CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Superabsorbent Polymers (SAPs)

Superabsorbent polymers can absorb a large amount of water compared with general water absorbing materials. Because of their excellent characteristics, superabsorbents has raised a considerable interests and researches [3].

2.1.1 Classification of Superabsobent Polymers

Classification of SAPs from composition and preparation methods (networks formation, introduction of hydrophilic groups and product form) are shown in Table 2.1 [3].

Table 2.1 Four Classifications of Superabsorbent Polymers

A. Polymer composition	
a) Starch	Graft polymerization
	Carboxymethylation
b) Cellulose	Graft polymerization
	Carboxymethylation
c) Synthetic polymer	Poly(acrylic acid)
	Poly(vinyl alcohol)
	Polyacrylamide
	Polyoxyethylene

Table 2.1 Four Classifications of Superabsorbent Polymers (continued)

B. Network formation

- a) Graft polymerization
- b) Crosslinked copolymerization
- c) Network forming reation of water-soluble polymer
- d) Self-crosslinked polymerization
- e) Radiation crosslinking
- f) Introduction of crystal structure

C. Hydrophilic groups

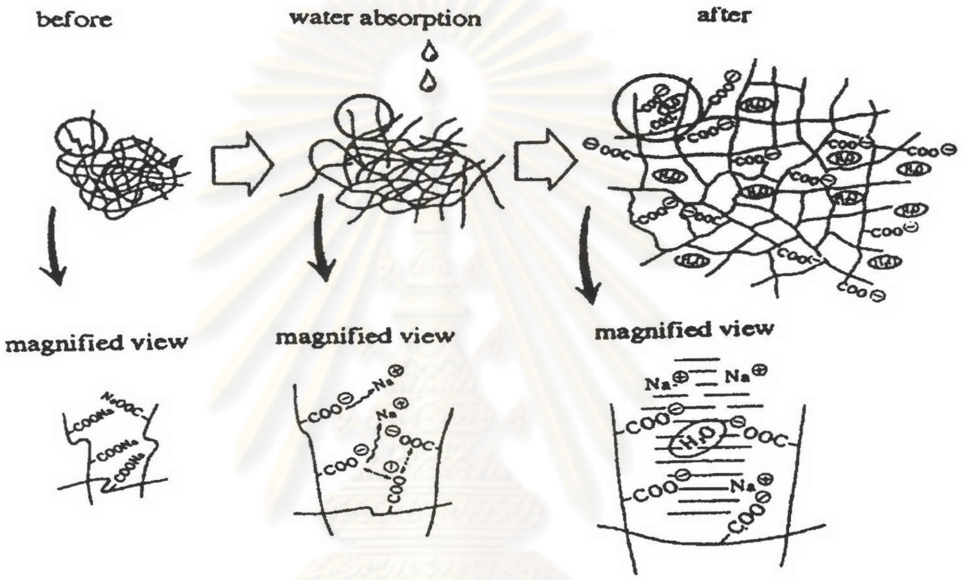
- a) Polymerization of hydrophilic monomers
- b) Carboxymethylation of hydrophilic monomers
- c) Graft polymerization of hydrophobic polymers with hydrophilic monomers
- d) Hydrolysis of nitrile or ester group

D. Product form

- a) Powder
  - Globular
  - Amorphous
- b) Film
- c) Fiber
  - Short fiber
  - Long fiber
  - Non-woven fiber

2.1.2 Physical Behavior of Superabsorbents

Superabsorbent polymers (SAPs) are crosslinked network of flexible polymer chain. The most efficient water absorbers are polymer networks that carry dissociated, ionic functional groups. The factors that supply absorbing power to polymers are osmotic pressure based on movable counter-ions, and affinity between the polymer electrolyte and water. The factor that suppresses absorbing power, in contrast, is found in the elasticity of the gel resulting from its network structure. The absorption mechanism before and after swelling in a dilute salt solution of an example of a superabsorptive resin, in the case of a crosslinked polymer with sodium carboxylate groups is shown in Figure 2.1 and 2.2.



Figures 2.1 Water absorption in ionic polymer network

Before absorption, long chains of polymers are interwoven, and polymers make a three-dimensional structure by crosslinking between the chains to make a dense phase. These SAPs instantaneously absorb water and swell with dissolution of Na$^+$, owing to the hydrophilic ionic groups, and becoming a gel [3].

During absorption, water moves into a particle of superabsorbent polymer because the activity of water is initially lower in the interior of the particle. As water diffuses into the particle, the particle volume increases and the polymer chain that form the superabsorbent polymer network must also move general by in a direction opposite to that of the water molecules, in order to accommodate the volume of the additional molecules of water. After absorption, the change in volume is apparent due to polymer molecules are much larger than water molecules, they diffuse much more slowly. Not only are the polymer molecules larger, but they are also connected one to the other by the crosslinks, that the polymer does not eventually dissolve in the water and become useless as a superabsorbent.

