

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Starch [1]

Starch, the principally reserve polysaccharide in plants, constitutes a substantial portion of the human diet. It is the principal component of most seeds, tubers, and roots. Today, starch is used extensively in paper, textile, explosives, foods, alcoholic beverage, clothing, fuel and adhesive industries.

Starch is abundantly available, inexpensive, a desirable source of calories, and occurs in the form of granule with a density of approximately $1.5 \times 10^{-3} \text{ kg/cm}^3$. In a granule form, starch is semi-crystalline, insoluble in cold water but imbibes water reversibly and swells slightly. The granules vary in shape and size ranging from about 1 to 100 μm in diameter depending on the source. For cassava starch, the size of granules range from 5 to 35 μm . The largest sizes are usually 25 to 35 μm and the smallest ones are 5 to 15 μm .

2.1.1 Chemical Structure of Starch [2]

Chemically, starch is a polymeric carbohydrate consisting of anhydroglucopyranose units linked together primarily through α -D-1,4-glycosidic bonds. It is a heterogeneous material consisting at the extremes of two major types of polymers, amylose and amylopectin. In addition to amylose and amylopectin, starch also contains lipid, residues of protein, and trace amounts of phosphorus.

2.1.1.1 Amylose [2]

Amylose is essentially a linear polymer in which the anhydroglucopyranose units are predominantly linked through α -D-1,4-glycosidic bonds. Its molecular size varies depending upon the plant source and processing conditions employed in extracting starch.

Amylose may contain anywhere from about 200 to 2000 anhydroglucopyranose units. At one end of the polymeric molecule, the anhydroglucopyranose 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, an anhydroglucopyranose unit contains one primary hydroxyl group and three secondary hydroxyl groups. The other anhydroglucopyranose units along the chain contain one primary and two secondary hydroxyl groups. Figure 2.1 shows a schematic diagram of the amylose molecule.

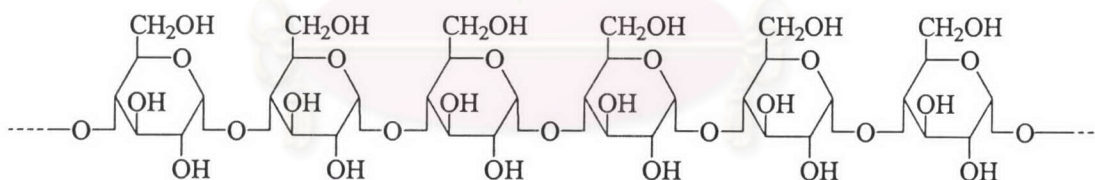


Figure 2.1 Linear structure of amylose

The abundance of hydroxyl groups imparts hydrophilic properties to the polymer, giving it the affinities for moisture absorbability 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 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 bonds at those sections where close alignment has occurred.

In general, the linearity of amylose favors the formation of strong film. For the phenomenon in which intermolecular association occurs 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 [2]

Amylopectin is a branched polymer containing, in addition to anhydroglucopyranose units linked together as in amylose through α -D-1,4-glycosidic bonds, periodic branches at the carbon-6 position. These branches are linked to the carbon-6 by α -D-1,6-glycosidic bonds. Each branch contains about 20 to 30 anhydroglucopyranose units. A schematic diagram of the amylopectin molecule is shown in Figure 2.2.

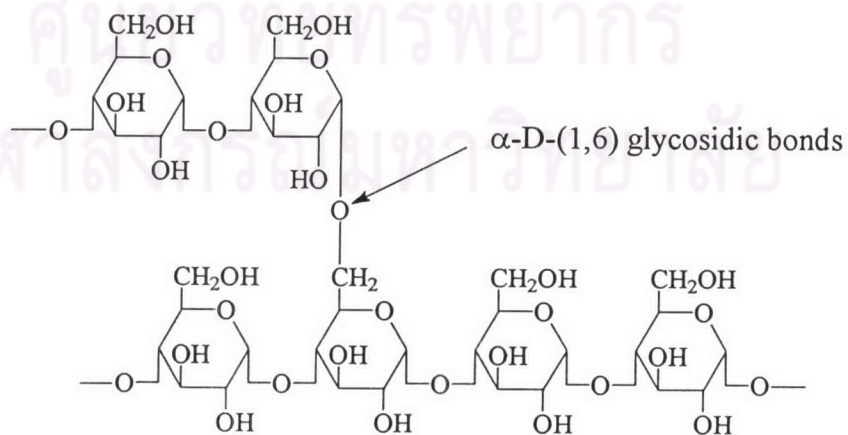


Figure 2.2 Branched structure of amylopectin

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 a strong and flexible film as that of the linear amylose does. Furthermore, it does not form a complex with iodine which gives deep blue coloration.

