls on adjacent polymers. As a result, the affinity of the polymer for water is reduced and the sol becomes opaque. This phenomenon of intermolecular association between amylose molecules is commonly called retrogradation.

Amylopectin is a branched polymer containing, in addition to anhydroglucose units linked together as in amylose through α-D-(1$\rightarrow$4) glucosidic bonds, periodic branches at the carbon-6 position. These branches are linked to the carbon-6 positive by α-D-(1$\rightarrow$6) glucosidic bonds (Figure 2.3). Each branch contains about 20 to 30 anhydroglucose units. The large size and branched nature of amylopectin reduce the mobility of the polymers and interfere with any tendency for them to become oriented closely enough to permit significant levels of hydrogen bonding. As a result, aqueous sols of amylopectin are characterized by clarity and stability as measured by resistance to gelling on aging. Amylopectin sols do not form as strong and flexible films as the linear amylose.
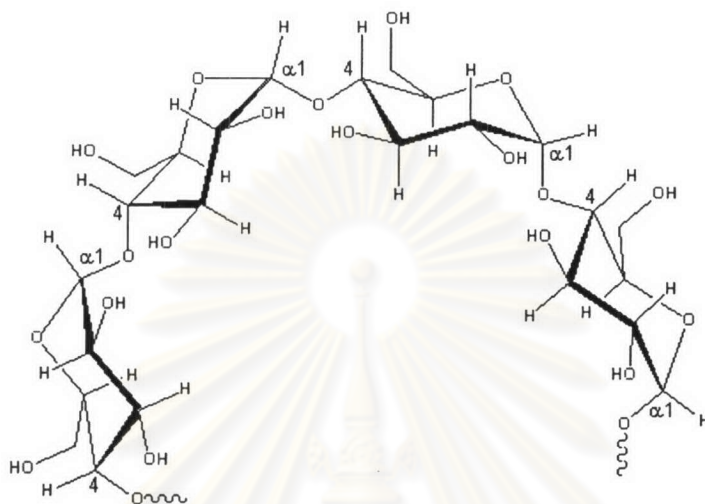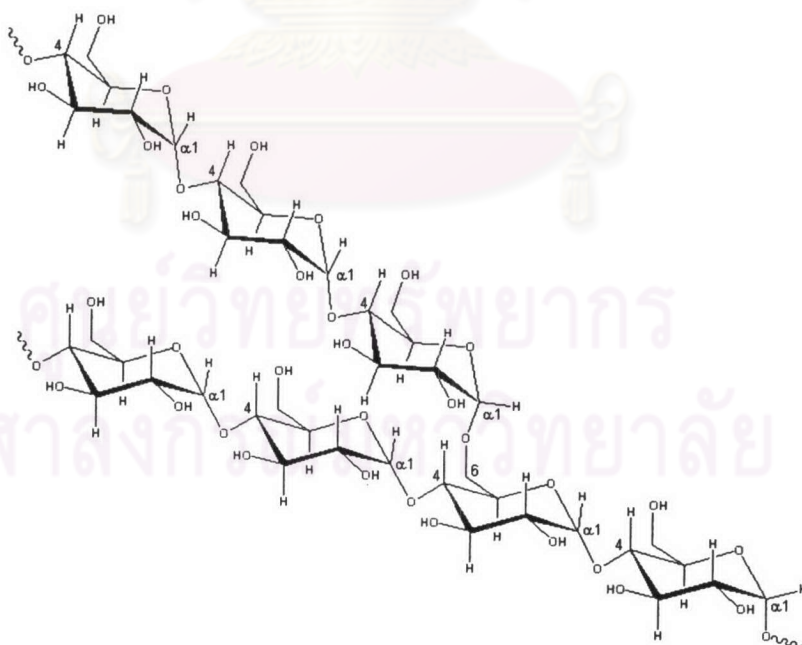
Amylose

Amylopectin

Figure 2.3 Partial structures of amylose and amylopectin

The amylose and amylopectin fractions are oriented in the starch granule in radial fashion. Wherever the linear segments of the amylopectin or amylose run closely parallel, hydrogen bonding between adjacent segments may occur forming micellar crystallites, which are responsible for the granule integrity and for imparting birefringence properties.