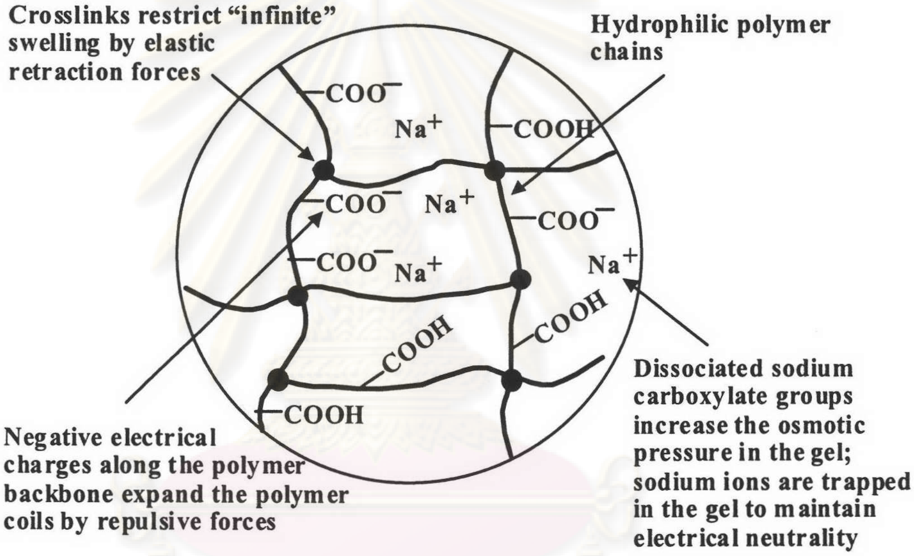


Figure 2.2 Mechanism of swelling of superabsorbent polymers

The water absorbency and the strength of SAPs can be expressed by Equation 2.1 (Flory's equation) and Equation 2.2, respectively [5].

$$Q5/3 = [(i/2\nu_u S^{*1/2})^2 + (1/2 - \chi_1)/\nu_1] / (\nu e/V_0) \tag{2.1}$$

$$G = RT\, \nu_e/V_0 \tag{2.2}$$

Where Q is degree of swelling, i/ν_u is charge density of polymer, S^* is ionic strength of solution, $(1/2 - \chi_1)/\nu_1$ is polymer-solvent affinity, $\nu e/V_0$ is crosslinking density, and G is rigidity.

2.1.3 Application of Superabsorbent Polymers

Superabsorbent polymers have been widespread applications in the field of bioengineering, biomedicine, pharmaceutical, veterinary, food industry, agriculture, photographic technology and other. It is used as controlled release system of drugs, for production of contact lenses and artificial organs in biomedicine, as an adsorbent for removal of some agents in environmental applications, immobilized enzyme kinetics in bioengineering and also as a carrier of water, pesticides and fertilizer in agriculture field [6]. Another characteristic of the swollen polymer is its rubbery nature, which has been used to control the consistency of products as diverse as cosmetics or concrete or to contribute a soft, yet dry, feel to a product like a hot or cold pack for sore muscles. The soft, rubbery nature may also be employed to impart sealing properties to products that are in contact with water of aqueous solutions, for examples, underground wires and cable [7]. The application of these polymers classified from the market field and the properties of polymers is indicated in Table 2.3 [3].

Table 2.2 Possible Applications of Superabsorpbent Polymers

Properties fields	**Water absorption and retention**	**Swelling in volume**	**Gelling ability**	**Increase in Viscosity**
Sanitary Products	• Sanitary napkins • Diapers • Breast pads			
Agriculture-gardening	• Water-retaining agents in soil • Seed coatings • Drying preventives for samplings • Artificial moss		• Cultivation plot for mushroom • Seed beds in fluid	
Civil engineering, architecture	• Dew preventing agents in walls • Water-retaining agents in concrete	• Water sealing agents • Substitutes for sandbags	• Sludge solidification agents • Lubricants in drilling works • Slurry explosives	• Mud shielding works
Cosmetics, Toiletries	• Sweat absorbing and kitchen papers		• Gelaromatics • Pocket warmers • Disposable • chamber pots	
Medical	• Wound dressings • Sheets for surgical operation	• Control release agents for drug • Disintegrators in tablets	• Gelation of blood wastes	• Wet plasters
Food industry	• Agent for preservation of freshness		• Gelling agents • Cold keeping • hydrogels	• Viscosity enhancing additives
Others	• Fog preventing film • Dehydrating agents in oil • Moisture sensor • Ink jet for printer	• Toys swelling when soaked in water	• Hydrogel for fire fighting • Artificial snow • Water bed	• Emulsion paints

2. 2 Mechanism for Free Radical Copolymerization

Free radical addition polymerization of vinyl monomers is summarized. Several excellent texts on this subject exist, and the reader is directed to one of these for more comprehensive information. Free-radical for initiation of addition polymerization is usually generated by the thermal decomposition of organic peroxides or azo compounds. The initiator molecule, represented by I, undergoes a first-order decomposition with a rate constant k_d to give two free radicals, $R^{\bullet}$:

$$I \xrightarrow{k_d} 2R^{\bullet} \qquad (2.3)$$

These radicals may adds a monomer by grabbing an electron from the electron-rich double bond, forming a single bond with the monomer, but leaving an unshared electron at the other end:

Where $P_1^{\bullet}$ represents a growing polymer chain with 1 repeating unit.

$$R^{\bullet} + M \xrightarrow{k'} P_1^{\bullet} \qquad (2.4)$$

Additional monomer units add rapidly to this growing end, depicted in Eq. 2.4. This step is called *propagation*:

$$RM^{\bullet} + M \xrightarrow{k_p} P^{\bullet}{}_{(x+1)} \qquad (2.5)$$

Growing chains can be terminated in one of two ways. Two can bump together and stick, their unshared electron combining to form a single bond between them.

(combination):

$$P^{\bullet}_{x} + P^{\bullet}_{y} \xrightarrow{k_{tc}} P_{(x+y)} \tag{2.6}$$

Where $P_{(x+y)}$ is dead polymer chain of (x+y) repeating units.

