

CHAPTER II

THEORY and LITERATURE REVIEW

2.1 Theoretical Background

2.1.1 Starch

Starch is a reserve carbohydrate found principally in the seeds, roots, tubers, fruits, and sometimes in the pith of plants. It occurs as very small water-insoluble 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 (5). 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 (6).

2.1.1.1 Chemistry of Starch

Starch is composed of carbon, hydrogen and oxygen in the ratio of 6:10:5 as an empirical formula of $\text{C}_6\text{H}_{10}\text{O}_5$, placing it in the class of carbohydrate. It is a condensation polymer of glucose. The glucose units in the starch are present as anhydroglucose units (AGU), the linkage between the glucose units being formed as if a molecule of water is removed during a step polymerization.

The linkage of one glucose to another through the C-1 oxygen is normally known as a 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 (7).

2.1.1.2 Molecular Structure

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 particular starch are 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-glucopyranose" 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. Most starches such as regular corn, wheat, potato, and cassava

contain approximately 28% amylose (5). For cassava starch, the amylose content is about 16.5-22.2% (6).

Starch molecules have a multitude of hydroxyl groups impart hydrophilic to starch. In addition to their affinity for water, these hydroxyl groups also tend to attract each other, forming hydrogen bonds. The linear amylose molecules can readily align themselves next to each other and form interchain hydrogen bonds through the hydroxyl groups. When sufficient interchain hydrogen bonds are formed, the individual amylose molecules are associated to form molecular aggregates with reduced hydration capacity and hence, lower solubility.

b) Amylopectin (1)

Amylopectin has a highly branched structure consisting of short linear amylose chains with a D.P. ranging from 12 to 50 AGU and an average chain length of about 20 AGU, connected to each other by alpha-1,6-linkage (Figure 2.2).

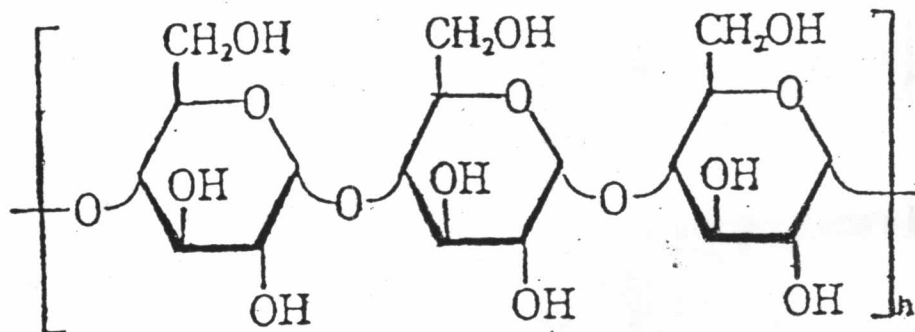


Figure 2.1 Chemical structure of amylose chain.

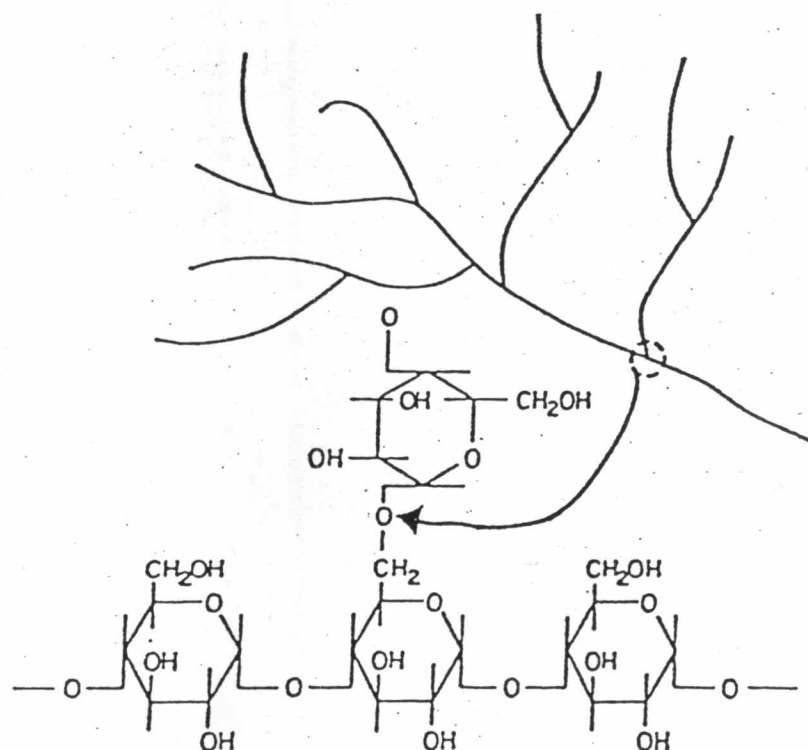


Figure 2.2 Branched structure of amylopectin and chemical configuration at the branch point.