2.2.2 Gelatinization Phenomena

Undamaged starch granules are insoluble in cold water, but can reversible imbibe water and swell slightly. However, as the temperature increases, the starch molecules vibrate more vigorously, breaking intermolecular bonds and allowing their hydrogen bonding sites to engage more water molecules. This penetration of water and the increased separation of more and longer segments of starch chains increase randomness in the general structure and decrease the number and size of crystalline regions. Continued heating in the presence of abundant water results in a complete loss of crystallinity as judged by loss of birefringence and the nature of the X-ray diffraction pattern. The point at which birefringence first disappears is regarded as the gelatinization temperature. It usually occurs over a narrow temperature range, with larger granules gelatinizing first and smaller granules later, although this is not a universal pattern (Table 2.4). Highly swollen granules can be easily broken and disintegrated by mild stirring, and these results in a large decrease in paste viscosity.

Important causes on swelling granule starch are as follows :

1   Oriental molecular in granule starch
2.   Amylose per amylopectin ratio
3.   Molecular weight distribution of amylose and amylopectin
4.   Other composition of starch exactly

Table 2.4 Starch Granule Characteristics (10)

Source	Diameter (μm)		Gelatinization temperature (°C)
	Range	Mean	
Corn	21-96	15	61-72
White potato	15-100	33	62-68
Sweet potato	15-55	25-50	82-83
Tapioca	6-36	20	59-70
Wheat	2-38	20-22	53-64
Rice	3-9	5	65-73

Swelling and the subsequent disruption or pasting of the granule are of great technological importance; this phenomenon can be readily followed by using a Brabender Amylograph (Figure 2.4) shows the typical pasting behavior of starches from three genotypes of maize; normal maize, waxy maize and amylomaize. As the temperature of the water is increased, the granules swell to impinge on each other, and so increase the viscosity of the starch paste. This process continues until the "peak viscosity" is reached, for at this point the cohesive forces in the original granular structure become excessively weakened and the structure of the paste collapses as the integrity of the granules is lost. Figure 2.4 shows that waxy maize starch swells rapidly to give a peak viscosity, but the intermolecular forces in this granule are weak and they break down rapidly on further cooking. On cooling, however, there is very little set- back because of the absence of amylose. Normal maize starch takes a longer time to reach a much lower peak viscosity; the extent of break down of structure on prolonged stirring at high temperatures is smaller, but the degree of set-back is large because of aggregation of amylose. In contrast, the amylomaize starch granules are little affected, and no swelling at all is apparent on the amylograph (11).
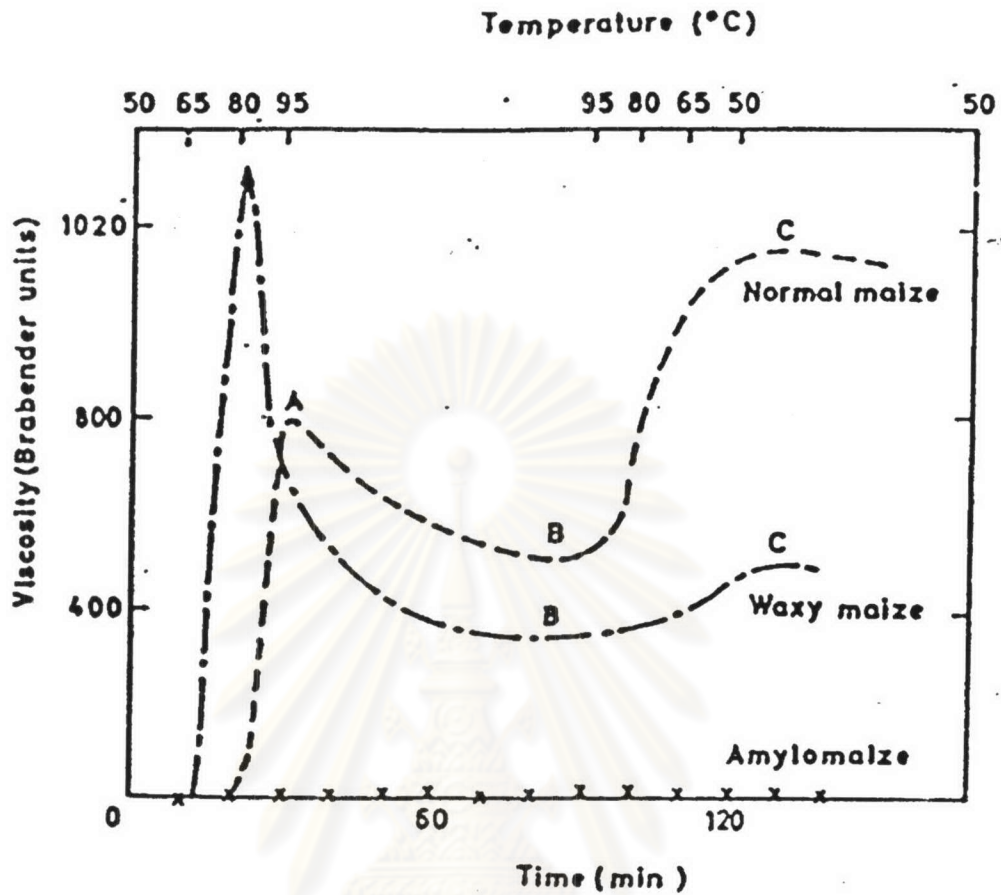
Temperature (°C)

