CHAPTER II

LITERATURE SURVEY

Starch is a reserve carbohydrate found principally in seeds, roots, tubers, fruits, and sometimes in the pith of plants. Starch and modified starch can be used to produce food and non-food products. Because of its cheap and being degradable product, so it can replace or being filled in non-degradable materials both original and modified form. Starch graft copolymer is one type of chemical modified starches. Figure 2.1 shows the structure of starch graft copolymers. When X representing $-CO_2H$, $-CONH_2$, $-CO_2(CH_2)_n^+$ or $-NR_3Cl^-$ groups, the graft products are water soluble and useful as thickeners, absorbents, sizes, adhesives, and flocculants. When X representing $-CN$, $-CO_2R$ or phenyl groups, the graft products are water insoluble and potentially useful as resin and plastics [11,14].

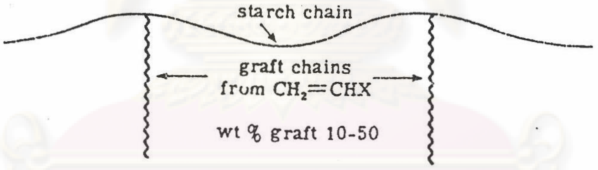


Figure 2.1 Structure of starch graft copolymers [11, 14].

2.1 Starch

Starch is a major form of carbohydrate storage in green plants and is considered to be the second largest biomass, next to cellulose, produced on earth [16]. It is a polymer that consists of six-membered-ring glucose repeating units. The molecular weight of starch varies from 10^4 to 10^7 daltons. Starch can be found in some algae and in all parts of higher plants including leaves, stems, and shoots, but mainly in the storage organs such as rhizomes, tubers, bulbs, and seeds. Its amount in any one source varies from a few percent to 60% found in cereal seeds. Starch is, of course, an extremely important source of energy in human diet, and indeed more than three-quarters of all food crops are cereals and starchy root crops [17]. Today, starch is used extensively in many industries including paper, textile, explosive, food, alcoholic beverage, clothing, petrochemical, and adhesive industries. Currently, it is also used for biodegradable plastics preparation.

2.1.1 Chemical Structure of Starch [18]

A uniqueness is that most starch granules compose of a mixture of two components: an essentially linear molecule called amylose and a highly branched molecule called amylopectin. In addition to amylose and amylopectin, starch also contains lipid (up to 1%), residues of protein (ca. 0.4%), and trace amounts of phosphorus (up to 0.09%).

2.1.1.1 Amylose

Amylose is essentially a linear polymer in which the anhydroglucose units predominantly link through α-D-(1$\rightarrow$4) glucosidic bonds. Its molecular size varies with the plant source and processing conditions employed in extracting the starch. It may contain about 200 to 2000 anhydroglucose units. At one end of the polymeric molecule, the anhydroglucose unit contains one primary and two secondary hydroxyl groups as well as an aldehydic reducing group in the form of an inner hemiacetal. This is called the reducing end of the molecule. The opposite end, or nonreducing end, contains an anhydroglucose unit containing one primary hydroxyl and three secondary hydroxyl groups. The other anhydroglucose units contain one primary and two secondary hydroxyl groups. A schematic diagram of the amylose is shown in Figure 2.2.

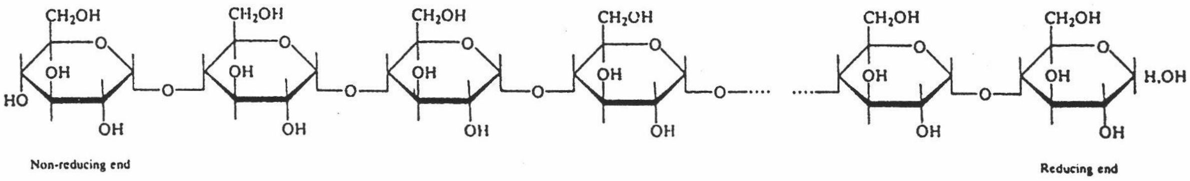


Figure 2.2 Chemical structure of amylose [17].

The abundance of hydroxyl groups imparts hydrophilic properties to the polymer, giving it the affinities for moisture absorpability and dispersibility in water. However, because of their linearity, mobility and polarity, amylose molecules have a tendency to orient themselves in a parallel fashion and approach each other closely enough to permit hydrogen bonding between hydroxyl groups on adjacent molecules. As a result, the affinity of the polymer for water reduces and the sol becomes opaque. In dilute solutions, the aggregate size of the associated polymers may increase to a point where precipitation occurs. At high concentrations, steric hindrance may interfere so only partial orientation between segments of the polymer 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 film. For the phenomenon in which intermolecular association between amylose molecules at high concentration is commonly called retrogradation (starch molecules associate and precipitate in an insoluble form). Amylose can form a complex with iodine giving a deep blue color which is used to identify amylose-containing starch.

2.1.1.2 Amylopectin

Amylopectin is a branched polymer containing, in addition to anhydroglucose units linked together as in amylose through α-D-(1→4) glucosidic bonds, periodic branches at the carbon-6 position (Figure 2.3). These branches link to the 6-carbon by α-D-(1→6) glucosidic bonds. Each branch contains about 20 to 30 anhydroglucose units.

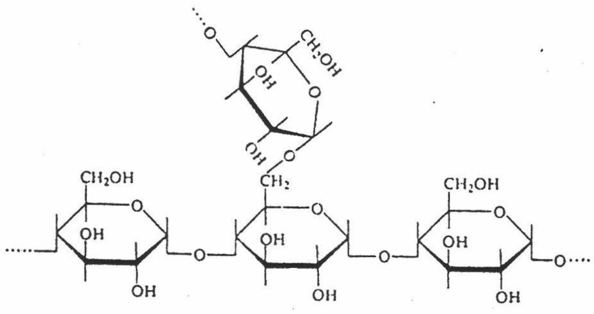


Figure 2.3 Chemical structure of amylopectin [17].

The large size and branched nature of amylopectin reduce the mobility of its molecules and interfere with their tendency to orient closely enough to permit significant levels of hydrogen bonding. As a result, aqueous sol of amylopectin is characterized by clarity and stability as measured by resistance to gelling on aging. Amylopectin sol does not form strong and flexible films as that of the linear amylose does. Furthermore, it does not form a complex which giving deep blue coloration with iodine.