Or, one can abstract a proton from the penultimate carbon of the other.

(disproportionation):

$$P^{\bullet}_{x} + P^{\bullet}_{y} \xrightarrow{k_{td}} P_{(x+y)} \tag{2.7}$$

The relative proportion of each termination mode depends on the particular polymer and the reaction temperature, but in most cases, one or the other predominates.

The foregoing description is based on a thermally decomposing initiator. Redox couples are another class of radical initiators that are particularly useful for preparing superabsorbent polymers. In such cases, an oxidizing agent and a reducing agent react to form at least one active radical, which then initiates polymerization [10]:

$$\text{Red} + \text{Ox} \xrightarrow{k_{red}} R^{\bullet} + \text{by products} \tag{2.8}$$

2.3 Specific Polymerization Techniques

Superabsorbent polymers are prepared using a large variety of techniques:

2.3.1 Suspension Polymerization

Suspension polymerization is a system in which monomer are suspended as the discontinuous phase of droplets in a continuous phase and polymerized. The reactor product is a slurry of suspended polymer particles. The monomer suitable for suspension polymerization usually water, as most monomer are relatively insoluble in water. The terms pearl polymerization and bead polymerization describe the smooth, spherical particles from some suspension polymerization.

2.3.2 Solution Polymerization

Solution polymerization allows efficient heat transfer. Solvent must be chosen carefully, otherwise chain transfer reactions may severely limit the molecular weight. Apart from the environmental concerns associated with organic solvent, a major problem in solution polymerization is that it is often difficult to remove solvent completely from the finished polymer. As a result there is considerable interest in using supercritical carbon dioxide as a polymerization solvent. Advantages are that carbon dioxide is nontoxic, inexpensive, and easily removed from the polymer recycled.

2.3.2 Graft Copolymerization

Water soluble polymers such as starch and poly(vinyl alcohol) are grafted into superabsorbent polymers in order to modify the properties. Certain process benefit from increased viscosity of the monomer solution, and the water soluble, graft substances can serve this purpose. Special initiators are useful to increase grafting efficiency with polymers containing hydroxyl sites and serve as a locus for the nascent free radical formed by oxidation of substrate.

2.3.4 Emulsion Polymerization

Emulsion polymerization resembles suspension polymerization in that water is used as a dispersing medium and heat transfer is very efficient but there are the similarity ends. Monomer is dispersed in the aqueous phase by an emulsifying agent such as a soap or detergent. Initiator radicals, usually of the redox type, are generated in the aqueous phase and diffuse into soap micelles swollen with monomer molecules. As monomer is used up in the polymerization reaction, more monomer migrates into micelles to continue the reaction. Termination of polymerization occurs by radical combination when a new radical diffuses into the micelle. Because only one radical is present in the micelle prior to termination extremely high molecular weights are obtainable, generally too high to be of practical value unless compounds called "chain transfer" agent are added that control the degree of polymerization. The overall process is complex, with reaction kinetics differing significantly from that of bulk or solution process.

2.4 Biodegradable Polymers

Biodegradable polymer technologies can be classified under three broad categories and several subcategories:

1. Aliphatic polyester based (petrochemical feedstock; agricultural feedstock; microbial synthesis)
2. Natural polymer based (starch and starch derivatives [starch esters]; cellulose and cellulose ester; proteins, other polysaccharides, and amino acids)
3. Blends, alloys, and graft copolymers of natural polymers and polyesters.

2.4.1 Natural biodegradable polymers

Biopolymers are polymers formed in nature during the growth cycles of all organisms. Included are:

The most important polysaccharides of concern to material applications are cellulose and starch. Increasing attention is being given recently to more complex carbohydrate polymers produced by bacteria and fungi, such as xanthan, curdlan, pullulan, and hyaluronic acid [2].

2.4.1.1 Starch

Starch is a polymer which occurs widely in plants. The principal crops used for its production include potatoes, corn and rice. In all of these plants, starch is produced in the form of granules, which vary in size and somewhat in composition from plant. In general, the linear polymer, amylase, makes up about 20wt% of the granule, and the branch polymer, amylopectin, the remainder. Amylose is crystalline and can have a number average molecular weight as high as 50,000, but it is soluble in boiling water.

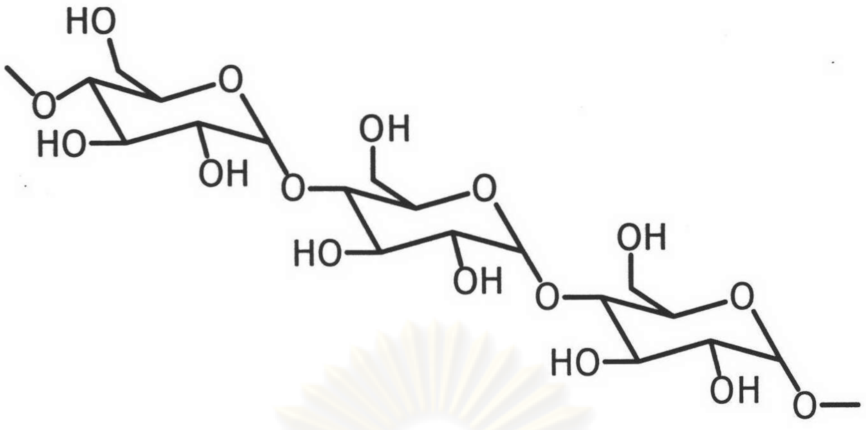


Figure 2.3 Chemical structure of amylose chain

Amylopectin is insoluble in boiling water, but in their use in foods, both fractions are readily hydrolyzed at the acetal link by enzyme. The α-link in both components of starch is attacked by amylases and the α-1,6-link in amylopectin is attacked by glucosidases.