2.1.2 Cassava Starch [3,4]

Cassava is an important food crop in many tropical countries in Africa, South America and Asia. However, in Thailand, this crop has been well recognized as more than a subsistent crop. It is important commercially as the raw material for a large and complex industrial system that has a significant impact to the country's economics. The roots of this crop contain high starch content and approximately half of the roots produced are used for starch industry. Cassava starch has many remarkable characteristics including high paste viscosity, high paste clarity and high freeze-thaw stability, which are advantageous to many industries. In addition, the native starch with high purity can be readily modified by physical, chemical and enzymatic processes into many diversified products in order to improve the starch functionality and, consequently, encourage more industrial applications.

Unlike other starch sources such as cereal grains and tubers, cassava roots contain a low quantity of impurities such as protein and lipid, and have high starch content. The standard for starch content in native cassava starch is not less than 96% (dry basis). Chemical compositions and general properties of cassava starch are shown in Table 2.1.

The most important characteristics of cassava starch are:

Odorless: The absence of unpleasant odor in cassava starch enables this product to be conveniently and readily blended with other flavoring ingredients.

Paste clarity: Cassava starch, when cooked, provides a paste with clear appearance. The paste clarity of cassava starch (1%) as indicated by % transmittance at 650 nm is in the range of 40-70%. The products of cassava starch are clear and suitable for combining with other coloring agents.

Stickiness: With a high ratio of amylopectin to amylose (80:20), cassava starch provides a high peak viscosity but low potential for retrogradation, resulting in starch gel with good freeze-thaw stability.

Starch from cassava roots is recognized as a pure starch suitable for a wide range of applications such as:

Food: Applications take advantage of odorless, clear paste and high freeze-thaw stability properties of this starch.

Chemicals: The amorphous region in amylopectin is recognized as a good acceptor site for active chemicals. With high amylopectin content ($\approx 80\%$) in cassava starch, it assures good susceptibility to any chemical molecule.

Fermentation: As feed stock of all fermentation processes, cassava starch delivers low-price carbohydrate source with good susceptibility to acid and/or enzymatic hydrolysis even at low temperature.

Adhesives & Glue: Clear appearance and sticky texture of cooked paste are very advantageous of using cassava starch in this area.

Table 2.1 Chemical compositions and general properties of cassava starch [4]

	Value
Chemical composition (% dry basis)	
- Protein	0.15-0.30
- Fat	0-0.01
- Ash	0.10-0.15
Granule size (μm by image analysis)	3-34
Amylose content (% by high performance size exclusion chromatography)	17-23
Amylose size (DP_n , by high performance size exclusion chromatography)	2040-4640
Swelling power at 85°C (0.1 g starch in 15 ml. of distilled water)	40-62
Solubility (%) at 85°C (0.1 g starch in 15 ml. of distilled water)	22-42
Paste viscosity (by rapid visco analyzer using 3 g. starch at 14% moisture content in 25 ml. of distilled water)	
- Pasting temperature (°C)	67.0-74.0
- Peak viscosity (RVU)	350-490
- Trough viscosity (RVU)	110-210
- Final viscosity (RVU)	180-290
- Breakdown (RVU)	160-340
- Setback (RVU)	50-110
Thermal analysis (by differential scanning calorimeter using 30% starch)	
- Onset temperature (°C)	60.0-65.0
- Peak temperature (°C)	67.0-74.0
- Conclusion temperature (°C)	79.0-87.0
- Enthalpy (J/g)	14.0-17.0

2.2 Poly(methyl methacrylate) [5,6]

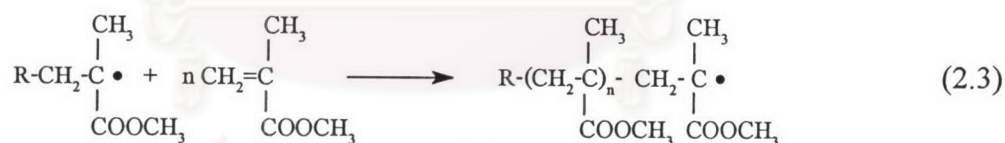
Poly(methyl methacrylate) (PMMA) is the most important member of acrylic polymers. It is hard, clear, colorless, transparent plastic that is usually available as molding and extrusion pellets, reactive syrups, cast sheets, rods, and tubes.