2.1.2 Starch Gelatinization [18]

Native starch is presented in semicrystalline granular forms with densities ca. 1.5 g/cm^3. Starch granules are insoluble in cold water but they can be solvated by heating with water, or by treating them with organic solvents (e.g. dimethyl sulfoxide), aqueous alkaline, or salt solutions (e.g. $CaCl_2$, KI).

For the dried starch granules, they show polarization crosses reflecting crystalline organization when examine microscopically under polarized light. The granules absorb water to a limited extent when expose to high humidity or when suspend in water. However, the swelling is reversible and the polarization crosses retaine when the humidity reduces or the starch is dried. The average increase in diameter of granules for various starches in passing from anhydrous conditions to a water-saturated atmosphere, together with increase in water sorption, are shown in

Table 2.1. When equilibrate under normal atmospheric conditions, starches usually contain 10 to 20% moisture depending upon the starch source.

Table 2.1 Effect of water-saturated atmosphere on granule diameter and water sorption of various starches [18]

Starch source	Average increase in granule diameter (%)	Water sorption/ 100 g dry starch (g)
Corn	9.1	39.9
Potato	12.7	50.9
Tapioca	28.4	47.9
Waxy corn	22.7	51.4

When the slurry of starch in water is heated above a critical temperature, which varies with the type of starch and other factors, the hydrogen bonds are 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 to form helices or coils, creating tangential pressures causing the granules to imbibe water and swell to many times their original volume.

During the swelling, the amylose tends to reach out of the granule and, along with the amylopectin, become highly hydrated. The suspension becomes clear and the viscosity of the suspension rises and continues to rise 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. This causes viscosity drops. During the process as the polymeric molecules are released, the sol often develops a cohesive, rubbery texture. As the 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 a gel if the concentration is sufficiently high. Sols of cereals starches, having relatively high levels of moderately sized amylose molecules, become opaque and form gels on cooling. Those of potato and tapioca, however, usually maintain their clarity much better than other starches and do not form opaque gels while they thicken on cooling. Waxy corn starch, unlike regular corn starch, behaves like tapioca or potato. Its sol shows even less tendency to thicken on cooling than tapioca or potato. The difference in behavior between starches such as tapioca and potato and starches such as corn and wheat may be attributed to be lower amylose content and bulkier amylose molecules in the former starches, reflecting their higher molecular weights and possibly slight degree of branching.

As a general rule, root or tuber starches swell more rapidly in a narrow temperature range than the common cereal starches. For example, cassava starch, used in this experiment, shows the initial and final gelatinizations occured at 60°C and 80°C, respectively.

2.1.3 Cassava Starch

Cassava is the term usually applied in Europe and in the United States to the root of the plant, whereas, tapioca is the given name for the processed products of cassava [19]. The composition of cassava's root is shown in Table 2.2 [20]. The size of the cassava granules ranges from 5 to 35 μm. The amylose content in cassava starch is about 16.5-22%.

Table 2.2 The composition in cassava's root [20]

Composition	Percent
Moisture	69.8
Starch	22.0
Sugar	5.1
Protein	1.1
Fat	0.4
Fiber	1.1
Ash	0.5

Cassava is recognized as one of the most important crops to the Thai economy [21]. It is the third most important crop after rice and sugarcane. The production of the crop is on average about 18 million tons in each crop year from a planted area of 1.5 million hectares; and about half of this amount (9 to 10 million tons) is converted to starch. This product capacity was 5% of the global total in 1999 [22]. In 1994, Thai Tapioca Flour Industries Association estimated the annual starch export growth rates between 1987 and 1992 as follows: native 10.5%, modified 33.8%, sorbitol 48.9%, monosodium glutamate (MSG) 12.8%, glucose syrup 9.4%, and sago 8.3% while the domestic cassava starch utilization by industry presented as percents of 1,121,625 tons of starch produced in 1994 for domestic usage is shown in Table 2.3 [23].

Table 2.3 Domestic utilization of starch in Thailand in 1994 [23]

Products	Percent of total domestic use
Chemically modified starch	25.4
MSG (80%) and lysine (20%)	12.1
Glucose/fructose syrup	12.0
Food processing	11.9
Paper	11.5
Physically modified starches	7.4
Sago pearl	3.6
Plywood	2.1
Textile	1.9
Sorbitol	1.6
Adhesives	1.2
Others	9.5

2.2 Polystyrene [24]

Although known since 1845, polystyrene became a commercial product only after the Second World War as a result of high production of styrene for the synthetic rubber. Styrene, along with most of its substituted derivatives, can be as either an electron donating or an electron attracting center. Therefore, in addition to free radical polymerization, these monomers can be polymerized by all other primary propagation mechanisms: anionic, cationic, and coordination.

The world production of 3.3 million tons in 1970 is surpassed by 5 million tons in 1980. In USA, the 2.5 million tons production of polystyrene (PS) and its copolymers in 1983 had reached 3.8 million tons in 1993. However, the production rate of PS is lower than that of total thermoplastics, due not only to the low number of applications, but especially to the fact that styrene production is oriented to prepare copolymers and to crosslink unsaturated polyester resin.

Styrene, likes many other aromatic compounds, is toxic and its concentrations in the atmosphere should not exceed 10 ppm. Styrene polymerization takes place in most cases through the radical thermal mechanism, with or without initiators (peroxides). The system needs heat only for starting since the reaction is exothermic (71 kJ/mol). As the temperature or initiator concentration increases, the reaction rate increases and in the meantime, polystyrene molecular weight (MW) decreases. The chemical structures of styrene monomer and polystyrene are shown in Figure 2.4.

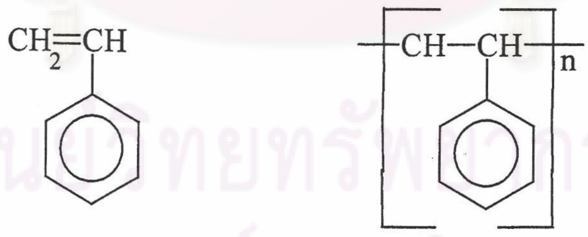


Figure 2.4 Chemical structures of styrene monomer (left) and polystyrene (right).