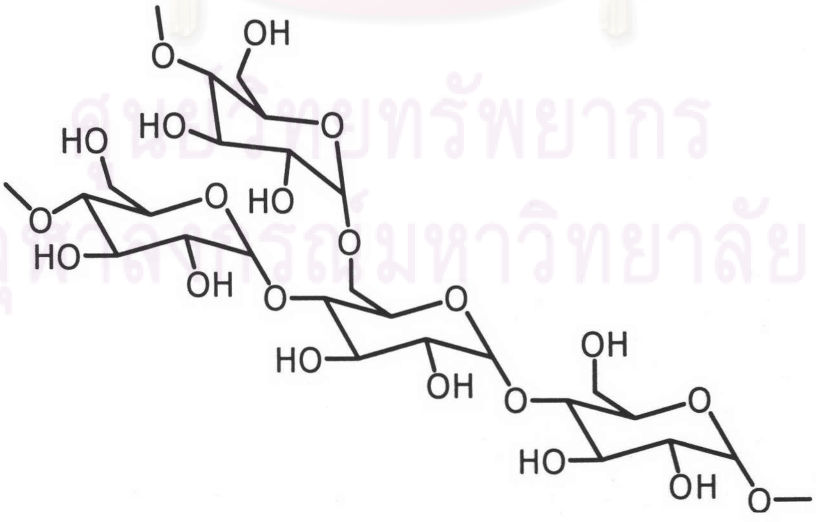


Figure 2.4 Branched structure of amylopectin

2.4.2 Starch Graft Copolymer

In addition to the α-1,4 and α-1,6-glycosidic linkage in starch, the hydroxyl groups on both the primary and secondary carbon atoms offer the opportunity for chemical modification, incorporating near and useful properties. Graft copolymer have been prepared using starch as a backbone. Grafting synthetic copolymers onto starch often superimposes the physical and chemical characteristics of the copolymer

Use of starch as an extender and replacement for synthetic polymers is currently an active research area. Incorporation of starch into other polymers not only reduces our dependence on petrochemical-derived monomers but also provides materials in which the starch portion can biodegrade rapidly in the environment. Free-radical graft polymerization is an excellent method for preparing these starch synthetic composites [9]

Graft copolymerization of vinyl monomer to polysaccharide substrate is used for the preparation of absorbent polymers. The polymerization kinetic is the initiation step and chain transfer reactions. Practical graft polymerization attempts to initiate the polymerization using a redox reaction of oxidant with oxidizable groups of the polysaccharide. Many of the metal ion systems investigated also initiate polymerization in the absence of the polysaccharide and so contribute to homopolymerization of the monomer with reduction in the amount of graft copolymer. Another complication is the generally observed termination of propagating chains with metal ion. This reduced the backbone molecular weight and hence the modulus of the swollen network. A third complication is chain transfer of propagating chains to polysaccharide [10].

2.4.3 The Use of Enzyme in Starch Hydrolysis

Starch is the commonest storage carbohydrate in plants. It is used by the plants themselves, by microbes and by higher organisms so there is a great diversity of enzymes able to catalyse its hydrolysis of the two components of starch, amylopectin presents the greater challenge to hydrolytic enzyme systems. This is due to the residues involved in α-1,6-glycosidic branch points which constitute about 4-6% of the glucose present. Most hydrolytic enzyme are specific for α-1,4-glucosidic links yet the α-1,6-glucosedic links must also be cleaved for complete hydrolysis of amylopectin to glucose. Some of the most impressive recent exercises in the development of new enzymes have concerned debranching enzymes.

It is necessary to hydrolyze starch in a wide variety of processes which may be condensed into two basic classes: (1) processes in which the starch hydrolysate is to be used by microbes or man, and (2) processes in which it is necessary to eliminate starch.

There are three stages in the conversion of starch (Figure 2.5): (1) *gelatinization*, involving the dissolution of the nanogram-sized starch granules to form a viscous suspension; (2) *liquefaction*, involving the partial hydrolysis of the starch, will concomitant loss in viscosity; and (3) *saccharification*, involving the production of glucose and maltose by further hydrolysis. Gelatinization is achieved by heating starch with water, and occurs necessarily and naturally when starch foods are cooked. Gelatinized starch is readily liquefied by partial hydrolysis with enzymes or acids and saccharified by further acidic or enzymatic hydrolysis.

