

CHAPTER II

THEORY and LITERATURE REVIEW

2.1 Theoretical Background

2.1.1 Starch

Starch is a reserve carbohydrate occurring in a granular form in the organs of plants. The granules are deposited principally in the seeds, roots, tubers, fruits, and sometimes in the stem piths, as a reserve food supply for periods of dormancy, germination and growth. It occurs as tiny, water-insoluble, white granules, usually associated with proteins, fats, and inorganic salts. The granules vary in shape and size ranging from about 1 to 1000 μm in diameter depending on the sources (7). For cassava starch, the size of the granules ranges from 5 to 35 μm . The largest are usually 25 to 35 μm and the smallest are 5 to 15 μm (8).

The commercial sources of starch are the seeds of cereal grains (corn, wheat, sorghum, and rice), tubers (potato), roots (tapioca, sweet potato, and arrowroot), and the pith of the sago palm. Each starch is described according to its plant source as corn starch, tapioca starch, wheat starch, and so on. The properties of the starch vary

with the plant source from which it is derived.

The commercial starches can be divided into three groups. The first group comprises the tuber, root, and pith starches. The second group comprises the common cereal starches. These two groups are distinctly different from each other with respect to chemical composition and physical properties. The third group comprises the waxy starches. These starches are obtained from cereals, but the physical properties of the waxy starches are similar to those of the root starches (9).

2.1.1.1 Chemistry of Starch

Starch is a carbohydrate, composed of carbon, hydrogen and oxygen atoms in the ratio of 6:10:5 ($C_6H_{10}O_5$)_n. It can be considered as a condensation polymer of glucose, consisting of anhydroglucose units (AGU). The linkage between the glucose units being formed as if a molecule of water is removed during a step polymerization. These units are linked to one another through the C-1 oxygen, normally known as glucoside bond. The glucoside linkage is an acetal, stable under alkaline conditions and hydrolyzable under acid conditions. The hydroxyl groups can react to form ethers and can be oxidized to aldehyde, ketone, and carboxyl groups (10).

2.1.1.2 Molecular Structure

Starch is not a uniform product. Most starches consist of a mixture of two polysaccharide types: amylose, an essentially linear polymer; and amylopectin, a highly branched polymer. The relative amounts of these starch fractions in a particular starch are a major factor in determining the properties of that starch.

a) Amylose

The linear polymer consists of a chain of glucose units connected to each other by 1-4 linkages. These glucose units are in the " α -D-glucoopyranose" form (Figure 2.1). The amylose polymer fraction of starch will show a distribution of molecular sizes, and the average degree of polymerization (D.P.) will vary with plant variety from which the starch is obtained. Depending upon the type of starch, the D.P. will range from about 250 to 4000 AGU per amylose molecule, corresponding to a molecular weight of approximately 40,000 to 650,000. Generally, starches contain about 15-25% amylose. For cassava starch, the amylose content is about 16.5-22.2% (2). A stable formation of amylose is that of a helix, which explains the characteristic solution behavior of native amylose. Amylose is embedded in a continuous network of amylopectin in starch. The network hinders the formation of complete helix structure.

The abundance of hydroxyls imparts hydrophilic properties to the polymer, giving it an 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. In the dilute solutions, the aggregate size of the associated polymers may increase to a point where precipitation may occur. At higher concentrations, steric hindrance may interfere so only partial orientation between the polymers may occur, producing a gel consisting of a three-dimensional network held together by hydrogen bonding at those sections where close alignment has occurred. In general, the linearity of amylose favors formation of strong films (9).

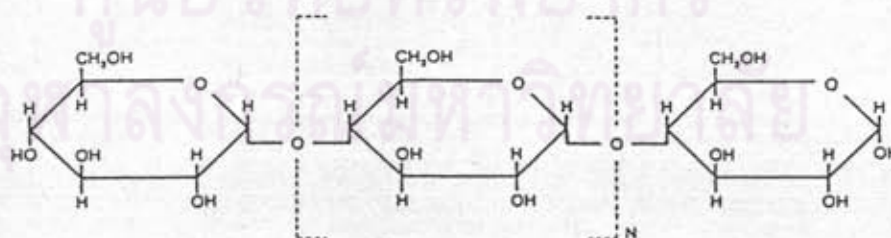


Figure 2.1 Chemical structure of amylose chain.

b) Amylopectin

Amylopectin is a branched polymer containing, in addition to AGUs 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 6 carbon by α -D-(1 \rightarrow 6) glucosidic bonds. Each branch contains about 20 to 30 anhydroglucose units. A schematic diagram of the amylopectin molecule is shown in Figure 2.2. In addition, many subsidiary branches may extrude off the main branch. Amylopectin occurs as a network in starch, and so, is insoluble in water. But amylopectin is dispersed in cold water by rapid stirring. On drying, an amylopectin powder is formed which cannot form long helix sequences, and thus crystallizes, because of the high degree of branching. The amorphous powder, however, can be redispersed in water.

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 (9).

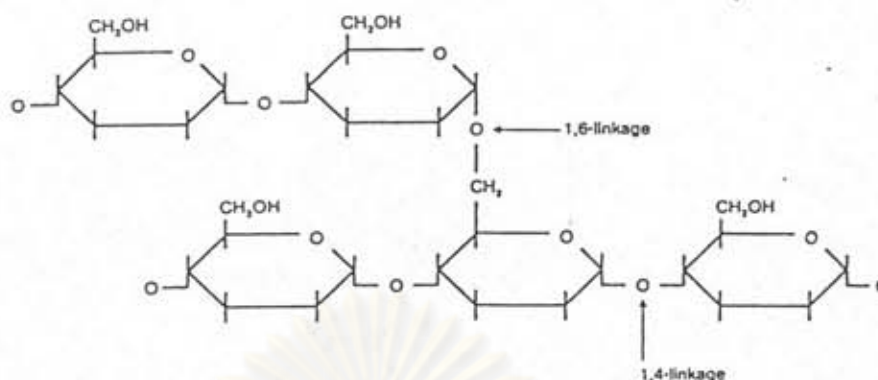


Figure 2.2 Branched structure of amylopectin and chemical configuration at the branch point

2.1.1.2 Graft copolymer and copolymerization

A graft copolymer consists of a polymeric backbone with covalently linked polymeric side chains. In principle, both the backbone and side chains could be homopolymers or copolymers. Graft copolymers are of great interest in the field of absorbency in a number of aspects. Grafting can be carried out in such a way that the properties of the side chains can be added to those of the substrate polymer without greatly changing the latter.

2.1.1.2.1 Methods of Grafting copolymerization

In the context of this thesis, the backbone polymers for grafting are starch. The grafted side chains are hydrophilic in nature, either cationic, anionic, and nonionic. These can be prepared by directly grafting

such monomer as acrylic acid, or by grafting monomer such as acrylonitrile and hydrolyzing to acrylic acid and its salts (11).

In principle, there are two general methods for the synthesis of graft copolymers.

(1) Side chain polymer could be linked directly by a suitable chemical reaction to the backbone polymer.

There are many advantages to this approach which is, in principle, a simple synthetic method. There could be fewer problems of homopolymer formation. More importantly, the length and number of side chains could be readily controlled. This could lead to superior properties, including absorbency because of the higher degrees of substitution and shorter side chains. However, the difficulty of inducing polymer reactions presents a real problem. This method is difficult except in solution and perhaps the most successful has been by treating living polymers to a suitably reactive backbone.

(2) The backbone polymer could have active sites such as free radicals or ions formed upon it. These can then be used to polymerize a suitable monomer to produce the side chain of polymer.

This general method has been much more successful and a large number of techniques have been developed. Essentially, there are free radical processes although ionic grafting has been accomplished by more difficult experimental techniques.

2.1.2.2 Free radical initiation

Radicals can be produced by a variety of redox, thermal, and irradiation methods. In order to function as a useful source of radicals, an initiator system should be readily available, stable under ambient or refrigerated conditions, and possess a practical rate of radical generation at temperatures which are not excessively high (approximately $< 150^{\circ}\text{C}$) (12).

a) Redox Initiation

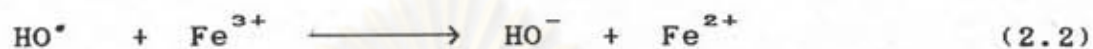
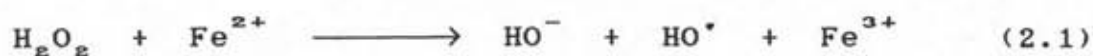
Redox initiation is often an efficient method of initiating a graft polymerization. It usually results in grafting with a minimum of homopolymerization since only the polymeric radical is formed.