Large scaled polymerization can take place via bulk, solution or suspension techniques. Polymerization conditions determine PS purity, styrene content, MW, degree of branching and polydispersity. PS obtained through continuous mass polymerization does not contain emulsifier, salts, initiator or foreign impurities, providing superior dielectric properties.

The polymer with a MW of 50,000 is normally used for coatings and with MW of 20,000 to 300,000 is suitable for processing through compression or injection molding.

PS shows good dielectric properties, chemical stability, and water stability. It is soluble in chlorinated and aromatic hydrocarbons and insoluble in kerosene and alcohols. At room temperature it is hard, transparent, and has a density of 1.05 g/cm^3. Above 150°C in air, it becomes darken and thermal degradation starts. The weaknesses are its brittleness, low thermal stability, low resilience, and high flammability.

PS is very suitable for processing through extrusion, injection and blowing. PS has a lot of applications in electro and radio technique laboratory equipment, food and pharmaceutical supplies packaging, pipes for acids, etc. More recently, more and more polymers of styrene derivatives and styrene-based copolymers are also used to replace PS. Poly(2,5-dichlorostyrene), styrene-acrylonitrile copolymer and acrylonitrile-butadiene-styrene grafted copolymer are the examples of new modified styrene used in industries.

2.3 Graft Copolymer and Copolymerization

Figure 2.5 Structure of graft copolymer [25].

A graft copolymer is a polymer comprising molecules with one or more species of blocks connected to the main chain as side chains, having constitutional or configurational features that differ from those in the main chain, exclusive of branch points as schematically presented in Figure 2.5. As a sequence of A monomer units is the main chain or backbone, the sequence of B units is the side chain or graft, and X is the unit of the backbone which the graft is attached. In graft copolymers the backbone and the side chains may both be homopolymeric, the backbone may be homopolymeric and the side chains copolymeric or vice versa, or both backbone and the side chains may be copolymeric but different in chemical compositions. Branching in one or more stages and cross-linking may also occur [25].

The simplest case of graft copolymer can be represented as poly(A)-graft-poly (B). Grafting has been utilized as an important modification technique for the chemical and physical properties of synthetic polymers because of their tremendous industrial potential [15].

2.3.1 Method of Grafting Copolymerization

In principles, there are two general methods for the synthesis of a graft copolymer [26].

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

(b) The backbone polymer could have active sites such as free radicals or ions formed upon it which are used to polymerize a suitable monomer to produce the side chain of polymer.

There are many methods for synthesis of graft copolymer but free-radical polymerization methods are the oldest and most widely used procedures, because they are relatively simple. However, the methods summarized in this thesis are described for starch graft copolymerization.

2.3.1.1 Free Radical Polymerization [27]

Radical can be produced by varieties of thermal, redox, photochemical, and irradiation methods. In order to function as a useful source of radicals, an initiator system should be readily available and stable under ambient or refrigerated conditions, which process at a practical rate of radical generation at temperatures that is not excessively high.

(a) Thermal Decomposition of Initiators

The thermal homolytic dissociation of initiators is the most widely used mode of radical generation for initiation. Only few classes of compounds, including those with O-O, S-S and N-O bonds, process the desired range of dissociation energies. However, it is only the peroxides which are extensively used as radical sources. The other classes of compounds are usually either not readily available or not stable enough. Several different types of peroxy compounds are widely used. One of them is benzoyl peroxide which is widely used in general polymer laboratory.

Benzoyl peroxide is a white, crystalline solid having melting temperature in the range of 103 to 105°C. It can explode when heating above 105°C. It is slightly soluble in water and soluble in organic solvents. Benzoyl peroxide can be used as a bleaching agent and a drying agent; however, it is usually used as an initiator or a catalyst in free radical polymerization [28]. Benzoyl peroxide is one type of diacylperoxides, RC(O)OO(O)CR, which decomposes by an initial cleavage of oxygen-oxygen bond. Benzoyl peroxide undergoes the initial bond scission (β-scission) as shown in Figure 2.6 with a first order rate constant of $1 \times 10^{14} e^{-29,900/RT} s^{-1}$ [29].

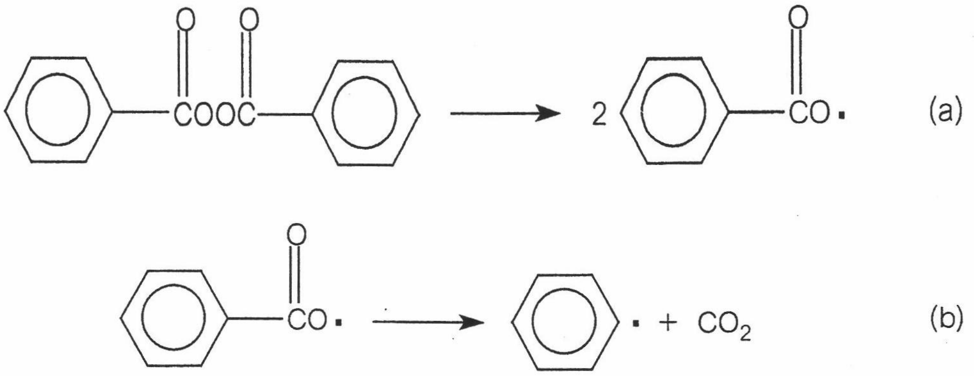


Figure 2.6 Dissociation of benzoyl peroxide [29].

This rate constant indicates that benzoyl peroxide is a useful thermal initiator in the temperature range of 60 to 80°C. Despite the relatively low temperatures at which this initiator is useful, the benzoyl radicals (benzoyloxy radicals) formed by the initial bond rupture may decompose by the reaction shown in Figure 2.6 (b) before they can react with monomer. However, the occurrence of reaction (b) has slightly effect on the overall rate of initiation, because the phenyl radicals formed in (b) can add themselves to the monomer to bring about the initiation. So that, both benzoyl and phenyl radicals are important as initiating species. In solution, there is a small possibility for reformation of benzoyl peroxide (ca. 4% at 80°C in isooctane) and only minute amounts of phenyl benzoate or biphenyl are formed within the cage. Therefore, in the presence of a reactive substrate (e.g. monomer), the production of radicals can be almost quantitative. Figure 2.7 shows overall dissociation reaction of benzoyl peroxide [30].