Figure 2.4. Typical pasting behavior of starches from three genotypes of maize (7) .

2.3 Modification of Starch

The term "native starch" is defined as the product extracted from cassava roots, which is called "starch"-not "flour". The physical properties of native unmodified starches and of the colloidal sols produced from these starches on heating limit the usefulness of starch in many applications. Modification of native starch can be grouped into three main classes. There are physical modification, chemical modification and biological modification. The latter can be subdivided into four groups: cross-linking, degradation, derivertization and graft and block polymerization (12). Modified starches were developed one or more of these shortcomings and thus expand the usefulness of starch for a myriad of industrial applications. The I.S.O. (International Organization for Standardization) Technical Committee 93 distinguishes only between native starch and

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modified starch, the latter being defined as native starch treated in such a way to modify one or more of its original physical or chemical properties. The term "modified starch" thus includes: pregelatinized starch, oxidized starch, thin boiling starch, dextrin dialdehyde starch, starch ester and starch ether etc. (13). In recently, important modified starch and to provide products with the properties required for a myriad of industrial applications that is chemical modification.

Table 2.5 Types and properties of modified starches (14)

Type of modification	Properties	Uses
1. Physical	-soluble cold water - low pregelatinization temperature	-snack extrusion at low temperature
2. Biological	-low viscosity at high temperature	-instant fruit -pie filling -beggary -candy
3. Chemical **3.1 Derivatization**	-low retrogradation -low pasting temperature -high paste and viscosity -high water- holding capacity	-freeze/thaw stability -UHT custards -frozen pizza and topping
3.2 Hydrolysis	-low viscosity -higher binder	-candy -chocolate
3.3 Oxidation	-low pasting temperature -decrease retrogradation of amylose -clarity pasting	-tablet binder -sauces
3.4 Cross-linking	-increase distribution of solid -lower retrogradation and swelling	- pie filling - pudding cheese and sauces

2.3.1 Chemically Modified Starches

2.3.1.1 Acid Conversions or Acid Modified Starch

Acid hydrolysis below the gelatinization temperature takes place in amorphous regions of the granules leaving the crystalline regions relatively intact. Some properties of acid-treated starches, relative to this parent starches, include decreased hot-paste viscosity, decrease intrinsic viscosity, decrease gel strength and increased gelatinization temperature. Commercial acid-modified starch is produced by reacting 40% slurry of corn or waxy maize starch with hydrochloric or sulfuric at 25-50°C. Time of treatment is determined by the viscosity decrease and may vary from 6 to 24 hr. The mixture is neutralized with soda ash or dilute sodium hydroxide, and the modified starch is then filtered and dried. These starches are used in the manufacture of gum candies and confection because of their ability to form hot, concentrated paste that gel firmly on cooling.

2.3.1.2 Hydroxyethylated Starch

Hydroxyethylstarch ethers of the degree of substitution (DS) 0.05-0.10 have been produced by reacting starch with ethylene oxide at 50°C. Wet-milled but undried starch is used for hydroxyethylation. The derivative is easily filterable and can be produced economically in a fairly pure form. The introduction of hydroxyethyl groups at low DS results in extensive modification of physical properties. Among them are reduced gelatinization temperature, increased rate of granule swelling and lowered tendency of starch pastes to gel and retrograde. Other hydroxyalkylstarches use as food additives in salad dressings, pie fillings and other food-thickening applications.