A prime advantage of redox initiation is that a radical production occurs at reasonable rates over a very wide range of temperatures, depending on the particular redox system, including initiation at moderate temperatures of $0-50^{\circ}\text{C}$ and even lower (12).

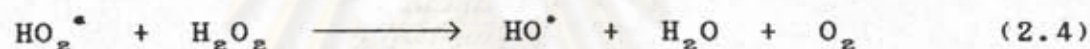
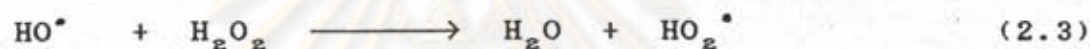
Some redox systems involve a direct electron transfer between a reductant and an oxidant, while others involve the intermediate formation of reductant-oxidant complexes; the latter are charge transfer complexes in some cases (12).

b) Types of Redox Initiator

Peroxides in combination with a reducing agent are common sources of radicals, for example,

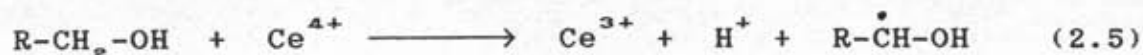


The HO^\bullet radical further decomposes the H_2O_2 molecules.



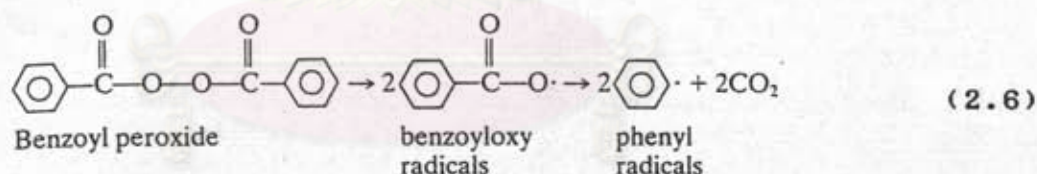
However, decomposition of H_2O_2 by HO^\bullet radicals takes place to an appreciable extent only if H_2O_2 is present in large excess over Fe^{2+} ions.

Organic-inorganic redox pairs can also initiate a polymerization, usually but not always by oxidation of the organic component, for example, the oxidation of an alcohol group by Ce^{+4} , V^{+5} , Cr^{+6} , Mn^{+3} as follow:



c) Thermal Decomposition of Initiators

The thermal, homolytic dissociation of initiators is the most widely used mode of generating radicals to initiate a polymerization. The number of different types of compounds which can be used as thermal initiators is rather limited. One is usually limited to compounds with bond dissociation energies in the range 100-170 kJ/mole. Only a few classes of compounds -including those with O-O, S-S, N-O bonds- possess the desired range of dissociation energies. However, it is only the peroxides which find extensive use as radical sources. The other classes of compounds are usually either not readily available or not stable enough. Several different types of peroxides are widely used, such as benzoyl peroxide :



d) Radiation

Grafting by irradiation of certain polymers either in the presence or absence of a vinyl monomer has been one of the most successful methods and has been applied to an enormous number of polymer-monomer systems. Chemical bonds of organic materials are usually ruptured when they are irradiated to electromagnetic wave or particulate radiation of 100 eV or greater. Among the commonly used energy sources are Cobalt-60, electron accelerator,

and nuclear reactor. Free radicals have been detected in irradiated organic systems, and if vinyl monomers are irradiated, polymerizations take place through a free radical mechanism. When organic polymers are irradiated, simultaneous crosslinking and degradation of the chains occur due to the formation of free radicals on the polymer backbone. Irradiation in the presence of oxygen, an effective free radical scavenger, produces peroxides and hydroperoxides within the polymer. Free radicals or peroxides formed on the polymer backbone by the radiation can be used to initiate the polymerization of different vinyl monomers, leading to graft copolymer formation.

The two common γ sources available are the Co-60 and Cs-137, though the Co-60 is the one commonly used in commercial isotope radiation plants. The reasons for this are not too difficult to find. The Co-60 source is relatively cheap, and has a useful half life of 5.25 years, the source itself is unaffected by high energy radiations from external sources, and may be used up to a temperature of 1300 K. The emission of two gamma rays per disintegration provides a total of 2.5 MeV energy per disintegration. Commercial operations require the use of multi-kilocurie sources, with continuous exposure providing high penetration levels. Several source geometries are available to satisfy particular requirements. The Co-60 sources which is used on a commercial scale lend themselves to ready automation, are reliable, highly penetrating, and provide

continuous irradiation during exposure. As stated above, the source gradually lose its strength, though in a controlled manner. This loss of strength means that the sources need replacing at an approximately 2-5 year interval. The need for automation in product delivery for irradiation is a limiting factor in the degree of flexibility in exposure doses in terms of the distance between the radiation sources and the sample being irradiated.

Radiation is a very convenient source for graft initiation as it allows a considerable degree of control to be exercised over structural factors such as the number and length of the grafted chain by a careful selection of the dose and dose-rate. Preirradiation and mutual irradiation are two different techniques used for radiation grafting (12,13).

e) Chain Transfer and Copolymerization

An active site capable of initiating graft copolymerization may be formed on a polymer via a "chain transfer" step in vinyl addition polymerization. For an initiation by chain transfer, the efficiency of the grafting reaction is dependent on the tendency of a propagating radical to transfer to a polymer (14).

In this method radicals are created on the polysaccharide backbone by the following reactions :



R^{\bullet} can be the growing chain of polymers formed by polymerization with a radical initiator in the presence of the polysaccharide, or by the primary radical from the initiator itself. The chain transfer reaction can be enhanced by the deliberate introduction of such groups as halogens and sulhydryls. The efficiency of this type of grafting reaction is also greatly improved by increasing the ratio of Polysaccharide to monomers such as by using a simple swollen system or with the correct choice of swelling agents. With the primary radical approach, the initiator can be absorbed first into the polysaccharide. With redox initiation such as the ferrous ion-hydrogen peroxide system, the iron can be absorbed into polysaccharide or even exchanged with the residual carboxylic acid group, and the hydrogen peroxide added with monomer. These methods can often be adapted to locate the grafting near the surface or throughout the substrate (11).

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2.2 Terminology and Definition

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

2.2.1 Gelatinization of Starch

Native starches are insoluble in water below their gelatinization temperature. This is a very important property, which enables the starch granules to be easily extracted from the plant source in an aqueous system. Starch granules are insoluble in cold water due to the hydrogen bonds, formed either directly via neighboring alcoholic OH groups of the individual starch molecules or indirectly via water bridges. The hydrogen-bonding forces are weak, but there are so many hydrogen bondings in a starch granule that make the starch insoluble in cold water. Starch granules only swell slightly in cold water (a 10-15% increase in diameter), but this swelling is reversible. The granules shrink back to their original dimensions on drying (9).

When a slurry of starch in water is heated above a critical temperature, a point is reached where the polarization cross starts to fade at the hilum, and this rapidly extends to the periphery of the granule. Simultaneously, the granule starts to swell irreversibly. The term "gelatinization" is applied to this loss of polarization and concurrent initiation of swelling. This gelatinization temp-

erature varies with the type of starch and other factors; the hydrogen bonds responsible for the structural integrity of the granule weaken, allowing the penetration of water and hydration of the linear segments of the amylopectin. As this occurs, the molecules start form helices or coils, creating tangential pressures causing the granules to imbibe water and swell to many times their original volume (15).

During the swelling, the amylose tends to leach out of the granule and, along with the amylopectin, becomes highly hydrated. The suspension begins to clarify and the viscosity of the suspension rises until it approaches a peak where the granules have approached their maximum hydration. As heating is continued, the granules tend to rupture, collapse, and fragment, releasing the polymeric molecules and aggregates. The viscosity drops. During the process as the polymeric molecules are released, the sol often develops a cohesive, rubbery texture. As the resulting sol is cooled, the clarity decreases and the viscosity tends to rise and, in the case of regular cereal starches such as corn or wheat, the sol forms gel if the concentration is sufficiently high (15).

In gelatinizing, starch undergoes a radical alteration in molecular arrangement, with a concomitant change in properties. From a practically insoluble product of semi-crystalline structure, it becomes an amorphous substance, miscible with water in any proportions at suffi-

ciently high temperatures, giving a viscous solution which at lower temperatures, set to a semi-solid, elastic mass, a jelly or gel.

This process may be brought about by the action of chemical, or by heating in the aqueous medium; only the latter case is of current interest. The onset of gelatinization is characterized by a loss of structure of the granules, which also promotes swelling; both processes can easily be followed under the microscope. With cassava starch, gelatinization sets in at about 60°C, and the process is complete below 85°C. The point of gelatinization to a certain extent depends on granule size, the small granules being more resistant to swelling (16).