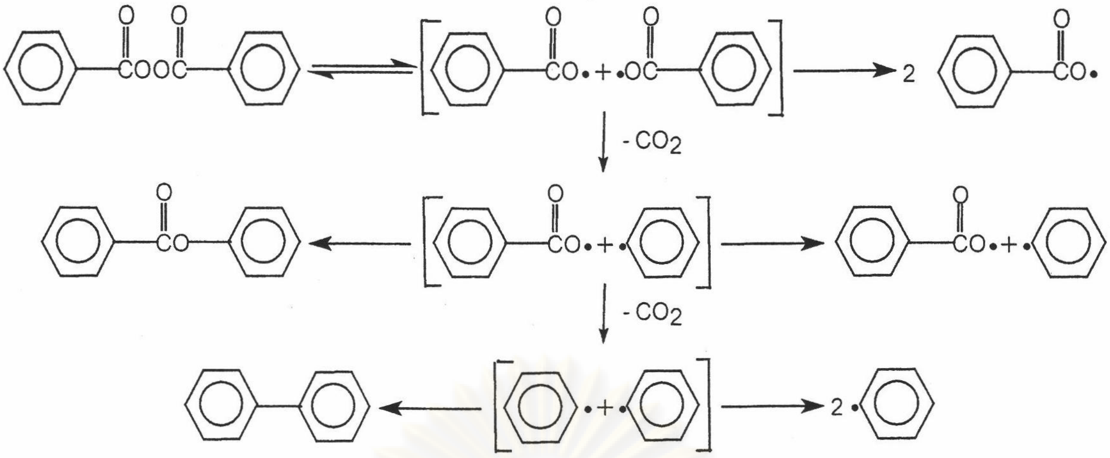


Figure 2.7 Overall reaction dissociation of benzoyl peroxide [30].

Benzoyl peroxide can be used as an initiator for graft copolymerization. Sheng and Hu grafted styrene onto random ethylene-propylene-diene monomer copolymer (EPDM) with benzoyl peroxide (BPO) and 2,2-azo-bis-isobutyronitrile (AIBN) [31]. They found that the grafting percent depended on the reaction parameters such as monomer concentration, time and temperature. However, the result showed that BPO was superior to AIBN and by chemical analysis, it was found that the double bond in EPDM-*g*-styrene did not react.

Mehmet and Fazli grafted acrylic acid onto poly(ethylene terephthalate) fibers using BPO as initiator [32]. They found that the grafting yield increased with BPO concentration up to concentration of 4.0×10^{-3} *M* and slightly decreased at higher initiator concentration. They concluded that the grafting took place mainly in the subsurface regions of the fibers and this occurred a diffusion barrier after the grafting value of 8-9%.

Meral and Mehmet grafted ethyl acrylate onto monofilament polyester [33]. They found that breaking tenacity and densities of grafted fibers decreased while breaking elongation increased with grafting yield. However, scanning electron micrographs showed that the fiber geometry and its diameter were not affected by grafting.

Boonsri studied the new method to modify the hydrophilicity of polyester fabrics by grafting with poly(methacrylic acid) and found that swelling of fabrics was necessary for grafting occurrence[34]. However, when the percent of grafting increased, the fabrics tended to be stiffer than ungrafted fabrics but they could be softened by controlled treatment with aqueous solution of sodium hydroxide.

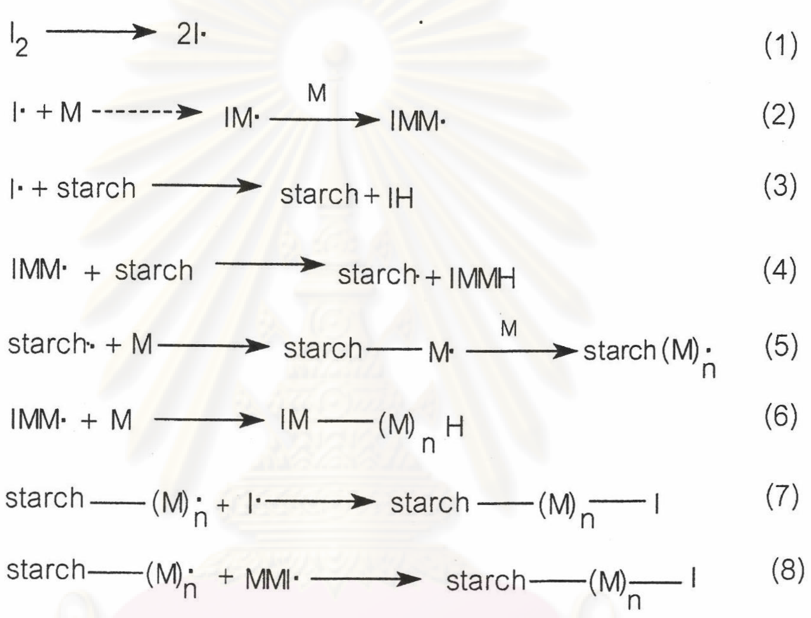
Havva, et al., tried to graft methyl methacrylate upon gelatin by benzoyl peroxide in aqueous medium. They found that the properties of graft copolymer depended on grafting percentage. For example, the thermal stability of graft copolymer increased after grafting [35].

There are some studies about graft polymerization in which starch was as a substrate and BPO as an initiator:

Srivastava, Pande and Misra studied the new method for determination of grafting percentage in starch-polyacrylonitrile graft copolymer [36]. They prepared the graft copolymer by using various initiators such as BPO, ceric sulphate, potassium persulphate and Fenton's reagent, and calculated percent of grafting between estimating glucose in the hydrolysate of the copolymer by titration and the nitrogen analysis.