PMMA for molding or extrusion is produced commercially by suspension polymerization or bulk polymerization of methyl methacrylate (MMA). To minimize polymerization reaction exotherm and shrinkage, bulk polymerization, which is used in the production of sheets, rods and tubes, is carried out with reactive syrup of partially polymerized MMA, which has a viscosity convenient for handling. An example of polymerization reaction of MMA to PMMA is showed below.

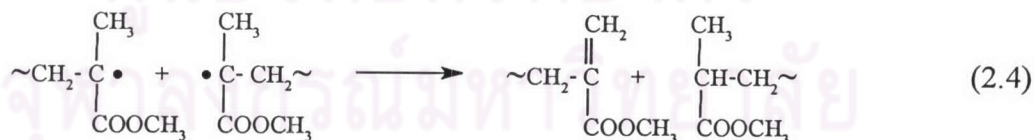
Initiation



Propagation



Termination



The bulky nature of the pendant group (-O-CO-Me), and the absence of complete stereoregularity makes PMMA an amorphous polymer. Isotactic and syndiotactic PMMA may be produced by anionic polymerization of MMA at low temperatures. However, these forms of PMMA are not commercially available. Modified PMMA can be obtained by copolymerizing MMA with monomers such as acrylates, acrylonitrile, and butadiene.

PMMA is characterized by crystal-clear light transparency, and good chemical resistance and electrical and thermal properties. It has a useful combination of stiffness, density, and moderate toughness. PMMA has a moderate T_g of 105°C , a heat deflection temperature in the range of 74 to 100°C , and a service temperature of about 93°C . However, on pyrolysis, it is almost completely depolymerized to its monomer.

The outstanding optical properties of PMMA combined with its excellent environmental resistance recommend it for applications requiring light transmission and outdoor exposure. PMMA is used for specialized applications such as hard contact lenses. The hydroxyl ester of methacrylic acid is the monomer of choice for the manufacture of soft contact lenses. Typical applications of PMMA are given in Table 2.2.

Table 2.2 Typical applications of poly(methyl methacrylate) [5]

Area	Applications
Construction	Enclosures for swimming pools, shopping malls and restaurants, tinted sunscreens to reduce air-conditioning and glare, domed skylights
Lighting	Lighted signs, luminous ceilings, diffusers, lenses and shields
Automotive	Lenses, instrument panels, signals and nameplates
Aviation	Windows, instrument panels, lighting fixture covers, radar plotting boards, canopies
Household	Housing, room dividers, decorating of appliances, furniture, vanities, tubs, counters
Others	Display cabinets and transparent demonstration models in museums, exhibits, and department stores

2.3 Graft Copolymerization

2.3.1 Principles of Graft Copolymerization

Copolymerizations are the reactions which lead to the formation of polymers containing two or more discrete types of monomer units. Graft copolymer, also called branched or comb polymer, is one of the basic types of copolymers. It is a polymer of molecules with one or more species of block connected to the main chain as side chains. These side chains have constitutional or configurational features that differ from those in the main chain. As schematically presented in Figure 2.3, a sequence of “A” monomer units represents the main chain or backbone while a 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 may be copolymeric or vice versa, or both backbone and side chains may be copolymeric but different in chemical compositions [7].



Figure 2.3 Schematic structure of graft copolymer [7]

The simplest case of a graft copolymer can be represented as: poly(A)-g-poly(B), where a polymer named first [poly(A)] is the backbone while that named second [poly(B)] is the side chain [8]. Thus, poly(methyl methacrylate)-g-polystyrene indicates a backbone of poly(methyl methacrylate) and the grafts of polystyrene.

In principle, there are two general methods for synthesizing graft copolymer [9].

- (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. These can then be used to polymerize a suitable monomer to produce the side chain of polymer.

Graft copolymerization is generally initiated via the formation of an active site on a substrate polymer molecule followed by its reaction with a monomer. Most graft copolymers are formed by free radical polymerization. Irradiation and chemical initiations can be used to generate the polymer radicals that lead to copolymers [2].

2.3.2 Synthesis of Starch Graft Copolymer [10]

The structure of a starch graft copolymer is shown schematically in Figure 2.4, where AGU represents an anhydroglucopyranose unit, and M is the repeating unit of the monomer used in the polymerization reaction.