As result of heating, starch forms a continuous system, referred to as a starch cook or starch paste. In a starch cook or paste, there is a mixture of hydrated, swollen granules and granular particles, held together by a typical maze of associative forces, as schematically presented in Figure 2.3. For complete swelling and binding the available water, the starch concentration must equal to or higher than the critical concentration, which is 0.1%, 1.0%, 1.4%, 4.4%, 5.0%, and 20.0% for potato, sago, cassava, corn, wheat, and high-amylose corn starch, respectively (17).



Figure 2.3 Structure of molecules in a cooked starch paste

Rodehded, C., and B. Ranby (18) studied the grafting of acrylonitrile with granular and gelatinized starch. It was found that the efficiency of the grafting was higher with gelatinized starch rather than with granular one. The accessibility of starch for grafting is enhanced, which will increase the extent of conversion. The resulting starch-g-PAN from gelatinized starch gave about eight times higher molecular weight than that from granular starch. A higher molecular weight of the graft copolymer has shown to give higher water absorption (19).

2.2.2 Percent add-on

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

$$\text{percent add-on} = \frac{\text{Polymer in grafts}}{\text{Weight of the grafted sample}} \times 100 \quad (2.9)$$

Usually, one has to cleave the polymer attached from the starch matrix by acid hydrolysis. The graft copolymer is under reflux in dilute acid solution in which the grafted polymers are separated from the starch backbone.

2.2.3 Grafting efficiency (G.E.)

It is a term to describe graft copolymerization which 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 low grafting efficiency would afford mainly a physical mixture of starch and homopolymer. The grafting efficiency can be calculated as follows:

$$\% \text{ G.E.} = \frac{\text{Weight of grafted polymer} \times 100}{\text{Weight of (homopolymer+ grafted polymer)}} \quad (2.10)$$

2.2.4 Percentage Conversion

Monomer conversion is defined as the extent of the monomer which is charged to the system and then becomes a respective polymer (polymers). For this particular case, the conversion of acrylic acid to be a graft copolymer and a homopolymer is referred to as the percentage conversion.

$$\% \text{ conversion of monomer} = \frac{\text{Polymer formed}}{\text{Monomer charged}} \times 100 \quad (2.11)$$

2.2.5 Grafting ratio

It is a term used to describe a graft copolymerization which is defined as the percentage ratio between the grafted polymer and starch. This ratio can be calculated as follows:

$$\% \text{ grafting ratio} = \frac{\text{Polymer in grafted} \times 100}{\text{Weight of substrate (or starch)}} \quad (2.12)$$

2.2.6 Grafting frequency (AGU/chain)

It is expressed as an average number of anhydroglucose units (AGU) separating each grafted branch. It can be calculated as follows:

$$\text{grafting frequency (AGU/chain)} = \frac{\text{glucose (mole)}}{\text{synthetic polymer (mole)}} \quad (2.13)$$

where

$$\text{synthetic polymer (mole)} = \frac{\% \text{ add-on}}{\text{molecular weight}} \quad (2.14)$$

$$\text{glucose (mole)} = \frac{100 - \% \text{ add-on}}{\text{glucose molecular weight (162)}} \quad (2.15)$$

2.3 Survey of Related Literature.

Considerable studies on the synthesis, properties and of cellulose graft copolymers have been carried out since 1952. Graft copolymerizations onto starch are carried out in much the same way as graft copolymerizations onto cellulose. The hydrolyzed starch-g-PAN copolymers were not the first types of polymers which were used as superabsorbents for aqueous fluids; however, their discovery did much to spark the tremendous interest in this field. Recent reviews on the synthesis, properties, and application of starch graft copolymers have been compiled (1-2, 11, 20-22). Corn starch is most often used as the substrate for graft copolymerizations, however, starch from wheat, sorghum, rice, and potato will give hydrolyzed starch-g-PAN copolymers with similar properties. The grafting monomers used cover a very wide variety of vinyl monomers such as acrylonitrile, acrylamide, acrylic acid, monomer with amino substituents, acrylic acid esters, styrene, butadiene, vinyl chloride, and N-vinyl-2-pyrrolidone.

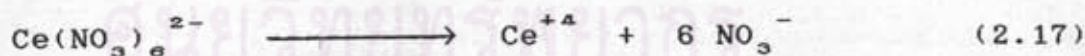
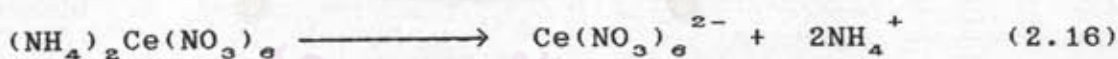
Although other absorbent polymers, both natural and synthetic, have since been prepared for this application, grafted starch still holds an important place in the market. The development of the grafted starch products, essentially involving acrylic acid grafted side chains, immediately attracted worldwide attention because of their tremendous water sorbing and retention properties. Related works on the study of starch graft copolymers, classified

by the type of initiators, are listed below.

2.3.1 The Ce^{+4} Initiation

Due to its ease of application as well as its grafting efficiency, the Ce^{+4} ion method has considerable importance in the grafting reaction. This technique is based on the fact that when starch is oxidized by a ceric salt such as ceric ammonium nitrate, free radicals capable of initiating vinyl polymerizations are formed on the starch by a single electron transfer. Since the radicals produced are almost exclusively on the starch, homopolymer formation is theoretically minimized.

Ceric ammonium nitrate exists as a complex salt and is ionized in solution, yielding free ammonium ions and nitratocerate ions. The nitratocerate ions subsequently decompose to yield Ce^{+4} cations and nitrate anions.



The mechanism of Ce^{+4} initiation is the cleavage of the glycol groups of the anhydroglucose units. The Ce^{+4} ions forms a complex with the starch, propably at the C_2 and C_3 hydroxyls, which then causes one of the hydrogen atoms on C_2 or C_3 to be oxidized while the Ce^{+4} ion is reduced and a free radical is formed on the starch at the C_2 or C_3 atom. The bond between C_2 and C_3 is then broken

with the formation of an aldehyde group on the C_2 or C_3 , which does not have the free radical form. It has been concluded that both C_1 - C_2 glycol end group and C_2 - C_3 glycol groups along the polysaccharide chains form reactive grafting sites as shown in Figure 2.4. The free radical then reacts with the monomer to form a starch grafted copolymer.

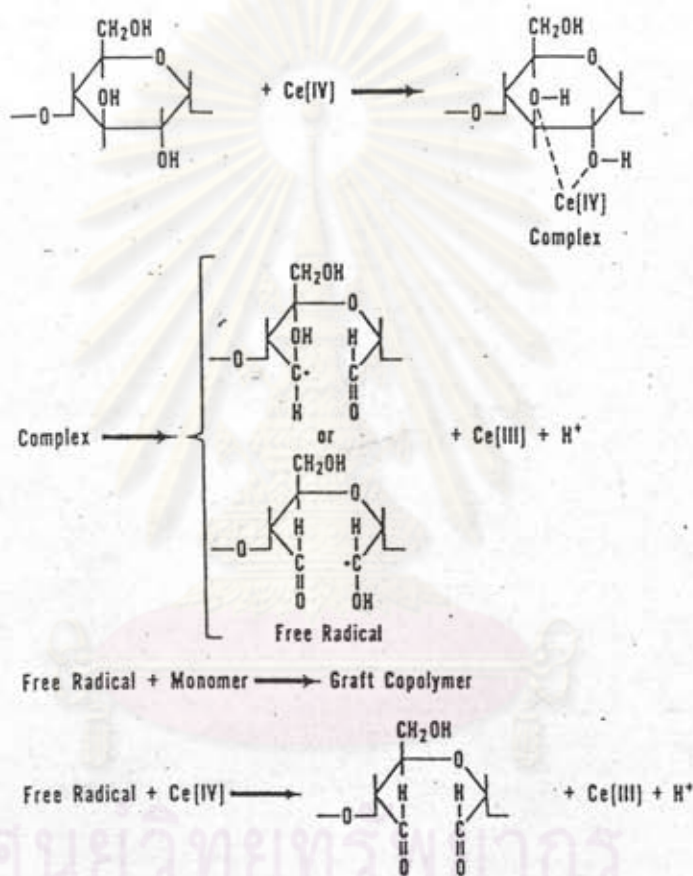


Figure 2.4 Reaction Scheme to synthesize a starch grafted copolymer by Ce^{+4} ion

Reyes, Z., C.E. Rist, and C.R. Russell (23) studied the grafting of AN and acrylamide to starch. The variables affecting the grafting of AN and acrylamide were investigated with granular wheat starch dispersed in aqueous N,N-dimethylformamide. The results showed that the concentra-

tions of monomer and initiator are the major factors influencing the grafting of AN. The grafting of acrylamide is also influenced by these variables, but to a much less degree.