Mirsa, et al. attempted to prepare acrylonitrile (AN) and methylacrylate (MA) grafted onto starch in aqueuos medium [37]. They found that the percent grafting depended upon concentration of initiator, concentration of monomer, time, and temperature. In this experiment, it was found that AN was more reactive than MA. They also compared the relative reactivities of BPO and AIBN for graft copolymerization of vinyl acetate onto potato starch [38] and found that BPO (53.6%) appeared to be more reactive than AIBN (23.5%).

The following chain transfer mechanism (Figure 2.8), suggested by Flory in early 1937 and elaborated by Hoffman and Bacskai, is postulated for the grafting of vinyl monomers onto starch in the presence of free radical initiator. The mechanism invoked to explain grafting of vinyl monomers onto starch is chain transfer process [37]. In chain transfer process, the initiator fragment (I·) arising from the decomposition of initiator usually abstract a hydrogen atom from the polymeric backbone leading to generation of active sites on the backbone polymer where grafting of appropriate vinyl monomer can occur.



$$I_2 \longrightarrow 2I\cdot \tag{1}$$

$$I\cdot + M \dashrightarrow IM\cdot \xrightarrow{M} IMM\cdot \tag{2}$$

$$I\cdot + \text{starch} \longrightarrow \text{starch} + IH \tag{3}$$

$$IMM\cdot + \text{starch} \longrightarrow \text{starch}\cdot + IMMH \tag{4}$$

$$\text{starch}\cdot + M \longrightarrow \text{starch}\text{---}M\cdot \xrightarrow{M} \text{starch}\,(M)_n^{\cdot} \tag{5}$$

$$IMM\cdot + M \longrightarrow IM\text{---}(M)_n H \tag{6}$$

$$\text{starch}\text{---}(M)_n^{\cdot} + I\cdot \longrightarrow \text{starch}\text{---}(M)_n\text{---}I \tag{7}$$

$$\text{starch}\text{---}(M)_n^{\cdot} + MMI\cdot \longrightarrow \text{starch}\text{---}(M)_n\text{---}I \tag{8}$$

Figure 2.8 The chain transfer mechanism for grafting of vinyl monomers onto starch [37].

For this mechanism, it is expected that free radical sites on starch may also form on C_2-OH, C_3-OH or C_6-OH (Figure 2.9). C_6-OH being a primary hydroxyl group is expected to show greater reactivity. If hydroxyl groups provide active sites, starch would be expected to show identical reactivity towards grafting. Misra studied that the grafting of poly(vinyl acetate) onto starch took place to a greater extent than onto cellulose. This may indicate that generation of active sites by process involving abstraction of hydrogen from starch by the initiator fragment (I·) being important. Since starch is easily dispersible in water, (I·) has greater chance to react with starch. Thus, wastage of (I·) by cage recombination is minimum when grafting is carried out in the presence of starch. Havva, et al. reported the termination of graft copolymerization may take place by either chain transfer or combination reaction [35].

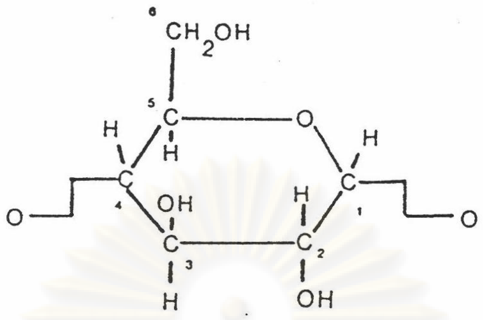


Figure 2.9 A schematic diagram of numbering system for carbon positions in anhydroglucose units [18].

(b) Redox Initiation

Redox initiation or oxidation-reduction reactions produce radicals that can be used to initiate graft copolymerization. A prime advantage of redox initiation is that radical production occurs at reasonable rates over a very wide range of temperature. A wide range of redox reactions, including both inorganic and organic components either wholly or in part, may be employed for this purpose. Some redox systems involve direct electron transfer between reductant and oxidant, while others involve the intermediate formation of reductant-oxidant complexes; the latter is charge-transfer complexes in some cases.

The types of redox initiators widely used in graft copolymerization were as follows:

(i) Ceric ion salts (ceric ammonium nitrate), suggested by Mino and Kaizerman in 1958, has been used to graft copolymerize a number of monomers onto polysaccharides. Reactions of ceric salts with alcohols have been studied, and researched using model compounds to determine the chemistry involved when a glucopyranosyl unit reacted with ceric ion. On the basis of available evidence, one reaction path for ceric-initiated graft copolymerization is presented in Figure 2.10. After initial formation of a starch-ceric complex, the ceric ion (Ce^{4+}) reduces to cerous (Ce^{3+}), a hydrogen atom is oxidized, and a free radical is formed on starch. The starch free radical may then react with monomer to initiate graft copolymerization or may loose through further reaction with the ceric ion. This method is grafting yields substantially pure graft copolymers since the free radicals are produced exclusively on the backbone.

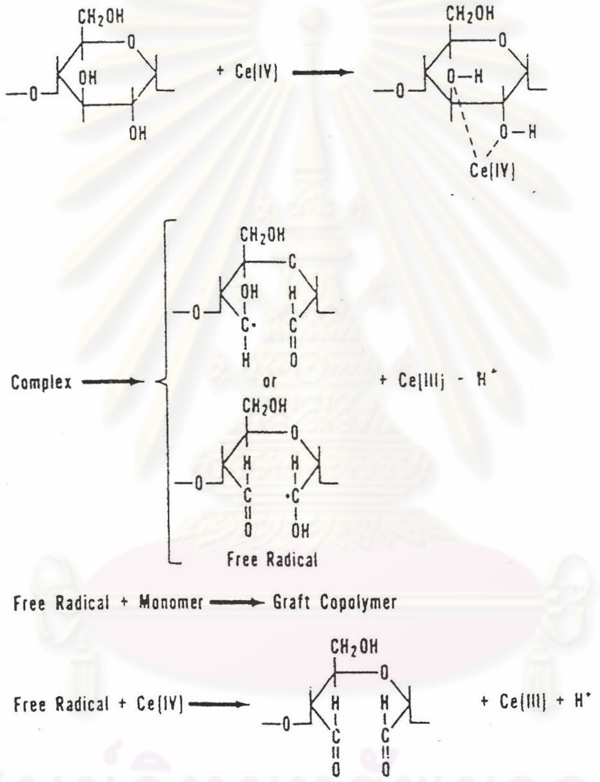


Figure 2.10 Initiation of graft polymerization by ceric ion [39].