2.3.1.3 Starch Phosphate Monoesters

Starch phosphate monoesters may be prepared by reacting a dry mixture of starch and acid salts of ortho-, pyro- or tripolyphosphate at elevated temperature. Typical reaction conditions involve heating for 1 hr at 50-60°C. The degree of substitution obtained is generally less than 0.25, but higher DS derivatives can be prepared by elevating the temperature and concentration of phosphate salt and by extending the reaction time. Compared with their parent starches, the monophosphate esters have a lower gelatinization temperature and swill in cold water at 0.07 and higher. In common with other derivatives, starch phosphates exhibit increased paste viscosity and clarity and decreased set-back or retrogradation. Starch monophosphates are useful in frozen foods because of their excellent freeze-thaw stability. They are often employed as thickeners in frozen gravy and frozen cream pie preparations.

2.3.1.4 Cross-linked Starch

Cross-linking may be produced by reacting starch in aqueous suspension with phosphoryl chloride, by reacting dry starch with trimetaphosphate or by reacting starch slurry with 2% trimetaphosphate (pH 10-11) for 1 hr at 50°C. The most notable change effected by phosphate cross-linking is an increase in stability of the swollen granule. Depending on the degree of derivatization, the hot-paste viscosity may be greater or less than that of the parent starch. More highly cross-linked starches are very stable at high temperatures, low pH and conditions of mechanical agitation. If the starch is sufficiently cross-linked, swelling can be inhibited, even in boiling water. Cross-linked starch is used mainly in baby foods, salad dressings, fruit pie filling and cream-style corn, in which it functions principally as a thickener and stabilizer.

2.3.1.5 Acetylated Starch

Low-Ds starch acetates are produced by treatment of granular starch with acetic acid or preferably acetic anhydride, either alone or in the presence of a catalyst, such as acetic acid or an aqueous alkaline solution. A common commercial product is made by exposing starch to acetic anhydride at pH 7-11 and $25^{\circ}C$ to give DS 0.5. Low-DS starch acetates have low gelatinization temperature and good resistance to retrogradation after pasting and cooling. They are used in foods because of the clarity and stability of their pastes. Application includes frozen fruit pies and gravies, baked goods, instant puddings, pie fillings and gravies. Higher DS products exhibit a decreased ability to form gels.

2.4 Hydroxypropylated Starch

2.4.1 Reaction Mechanism

Chemical modification can improve the functional properties of starch for food or nonfood uses. Reaction of starch with propylene oxide to form the hydroxypropylated starch derivative is used primarily for the food industry. This modification improves the cold-storage stability, clarity and textural properties of the starch paste. Besides the propylene oxide treatment, the starch may also be cross-linked with phosphorous oxychloride or epichlorohydrin to improve cooked paste viscosity stability.