Fanta, G.F., R.C. Burr, C.R. Russell and C.E. Rist (24) investigated the influence of selected reaction condition on both the grafting frequency and the molecular weight of grafted PAN for the reaction of gelatinized wheat starch with AN. In the design of experiments, conditions were sought that might lead to a large number of relatively short PAN chains grafted to starch backbone as opposed to a small number of high molecular weight grafts.

Burr, R.C., G. F. Fanta, C.R. Russell, and C.E. Rist (25) determined accurately how the degree of swelling and the extent of granule disruption would influence the composition of graft copolymer prepared from gelatinized wheat starch with AN under a constant condition. They obtained a more frequently grafted copolymer whose grafted chain had molecular weights on the order of 150,000. In contrast to previous results (11), grafting AN to gelatinized wheat starch has afforded a product with grafted chains having few numbers, but high in molecular weight (about 800,000).

Burr, R.C., G.F. Fanta, C.R. Russell, and C.E. Rist (26) prepared a starch-g-PAN copolymer in a number of aqueous-organic solvent system. The organic solvents used in this experiment were methanol, tetrahydrofuran (THF), DMF, t-butanol, acetic acid, and acetonitrile. They found that, with an exception of acetonitrile, the graft copolymers had more grafts than those prepared in water alone and these were lower molecular weight.

Gugliemelli, L.A., M.O. Weaver, and C.R. Russell (27) isolated grafted copolymers from starch backbone by periodate-alkali method. They found that the graft copolymers could be isolated readily under mild condition at room temperature.

Fanta, G.F., R.C. Burr, C.R. Russell, and C.E. Rist (28) studied the influence of a variety of starch, size of the starch granules, reaction time, and possible reasons for the influence of reactant concentration on the composition of the copolymers. The results showed that neither the origin of the starch nor the relative amounts of amylose and amylopectin affect materially the molecular weights and frequencies of the grafts. Since the grafting frequencies were not greatly different from each other and showed no dependence on granule size, the evidence suggest that granules of starch were grafted internally. If the grafting frequencies were plotted against reaction time, it

showed that the number of grafted chains levelled off more rapidly and to a lower final value with 50.9 g of AN than with 10.0 g. The grafting frequencies and molecular weight of grafted PAN changed from 600 anhydroglucose units (AGU)/graft and 120,000 to 280 AGU/graft and 36,000 when concentration of starch and AN were varied from 0.27 and 1.20 to 0.023 and 0.235 moles/dm³ of water, respectively.

Gugliemeili, L.A., M.O. Weaver, C.R. Russell, and C.E. Rist (29) prepared and hydrolyzed a starch-g-PAN graft copolymer consisting of one part starch and one part PAN (M.W. 794,000) with aqueous KOH saponified at 80° and 100°C to polyelectrolytes containing the carboxyl and amide functionalities but void of infrared-detectable amounts of nitrile.

Weaver, M.O., L.A. Gugliemelli, W.M. Doane, and C.R. Russell (30) prepared three starch-g-PAN copolymers containing ratios of starch: PAN at 1:1.90, 1:1.16, and 1:0.64 by graft polymerization of AN onto gelatinized starch. A fourth graft, made from granular starch had an starch: PAN ratio of 1:2.16. These grafts were hydrolyzed in aqueous KOH under various conditions to give a series of products with varying amounts of carboxylic acid and amide groups. Maximum conversion of nitrile to carboxyl was 65%. Their viscosities reflected the amount of PAN add-on, with the highest add-on giving the highest viscosity.

Fanta, G.F., F.L. Baker, R.C. Burr, W.M. Doane, and C.R. Russell (31) determined the location of PAN within a starch granule matrix for two wheat starch-PAN graft copolymers which contained 22% and 44% grafted PAN. Granules of graft copolymers were fractured by ballmilling. The milled copolymer was then heated under reflux in dilute hydrochloric acid to remove starch moiety, and the fracture surface in the remaining PAN was examined with a scanning electron microscope. They found that, areas in the grafted granules which contained little or no PAN thus appeared as voids in the fracture surfaces. Electron micrographs suggested that granules of low add-on graft copolymer were largely surface grafted. In the higher add-on product, grafting had taken place throughout most of the granule interior; however, small areas in the centers of some granules still contained little or no PAN.

Taylor, N.W., and E.B. Bagley (32) prepared a starch-g-PAN copolymer with subsequent hydrolysis of PAN moiety to a mixture of carboxylate and carboxamide. In many ways these mixtures behaved like ordinary polyelectrolytes solutions, but dilution experiments revealed that linear reduced viscosity-concentration plots could be obtained even under ostensibly isoionic dilution conditions. These results, combined with a determination of gel content from centrifugation studies, led to the conclusion that high viscosity HSPAN water mixtures consist of swollen, deform-

able gel particles closely packed in an intimate contact. Under high dilution or at high ionic strength condition, the gel particles no longer are tightly packed, solvent is present in excess, the viscosity drops precipitously, and thickening action effectively disappears.

Fanta, G.F., F.L. Baker, R.C. Burr, W.M. Doane, and C.R. Russell (33) prepared a series of hydrolyzed starch-g-PAN copolymers, the only differences being in the degree of swelling and gelatinization of starch granules. This variable was governed by the temperature at which starch-water slurries were heated before graft polymerization. Comparison of scanning electron micrographs of each starch-g-PAN copolymers with those of the corresponding saponified product showed particles which retain the outward appearance of graft polymerized starch granules.

Weaver, M.O., R.R. Montgomery, L.D. Miller, V.E. Sohns, G.F. Fanta, and W.M. Doane (34) developed a process for making the starch-g-PAN copolymer (Super Slurper) in multipound quantities from laboratory scale-up studies. This process avoided intermediate isolation steps, permitted efficient removal of the unreacted monomer, kept the concentration of extraneous salts low, and gave a high solid concentration for the drying step. Variation in drying procedure allowed Super Slurper to be made in a film, mat, powdery or flake form. Shearing the hydrolysis mixture

prior to isolation and avoiding extended exposure or isolated the product to an elevated temperature gave Super Sluper with a highest absorptive capacity.

Fanta, G.F., R.C. Burr, W.M. Doane, and C.R. Russell (35) prepared starch-g-PAN copolymers of corn starch from monomer mixtures obtained when selected comonomer which was substituted for the portion of the AN. Graft copolymers were then saponified and saponified polymers were dried to form absorbents for aqueous fluid. Use of 2-acrylamide-2-methylpropanesulfonic acid (AASO_3H) as a comonomer resulted in the significantly shorter saponification times, more absorbent products and gave saponified graft copolymers from both granular and gelatinized starch which absorbed larger amounts of aqueous fluids than their counterparts prepared from AN alone. Incorporation of acrylamide into the polymerization mixture similarly shortened the time needed for saponification, but the absorbencies were in most case the same or somewhat less than the products prepared in the absence of comonomer. The effect of five other comonomers on saponification time and on absorbency of saponified graft copolymer was examined. Acrylic acid increased water absorbency and shortened the saponification time. A shorten saponification time was also obtained with 10 mole% methyl acrylate. Although inclusion of vinyl sulfonic acid also gave a saponified polymer with higher absorbency, the saponification time was somewhat

longer. When 10 mole% of either methyl methacrylate or styrene was included with AN in the graft polymerization, The absorbency values of products were lower than those of saponified starch-g-PAN and there was little or no reduction in the saponification time. Substituent flour or corn meal for starch in the ceric initiated graft polymerization of AN which gave a polymer which after saponification, had a higher absorbency for aqueous fluid than saponified starch-g-PAN.

Fanta, G.F., M.O. Weaver, and W.M. Doane (36) reported on the absorbency test of starch-PAN graft copolymers in water and simulated urine (97.09% deionized water, 1.94% urea, 0.80% NaCl, 0.11% $MgSO_4 \cdot 7H_2O$, and 0.06% $CaCl_2$). They found that, with graft copolymers, more than 50% of absorbence capacity is reached in 30 seconds. "Total" capacity is reached in about 10 minutes. This graft copolymers can absorb a large amount of aqueous fluids. This graft copolymer has potential uses in disposable diapers, sanitary napkins, bandages, bed pads, and the like replace cellulose fibers.