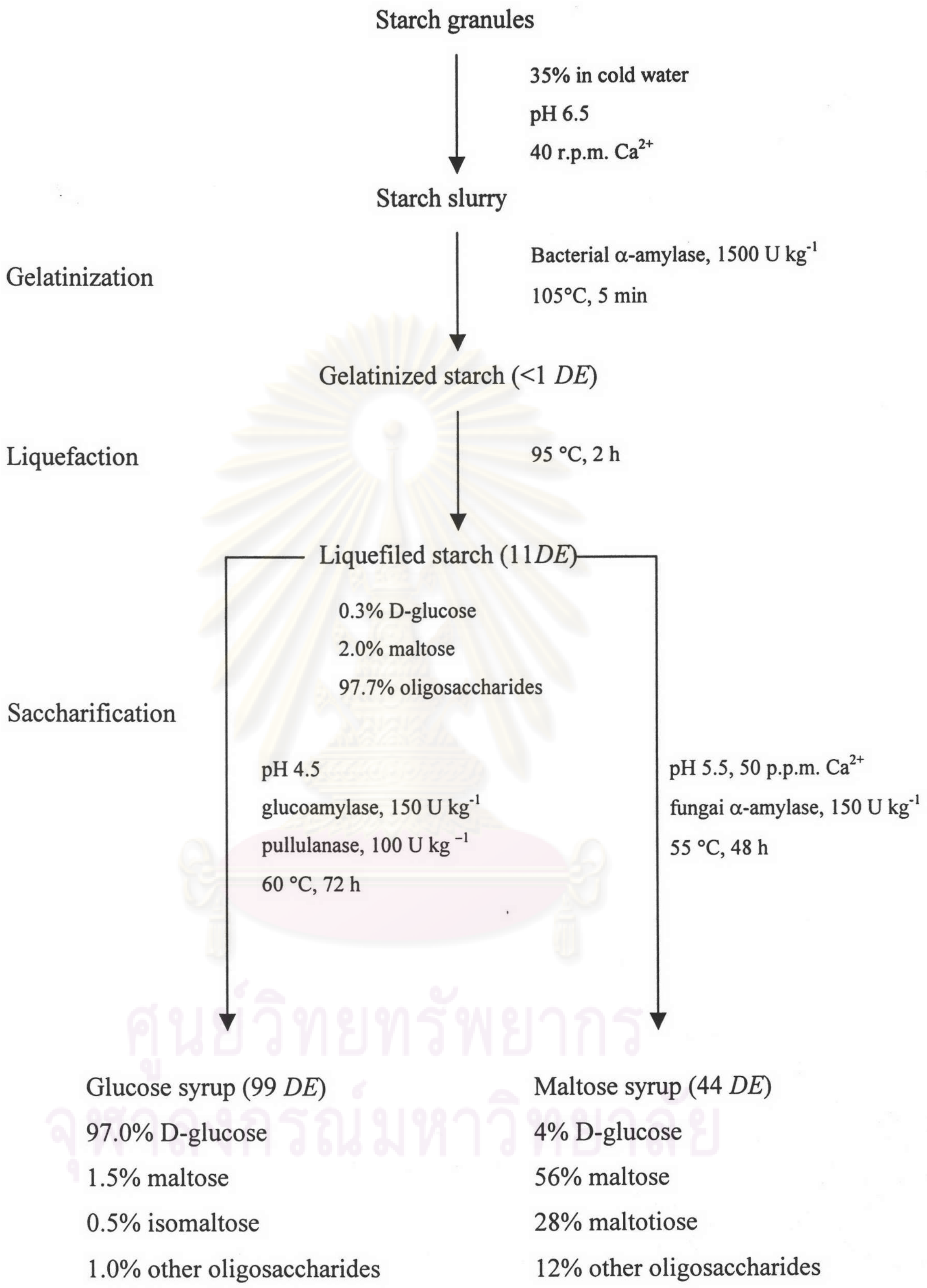


Figure 2.5 The use of enzyme in processing starch. Typical conditions are given.

Enzymes are essentially biological catalysts, with the same action as chemical catalysts. By lowering the activation energy they can induce an increase in reaction rates in an environment otherwise unfavorable for chemical reaction, for example, water at pH 7 and 30 °C. In the presence of enzyme, a rise in reaction rate of $10^8 - 10^{20}$ can often be observed. The vast majority of enzymes are proteins having a polypeptide chain with a complex three-dimensional structure. Enzyme activity is closely related to conformational structure.

The three-dimensional structure of enzyme with folds and pockets creates certain regions on the surface with characteristic primary structures (i.e. specific amino acid sequences), which form an active site. At the active site the interaction between the enzyme and substrate takes place leading to chemical reaction, giving a particular product.

For enzyme with absolute specificities the "key-and-lock" theory which implies an unchangeable rigid conformation, is a plausible model. The initial contact between an enzyme and substrate forms an optimal orientation at the active site giving good possibilities for maximum bonding (enzyme-substrate), often the cofactor induces these change when binding to the enzyme [2].

The nomenclature of the enzymes used commercially for starch hydrolysis is somewhat confusing and the EC numbers sometimes lump together enzymes with subtly different activities (Table 2.4) [11].

Table 2.3 Enzymes used in starch hydrolysis

Enzyme	EC number	Source	Action
α-Amylase	3.2.1.1	*Bacillus amyloliquefaciens*	Only α-1,4-oligosaccharide links are cleaved to give α-dextrins and predominantly maltose(G_2), G_3, G_6 and G_7 oligosaccharides
		B. licheniformits	Only α-1,4-oligosaccharide links are cleaved to give α-dextrins and predominantly maltose(G_2), G_3, G_4 and G_5 oligosaccharides
		Aspergillus oryzae, A. niger	Only α-1,4-oligosaccharide links are cleaved to give α-dextrins and predominantly maltose and G_3 oligosaccharides
Saccharifying α-amylase	3.2.1.1	*B. subtilis (amylosacchariticus)*	Only α-1,4-oligosaccharide link are cleaved to give α-dextrins and maltose, G_3, G_4 and up to 50% (w/w) glucose
β-Amylase	3.2.1.2	Malted barley	Only α-1,4-links are cleaved from non-reducing ends, to give limit dextrins and β-mailtose
Glucoamylase	3.2.1.3	*A.niger*	α-1,4 and α-1,6-links are cleaved from non-reducing ends, to give limit dextrins and β-glucose
Pullulanase	3.2.1.41	*B.acidopullulyticus*	Only α-1,6-links are cleaved to give straight chain maltodextrins

For example, α-amylases may be subclassified as liquefying or saccharifying amylases but even this classification is inadequate to encompass all the enzymes that are used in commercial starch hydrolysis. One reason for the confusion in the nomenclature is the use of the anomeric form of the released reducing group in the product rather than that of the bond being hydrolyzed; the products of bacterial and fungal α-amylases are in the α-configuration and the products of β-amylases are in the β-configuration, although all these enzymes cleave between α-1,4-linked glucose residues.