The mechanism for the base-catalyzed reaction of propylene oxide with starch is considered to be substitutive nucleophilic bimolecular or S_N2 type. The reactive nature of propylene oxide is due to its highly strained three-membered epoxide ring. Bond angles in the ring average 60° resulting in a very unstable (reactive) molecule. Reaction kinetic is second order and dependent of concentration of the reactants. Steric factors, however, direct the reactivity to the less hindered or primary carbon of the propylene oxide resulting in the 2-hydroxypropylated starch derivative.
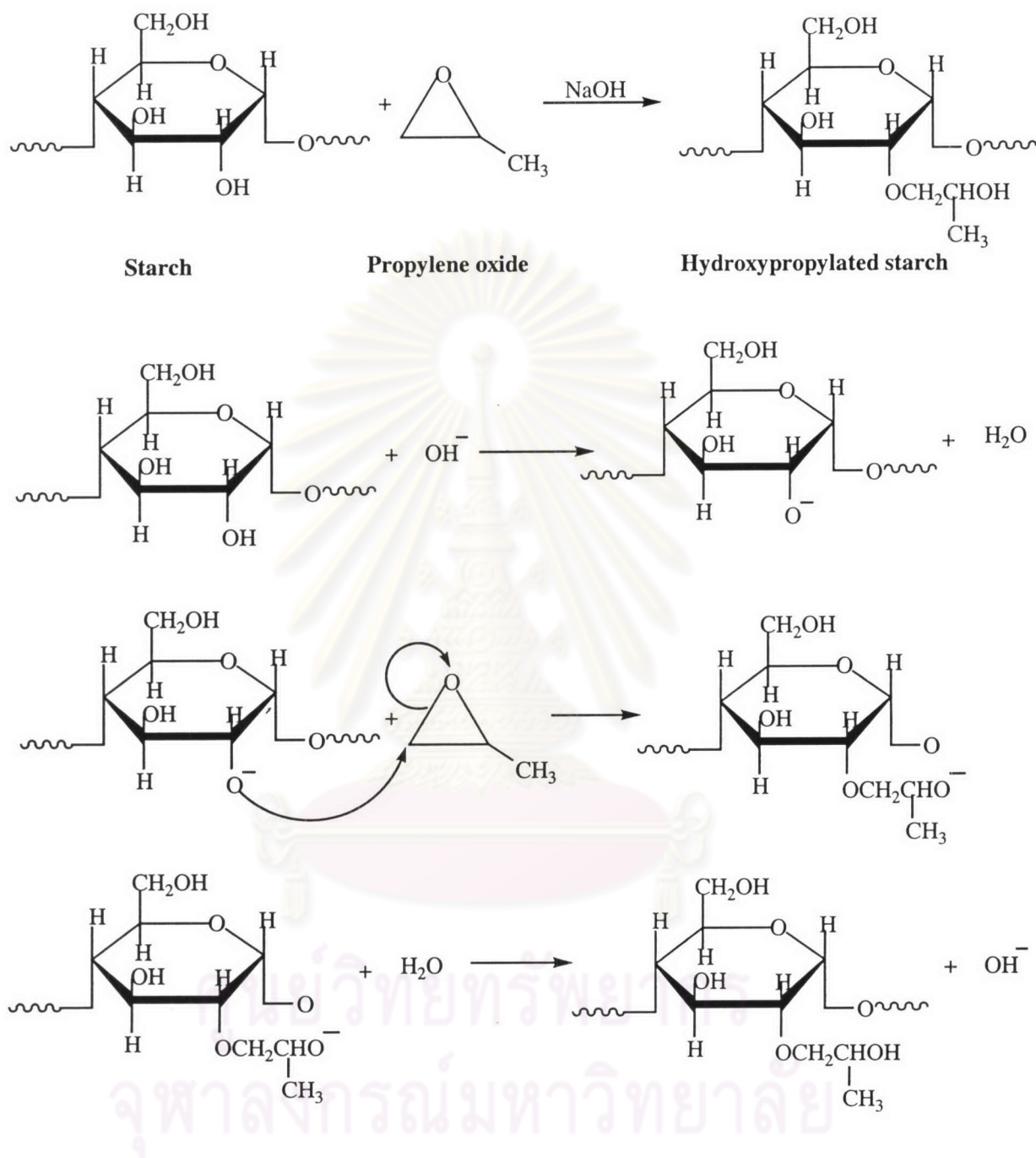
Scheme 2.1 The generally accepted mechanism for the reaction of propylene oxide and starch under alkaline conditions.

2.4.2 Reaction Conditions

2.4.2.1 Aqueous Reactions

The reaction of propylene oxide and starch is considered base catalyzed. Aqueous slurry reactions are generally catalyzed by 0.5 to 1% sodium hydroxide based on the dry weight of the starch. The sodium hydroxide is added as a 5 to 7% solution to the starch slurry with rapid agitation. Sodium sulfate may also be added to the starch slurry prior to caustic addition to protect the starch and keep it from swelling during reaction with the propylene oxide. Salt levels may range from 5 to 15% based on dry substance starch depending on the level of propylene oxide to be used. Reaction temperatures are generally in the 37 to $50^{o}C$ ranges. At temperatures below $37^{o}C$, reaction very slowly; above $50^{o}C$, the risk of swelling or pasting the starch granules unless high levels of salt are used is a concern.

Propylene oxide levels generally range from 5 to 10% based on the dry weight of the starch. Most of the propylene oxide reacted starches are intended for food use and must conform to Food and Drug Administration (FDA) guidelines for chemical modification. Propylene oxide-starch reactions take approximately 24 hrs to complete under the conditions described.