Fanta, G.F., E.B. Bagley, R.C. Burr and W.M. Doane (37) used methanol as a precipitant to isolate saponified starch-g-PANs from aqueous alkaline saponification mixture to give a product with higher water absorption and better storage stability than that resulting from precipitation

with ethanol, acetone, or isopropanol. Storage stability is strongly dependent on moisture content of the polymer and is enhanced if excess alkali in the saponification mixture is neutralized before the product is isolated. Although absorbent polymers prepared from granular starch have lower absorbencies than products prepared from gelatinized starch, granular-based polymers also lose a small percentage of their original absorbency on storage.

Fanta, G.F., R.C. Burr, and W.M. Doane (38) examined the influence of the molar ratio of corn starch : Ce^{+4} (between 10-1000 glucopyranosyl units, AGU, per Ce^{+4}) on the properties (absorbency and water solubility) of HSPAN, with the goal of minimizing the amount of CAN used to initiate a graft polymerization. They found that, with granular starch, Ce^{+4} ion concentration ranging from 10 to 500 AGU/ Ce^{+4} all yield starch-g-PAN with about the same % add-on. The of Ce^{+4} ion had little effect on viscosity average molecular weight in the 50-200 AGU/ Ce^{+4} range; however, at 10 and 500 AGU/ Ce^{+4} , graft molecular weights were lower and higher, respectively. The amount of CAN had a great effect on water solubility of HSPAN than it did on water absorbency, and relatively high water solubilities were observed at both 10 and 500 AGU/ Ce^{+4} . Ceric-initiated graft polymerization onto other varieties of corn starch, such as acid modified, waxy, and high-amylose, were also investigated. It is appeared that waxy corn starch requires

more CAN to initiate a graft polymerization than do the other varieties of corn starch, particularly when it is gelatinized. With the exception of the product made from gelatinized high-amylose starch, water absorption of other varieties of corn starch were all higher than those of products made with normal corn starch. Additionally, the preparation of starch-g-PAN can be achieved by an incremental addition of CAN. They showed that, HSPAN with significantly higher water absorbency and higher molecular weight for grafted PAN could be prepared by this procedure.

Fanta, G.F., R.C. Burr, and W.M. Doane (39) found that, crosslinking occurred during the graft polymerization of AN onto starch by way of chain combination of growing PAN macroradicals. Crosslinking also occurred between starch and PAN during alkaline saponification. Soluble (and thus uncrosslinked) starch-g-PAN polymers were rendered partially insoluble by alkaline saponification, as was a synthetic mixture of starch and PAN. Although PAN would self-crosslink if saponifications were carried out in ethanol-water systems containing predominantly ethanol. PAN: PAN crosslinking did not take place during aqueous saponifications. Since the individual grafted starch granules were crosslinked, these granules maintain their integrity after alkaline saponification and exist in the saponificate as highly swollen gel particles. When the saponificate was dried, these gel particles coalesce into

either films or macroparticles which would not redisperse back into gel when placed in water. These properties may be similarly explained by assuming interdiffusion of polymer chain ends on the surface of individual gel particles, followed by hydrogen bonding between these polymer chains. If a dry saponified starch-g-PAN was heated, its ability to absorb water was reduced; however, this absorbency loss was not related to the loss of hydrogen-bonded water from the graft copolymer.

Fanta, G.F., R.C. Burr, and W.M. Doane (40) investigated the method by which methanol was added to the precipitated saponified starch-g-PAN from an alkaline saponification mixture. The method influences the particle size of copolymer and thus the properties of the absorbent. Slow methanol addition, coupled with thorough mixing to ensure complete absorption of methanol by the reaction mass, would separate individual micron-sized fragments of HSPAN gel and would yield a product with small enough particle size to produce a smooth, free-flowing gel dispersion when added to water. This product was perhaps more suitable as a thickener than as a water absorbent. More rapid addition of methanol, resulted in incomplete absorption by the reaction mass and caused individual gel fragments to coalesce to form millimeter-sized chunks of water-swollen HSPAN. Subsequently dewatering with excess methanol produced a granular product with good absorption. Gel-blocking was re-

duced by adding either stearic acid or poly(vinyl acetate) to methanol-precipitated.

Patel, A.R., K.C. Patel, and R.D. Patel (41) prepared and investigated graft copolymers of six cereal starches (corn, wheat, rice, great millet, bulrush millet, and common millet starch) with PAN. The molecular weights, the frequencies of grafting, and the absorbencies of the saponified product were almost independent of the source of granular starches. The percent yield and percent add-on of graft copolymers from gelatinized starches were almost the same as those from granular cereal starches. However, their molecular weight, corresponding frequency of gelatinized starch graft copolymers had increased five times, the absorbency of which was doubled.

Ziderman, I., and J. Belayche (42) studied on water sorbence by saponified PAN-grafted polysaccharides in relation to practical end uses. Graft copolymers prepared from wheat flour, corn flour, cotton wool, and rayon fibers swelled to a gel, exhibiting a 10- to 20-fold increase in sorbency over the starting materials. They found that, a further enhanced water capacity was obtained when homopolymer was not removed. Soaking the wheat flour copolymer in salts or dilute mineral acids nullified the enhanced water sorbence, which could be reversibly restored by neutralization of acrylic acid functionality with alkali.

Sandle, N.K., O.P.V. Verma, and I.K. Varma (43) investigated thermal behavior of several starch-g-PAN copolymers having different percentage graft-on, by changing the AN concentration in the initial feed. Thermal behavior was investigated using dynamic thermogravimetry in a nitrogen atmosphere. They found that, the decomposition of starch took place mainly in a one-step reaction, and about 80% of starch is degraded from 280 to 340°C. The decomposition of PAN also took place mainly in one step with a loss of 52.5%. In the case of graft copolymers, the low grafted samples degraded predominantly in a one-step reaction, whereas highly grafted samples degraded in two or three distinct steps. The percentage weight loss during first step degradation was decreased as the percentage graft-on increases. An increase in percentage graft-on resulted in an increase in anaerobic char yield at 550°C. A graft copolymer sample having a 97.7% graft-on had a char yield of 52%, which was higher than that of PAN.

Bazuaye, A., E.F. Okieimen, and O.B. Said (44) prepared graft copolymers of AN on bleached holocellulose and starch at 29°C using the continuous initiation and depleted initiator methods. They found that, the extent of graft copolymer formation (grafting level and molecular weight of grafted chains) on starch was higher than on the bleached holocellulose. The extent of graft copolymer formation using the depleted initiator method was higher than that ob-

tained using the continuous initiation method but grafts from the latter method were more frequent on the polymeric substrates.

Bazvaye, A., F.E. Okieimen, and O.B. Said (45) prepared starch-g-PAN copolymers by varying the amount of initiator, and monomer. The results showed that, at each monomer concentration, the maximum graft level was attained at 10.0 m.mol Ce^{+4} /g starch. The ceric ion concentration at which the maximum graft level was attained was considered to indicate the ability and extent of the backbone polymer to reduce Ce^{+4} to Ce^{+3} .

Gurruchaga, M., I. Goni, M.B. Vazquez, M. Valero, and G.M. Guzman (46) studied the homopolymerization of methyl methacrylate in the absence of reductant and the influence of photoactivation of the initiator. They found that, poly(methyl methacrylate) was formed from the beginning of the reaction and its amount increased with time. Nevertheless, the most important was not only the increase in the amount of homopolymer but its formation in the absence of polysaccharide. In addition, they found that, percentage grafting increased in the presence of sunlight which implied the initiation was more efficient under these condition.

Okieimen, F.E., J.E. Nkumah, and F. Egharevba (47) prepared graft copolymers of acrylic acid on starch by the use of various initiator concentrations in aqueous media at 29°C. The attachment of the grafts to starch led to marked improvement in the water retention capacity and metal ion binding capacity of the polymeric substrate. The equilibrium sorption data for Cu^{+2} ions on starch graft copolymers fitted the Freundlich isotherm, with the coefficient and exponent of the isotherm being 0.40 and 0.60 respectively. The distribution coefficient for Cu^{+2} ions between the polymeric substrate and the bulk aqueous phase depended on the concentration of the metal ion in solution, including that Cu^{+2} ions which may be strongly adsorbed on the starch graft copolymers.

Castel, D., A. Ricard, and R. Audebert (48) reported about the influence of several structural parameters on the swelling properties in water or saline solution of starch-based superabsorbent gels. They prepared both anionic and cationic superabsorbent gels. Anionic gels were obtained by saponification of grafted PAN onto starch. Cationic gels have been synthesized by copolymerization with cationic monomer (trimethylaminoethylacrylate chloride) and a crosslinking reagent such as N,N-methylene bisacrylamide. The influence of several structural parameters on the swelling properties of these absorbents had been studied in terms of crosslink density, ionic content, and compo-

sition of the starch. They found that, the absorbency decreased with an increase in crosslink density. The water absorption increased with the ionic content of graft copolymer up to a maximum value of an excessive change in any of these parameters leading to a decrease in swelling. The PAN branch length depended on the origin of the starch. A high molecular weight PAN was grafted onto the waxy corn, a starch with high amylopectin content. In saline solution, the absorbency of both ionic gels decreases significantly. For cationic absorbents the swelling depends on the ionic strength but not on the ion valency. On the other hand, anionic absorbents are significantly affected by multivalent cations.