2.1.2 Graft Copolymerization of Vinyl Monomer onto Starch via Radiation-Induced Synthesis (8)

As mentioned previously that water-absorbing polymer can be made by modification of starch and cellulose through grafting with a petroleum derived monomer to form a graft copolymer. The grafted material can either be synthesized by a free radical or anionic process with some vinyl monomers such as acrylonitrile, acrylamide, acrylic acid and so on.

The newly used method of free radical initiation of starch is interacted with electromagnetic radiation.

When electromagnetic radiation passes through matter its intensity decreases, primarily as a result of scattering and energy absorption by some of the irradiated molecules.

Three major processes are operative as follows:

- a) The photoelectric effect.
- b) Compton scattering.
- c) The production of electron pairs.

For gamma rays from Co^{60} the predominant effect in organic material is Compton scattering. In the Compton effect the incident gamma ray interacts with an orbital electron ejecting the electron from its orbit and producing another photon of lower energy. Both the electron and photon subsequently interact with the material or the surroundings giving rise to essentially two processes, one of ionization and the other of excitation. In the case of ionization the Compton electron transfers sufficient energy to the orbital electron of another atom to overcome the forces binding it to the nucleus. The electron is therefore ejected, leaving behind a positive ion. If the energy transferred is insufficient to cause ejection of an electron, the energy level of the atom is raised and the atom is said to be in an excited state. The ions and excited molecules are very reactive; they either react with other materials present in the system or decompose into free radicals and atoms or molecules. The free radical produced upon irradiation of polymeric systems can be used to initiate graft polymerization.

2.1.2.1 The Different Method of Radiation Grafting of Starch-g-Polyacrylonitrile.

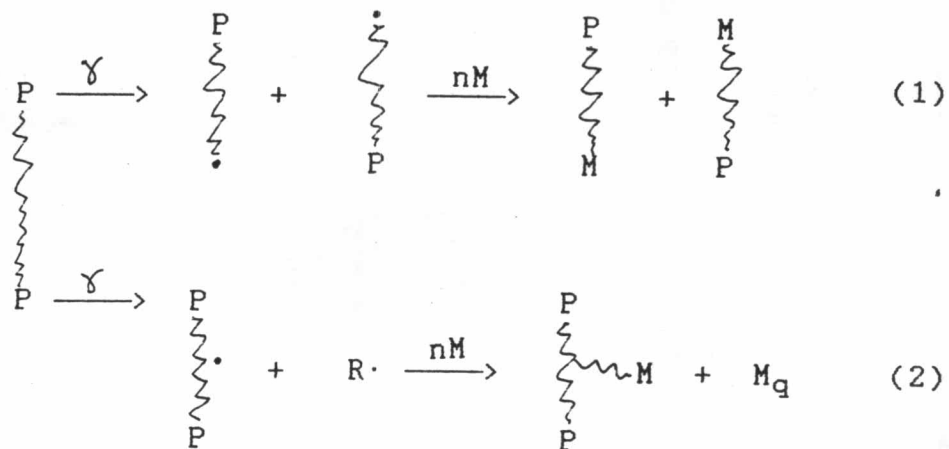
As already indicated above that the irradiation of organic macromolecules leads predominantly to the formation of free radicals. If the irradiation is carried out in air, an effective free radical scavenger, peroxides and hydroperoxides are formed within the polymer. If, however, the polymeric substrate is highly crystalline and in particular if the irradiation is carried out at low temperature and in the complete absence of air, the free radicals can be trapped in the system and can remain "active" for a considerable time. The free radicals, peroxides, and hydroperoxides formed or trapped in polymeric substrates upon irradiation can be used quite conveniently to initiate block and graft copolymerization. Experimentally, then, radiation synthesis of graft copolymer of acrylonitrile onto cassava starch can be accomplished by the following techniques.

2.1.2.1.1 The Direct or Simultaneous or Mutual Irradiation Technique.

In its simplest form, the direct grafting technique involves the irradiation of a polymeric substrate in the presence of a monomer and in the absence of oxygen. Graft copolymerization of the monomer to the polymer is then initiated through the free radicals generated at the latter stages. A number of

important factors must be considered, however, before applying the direct radiation technique to given polymer-monomer system. Ionizing radiation as such is unselective. One must therefore consider not only the effect of radiation on the polymeric substrate but also the effect on the monomer, the solvent, or any other substances present in the system.

In general, polymers either degrade or crosslink under irradiation. If the polymer degrades then irradiation in the presence of a monomer will lead predominantly to block-type copolymers; if the polymer crosslinks, graft structures will result. This may be represented schematically as follows:



Here $P \text{---} \cdot$ and $\cdot \text{---} P$ represent polymeric free radicals derived from $P \text{---} P$, $R \cdot$ represents a low weight radical or hydrogen atom and M represent a monomer atom.