2.4.2.2 Nonaqueous Reactions

2.4.2.2.1 Dry Reaction

So-called "dry" reactions of starch with propylene oxide require a limited amount of moisture. At starch moisture levels of less than 5%, the reaction proceeds very ineffectively. Commercial reactions are carried out in a heated, pressure-type mixer or reactor with good agitation. The alkaline catalyst is added to the starch and thoroughly mixed in. The vessel or reactor is purged with nitrogen and propylene oxide is introduced as a gas at a reaction temperature of $85^{o}C$ and pressure at 45 psi. When the desired amount of propylene oxide has been introduced, reaction can also be catalyzed with a salt such as sodium sulfate or sodium phosphate. Starch wet cake

or slurry is salted and dried. Salt content is 1 to 2% based on dry substance starch. Reaction pH becomes alkaline from salt-propylene oxide interaction. After propylene oxide reaction, the reactor is purged with nitrogen and starch pH is adjusted with dry citric acid.

2.4.2.2.2 Organic Liquid Slurry Reaction

The starch is slurry in the desired organic medium and catalyst and reactant are added. The advantage of this procedure over the aqueous slurry or dry reaction technique is that high levels of substitution can be achieved in a short time at high temperatures and in a continuous manner if desired. The product is recovered by filtration or centrifuging and can be washed to remove by-products. The main disadvantage to this system is recovery and purification of the organic liquid. Organic liquids like methanol, ethanol and isopropanol are the most commercial interest.

2.4.3 Degree of Substitution (DS)

The DS indicates the average number of sites per anhydroglucose unit on which there are substituent groups. Thus, if one hydroxyl on each of the anhydroglucose units in a starch is etherified with hydroxypropyl groups, the DS is 1. If all three hydroxyls are etherified, the DS is 3. Most of the commercially available modified starches have low DS values ranging up to about DS 0.1, which would represent on average 1 substituent group per every 10 anhydroglucose units.

The formula for calculating the DS of a starch derivative will vary depending upon the molecular weight and functionally of the substituent group; thus, for hydroxypropylated starch,

$$DS = \frac{162W}{100M-(M-1)W}$$

Where   W   = The percentage by weight of substituent.

M   = The molecular weight of monomeric units of

the polymeric substitutent.

162   = Molecular weight of anhydroglucose unit

For the spectrophotometric determination of the hydroxypropyl ether groups in hydroxypropylated starch ethers, Johnson (15) described a method whereby the ether group is hydrolyzed with sulfuric or phosphoric acid. The propylene glycol formed is dehydrogenated with these acids to propionaldehyde and the enol form of allyl alcohol, which products give a purple color with ninhydrin. This ninhydrin color reaction is specific for propionaldehyde, and does not react with other compounds that may be formed. Otherwise the method is specific for the hydroxypropyl group in this group of substances.

In proton NMR spectroscopy, best results are obtained at lower levels of substitution, hydroxypropyl substitution of 10% or less. An internal standard of acetic acid is compared with the resonance of the hydroxypropyl terminal methyl group. Precision and accuracy of this method is dependent upon measuring the intensity of very weak spectral lines.

Another indirect method of special interest for in-process control is the starch "pasting temperature drop". As the starch undergoes hydroxypropyl substitution, the pasting temperature decreases. The magnitude of this decrease is correlated to substitution by one of the direct analytical methods. The Brabender viscoamylograph is a convenient instrument to use for determining pasting temperature decrease.

2.4.4 Reaction Efficiency (RE)

The efficiency of hydroxypropylation is greatly influenced by the reagents used. The reaction efficiency is defined as the percentage of the reagent reactor or substituted upon starch. The remaining reagent is consumed to form by-products. The efficiency depends upon the diffusion or penetration of alkali catalyst and etherifying agent into starch granules and the chances of collisions of the starch alcoholate nucleophile with the propylene oxide molecule. The elevated temperature of reaction helps in diffusion of alkaline catalyst and penetration of etherifying reagent more readily into the reaction point inside the starch granule and thus economizes the reagent consumption (16).