Kiatkamjornwong, S. and J.G. Faullimmel (49,50) prepared a superabsorbent polymer synthesized by grafting copolymerization of AN on to the 80°C gelatinized cassava starch. In addition to cassava starch-g-PAN, a homopolymer of PAN was a by-product which was later removed by extraction with DMF. The purified graft copolymer was subsequently saponified with an 8.5% KOH solution at 85°C to convert the nitrile groups into a mixture of acrylamide and carboxylate groups which were responsible for water absorbency. The water absorption capacity in pure water ranged from 120 to 270 time its original dried weight. Water absorption capacity in saline ($MgCl_2$) solution decreased dramatically with increasing the salt concentrations. Water

retention in sand and in mixed sand-copolymer at different copolymer concentrations was also performed. Increasing the concentrations of the copolymer in sand increased the water retention capacity.

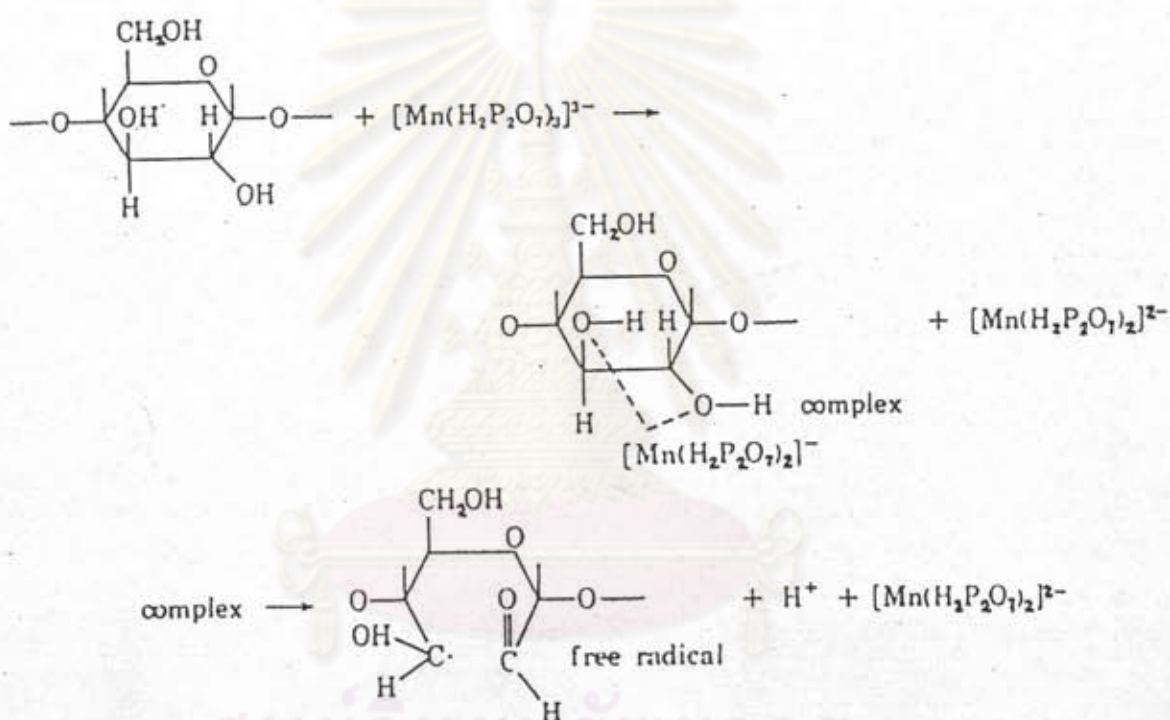
2.3.2 The Mn^{+3} Initiation

The use of trivalent manganese ion (manganic pyrophosphate) as an initiator has been reported. The mechanism of Mn^{+3} initiation is similar to that proposed for the Ce^{+4} initiation as shown in Figure 2.5.

Mehrotra, R., and B. Ranby (51) studied the graft copolymerization of vinyl monomers onto starch. The results showed that grafting efficiency and polymer yields were high when starch and starch derivatives were grafted with AN and methyl methacrylate. When acrylamide was used as a grafting monomer, in contrast to AN, low grafting efficiencies and considerable amounts of homopolymer were obtained. The average molecular weight of the synthetically grafted polymer chains were of the order of 10^5 for AN and of the order of 10^6 for methyl methacrylate as a monomer. Consequently, the average number of AGU separating the grafted chains was in the range of 600-1,600 for AN and over 25,000 for methyl methacrylate. Reaction mechanisms responsible for initiation of graft copolymerization were discussed as follows: (a) Glycol cleavage in the AGU by

Mn^{+3} ions leading to the formation of a radical; (b) enolization and further oxidation of oxidized starch by Mn^{+3} ions also leading to radical species. Mechanisms of homopolymerization were proposed through the Mn^{+3} oxidation of enols which were properly formed by a vinylogous addition of water molecules to acrylamide and methyl methacrylate.

Initiation:



Propagation:



Termination:

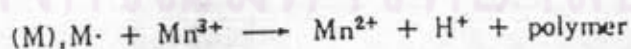


Figure 2.5 Reaction Scheme to the synthesis of starch grafted copolymer by Mn^{+3} . Reproduced from Ref (51).

Mehrotra, R., and B. Ranby (52) examined the effect of reaction conditions on the composition of granular native potato starch-g-PAN copolymers onto starch slurries at 30°C. They found that, when the Mn^{3+} ion concentration was increased from 0.15×10^{-3} M to 3.0×10^{-3} M (other conditions were kept constant), an increase in conversion of monomer to polymer and % add-on was observed, whereas frequency of grafts (AGU/chain) decreased. Also, the average molecular weight of the graft showed a decrease from 2.2×10^5 to 1.5×10^5 . Increasing the concentration ratio of starch to monomer during polymerization by a factor of 3 produced an increase in the conversion of monomer to polymer, as well as an increase in AGU/chain, i.e. an increase in grafting frequency was obtained. The value of % add-on and average molecular weights of the grafts showed, however, a decreasing tendency. In this investigation, little or no PAN was formed as a homopolymer in a physical mixture with the starch substrate.

Mehrotra, R., and B. Ranby (53) prepared gelatinized potato starch-g-PAN copolymers. The results showed that, total conversion of AN to PAN and % add-on were almost constant and showed only slight variation with increasing starch pretreatment temperatures. Average molecular weight of grafts showed, however an increase by a factor nearly 10 (i.e., from 0.4×10^5 to 4.0×10^5) after swelling and gelatinization of the starch, and the grafting frequency also

increased in proportion. Increasing Mn^{3+} concentration increased the conversion of monomer and % add-on, whereas the average molecular weight of grafts and the grafting frequency decreased. A selective solution of the PAN homopolymer by DMF extraction indicated that grafting efficiencies were high in all cases.

Ranby, B., and C. Rodeled (54) investigated water vapor absorption and aqueous retention of hydrolyzed starch-g-PAN copolymers. The water vapor absorption like other polysaccharides, at relative humidity (RH), was of upto 95-97 %. At higher RH values, the water vapor absorption increased very rapidly. In contact with distilled water, the modified starch becomes "superabsorbent" by retaining very large amounts of water (upto 800 g/g).

Rodehed, C., and B. Ranby (55) prepared a sample of starch-g-PAN (grafting ratio 82%) at 303 K in aqueous acid solution with gelatinized starch as a substrate. Subsequent alkaline hydrolysis converted the nitrile groups to the carboxamide (30%) and carboxylate (70%) groups. The swelling of the copolymer formed which retained about 700 g water per g dry polymer, had been studied in alcohol/water mixtures of increasing alcohol content at 294, 304 and 314 K. The main transition for both alcohol/water mixtures was a collapse of the gels at 50-60 volume % ethanol and 60-70 volume% methanol, respectively. Increasing the tempe-

rature from 294 to 314 K increased the liquid retention.