Gugliemelli, et al., grafted acrylonitrile onto gelatinized cationic starch to produce stable latex-like copolymer dispersion and then they produced the film of graft copolymer by coalescence of the dispersed particles [40]. Ronald, Rodney, and Thomas prepared starch-*g*-poly(methyl acrylate) copolymers with molecular weight less than 500,000 [41]. They extruded this copolymer in form of biodegradable mulch film which showed excellent initial tensile strength and elongation.

While Mingzhu, et al., synthesized starch graft methyl acrylate similar to Ronald but they changed the type of starch from corn to potato and they studied the kinetic of graft copolymerization [42]. In addition, Athawale, Rathi and Vidyagauri grafted methacrylamide onto maize starch [43] where Anthawale and Lele also grafted methacryonitrile onto maize starch [44].

Athawale and Rathi studied the role and relevance of polarity and solubility of vinyl monomers in graft polymerization onto starch [45]. They reported that, for graft copolymerization of vinyl monomers in aqueous medium using ceric ammonium nitrate as initiator, the grafting efficiency decreased with decreasing monomer polarity in the following order: acrylonitrile > acrylic acid > methyl methacrylate > vinyl acetate > styrene.

(ii) Persulfate salts, generally, ammonium persulfate or potassium persulfate are used as initiators for graft copolymerizations. When an aqueous solution of persulfate is heated, it decomposes to yield sulfate radical along with other free radical species. Starch-*g*-poly(*N*-methylol acrylamide-methacrylic acid) cation exchange composites are synthesized by polymerizing the highly concentrated mixture using ammonium peroxydisulfate as initiator and with different reductants, such as sodium thiosulfate, sodium pyrosulfate, and glucose. Sodium thiosulfate is the best reductant for preparing the composites with lowest solidification time and highest insoluble yield and carboxyl content.

(iii) Ferrous ammonium sulfate-hydrogen peroxide is also used to form radical reactive sites on starch by chain transfer reaction. Hydroxyl radicals are produced from the hydrogen peroxide-ferrous ion system, and these free radicals then abstract hydrogen atoms from starch. In further development, hydrogen peroxide has been replaced by organic hydroperoxides or inorganic persulfate salts while such reducing agent as sodium bisulfite has been substituted for ferrous ion. Trimnell, Fanta and Salch [46] compared the method to synthesize graft copolymer of methyl acrylate onto granular starch by Fe^{2+}/H_2O_2 and ceric initiating system. They found that Fe^{2+}/H_2O_2

system gave higher levels of homopolymer produced on starch granule surface than ceric initiating system when detected by scanning electron microscopy (SEM) and attenuated total reflectance (ATR) infrared spectroscopy.

(iv) Manganese derivatives, Mn^{4+} (as MnO_2 from a $KMnO_4^-$ acid system) and Mn^{3+} (as manganic pyrophosphate) have been employed for graft polymerization of vinyl monomers onto starch. For the Mn^{4+} initiator, starch is generally immersed in $KMnO_4$ solution to deposit MnO_2 on it. In the presence of acid, formation of primary radical species occurs as a result of the action of acid on the deposited MnO_2. Hence, different primary radical species are created depending on the type and nature of the acid used. The mechanism of this initiating system is to produce starch macroradicals via direct abstraction of hydrogen atom from the hydroxyl groups of the starch molecules. In the presence of vinyl monomer, the starch macroradicals are added to the double bond of the vinyl monomer, resulting in a covalent bond between the monomer and starch and the creation of free radical on the monomer (i.e., a chain is initiated). Subsequent addition of monomer molecules to the initiated chain propagates the grafting onto starch. The termination of the growing grafted chain may occur via coupling (combination), disproportionation, reaction with the initiator, and/or chain transfer.

The following reaction mechanism of manganic pyrophosphate initiator is presented to account for the synthesis of starch graft copolymer by cleavage of the glycol groups of the anhydroglucose units in amylose and amylopectin by manganic pyrophosphate, with the dissociation of the glycol-Mn^{3+} complex. Jian, et al. grafted methyl methacrylate onto canna starch using pyrophosphate as an initiator [47]. In this experiment, they described the mechanism of this initiator such as ceric initiator and they also used the Arrhenius equation to calculate the apparent activation energy for this graft copolymer which were about 27.1 kJ/mol.

(c) Irradiation

Radiation initiated graft copolymerization involves two simultaneous or consecutive processes in which active sites are formed on or near the surface of existing polymer by irradiation, followed by polymerization of monomer on these sites. There are four main methods of radiation-initiated graft copolymerization [48]. The first technique is direct or mutual method. In this technique the monomer (which may be gas or vapor, liquid, or solution) is irradiated in contact with the polymer in air, or better, under an inert atmosphere. The polymer is generally irradiated in contact with excess monomer, but several variations are possible and the polymer may, for example, be impregnated with monomer before irradiation. In radical graft polymerization, irradiation produces macroradicals, $P_{\dot{A}}$, in the polymer (P_A) and these initiate polymerization of the monomer (B) to give a graft polymer P_A-P_B. The irradiation also generates radicals, B•, from the monomer that initiate polymerization to give the homopolymer, -BBBBBB-. Low molecular weight radicals formed by radiolysis of polymer can also initiate homopolymerization. In the case of radiation sensitive monomers (e.g., acrylic and methacrylate, etc.), homopolymerization proceeds at a greater rate than grafting. Homopolymerization is one of main disadvantages of the direct method. However, grafting predominates if the yield of radicals from the monomer is considerably less than of radicals from the backbone polymer, if the polymer is treated before irradiation with a solution of monomer in a radiation sensitive solvent (for swelling) [49], and if the polymer is added with such compounds as acid [50], inorganic salts, urea, and polyfunctional monomers.