2.4.5 Brabender Viscoamylograph

The Brabender Viscoamylograph is a viscometer designed to permit a continuous measurement of the viscosity of a starch water mix during cooking and, if desired, during cooling. A suspension of starch in water is heated in a revolving cup driven at a constant speed. The starch slurries were heated rapidly to $50^{o}C$, then at a rate of $1.5^{o}C$/min to $95^{o}C$. They held at that temperature for 30 min and then cooled to $50^{o}C$. They were held again at $50^{o}C$ for 30 min.

The amylograph finds worldwide usage in the characterization of starch pastes. Six significant points on the curve are generally recognized.

a. Pasting Temperature - Denotes initiation of paste formation; varies with starch type, modification and with additives present in the slurry.

b. Peak Viscosity - Cited irrespective of the temperature at which the peak is attained. Generally, cooking must proceed through this stage to obtain a usable paste.

c. Viscosity at $95^{o}C$ - Reflects ease of cooking the starch.

d. Viscosity after 30 min at $95^{o}C$ - Indicates pastes stability or lack thereof, during cooking under relatively low shear.

e. Viscosity at 50°C - Measures the setback that occurs on cooling the hot paste.

f. Viscosity after 30 min at 50°C - Indicates stability of the cooked under simulated uses conditions.

2.4.6 Application of hydroxypropylated starches

Hydroxypropyl-modified starches have a very wide spectrum of application. They are being used in both food and non-food product. One of the largest areas of application is as a thickener in a multitude of food and food related products. The outstanding storage stability and freeze/thaw properties of these starches make them a premiere product for the food industry.

Nonfood uses for hydroxypropyl starch are also numerous. In many of the nonfood applications the coating or film forming properties of the starches is the most important. In the sizing of textile and paper products, for example, the clear, flexible, water-soluble coating, formed by hydroxypropyl starch is desired. In other uses such as a binder for building materials or gelling aid for perfumes or organic liquids, the adhesive properties and solvent soluble properties of the starch are utilized.

Levels of chemical substitution for food starches and some industrial starches that can come in contact with food are governed by FDA regulations. These regulations define the maximum amount of chemical reagent that can be used and, in some cases, the residual amount of certain by-products that remain. Of special concern for hydroxypropyl starch is the propylene chlorohydrin residues. (7-13)

2.4 Literature Reviews

Pal, *et al.* (16) studied the conditions for the preparation of hydroxypropyl derivatives of corn and small sized (1-2 μm) waxy amaranth starch. The synthesis was followed in terms of molar substitution (MS). The parameters optimized included propylene oxide concentration, reaction time, starch/water ratio and the quantity of alkali required in the process. The two starches differed considerably, and were unique in their own respect. The optimization conditions of one starch type cannot be extended to another.

Liu, *et al.* (17) investigated the physical properties and enzymatic digestibility of hydroxypropylated starches. The high amylose, waxy and normal maize starches were studied. For normal and high amylose starch, hydroxypropylation decreased the temperature at peak viscosity and caused a large increase in both the peak and cool paste viscosities. Hydroxypropylation had little effect on the pasting properties of waxy starch. All the hydroxypropylated starches have lower gelatinization parameters than their unmodified and control starches, but hydroxypropylation increased swelling power and solubility. After hydroxypropylation, the hardness and adhesiveness of all the starch gels decreased. Hydroxypropylation increased the clarity and enzymatic digestibility of all starches.

Kavitha, and BeMiller (18) studied the characterization of hydroxypropylated potato starch. Unmodified and modified (hydroxypropylated) potato starch were fractionated on a size-exclusion column to obtain amylose and amylopectin fractions. The molar substitution (MS) of modified whole starch was determined to be 0.099, of amylopectin, 0.096, and of amylose, 0.113. The location and distribution of modifying groups on amylopectin and amylose were determined by enzyme-catalyzed hydrolysis, using various combinations of isoamylase, β-amylase, α–amylase and amyloglucosidase and comparing elution profiles of unmodified and modified amylopectin and amylose digests by size-exclusion chromatography. It was confirmed that amylose was modified to a greater extent than amylopectin, and that further modification of amylopectin

occurred close to branch points, probably because amorphous regions are more accessible to the modifying reagent. It was also evident that amylose, likewise, was not uniformly modified.