Rodehed, C., and B. Ranby (56) prepared starch-g-PAN copolymers. Both granular native starch and water-swollen gelatinized starch were used as substrates. Conversion of monomer, grafting ratio, and percent add-on tended to increase with increasing amounts of monomer charged. The amount of homopolymer formed was extremely low at approximately 1%. The efficiency, measured as conversion, was consistently higher with gelatinized starch as a substrate. The molecular weight of the grafts on gelatinized starch was approximately eight times higher than those on granular starch. The water retention value increased linearly with increasing % add-on. The saponified PAN branches alone had a water retention value of three times higher than that of the origin starch grafted copolymer.

Rodehed, C., and B. Ranby (57) studied the absorbed water in a saponified starch-g-PAN copolymer by differential scanning calorimetry. The grafted copolymers had a moisture content in the range of 0-1.05 g water per g of dry polymer. Molar heat capacity measurements at temperatures higher than 273 K gave a partial molar value between those of ice and bulk liquid water. No crystallizable water was detected in copolymers with water contents lower than 0.44 g/g dry polymer. In copolymers containing larger amounts of water, both the amount of bound uncrystallizable

water and the amount of free crystallizable water increased linearly. Two melting endotherms were detected, suggested that the free water could be divided into two components with different melting points, i.e 268 and 274 K, respectively.

Rungsriwong, N. (58) prepared cassava starch-g-PANs by a grafting copolymerization reaction of AN onto the polysaccharide backbone. Two types of high water absorbing polymer were obtained by using two gelatinization temperature of 65 and 80°C. The saponified starch-g-PAN was characterized in terms of the grafting efficiency and frequency, the % add-on, and the viscosity average molecular weight. Finally, the water absorption as a function of the amount of AN grafted onto starch, was determined with deionized water and salt solutions at different concentrations of NaCl, CaCl₂, and MgCl₂. The results indicated that water absorption increased with increasing % add-on and viscosity average molecular weight, but decreased as the concentration of salt increased. Water retention in sand was also determined and showed that an increase in the water holding capacity of sand was proportional with the amount of absorbent used.

Faullimmel, J.G., S. Kiatkamjornwong, and N. Rungsriwong (59) prepared saponified starch-g-PANs by a grafting copolymerization of AN onto the polysaccharide backbone. Prior to the grafting reaction, starch was gelatinized at 65°C. Following the reaction, the amount of homopolymer, PAN, obtained as a byproduct, was removed from the grafted starch by DMF extraction. The purified product was then saponified with an 8.5 % KOH solution resulting in the disappearance of the nitrile group and the formation of carboxylate and carboxamide functional groups.

Faullimmel, J.G., S. Kiatkamjornwong, and N. Rungsriwong (60) reported on the absorbency test of saponified cassava starch-g-PAN copolymers in deionized water and other solutions. They found that the absorption in deionized water was of a linear relationship between water absorption and % add-on. The highest absorbency value was as high as 200 g/g, which was above the value of similar materials currently available on the market. Water absorbency in NaCl, CaCl₂, and MgCl₂ solutions at concentrations of 0.5, 1.0, and 2.0% W/V dramatically decreased the water intake by the copolymer. It was suggested that this was due to an osmotic pressure effect: as the salt concentrations increased, the osmotic pressure differential between the inside and outside of the gel decreased more rapidly, thus allowing less water to be absorbed. Water retention in sand by mixing the sand itself with the grafted copolymer at

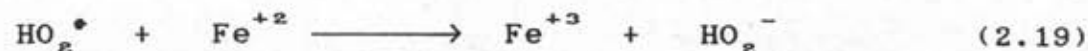
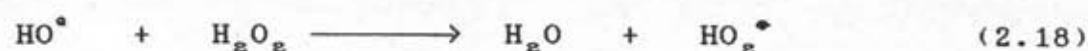
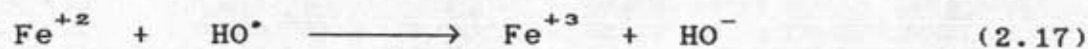
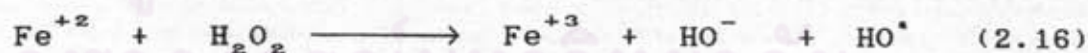
the concentrations of 0.5, 1.0, 1.5, and 2.0% showed a linear relationship of water increase with increasing amount of the absorbent added.

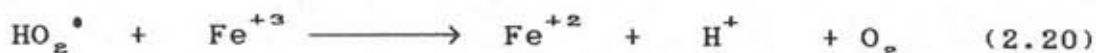
Faullimmel, J.G., S. Kiatkamjornwong, and N. Rungsriwong (61) reported on the effect of gelatinization temperature on water absorption of saponified cassava starch-g-PAN copolymers. They found that at a gelatinization temperature of 80°C, the resulting saponified starch-g-PAN had better absorption properties than the one synthesized with the starch gelatinized at 65 °C.

2.3.3 The Fe⁺² -H₂O₂ Initiation

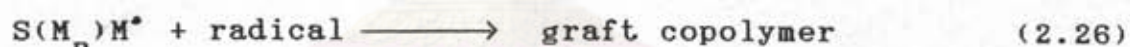
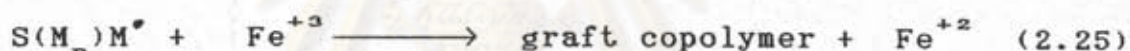
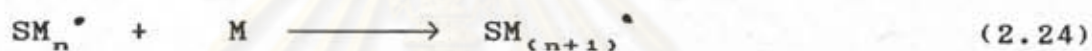
A mechanism for the grafting polymerization of a vinyl monomer (M) onto a polysaccharide (SH) is shown below (62).

Redox system





Graft copolymerization



When the initial Fe^{+2} concentration was kept constant, it usually influenced the number of HO^\bullet radicals formed which in turn were responsible for the relative amount of homopolymer and copolymer. The variation in the H_2O_2 - Fe^{+2} ratio affected the first five reactions of the mechanism. At very low ratio only the steps (2.16) and (2.17) occurred and the steps (2.18), (2.19) and (2.20) did not take place. As this ratio increased the competition for the HO^\bullet radicals in (2.17) and (2.18) became more pronounced. At high H_2O_2 - Fe^{+2} ratio however, the competition for the HO_2^\bullet radical in (2.19) and (2.20) would be predominate. In order

to favor the graft copolymer formation over homopolymer formation, the HO^\bullet radical should effectively abstract a hydrogen atom from the polysaccharide chain rather than initiate homopolymerization. This favorable situation could be arrived at by keeping the Fe^{+2} ions in the proximity of the polysaccharide chain during the reaction.

Fanta, G.F., R.C. Burr, C.R. Russell, and C.E. Rist (63) prepared graft copolymers of AN onto starch. Molecular weights and grafting frequencies of the graft copolymer showed a dependence on granule swelling similar to that found with ceric ammonium nitrate. Molecular weight of PAN branches grafted to swollen and unswollen starch was independent of the reaction time; however, grafting frequencies with swollen and unswollen starch tended to converge toward a common value with increased reaction time and increased dilution.

Fanta, G.F., R.C. Burr, M. William, and W.M. Doane (64,65) prepared graft copolymers of AN onto ground, water-wash straw. Wheat straw-g-PAN, containing 40% PAN, was saponified with sodium hydroxide and isolated under three sets of saponification and work-up conditions. Each reaction mixture was separated into a water-soluble and water-insoluble fraction, which were individually analyzed for percentages (by weight) of the synthetic polymer (saponified PAN), cellulose, hemicellulose, and lignin. Water

solubles amounted to 14-24% of the total product and contained 70-74% synthetic polymer, the remainder being hemicellulose and lignin. Although water-insoluble fraction contained 52-54% saponified PAN, their absorbencies were low (14-17 g H₂O/polymer).

Vazquez, B., I. Goni, M. Gurruchaga, M. Valero, and G.M. Guzman (62) studied the best condition of graft copolymerization of methacrylic acid onto potato starch. The variables were studied: initiator and monomer concentrations, time and temperature. They found that, the optimum graft yield was obtained at 7.3×10^{-3} M H₂O₂ concentration and it was favored by increasing the methacrylic acid concentration and reaction time.

2.3.4 The Radiation Initiation

Fanta, G.F., F.L. Baker, J.A. Stolp, R.C. Burr, and W.M. Doane (66) studied the location of grafted polymer within the starch granule matrix by scanning electron microscopy for two wheat starch grafted copolymers prepared by graft copolymerization of a mixture of acrylamide and N,N,N-trimethylaminoethyl methacrylate methyl sulfate (TMAEMA⁺MS). For a graft copolymer containing 16 % synthetic polymer, prepared by the simultaneous irradiation of a starch-monomer mixture, grafting took place throughout most of the granule interior. However, a graft copolymer containing

31% synthetic polymer, prepared by a reaction of preirradiated starch with a water solution of monomers, was grafted largely near the granule surface. In contrast to starch-g-poly(acrylamide-co-TMAEMA MS) prepared by simultaneous irradiation, irradiation of a starch-styrene mixture gave predominantly surface grafting. All graft copolymers had the outward appearance of the starch granules, and this appearance was retained even after removal of the starch moiety by hydrolysis. The size distribution of wheat starch granules, as determined by Coulter counter measurement, was not greatly altered by graft copolymerization of acrylamide-TMAEMA MS; however, graft copolymerization of styrene onto starch significantly increased the granule size.