It will be appreciated that, in the direct

irradiation technique, a certain amount of homopolymer will always be formed both because of the effect of the radiation on the monomer and as a normal consequence of the grafting reaction (see eq.2). Contamination of the grafted product with homopolymerization (polyacrylonitrile) give a product with poor water absorption capacity, and other interior physical properties. To avoid such a homopolymer formation the main problem is to ensure a true molecular contact between the monomer and the polymer itself by adding either cupric sulphate, or lead (II) nitrate, or aluminium (III) nitrate in the aqueous solution of gelatinized starch-acrylonitrile. The anions were found to have no effect on the grafting or homopolymerization, but both processes were suppressed by the cations (9). To suppress only homopolymerization, a piece of copper or aluminium foil was inserted in the reactor tube to observe as the effect of vessel material on graft copolymerization (10).

2.1.2.1.2 Preirradiation Technique

In principle, the preirradiation method should not yield homopolymer because the monomer is never directly exposed to radiation. In some cases, however, there is evidence that irradiation in air leads to the formation of hydroperoxides on the polymer backbone. The hydroperoxides on heating, decompose to give hydroxyl radicals which can initiate the homopolymerization

of the added monomer.

2.1.2.2 Kinetic Features of Radiation Grafting

In principle, the conventional free radical polymerization scheme should be applicable to radiation-grafting systems as, in general, the reaction involves the polymerization of vinyl monomer by a polymeric radical. In practice, however, the situation is not quite as straightforward as this because of the number of specific features that result from the special reaction conditions prevailing in most grafting systems. The gel effect, chain transfer, phase separation, and diffusion effects are but just a few of the many factors which can seriously affect the reaction kinetics.

Kinetic feature of the direct irradiation technique, if one assumes that the graft polymerization occurs by a radical chain process then the overall reaction scheme can be divided into three main steps: initiation, propagation, and termination. This may be represented as follows:

Initiation:



$$r = kI \quad (2.2)$$

Propagation of initial radical:



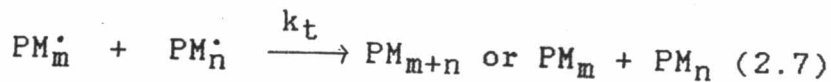
$$r_i = k_i[P\cdot][M] \quad (2.4)$$

Propagation:



$$r_p = k_p[PM_n\cdot][M] \quad (2.6)$$

Termination by two growing radicals:



$$\begin{aligned} r_t &= 2k_t[PM_m\cdot][PM_n\cdot] \\ &\approx 2k_t[PM_n\cdot]^2 \end{aligned} \quad (2.8)$$

If one makes the normal assumption that the length of the polymer chains is long, then reaction 2.3 can be neglected with respect to reaction 2.5, and one obtains the following relation for the rate of graft polymerization:

$$r_p = k_p[PM_n\cdot][M] \quad (2.9)$$

Introducing the conventional steady-state assumption that the rate of change of the radical concentration is small compared to its rates of formation and disappearance,

then

$$k_i[P\cdot][M] = 2k_t[PM_n^{\cdot}]^2 \quad (2.10)$$

i.e.,

$$r_i = 2k_t[PM_n^{\cdot}]^2 \quad (2.11)$$

then

$$[PM_n^{\cdot}] = (r_i/2k_t)^{1/2} \quad (2.12)$$

On combining eqs 2.9 and 2.12 one obtains the rate of graft polymerization as the following:

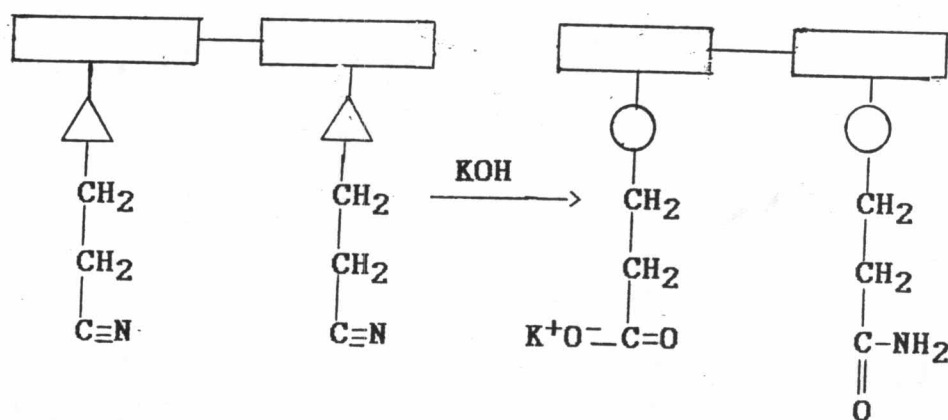
$$r_p = k_p[M](r_i/2k_t)^{1/2} \quad (2.13)$$

2.1.3 Saponification of the Graft Copolymer of Starch-g-Polyacrylonitrile.

Since the synthesis of high water-absorbing polymer involves simultaneously graft-copolymerization and homopolymerization, it is of great essential to remove the useless part, polyacrylonitrile, which does not contribute to water absorption, if a substantial amount is present. Dimethylformamide is used to extract the homopolymer while the grafted copolymer remains solid.