The α-amylases (1,4-α-D-glucan glucanohyrolases) are endohydrolases which cleave 1,4-α-D-glucosidic bonds and can bypass but cannot hydrolyse 1,6-α-D-glucosidic branchpoints. Commercial enzymes used for the industrial hydrolysis of starch are produced by *Bacillus amyloliquefaciens* (supplied by various manufacturers) and by *B. licheniformis* (supplied by Novo Industri A/S as Termamyl). They differ principally in their tolerance of high temperatures, Termamyl retaining more activity at up to 10°C, in the presence of starch, than the *B. amyloliquefaciens* α-amylase. The maximum DE obtainable using bacterial α-amylases is around 40 but prolonged treatment leads to the formation of maltose (4-α-D-glucopyranosyl-D-fructose), which is resistant to hydrolysis by glucoamylase and α-amylases.

2.4.4 Determination of Reducing Sugar

The DNS assay for reducing sugars is a colorimetric assay. Many biological compounds undergo reactions which result in the formation of reaction products that absorb light of a particular wavelength. Such reaction often serves as the basis for quantitative determination of biological compounds. While these reactions may be highly specific for a single biochemical, more often they are specific only for a class of biochemicals such as reducing sugar or protein. The DNS assay is commonly used to measure concentrations of reducing sugars [12].

A reducing sugar is any mono-, or polysaccharide that has a free or potentially free aldehyde or ketone group, *i.e.*, the C1 (aldehyde or C2 (ketone) carbon is not involved in a covalent linkage other than that of cyclization. The free aldehyde or ketone group can reduce alkaline solution of metal salts or carry out other reduction reactions. The DNS (dinitrosalicylic acid) assay is based on the reduction of 3,5-dinitrosalicylic acid by the sugars to 3-amino-5-nitrosalicylic acid which has a strong absorbance in the 540 to 600 nm range. This assay was developed by Miller (1959) and is still widely used today.

2.5 Terminology and Definition

Before proceeding to the experimental part, several technical terms need to be clarified for the better understanding of readers.

2.5.1 Percentage Add-on

It is refferred to as the weight percentage of synthetic polymer in the graft copolymer and is determined as follows:

$$\%\text{add-on} = \frac{\text{Weight of polymer grafted}}{\text{Weight of the grafted copolymer}} \times 100 \tag{2 9}$$

It is calculated by the acid hydrolysis method. The grafted polymers are separated from the starch backbone by heating the graft copolymer under reflux in a dilute acid solution.

2.5.2 Grafting Ratio

It is a term used to describe graft copolymerization, which is defined as the percentage ratio between the polymer grafted to the cassava starch and it can be calculated by the following expression.

$$\%\text{Grafting ratio} = \frac{\text{Weight of polymer grafted}}{\text{Weight of starch}} \times 100 \tag{2.10}$$

2.5.3 Grafting Efficiency

It is a term often used to describe graft copolymerization reactions and it is defined as the percentage of the total synthetic polymer formed that has been grafted to starch. High grafting efficiencies are desirable since a polymerization of the low grafting efficiency would afford mainly a physical mixture of starch and free polymers. It can be calculated as follows:

$$\%\text{Grafting efficiency} = \frac{\text{Weight of polymer grafted}}{\text{Weight of free polymers} + \text{Weight of polymer grafted}} \times 100 \qquad (2.11)$$

Literature Survey

Mostafa [13] reported the graft copolymer of acrylic acid onto rice starch using potassium permanganate/acid redox system as initiator. When starch was reacted with $KMnO_4$ solution, MnO_2 was deposited onto starch. He found that the highest graft yield was obtained with citric acid and the least with hydrochloric acid, with tartaric and oxalic acid in between. The graft yield increased by increasing the concentration of acid to a certain concentration beyond which grafting leveled off. A similar trend was observed when the magnitude of grafting was related to the amount of MnO_4 deposited. The graft yield increased by increasing the polymerization temperature from 30 to 50 °C.

Karadag et al., [6] have reported that the acrylamide/itaconic acid (AAm/IA) hydrogels were prepared by irradiating with γ radiation used in experiments on the uptake of some cationic dyes such as basic red 5 (BR-5), basic violet 3 (BV-3) and brilliant cresyl blue (BCB). The removal of the cationic dyes to AAm/IA hydrogels is studied by batch adsorption technique. In the experiments of the adsorption, L3 type (Langmiur) adsorption in Giles classification system was found. Adsorption studies indicated that monolayer coverages of AAm/IA hydrogael by these dyes were increased with the following order: BCB > BR-5 > BV-3.