Abbott, T.P., and C. James (67) reacted the monomer of 2-butenyl acrylate with starch by exposure to either Co^{60} irradiation or ceric ion initiation. They found that, the simultaneous irradiation technique would polymerize 2-butenyl acrylate to as much as 77% conversion. However, irradiation for 4 hrs (1.9 M rad) led to a lower polymer recovery than irradiation for 2 hrs due to degradation of the polymer backbone.

Chen, L.J., Z. Xin, And C.Z. Ping (68) studied graft copolymerization of corn starch with AN by gamma-irradiation. The graft copolymer produced by the reaction was

hydrolyzed by sodium hydrate and the water absorption polymer was obtained having a water absorption value of $875 \text{ cm}^3/\text{g}$. The effect of dose rate on water absorption was examined in the range of 4×10^5 to 10^6 rads/hr. They found the optimum dose rate was 8×10^5 rads/hr. The effect of total dose on water absorption was examined in the range of 4×10^5 to 1.2×10^6 rads, the result showed that all products produced in the range of 4×10^5 to 8×10^5 rads had high water absorption. The effect of reaction temperature on water absorption was investigated in the range of $20-40^\circ\text{C}$. The result showed that the optimum temperature was about 30°C .

Kiatkamjornwong, S. and J. Chvajarernpun (69) reported on the radiation modification on liquid retention properties of native cassava starch by graft copolymerization with acrylonitrile through by mutual irradiation to γ rays. The combined effect of radiation parameters in terms of an irradiation time and a dose rate to the total irradiation dose on the extent of the grafting reaction was studied which influenced the liquid retention value. Prior to radiation graft copolymerization, cassava starch was gelatinized at 85°C . Since homopolymer formation always takes place during graft copolymerization, the present research has successfully reduced its content, down to 1.6% with a water retention value of 665 g/g of its dry weight in deionized water, by inserting an aluminum foil to cover

the inner wall of the reactor. This finding helped eliminate the need of homopolymer removal by DMF extraction on a production scale. The infrared spectroscopic technique was used to follow up changes during the processes. A homopolymer of polyacrylonitrile was removed by DMF extraction, resulting in the graft copolymer which was subsequently subject to an 8.5% KOH solution in a saponification reaction at 100°C until a permanent light yellow color was obtained. The IR spectra indicated the presence of cassava starch as a framework of the graft copolymer (3,400 and 1,100-1,000 cm^{-1}) and the conversion of the $-\text{C}=\text{N}$ group at 2,243 cm^{-1} to a mixture of carboxylate and carboxamide groups (1,571 and 1,400 cm^{-1}). Grafting parameters denoting the degree of grafting copolymerization were determined in terms of the percentage of homopolymer, grafting efficiency, grafting ratio/add-on, grafting frequency, and viscosity-average molecular weight in relation to the extent of liquid retention in deionized water, NaCl solutions, MgCl_2 solutions, and fertilizer-liked salt solutions. The results obtained from statistical and physical interpretations indicated that the liquid retention depended on the percentage of add-on/grafting ratio, grafting frequency and molecular weight of grafted PAN; ionic strength of the saline solution and the valency of the corresponding cation. Incorporation of a small amount of this superabsorbent polymer in sand, with its water retention value of only 0.3 g/g, enhanced drastically the water retention of sand

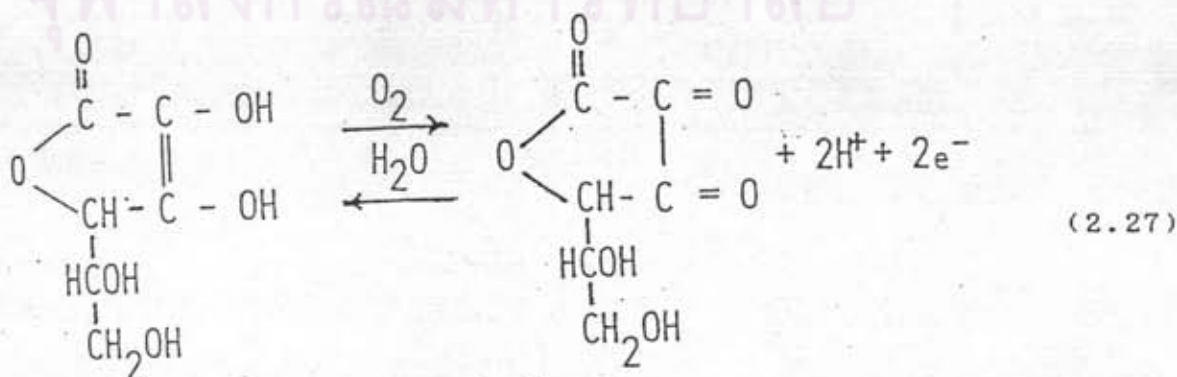
up to 250 times. The data suggested this polymer can be used in sandy soils of the Northeast region of Thailand to improve the local agricultural produce.

2.3.5 The Benzoyl Peroxide Initiation

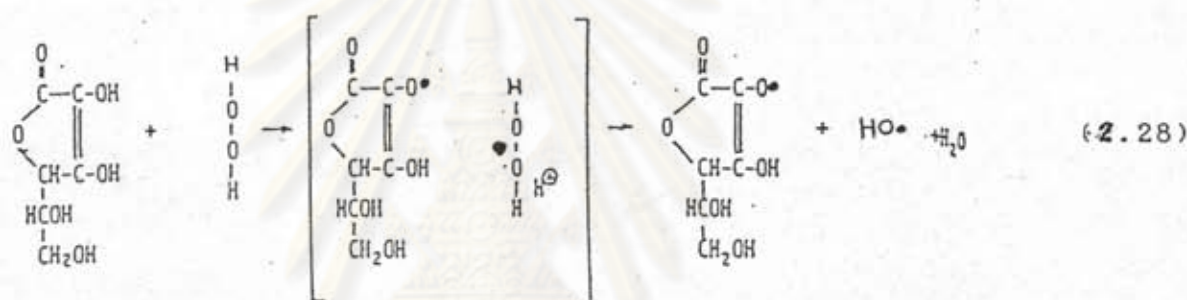
Misra, B.N., R. Dogra, I. Kaur, and D. Sood (70) prepared graft copolymers of vinyl monomers onto starch in an aqueous medium. They compared the reactivities of vinyl monomers towards grafting onto starch, so that the reactivity order can be assessed as follows: AN > MA. Percent grafting was found to depend upon the concentration of initiator, concentration of monomer, time and temperature.

2.3.6 The Hydrogen Peroxide - Ascorbic Acid Initiation

This method used a reducing agent or an antioxidant of L(+)-ascorbic acid (vitamin C) as an accelerator for organic peroxide. In an aqueous system, the most distinctive property of ascorbic acid is its reductant activity (71), manifested by its reversible oxidation to dehydroascorbic acid (DHA) as shown in Equation 2.27.



Apparently, this redox reaction proceeds by two successive one-electron transfer reactions, which suggests that its chemical property is responsible for its accelerative action with peroxides. Equation 2.28 outlines a possible proton-assisted one-electron transfer mechanism for an oxidation reaction of hydrogen peroxide with ascorbic acid (AA).



Masuda, F., K. Nishida, and A. Nakamura (72) prepared biodegradable water-absorbent polymers by polymerizing at least one monomer (having a polymerizable double bond which is water-soluble or becomes water-soluble by hydrolysis) onto polysaccharide (selected from various kinds of starch and cellulose) with a crosslinking agent if necessary, the resulting product is subjected to hydrolysis with NaOH.

Sanyo Chemical Industries (73) prepared starch-g-poly(acrylic acid) copolymers by stirring corn starch in

water at 55°C for 1 hour, cooling to 30°C, purging with nitrogen gas, mixing continuously with acrylic acid. A crosslinking agent solution contained water and methylene bisacrylamide in a teflon mixing head without a driving part through 5 jet nozzles at a jet speed of 1.2 m/s, passing through a polymerization reactor in 2 hours at 90-95°C to give an elastic gel which was then neutralized with NaOH, dried and pulverized.



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