To enhance the hydrophillic character of the starch-g-polyacrylonitrile, it will be hydrolyzed with an 8.5% potassium hydroxide. One usually observes color changes from initially a deep red solution which is due to the formation of naphthyridine intermediate structure from the adjacent nitrile groups. The intermediate rings are

consequently hydrolyzed which causes changes in color from red to light yellow. Saponification is another step to convert the polyacrylonitrile chains in the graft copolymer to a mixture of polycarboxamide and polycarboxylate. The resulting dry copolymer is responsible for high water absorption which may take up water several hundred times its dry weight. The following reaction in Figure 2.3 elucidates the saponification procedure:



□ represent starch backbone, △ represent grafted PAN,
○ represent polycarboxamide and polycarboxylate.

Figure 2.3 Saponification of the starch-g-polyacrylonitrile

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

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 sufficiently high temperatures, giving 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 process 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 (11).

As result of heating, starch forms a continuous system, referred to as 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 2.4. 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 (12).

Rodehded, C., and B.Ranby(13) 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 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 (14).



Figure 2.4 Structure of molecules in a cooked starch paste

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:

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

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

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:

$$\% \text{ grafting efficiency} = \frac{\text{Weight of grafted PAN} \times 100}{\text{Weight of homo-PAN} + \text{Weight of grafted PAN}}$$

2.2.4 Percentage Conversion

Conversion of a monomer is defined as the extent of the monomer to which is charged to become a respective polymer (polymers). For this particular case, the conversion of acrylonitrile to be graft copolymer (starch-g-polyacrylonitrile) and a homopolymer of PAN is referred to as the percentage conversion.

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

2.2.5 Grafting Ratio

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

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

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:

$$\text{grafting frequency (AGU/chain)} = \frac{\text{glucose (mole)}}{\text{PAN (mole)}}$$

where

$$\text{PAN (mole)} = \frac{\% \text{ add-on}}{\text{molecular weight}}$$

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

2.3 Preparation Scheme

In order to ease understanding of the entire synthesis process, Figure 2.5 reveals the preparation of saponified starch-g-polyacrylonitrile, high water-absorbing polymer. Further details of which is covered by the following Chapters.