Athawale et al., [14] studied the grafting of acrylic acid (AA) onto granular maize starch in aqueous medium initiated by ceric ion, gravimetrically under atmosphere. The effect of concentration of ceric ion, concentration of AA, reaction temperature, polymerization time and material-to-liquor ratio on the grafting has been studied in term of %GE and %Add-on. The optimum conditions obtained for the grafting of AA onto 2 g of granular maize starch were: [AA] = 0.2775 mol/L; [CAN] = 0.004 mol/L; time = 240 min; temp = 35°C; material-to-liquor ratio = 1:10. The graft copolymers were characterized by infrared spectroscopy, XRD, TGA and scanning electron microscopy. The XRD showed that the crystallinity of starch decreases owing to grafting. The SEM revealed that grafting is essentially a surface phenomenon. Grafting of acrylic acid affects the thermal stability of starch. Hydrogels were prepared by grafting AA onto gelatinized starch followed by neutralization with NaOH. The maximum water absorption obtained was 250 $g\ g^{-1}$.

Quintana et al., [15] studied the hydrogels of dimethylaminoethyl acrylate, methyl chloride quaternary and itaconic acid have been synthesized with different monomer ratios. The swelling process of the different xerogels immersed in water was monitored by the weight increase as a function of time. The swelling isotherms consisted of a steep initial portion and leveled off asymptotically to the equilibrium swelling limit. The experimental data suggest clealy that the swelling process obeys second-order kinetics. The rate constant and the equilibrium water content were determined for every monomer ratio from the experimental straight lines obtained according to that kinetics equation. Both magnitudes decreased as the itaconic acid content in the xerogel increased.

Chen et al., [16] synthesized superporous hydrogels base on monomers, N,N'-methylene bisacrylamide (N-MBA) as crosslinking agent, ammonium persulfate (APS) and N,N,N',N'-tetramethylethylenediamine (TEMED) as coinitiator and Pluronic F127 (PF127) as foam stabilizer. Crosslinking polymerization of monomer in a test tube and presence of carbon dioxide gas bubbles, which were generated by a reaction of sodium bicarbonate with an acid. The use of the $NaHCO_3$/acid system allowed easy control of the timing for gelation and foam formation. PF127 was the best foam stabilizer for most of the monomer systems. The resulting superabsorbents gave a fast swelling rate. The swelling ratio (Q) is 368±34 times its dry copolymer weight. Average diameter of the pores of superporous hydrogels is approximately 150 μm, and some pores are as large as 300 μm.

Sen et al., [17] investigated the average molecular weight between crosslinks ($\overline{M}_c$) of itaconic acid-containing poly(vinyl pyrrolidone) and maleic acid containing poly(acrylamide) hydrogels sensitive to pH changes of swelling medium. Polyelectrolyte hydrogels with varying compositions were prepared in the form of rods from ternary mixtures of N-vinyl 2-pyrrolidone/itaconic aicd/water. Gelation was achieved by irradiating the system with γ rays at ambient temperature. The equation modified by the authors recently for the determination of ($\overline{M}_c$) was observed to describe very well the swelling behavior of charged polymeric networks. In addition to the evaluation of $(\overline{M_c})$ from swelling data, the same equation also provided the simultaneous measurement of polymer-solvent interaction parameter of the system investigated.

Uyanik and Erbil [18] synthesized itaconic acid (methylene succinic acid)-acrylamide (IA-Aam) copolymer by using potassium persulphate. The potentiometric titation method was used to determine the itaconic acid-acrylamide (IA-AAm) copolymer compositions. The results were evaluated by various methods. The monomer reactivity ratios were found to be $r_{\mathrm{IA}} = 0.99 \pm 0.04$, $r_{\mathrm{AAm}} = 0.58 \pm 0.02$ with the Fineman-Ross method, $r_{\mathrm{IA}} = 1.05 \pm 0.10$, $r_{\mathrm{AAm}} = 0.62 \pm 0.06$ with the Kelen-Tüdös method, and $r_{\mathrm{IA}} = 1.36 \pm 0.11$, $r_{\mathrm{AAm}} = 0.77 \pm 0.06$ with the Tidwell-Mortimer method. As expected, IA is found to be the more reactive monomer in IA-AAm copolymers.

Kiatkamjornwong et al., [19] studied graft copolymerization of acrylamide and/or acrylic acid onto cassava starch by a simultaneous irradiation technique using gamma rays as an initiator. The extracted graft copolymers were subsequently saponified with a 5% aqueous solution of potassium hydroxide at room temperature to convert the carboxylic acid of acrylic acid to the carboxylate group. Cassava starch ratio 2:1, total dose 6.04 kGy, dose rate 2.24 kGy/h, and acrylamide-to-acrylic acid ratio 70:30 gave the saponified copolymer having the highest water absorption in distilled water as high as 1142 g/g its dry weight.

Athawale et al., [20] have reported the graft copolymers of pure granular maize starch with acrylamide, methacrylamide, acrylic acid and methacrylonitrile were synthesized using ceric ammonium nitrate as an initiator. The formation of graft copolymer was confirmed by gravimetric measurement, acid hydrolysis and IR spectroscopy. The thermal analysis of the pure granular maize starch and graft copolymers was carried out using TGA, DTG, DSC, DTA, and isothermal analysis. In order to determine the mechanism of decomposition of these polymers, the isothermal analysis was coupled with IR spectroscopy. The activation energies at every stage of decomposition for all the polymer samples were determined from their primary thermograms.. DTA studies indicated a delayed oxidative degradation of graft copolymers.