The second technique is preirradiation method. In this procedure the backbone polymer is irradiated in the absence of air and deaerated monomer placed in contact with the irradiated polymer. Grafting is brought about macroradicals trapped in the irradiated polymer, and homopolymerization does not occur. While the absence of homopolymerization is an advantage, disadvantages of this method are possible degradation of the backbone polymer, the significant temperature dependence, dependence on the crystallinity of the polymer, and a comparative low degree of grafting.

The peroxide method is the third technique which involves preirradiation of the polymer but in the presence of air or oxygen so that the formed macroradicals are converted to peroxides and hydroperoxides. An advantage of the peroxide method is the possibility of storing the irradiated polymer for a considerable time before grafting. However, the disadvantage of this technique is that hydroxyl radicals inducing homopolymerization of the monomer. This can be avoided by adding transition metal compounds that suppress hydroxyl radical formation.

The last technique is the crosslinking of two polymers. Irradiation of a mixture or solution of two polymers, P_A and P_B gives rise to crosslinking, that is, to the formation of the copolymer P_A-P_B.

For starch graft copolymer, free radicals on the starch backbone can be produced with ^{60}Co, electron beam and UV irradiation [51-52]. The first to the third methods are used to initiate starch graft copolymer, but starch is usually irradiated first and the activated starch is then allowed to react with monomer.

(d) Miscellaneous Initiation Systems

Besides these three chief grafting processes described above, alternative methods of synthesizing starch graft copolymers have been developed such as the anionic graft polymerization of lauryl methacrylate onto starch using potassium alkoxide as an initiator. When the alkoxide concentration increased, the grafting yield increased. The graft polymer composition depends on the reaction conditions. With increasing monomer concentration and temperature, the extent of formed poly(lauryl methacrylate) increases. In this experiment, graft polymers containing 30-65% poly (lauryl methacrylate) are obtained.

The anionic grafting of methacrylonitrile on starch in dimethyl sulfoxide initiated by the lithium and sodium alkoxide derivatives has been studied. The results were compared with those obtained previously with potassium alkoxide. As indicated by the monomer-starch balance at the end of the polymerization with lithium, the results were not highly reproducible but the results were reproducible with sodium. The yield of pure graft polymer with different alkoxides were in the order: potassium> sodium>lithium, lower alkoxide concentration was required for attaining complete conversion and optimal yield in the case of potassium alkoxide.

The synthesis of starch graft copolymers via reactive extrusion has been used to bring about chemical reactions between starch and vinylic polymers [53-54]. An example is the preparation of starch graft copolymer using reactive extrusion done by Chinnaswamy and Hanna [53]. In this experiment, they described the molecular mechanism of starch structural and molecular changes during extrusion process due to shear, high temperature, and pressure. The granular structure of starch disrupted and the ruptured granules were plasticized, throughly mixed and a viscous starch paste was formed. During this process, the starch molecules underwent degradation. This may happen from one or all of the following molecular mechanisms: (a) molecular reversion, (b) intramolecular rearrangement, (c) formation of anhydroglucose, and (d) recombination as outlined in Figure 2.11.

These molecular mechanisms of degradation or reformation of starch due to heat, shear, and high pressure can be manipulated in different ways to obtain a desired functional end product. Chemical agents such as urea, sodium chloride, sodium bicarbonate, citric acid, and dilute hydrochloric acid are known to accelerate starch molecular degradation. Similarly, starch molecule degrade by increasing the shear rate and residence time in the extruder, restricting the die nozzle opening, increasing barrel temperature, decreasing starch moisture content and combinations. Combinations of chemical agents and processing conditions yield a wide range of degraded starch products with different functional characteristics. It is known that the covalent bonded atoms or groups of atoms are literally torn off during starch degradation. Thus, this process offers a climate conductive to free radical formation on starch molecules which can be used to polymerize the starch with molecules having vinyl groups.

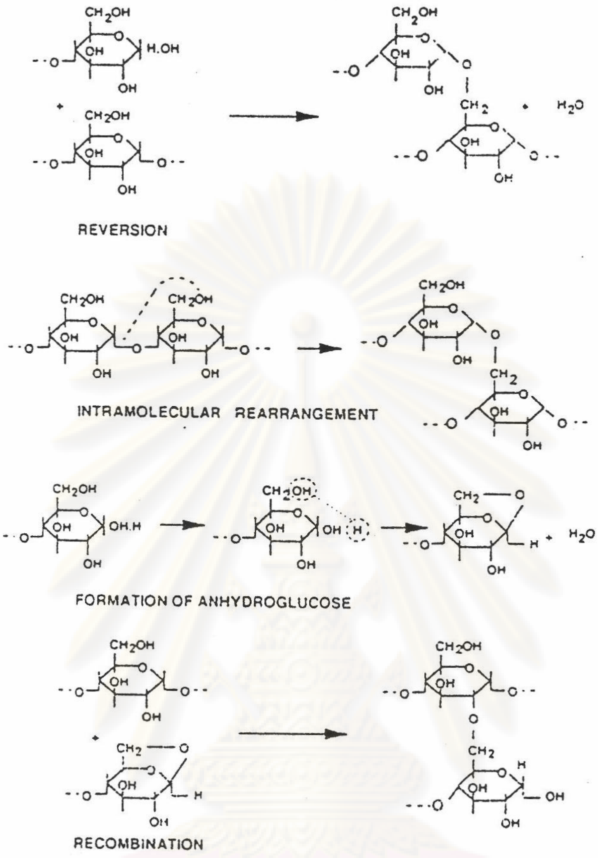


Figure 2.11 Molecular changes in starch during reactive extrusion processing of starch for graft polymerization [53].

Ring opening polymerization can be used to synthesize starch graft copolymer. Eui, Chang and Jung used this method to prepare graft polymerization of ε-caprolactone (CL) monomer onto corn starch [55]. They found that the yield of graft copolymer increased with increasing water content in the feed. This dued to the enhancement of starch gelatinization by the water. The starch gelatinization can generally induce the effective destruction and plasticization of granular structure of starch and, consequently, promote the reactions between the starch and CL monomer.