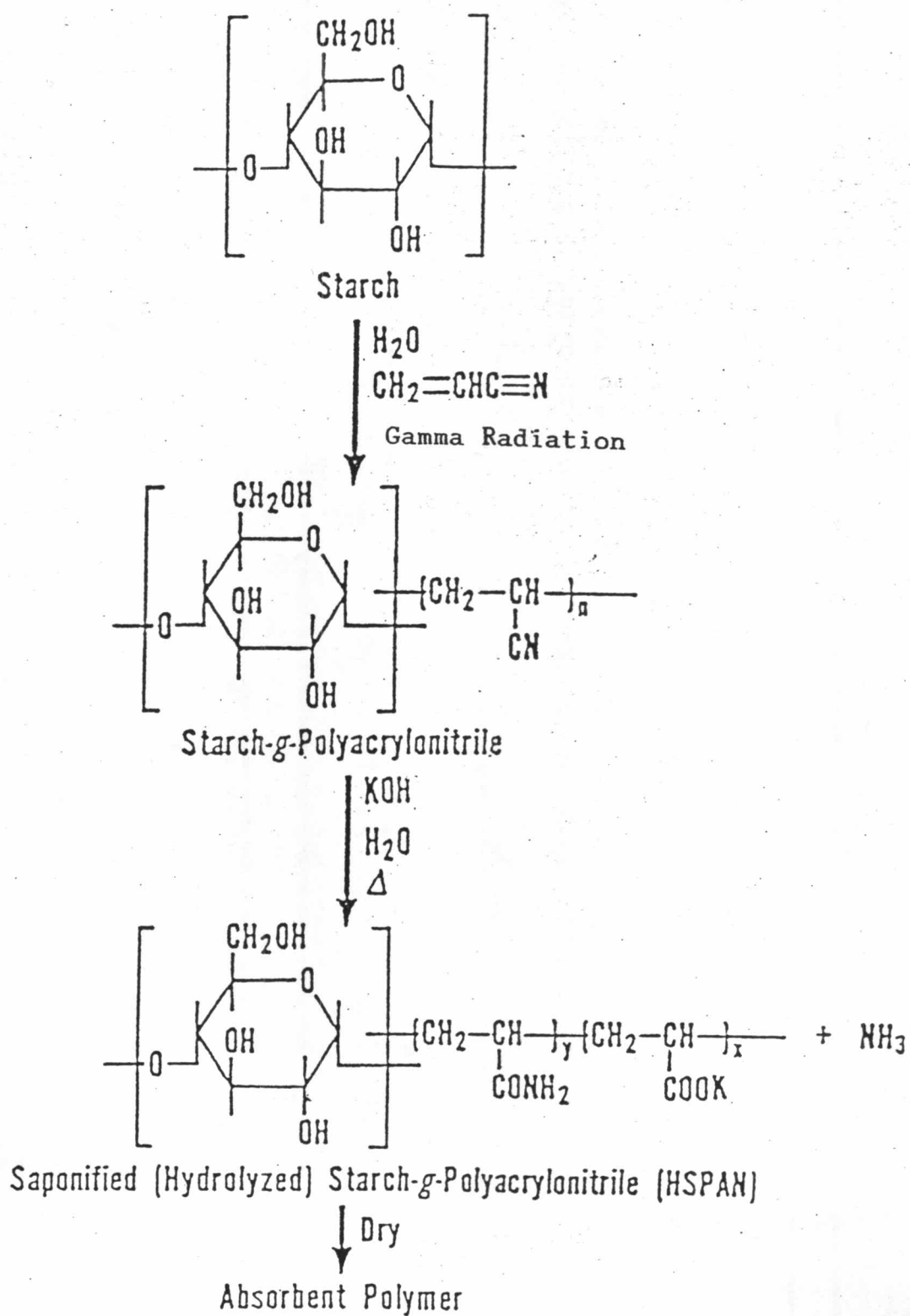


Figure 2.5 Preparation of saponified starch-g-polyacrylonitrile

2.4 Survey of Related Literature.

Extensive studies on the preparation, properties and application of cellulose graft copolymers have been carried out since 1952. Graft copolymerizations onto starch are carried in much the same way as graft copolymerization onto cellulose. A recent review on the synthesis and properties of starch graft copolymers has been compiled (15). Corn starch is most often used as the substrate for graft copolymerization, 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. Acrylonitrile, acrylamide, acrylic acid, monomer with amino substituents, acrylic acid esters, styrene, butadiene, vinyl chloride, and N-vinyl-2-pyrrolidone have been used in the synthesis of starch graft copolymer. 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 are listed below.

Reyes, Z., C.E. Rist, and C.R. Russell(16) studied the grafting of acrylonitrile and acrylamide to starch by ceric ion. The variables affecting the grafting of AN and acrylamide were investigated with granular wheat starch dispersed in aqueous N,N - dimethylformamide and ceric ammonium nitrate as a catalyst. The results showed that

the concentration of monomer and catalyst are the major factors influencing the grafting of acrylonitrile. 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 (17) investigated the influence of selected reaction condition on both grafting frequency and the molecular weight of grafted polyacrylonitrile for the reaction of gelatinized wheat starch with acrylonitrile catalyzed by ceric ammonium nitrate. In the design of experimentals, 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 (18) 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 acrylonitrile catalyst by ceric ammonium nitrate under 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 (15), grafting acrylonitrile (AN) to gelatinized wheat starch has afforded product with grafted chains, few number, but high in molecular weight (about 800,000).

Gugliemelli, L.A., M.O. Weaver, and C.R. Russell (19) isolated grafted copolymers from starch backbone by periodate-alkali method. They found that the graft copolymers can be isolated readily under mild condition at room temperature.

Burr, R.C., G.F. Fanta, C.R. Russell, and C.E. Rist (20) prepared starch-g-polyacrylonitrile copolymer in a number of aqueous-organic solvent system with ceric ammonium nitrate as the initiator. They found that, the graft copolymers had more grafted than those prepared in water alone.

Fanta, G.F., R.C. Burr, C.R. Russell, and C.E. Rist (21) 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. In the ceric ammonium nitrate-initiated graft copolymerization of acrylonitrile with starch. The results showed that 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/l of water, respectively.

Gugliemelli, L.A., M.O. Weaver, C.R. Russell, and C.E. Rist (22) prepared and hydrolyzed starch-g-PAN graft copolymer consisting of one part starch and one part polyacrylonitrile (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 (23) prepared three starch-polyacrylonitrile graft copolymers containing ratio of starch: PAN of 1:1.90, 1:1.16, and 1:0.64 by graft polymerization of acrylonitrile onto gelatinized starch catalyst by ceric ammonium nitrate. 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 amount 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(24) determined the location of PAN within 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 were examined with a scanning electron microscope.

Taylor, N.W., and E.B. Bagley (25) prepared S-PAN graft copolymer by ceric ion initiation method 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. This results, combined with a determination of gel content from centrifugation studies, led to the conclusion that high viscosity HSPAN water mixtures consist of swollen, deformable gel particles closely packed in 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., M.O. Weaver, and W.M. Doane (26) reported about the absorbency test of starch-PAN graft copolymers in water and other solution, They found that, this graft copolymers can absorb 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., F.L. Baker, R.C. Burr, W.M. Doane, and C.R. Russell (27) prepared a series of starch-g-PAN copolymers by ceric ammonium nitrate initiation. Comparison of scanning electron micrograph of each starch-g-polyacrylonitrile 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 (28) developed a process for making the starch-polyacrylonitrile copolymer in multipound quantities from laboratory scale-up studies. This process avoids intermediate isolation steps, permits efficient removal of unreacted monomer, keeps the concentration of extraneous salts low, and gives a high solid concentration for the drying step. Variation in drying procedure allows Super Slurper to be in film, mat, powder or flake form. Shearing the hydrolysis mixture prior to isolation and avoiding extended exposure of isolated product to elevated temperature gives Super Slurper with highest absorptive capacity.