Pulat et al., [21] studied the improve water wettability of polyurethane (PU), graft copolymerization of acryliamide (AAm) and itaconic acid (IA) was performed using benzoyl peroxide (BO) initiator. The grafting reaction was carried out by placing the membranes in aqueous solutions of AAm and IA at constant temperatures. Variations of graft yield with time, temperature, initiator and monomer concentrations were investigated. The optimum temperature, polymerization time, initiator and monomer concentrations for AAm were found to be 80°C, 2 h, $4.0\text{x}10^{-2}$ M and 1.2 M and IA, 80°C, 1h, $4.0\text{x}10^{-2}$ M and 1.5 M, respectively. The membranes were characterized by FTIR spectroscopy and scanning electron microscopy (SEM) analysis and the effect of grafting on equilibrium water content (EWC) of PU membranes was obtained by swelling measurements.

Rahmouni et al., [22] studied the influence of several physicochemical parameters on enzymatic hydrolysis and the in vitro release of sodium diclofenac (SDic) from cross-linked high amylose starch (Contramid) (CLA) tablets was evaluated. These parameters included pH, ionic strength of the medium, enzyme concentration, compression force and incorporation of gel-forming polymers. Pure CLA tablets were incubated in phosphate buffer (pH 6.8) containing α-amylase and the extent of enzymatic erosion was determined by gravimetry. Release of SDic from CLA tablets, in the presence of α-amylase, was measured using a USP type III dissolution apparatus. For low α-amylase concentrations (< 2250 IU/l), the drug release was mainly diffusion-controlled. At higher a-amylase concentrations (> 4500 IU/l) both diffusion and erosion contributed to the release of Sdic.

Kiatkamjornwong et al., [23] studied graft copolymerization of acrylamide and maleic acid onto cassava starch by a simultaneous irradiation technique using γ-rays as an initiator. Addition of 2% w w^{-1} diprotic acid of maleic acid into the reaction mixture yield a saponified starch graft copolymer with absorption in distilled water as high as 2256 g g^{-1} of its dried weight. The water absorption depends largely on the cationic type and concentration of these solutions in terms of ionic strength. This research explains a charge transfer mechanism for graft copolymerization of maleic acid and acrylamide onto cassava starch, and describes the influential parameters that affect grafting efficiency and water absorption.

Bhuniya et al., [24] have reported that maize starch was modified by allyl chloride adopting an interfacial reaction technique with acetyltrimethyl ammonium bromide as a phase-transfer catalyst and pyridine as an acid acceptor. The degree of substitution was determined from an increasing carbon content of the modified starch. The percentage of carbon and hydrogen of the allyl-modified starch was estimated by elemental analysis (C, H, and N), and the product characterization was done through

^{1}H NMR and ^{13}C NMR analyses. The allyl-modified starch was then copolymerized with methacrylic acid and a combination of methacrylic acid and acrylamide at 50 and 70°C with potassium persulfate as an initiator. The copolymer thus formed swelled in distilled water after neutralization with sodium carbonate. The percentage of absorption capacity of the hydrogels was determined with distilled water and 0.9% NaCl solution. The highest percentage of absorption, 6500%, was achieved for the developed hydrogel containing allyl starch and acrylic monomer in a 1:7:1 w w^{-1} ratio and acrylic monomer, namely, methacrylic acid and acrylamide in a 3:2:1 w w^{-1} ratio. The study on biodegradability of the developed hydrogel showed that the hydrogel is degradable in the presence of diastase (amylase).

Wu et al., [25] synthesized a novel starch-*graft*-acrylamide/mineral powder superabsorbent composite with water about 4000 times by graft-copolymerization reaction among acrylamide, potato starch and mineral ultrafine powder, followed by hydrolysis with sodium hydroxide. It is found that the composite doped with kaolinite powder possess higher water absorbency than those doped with bentonite or sercite powder, since the kaolinite powder can moderately disperse in the water and cross-link with acrylamide and starch. By controlling the amount of NaOH and reaction time during saponification process, the hydrophilic group on the composite can be adjusted, it is found that the collaborative absorbent effect of $-CONH_2$, $-COONa$ and $-COOH$ groups is superior to that of single $-CONH_2$, $-COONa$ and $-COOH$ group. The polymerization reaction mechanism and structure of the composite is proposed by the IR characterization,, the mineral ultrafine powder as a cross-linking point play an important role in the formation of network structure superabsorbent composite.

Caykara and Dogmus [26] studied equilibrium swelling ratio and swelling-shrinking kinetic of polyelectrolyte copolymeric hydrogels consisting of acrylamide and itaconic acid (AAm/IA) have been studied in water/nonsolvent (acetone, methanol, ethanol and 1-butanol) mixture as a function of solvent composition and IA content in the hydrogel. The phase transition of these hydrogels was generated by changing the solvent composition by progressive substitution of water by nonsolvent. For all P(AAm/IA) hydrogels, the form of the shrinking curves was determined to be strongly dependent on the type of the nonsolvent used. The rate of shrinking of these hydrogels increased in the order 1-butanol <ethanol <methanol <acetone.

Araujo et al., [27] studied the degradation behavior of blends of corn starch with poly(ethylene-vinyl alcohol) copolymer (SEVA-C). The characterization included long-term degradation trials on simulated physiological solution with α-amylase up to 200 days. The degradation solutions were analysed by several techniques. High-performance liquid chromatography (HPLC) and colorimetric method were used to monitor the liberation of carbohydrate as a consequence of starch hydrolysis by α-amylase. The hydration degree was followed by thermogravimetric analysis (TGA). Several degradation products such as carbohydrates ranging from C6 to C18 were identified. After α-amylase action, biodegradation was more pronounced in the first 100 days, after which the biodegradation rate decreased probably due to the structure and porosity of the material. The action of α-amylase solely led to the starch degradation, in contrast with other assays without enzymes where no carbohydrates were found in the degradation solutions.