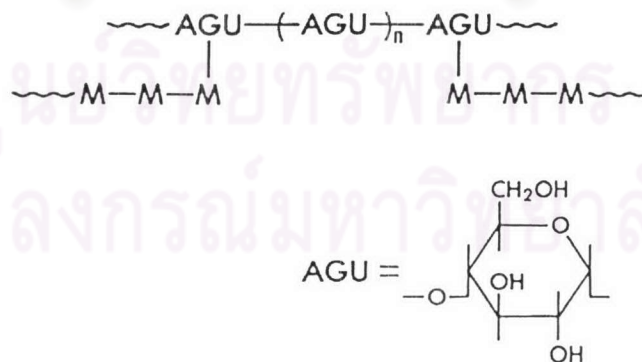


Figure 2.4 Schematic representation of starch graft copolymer [10]

Starch graft copolymers are synthesized by first generating free radicals on starch backbone and then allowing these free radicals to serve as macroinitiators for vinyl monomers. Generally, free radical initiated graft copolymers have high molecular weight branches that are infrequently spaced along the starch backbone. Copolymerizations can also be initiated anionically by allowing monomer to react with an alkali metal alkoxide derivative of starch. However, grafted branches produced by anionic initiation are of low molecular weight. Consequently, end-use applications of these anionically initiated polymers have thus far been limited.

In free radical graft copolymerizations, the average number of AGUs per high molecular weight graft (grafting frequency) will range from several hundred to several thousand; therefore, each starch molecule will have only a very few grafted branches. Grafting frequency, expressed in AGUs per graft, can be calculated from the weight percent synthetic polymer in the graft copolymer (percent add-on) and the average molecular weight of the grafted branches. Grafted polymer is easily separated from starch for molecular weight determination by degrading the starch component to low molecular weight sugars, e.g., with acid or enzyme.

Grafting efficiency is a term used to describe graft copolymerization reactions and is defined as the percentage of total synthetic polymer formed that has been grafted to starch. For example, if half of the synthetic polymer produced in a graft copolymerization was ungrafted homopolymer while the other half was chemically attached to starch, grafting efficiency would be 50%. High grafting efficiencies are, of course, desirable since a polymerization of low grafting efficiency would afford mainly a physical mixture of starch and homopolymer.

A number of free radical initiating systems have been used to synthesize graft copolymers, and they can be divided into two broad categories: irradiation initiation and chemical initiation [11].

2.3.2.1 Irradiation Initiation [12]

Irradiation initiated graft copolymerization can be accomplished by the following methods.

a.) The Direct Grafting Method

In its simplest form, the direct grafting method 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 on the latter.

A number of important factors must be considered before applying direct irradiation method to a given polymer-monomer system. Ionizing radiation as such is non-selective. One must, therefore, consider not only the effect of radiation on the polymeric substrate, but also its effect on the monomer, the solvent, or any other substances present in the system. Together with the radiation sensitivity of the polymer-monomer combination, one must also consider the effect of the radiation on the actual polymeric substrate. In general, polymer either undergo chain scission or crosslink under irradiation. If the former occurs in the presence of a monomer, this will lead predominantly to block copolymer. On the other hand, if the latter occurs, the network structures will be formed.

b.) Preirradiation in Air

In this method, the polymeric substrate is irradiated in air or oxygen to produce peroxide groups. These peroxide groups are reasonably stable and the polymer can be stored in the cold without loss of activity. If they are subsequently heated in the presence of monomer (as liquid or vapor) to about 150°C in the absence of air, the peroxide groups decompose liberating free radicals which can then initiate graft copolymerization.

c.) Grafting Initiated by Trapped Radicals

One of the primary effects of irradiation on polymers is the formation of free radicals. Although free radicals are highly reactive, it has been demonstrated that they can become trapped for extremely long periods (several days or months) in a viscous medium such as that encountered in a polymer at a temperature below its glass transition point. If the polymer is partly crystalline, the free radicals formed within the crystalline regions upon irradiation are still more firmly trapped, since the mobility of polymeric segments is much lower if these are involved in an organized structure. Although the free radicals are trapped, they are still highly reactive and provided the monomer which can diffuse through the polymer to reach the reactive sites. So, the trapped radicals can be used to initiate graft copolymerization.

Followings are some previous studies related to starch graft copolymerization initiated by irradiation.

In 1993, Kiatkamjornwong, Chvajareernpun, and Nakason [13] studied the effect of radiation modification on the liquid retention properties of native cassava starch, gelatinized at 85°C, by graft copolymerization with acrylonitrile carried out by mutual irradiation using gamma radiation. A thin aluminium foil was used to cover the inner wall of the reaction vessel so that the homopolymer concentration was reduced to less than 1.0%. The resultant saponified grafted product gave a distilled water retention value of 665 g/g of the dry weight of saponified grafted product. They used the infrared spectrophotometric technique to confirm the results of graft copolymerization and saponification reactions.