Fanta, G.F., R.C. Burr, W.M. Doane, and C.R. Russell (29) prepared polyacrylonitrile-containing graft copolymers of corn starch from monomer mixtures obtained when selected comonomer which was substituted for the portion of the acrylonitrile. Graft copolymers were then saponified and saponified polymers dried to form absorbents for aqueous fluid. Use of 2-acrylamide-2-methylpropanesulfonic acid as comonomer resulted in the shorter saponification times and more absorbent products. Incorporation of acrylamide into the polymerization mixture similarly shortened the time needed for saponification. Vinyl sulfonic acid, acrylic acid, methyl acrylate, methyl methacrylate, and styrene were also used as comonomer,

and their effect on saponification time and on absorbency of saponified polymer was examined. Substituted flour or corn meal for starch in the ceric initiated graft polymerization of acrylonitrile which gave polymer which after saponification, had a higher absorbency for aqueous fluid than saponified starch-g-polyacrylonitrile.

Fanta, G.F., E.B. Bagley, R.C. Burr and W.M. Doane (30) used methanol as a precipitant to isolate saponified starch-g-PAN 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 enhanced if excess alkali in the saponification mixture is neutralized before the product is isolated.

Fanta, G.F., R.C. Burr, and W.M. Doane(31) examined the influence of the molar ratio of corn starch : ceric ammonium nitrate (CAN) on the properties (absorbency and water solubility) of HSPAN, with the goal of minimizing the amount of CAN used to initiate graft polymerization. Ceric-initiated graft polymerization onto other variety of corn starch, such as acid modified, waxy, and high-amylose, were also investigated. Additionally, the preparation of starch-g-PAN can be achieved by an incremental addition of CAN. They showed that, HSPAN with higher absorbency could be prepared by this procedure.

Fanta, G.F., R.C. Burr, and W.M. Doane (32) investigated the method by which methanol was added to

precipitated saponified starch-g-polyacrylonitrile from an alkaline saponification mixture. It will influence the particle size of polymer and thus the properties of the absorbent. Slow methanol addition, coupled with thorough mixing to ensure complete absorption of methanol by the reaction mass, will separate individual micron-sized fragments of HSPAN gel and will yield a product with small enough particle size to produce a smooth, free-flowing gel dispersion when added to water. This product is perhaps more suitable as a thickener than as a water absorbent. More rapid addition of methanol, results in incomplete absorption by the reaction mass and causes individual gel fragments to coalesce to form millimeter-sized chunks of water-swollen HSPAN.

Sandle, N.K., O.P.V. Verma, and I.K. Varma (33) investigated thermal behavior of several graft copolymers of starch with acrylonitrile having different percentage graft-on which were prepared by using cerium(IV) initiation system. Thermal behavior was investigated using dynamic thermogravimetry in a nitrogen atmosphere. They found that, an increase in percentage graft-on resulted in an increase in anaerobic char yield at 550°C. A graft copolymer sample having 97.7% graft-on had a char yield of 52%, which was higher than that of polyacrylonitrile.

Patel, A.R., K.C. Patel, and R.D. Patel (34) prepared and investigated graft copolymers of six cereal starches (corn, wheat, rice, great millet, bulrush millet, and

common millet starch) with polyacrylonitrile by ceric ion initiation method. 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 is doubled.

Okieimen, E.F., and J.E. Ebhoaye (35) synthesised graft copolymers of acrylic acid on cellulosic materials by use of ceric ion in aqueous medium at different temperatures. The variation in the level of incorporating of poly(acrylic acid) grafts on the cellulose substrate and the dependence of the water and saline retentions of the graft copolymers on the graft level were examined.

Ziderman, I., and J. Belayche (36) studied about water sorbence by saponified polyacrylonitrile-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 reversible restored by neutralization of acrylic acid functions with alkali.

Okieimen, E.F., and J.E. Ebhoaye(37) prepared graft copolymer of acrylonitrile and of acrylic acid on cellulosic materials by using of ceric ion initiator in aqueous medium at 50 % (w/w) cellulose-monomer ratio. The variation of poly(acrylonitrile) grafts and the efficiency of grafting with ceric ion concentration, and poly(acrylic acid) grafts with temperature were examined. They found that, at constant initiator concentration, both the graft level and efficiency of grafting of PAN increased with time, and at a constant cellulose-acrylic acid ratio, the level of poly(acrylic acid) grafts onto the cellulose backbone decreased between 35 and 40°C. The water retention capacity decreased with increase in graft level.