2.3.2 Previous Studies on Graft Copolymerization of Starch and Styrene Monomer

Fanta, et al., prepared starch-*g*-styrene copolymer by grafting copolymerization reaction of styrene onto corn starch via simultaneous ^{60}Co irradiation method [56]. Copolymers were characterized in terms of the percent add-on, the molecular weight, and the molecular distribution. In a typical polymerization, 4 g of each starch and styrene were blended with 1 cm^3 water and 1.5 cm^3 of an organic solvent. They found that the highest 43% add-on and the highest 76% conversion of styrene to grafted polystyrene were obtained when the ethylene glycol and ethanol used as organic solvent were omitted and water alone was used. When water was also omitted, polymerization of styrene was negligible.

Bagley, et al., prepared copolymers containing 40-50% synthetic polymers grafted onto corn starch and cellulose [57]. The monomers including styrene, methyl methacrylate, methyl acrylate, and butyl acrylate, were chosen to produce grafted synthetic polymers with various glass transition temperatures (T_g). These graft copolymers were extruded, in absence of any added thermoplastic homopolymer, to give strong, continuous polysaccharide filled plastics which were biodegradable and exhibited little or no die swell. Starch-*g*-polystyrene and starch-*g*-poly(methyl methacrylate) were hard and brittle, while graft copolymers prepared from methyl and butyl acrylate were more flexible and leathery. The graft copolymers with lower T_g required less torque and could be extruded at lower temperatures. The surprising feature of these results was that the matrix polymers, starch and cellulose, were rigid and non softening materials.

Henderson and Rudin prepared starch-*g*-polystyrene by simultaneous ^{60}Co irradiation of mixtures of wheat starch and styrene at room temperature [58]. They found that the extent of conversion of monomer to polymer increased drastically with increasing water content up to a level of about 26% weight on starch. Methanol had approximately the same effect as water at equivalent concentration but ethanol was clearly less effective as a promoter of homopolymerization and graft copolymerization. Drying of the starch reduced the conversion to polymer with all promoters but caused the greatest deterioration in the ability of ethanol to promote polymerization. Water and methanol were better radical scavengers and polymerization promoters because they were better disrupt hydrogen bonds and permeated the starch structure.

They also prepared wheat starch-*g*-polystyrene by simultaneous ^{60}Co irradiation and strach-*g*-poly(methyl acrylate) by chemical initiation [59]. The respective percent add-on values were 46 and 45%, 68% of the polystyrene formed was grafted onto starch and the corresponding proportion of poly(methyl acrylate) was 41%. The molecular weight distributions of the homopolymer and graft portions were characterized and extrusion conditions were established for production of ribbon both samples. Both copolymer types were considerably weakened by soaking in water and this effect was more immediate and drastic for strach-*g*-poly(methyl acrylate). Both graft copolymers regained their original tensile strengths on drying but the poly(methyl acrylate) specimens did not recover their original unswollen dimensions and retained high breaking elongation characteristic of soaked specimens.

Fanta, et al. used potassium persulfate as initiator to synthesize starch-*g*-styrene and cellulose-*g*-styrene copolymers [60]. When starch was used as a substrate, it was found that polystyrene graft had mean M_w and M_n values of 515,000 and 190,000, respectively, whereas mean values of M_w and M_n for the homopolystyrene were 375,000 and 150,000, respectively. Since starch-g-polystyrene plastics were brittle, both dibutyl phthalate and glycerol as plasticizers were used to reduce the ultimate tensile strengths of extruded polymers without having a significant effect on brittleness, as approximated by the percent elongation at break. When cellulose was used as a substrate, it was found that percent add-on of cellulose-*g*-polystyrene was lower than that of starch-*g*-polystyrene even the amount of styrene monomer used in the preparation of the former was higher.

Expanded foam materials having a high degree of biodegradability were prepared by combining a starch graft copolymer (SGC) synthesized by Boehmer and Hanlon [61] with grain-based starch containing materials. The mixture of SGC and grain-based material was directly expanded at elevated temperature with an extruder or other expansion means. These products can be produced at lower cost and they had lower moisture absorption than the products prepared from high amylose starch alone and modified amylose with plasticizers.

From the experiments of Kollengode, Bhatnagar and Hanna [62], it was observed that the energy level of radiation significantly influenced extruded radial expansion ratio, bulk density, specific mechanical energy (SME), water solubility index (WSI), and degree of grafting as determined by δ^{13}C values for synthesized starch-*g*-polystyrene and starch-*g*-poly(methyl methacrylate) copolymers. It can be seen that the radical expansion ratio, SME, WSI and δ^{13}C % values of all graft copolymers decreased when the radiation dosage increased.

Suda, et al. mixed starch, styrene monomer and methanol as solution to synthesized starch graft copolymers via irradiation method [13]. Starch graft copolymers were mixed with cassava starch and polystyrene to produce polystyrene sheets by using two-roll mill. The degradability of these plastic sheets were investigated by out-door exposure, soil burial testing, UV irradiation, and bacterial exposure. It was found that all plastic sheets can degrade at the area of the starch by all degradation processes but the plastics took a longer time to degrade by the soil burial test.

The grafting of polystyrene onto dissolved starch in twin screw extruder has been studied by Graaf and Janssen [63]. This copolymerization was initiated using benzoyl peroxide and potassium persulfate as initiator. Parameters such as screw rotation rate, fully filled length of the extruder, wall temperature and throughput had been varied. They used maleic anhydride added in the grafting system to increase grafting of polystyrene onto starch. The total conversion of styrene could be controlled by adjusting extruder parameters while the molecular weights of polystyrene could be controlled by adding dodecylmercaptan which acted as a chain transfer agent to styrene phase. It was found that the grafting of polystyrene onto starch occurred at the interface between the dissolved starch and the styrene phase.

They also used starch-g-polystyrene as a compatibilizer for starch and polystyrene blend [64]. The results of tensile strength and impact strength provided of the same magnitude as they were blended material without compatibilizer. X-ray diffraction and differential scanning calorimetry (DSC) measurements revealed a highly ordered system.

It can be seen that preparations of graft copolymer from starch and styrene monomer have been previously based on irradiation method. Since alternative approaches have been used to synthesize graft copolymers from other monomers; hence, these approaches may be applied to prepare starch-*g*-polystyrene. Therefore, a new approach for graft copolymerization of starch and styrene monomer based on free radical polymerization was studied and it is presented in the following chapters.