Pal *et al.* (19) studied the pasting properties of hydroxypropyl derivative prepared from corn starch and waxy amaranths paniculatas starch. The properties studied were swelling power, Brabender characteristics, paste clarity and freeze-thaw stability. A remarkable improvement in freeze-thaw stability of both starches was the most significant finding of this work.

Shi and Bemiller (20) studied the effect of sulfate and citrate salts on derivatization of amylose and amylopectin during hydroxypropylation of corn starch. Common corn starch was modified in sodium sulfate solution and in potassium citrate solution. It was found that about 1.8 times at the amount of propylene oxide was needed to get the same molar substitution when potassium citrate was used. Hydroxypropylated starches were fractionated on a size-exclusion column to separate amylose from anylopectin, and MS values of the whole starch, the amylose, and the mylopectin were determined. In all preparations, amylose derivative to a grater extent than was amylopectin. The data indicate that, with common corn starch: (1) the greater the overall derivatization, the greater was the preference for derivatization of amylose was; and (2) the preference solution than in sokium sulfate solution when the MS values for the two preparations were essentially the same.

Graaf, *et al.* (22) developed a quantitative ^{1}H-NNR method for the determination of the molar substitution of acetylated and hydroxypropylated starches for MS ranging from 0.09 to 0.5. Results were checked using the Johnson method and a titration method for hydroxypropylated and acetylated starch, respectively. Hydroxypropyalted starch was produced using both a static mixer reactor and a co-rotating twin screw extruder. Acetylated starch was produced using a counter-rotating twin screw extruder. Quantitative analysis results of the ^{1}H-NMR method were in good agreement with

traditional analysis methods for all samples tested. Main advantage of the ^{1}H-NMR method is the considerable time saving as compared to the traditional analysis methods.

Wang (23) studied the process for preparing a hydroxyalkyl starch. A hydroxyalkylating agent treats the starch with an enzyme under conditions to increase the susceptibility of the starch to hydroxyalkylation. After the starch is treated, the starch is hydroxyalkylated with a hydroxyalkylating agent. The hydroxyalkylation reaction can proceed to provide a starch having an MS greater than about 0.2, while still remaining in granular form in the aqueous suspension. The method provides a granular starch a higher MS than is otherwise attainable via a reaction in aqueous media.

Eastman (24) investigated pasting temperatures of starch ethers. Hydroxypropyaltion of granular starch in a liquid medium comprising a lower alkanol under alkaline conditions in a confined zone at high temperature provides a novel improved hydroxypropyl substituted granular starch having a pasting temperature reduced from that of the granular starch before hydroxypropyl substitution by at least 6.5 ^{o}C for each 1% by weight of hydroxypropyl substitution.

Jarowenko (25) studied the method of preparing hydroxypropylated starch derivatives. An improved method for producing granular, cold-water dispersible hydroxypropylated starch comprises reacting a granular starch base with propylene oxide in the presence of sodium acetate or another water-soluble salt of a selected carboxylic acid. The resulting starch product, which upon purification is free of toxic by-products and has no perceptible off-taste, finds use as a thickener in food as well as in non-food applications.

Richardson, *et al.* (21) investigated the distribution of substituents in hydroxypropylated potato amylopectin starch (amylose deficient) modified in a slurry of granular starch (HPPAPg) or in a polymer solution of dissolved starch (HPPAPs). The molar substitution was determined by three different methods: proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy, gas-liquid chromatography (GLC) with mass

spectrometry, and a colourimetric method. The MS values obtained by ^{1}H-NMR spectroscopy were higher than those obtained by GLC mass spectrometry analysis and colourimetry. The relative ratio of 2-, 3- and 6-substitution, as well as un-, mono- and disubstitution in the anhydroglucose units (AGU) were determined by GLC –mass spectrometry analysis. Results obtained showed no significant difference in molar distribution of hydroxypropyl groups in the AGU between the two derivatives. For analysis of the distribution pattern along the polymer chain, the starch derivatives were hydrolyzed by enzymes with different selectivity. Debranching of the polymers indicated that more substituents were located in close vicinity to branching points in HPPAPg than in HPPAPs. Simultaneous α–amylase and amyloglucosidase hydrolysis of HPPAPg liberated more unsubstituted glucose units than the hydrolysis of HPPAPs, indicating a more heterogeneous distribution of substituents in HPPAPg.