Bazvaye, A., F.E. Okieimen, and O.B. Said (38) prepared starch-polyacrylonitrile graft copolymers by varying the amount of ceric ammonium nitrate, and the amount of monomer. The results showed that, at each monomer concentration, the maximum graft level was attained at 10.0 m.mol Ce(IV)/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(IV) to Ce(III).

Castel, D., A. Ricard, and R. Audebert(39) reported about the influence of several structure parameters on the swelling properties in water or saline water of starch-

based superabsorbent gels. They prepared both anionic and cationic superabsorbent gels. Anionic gels were obtained by saponification of graft PAN onto starch. Cationic gels have been synthesized by copolymerization with cationic monomer (trimethylaminoethylacrylate chloride) and a crosslinking reagent [N,N - methylene bis(acrylamide)]. The influence of several structural parameters on the swelling properties of these absorbents had been studied: crosslink density, ionic content, and composition of the starch. They found that, the absorbency decreased with an increase of crosslink density. It increased with the ionic content of graft copolymer up to maximum, an excess of changes leading to a swelling decrease. The PAN branch length depended on the origin of the starch. High molar weight PAN was grafted onto 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.

Mehrotra, R., and B. Ranby(40) used the pyrophosphate complex of trivalent manganese over the sulfate complex as initiator for 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 acrylonitrile and

methyl methacrylate. The average molecular weight of the grafted synthetic polymer chains were of the order of 10^5 for acrylonitrile and of the order of 10^6 for methyl methacrylate as monomer. Consequently, the average number of anhydroglucose units (AGU) separating the grafted chains was in the range of 600-1,600 for acrylonitrile and over 25,000 for methyl methacrylate. Reaction mechanisms responsible for initiation of graft copolymerization were discussed.

Mehrotra, R., and B. Ranby(41) examined the effect of reaction conditions on the composition of granular native potato starch-polyacrylonitrile graft copolymers initiated by manganic pyrophosphate onto starch slurries at 30°C. They found that, when the Mn^{3+} ion concentration was increased from $0.15 \times 10^{-3} M$ to $3.0 \times 10^{-3} M$ (other conditions 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 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 factor of 3 produced an increase in the conversion of monomer to polymer, whereas an increase in frequency of grafts (AGU/chain) was obtained. Value of % add-on and average molecular weights of the grafts showed, however, a decreasing tendency. In this investigation, little or no polyacrylonitrile was formed as homopolymer in physical

mixture with the starch substrate.

Mehrotra, R., and B. Ranby(42) prepared gelatinized potato starch-polyacrylonitrile graft copolymers initiated by manganic pyrophosphate. 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 temperature. 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 (AGU/chain) 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 (AGU/chain) decreased. Selective solution of PAN homopolymer by DMF indicated that grafting efficiencies were high in all cases.

Ranby, B., and C. Rodeled (43) investigated water vapor absorption and aqueous retention of hydrolyzed starch polyacrylonitrile graft copolymers, prepared by Mn^{3+} initiator. The water vapor absorption like other polysaccharide, at relative humidity(RH), was upto 95-97 %. At higher RH the water vapor absorption increased very rapidly. In contact with distilled water the modified starch becomes "superabsorbents" by retaining very large amounts of water (upto 800 g/g)

Ranby, B., and L. Gadda (44) prepared graft copolymers of dissolving pulp (MDC) and grease proof pulp

(GP)(both are bleached sulfite pulps from spruce) and low-substituted ethyl cellulose(EC) and hydroxyethyl cellulose (HEC), all samples in a never-dried state, with AN using Mn^{3+} ions, complex with pyrophosphate ion, as initiator gives high conversion of monomer (70 to 85%) and high grafting efficiency (80 to 98%). The grafted products retain both fiber morphology and their original water retention values (5 to 8 g/g). After hydrolysis of grafted samples in 1% aqueous NaOH at 100 °C, the water retention increases from 5 to 10 times higher level, i.e. 25 to 80 g/g, for never-dried samples and somewhat lower values for once-dried samples.

Rodehed, C., and B. Ranby(45) prepared a sample of starch-g-polyacrylonitrile (grafting ratio 82%) at 303 K using the Mn^{3+} complex ion as initiator in aqueous acid solution with gelatinized starch as substrate. Subsequent alkaline hydrolysis converts the nitrile groups to the carboxamide (30%) and carboxylate (70%) groups. The swelling of the copolymer formed which retains about 700g water per g dry polymer, has been studied in alcohol/water mixtures of increasing alcohol content at 294, 304 and 314 K. The main transition for both alcohol/water mixtures is a collapse of the gels at 50-60 volume % ethanol and 60-70 volume % methanol respectively. Increasing the temperature from 294 to 314 K increases the liquid retention and moves the transition to higher alcohol concentrations by 5-10 volume %.

Rodehed, C., and B. Ranby (46) used the Mn^{3+} initiation system to prepare starch-g-polyacrylonitrile copolymers. Both granular native starch and water-swollen gelatinized starch used as substrate. Conversion of monomer, grafting ratio, and percent add-on tend to increase with increasing amounts of monomer charged. The amount of homopolymer formed is extremely low, approximately 1%. The efficiency, measured as conversion, is consistently higher with gelatinized starch as substrate. The molecular weight of the grafts on gelatinized starch is approximately eight times higher than those on granular starch. The water retention value increased linearly with increasing % add-on. The saponified polyacrylonitrile branches alone had a water retention value that was three times higher than of the origin copolymer.

Fanta, G.F., R.C. Burr, C.R. Russell, and C.E. Rist (47) prepared graft copolymers of acrylonitrile onto starch with ferrous ammonium sulfate-hydrogen peroxide initiation. Molecular weights and grafting frequencies of graft copolymer showed a dependence on granule swelling similar to that found with ceric ammonium nitrate. Molecular weight of polyacrylonitrile branches grafted to swollen and unswollen starch was independent of 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 (48,49) prepared graft copolymers of acrylonitrile onto ground, water-wash straw using $\text{Fe}^{2+}\text{-H}_2\text{O}_2$ as initiator. Wheat straw-g-polyacrylonitrile, 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 synthetic polymer (saponified PAN), cellulose, hemicellulose, and lignin. Water solubles amounted to 14-24 % of 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 H_2O /polymer).

Misra, B.N., R. Dogra, I. Kaur, and D. Sood (50) prepared graft copolymers of vinyl monomers onto starch in aqueous medium by using benzoyl peroxide (BPO) as radical initiator. They compared reactivities of vinyl monomers towards grafting onto starch to follow the order: AN > MA. Percent grafting was found to depend upon concentration of initiator (BPO), concentration of monomer, time and temperature.

Zahran, A.H., J.L. William, and V.T. Stannett (51) prepared graft copolymers of acrylic acid and methacrylic acid to rayon and cotton using preirradiation technique with Co^{60} gamma rays. They found that, the rate of grafting

increased with increasing temperature and monomer concentration, as did the final degree of grafting. The amount and rate of grafting also increased with the total irradiation dose but tended to level off at higher doses. Methacrylic acid brought about less sorbency than the corresponding acrylic acid grafts.

Abbott, T.P., and C. James(52) 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 lower polymer recovery than irradiation for 2 hrs due to degradation of the polymer backbone.

Fanta, G.F., R.C. Burr, and W.M. Doane(53) prepared graft copolymers of acrylonitrile and acrylamide onto starch via simultaneous technique gamma radiation. Dose rate at the center of the chamber was 0.42-0.44 Mrad/hr.

Chen, L.J., Z. Xin, And C.Z. Ping(10) studied graft copolymerization of corn starch with acrylonitrile by gamma-irradiation. The graft copolymer produced in the reaction was hydrolyzed by sodium hydrate and the water absorption material was obtained having water absorption of 875 ml/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 rad, 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 °C. The result showed that the optimum temperature was about 30°C.

Zicheng, Z., L. Qian, L. Donghui, Z. Xin, L. Shuhua, and Z. Lihua (54) prepared polyacrylamide hydrogel by radiation techniques. Dose rate at the center of the chamber was 2.55 rad/s. The water retention value (WRV) was determined by measuring the quantities of water retained by polyacrylamide hydrogel at room temperature (g/g). The result showed that, the product with low gel fraction thus obtained had $WRV > 2000$ g/g.

McDowall, D.J., B.S. Gupta and V.T. Stannett (55) prepared graft copolymers of acrylic acid to rayon filaments by either the high energy preirradiation or ceric ion methods. A number of properties had been measured on the treated controls without monomer and on the grafted samples. This included elongations, initial moduli, and work rupture. In all cases, ceric ion gave somewhat lower properties compared with preirradiation. The moisture regains and water retention values showed some rather minor differences between the two types of grafting.

Kiatkamjornwong, S. and J.G. Faullimmel(63) prepared starch-g-polyacrylonitrile under a grafting copoly-

merization of acrylonitrile onto the 80°C gelatinized cassava starch via redox initiation mechanism using Ce(IV) as initiator in an acid medium. Water absorption of the newly synthesized copolymer was carried out in deionized water and in MgCl₂ solutions. The water absorption capacity in pure water was range from 120 to 270 times their original dried weight. Water absorption capacity in saline solutions decreased dramatically with increasing the salt concentrations.

Rungsriwong, N. (66) prepared Cassava starch-g-PAN by a grafting copolymerization reaction of acrylonitrile onto the polysaccharide backbone via a redox initiation mechanism with Mn(III) as the initiator. Two types of high water absorbing polymer were obtained by using two gelatinization temperature of 65 and 80 °C. 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 acrylonitrile grafted onto starch, was determined with deionized water and salt solutions at different concentrations of NaCl, CaCl₂, and MgCl₂. The results indicate that water absorption increases with increasing % add-on and viscosity average molecular weight, but decrease as the concentration of salt increases. Water retention in sand was also determined and showed that the increase in the water holding capacity of sand is proportional with the amount of absorbent used.