Then in 1997, Kiatkamjornwong and Meechai [14] investigated the enhancement of the gamma radiation grafting of acrylonitrile (AN) onto gelatinized cassava starch. They used infrared spectroscopy to follow the chemical changes in the grafting reaction and from saponification. The saponified starch-g-PAN was then characterized in terms of grafting parameters to provide a guide for the optimum total dose and the appropriate ratio of starch/acrylonitrile for a fixed dose rate of 2.5×10^{-1} kGy/min. They also carried out other dose rate to obtain the appropriate result of

grafting copolymerization and water absorption. They found that using a thin aluminium foil cover the inner wall of the reaction vessel is far more effective than any other metal films in the enhancement of the grafting reaction and the water absorption as well.

Two years later (1999), Kiatkamjornwong, Sonsuk, Wittayapichet, et al. [15] prepared cassava starch-g-polystyrene by a simultaneous irradiation technique from Co-60 source. The mixture of cassava starch, styrene and methanol solution was irradiated by gamma rays to various total doses at a fixed dose rate. The resultant graft copolymers were used as a part of the styrene-based polymer for studies of the degradation of plastic. They studied the characteristics of the copolymers in terms of the homopolymer content, grafting efficiency, grafting ratio, conversion, and percentage add-on. They found that the highest percentage grafting efficiency was 62.2%, obtained at a total dose of 10 kGy.

Afterwards, in 2001, chemical modification of cassava starch for degradable polyethylene sheets was studied by Kiatkamjornwong, Thakeow, and Sonsuk [16]. The irradiation grafting technique was used to graft acrylic acid onto cassava starch. Cassava starch-g-poly(acrylic acid) was further modified by esterification and etherification with poly(ethylene glycol) 4000 and propylene oxide, respectively. They characterized the modified product by NMR spectroscopy and contact angle measurement. Then, this modified product was used for blending with low density polyethylene (LDPE) sheets for evaluations of mechanical, thermal and degradation properties. They found that the blends of LDPE with ethylene-*bis*-stearamide wax had properties similar to the LDPE blends with the modified starch in terms of surface wettability, tensile properties, and hardness, but with a much better degradation in soil due to the much higher water absorption.

In 2002, Zhai et al. [17] prepared a series of excellent poly(vinyl alcohol) (PVA)/starch blend hydrogels by gamma and electron beam radiation at room temperature. They investigated the influence of dose, the content of starch in blend systems on the properties of the prepared hydrogels. They reported that the gel strength was improved obviously after adding starch into PVA hydrogels, but the swelling

properties decreased slightly due to poor hydrophilicity of starch. In order to elucidate the effect of component of starch on the properties of PVA/starch hydrogels as well as the formation mechanism of PVA/starch blend hydrogels under irradiation, the two components of starch, amylose and amylopectin, were chosen to blend with PVA to prepare hydrogels, respectively. The results indicated that amylose was a key component that influenced the properties of PVA/starch blend hydrogels. The further analyses of FT-IR spectra, DSC and TGA thermograms of the prepared gels after extracting sol manifested that there was a grafting reaction between PVA and starch molecules besides the crosslinking of PVA molecules under irradiation.

Also in 2002, Kiatkamjornwong, Mongkolsawat, and Sonsuk [18] carried out graft copolymerizations of acrylamide and maleic acid onto cassava starch by a simultaneous irradiation technique using gamma rays as an initiator. They studied various important parameters of total dose, dose rate, monomer-to-cassava starch ratio, and maleic acid content. Cassava starch grafted poly[acrylamide-*co*-(maleic acid)] performed as a superabsorbent polymer. Addition of 2% w/w diprotic acid of maleic acid into the reaction mixture yields a saponified starch graft copolymer with a water absorption in distilled water as high as 2256 g/g of its dried weight. The morphology of the superabsorbent polymers reveals some relationships between the porosity, network structure, and extent of water absorption.

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2.3.2.2 Chemical Initiation

In addition to irradiation initiation, free radicals on starch backbone can be generated by chemical methods. Grafting of vinyl monomers onto starch via chemical initiation has been accomplished by using various types of free radical initiator. In the following text, various initiators used in graft copolymerization of vinyl monomers onto starch are reported.

a.) Initiation by Ceric Ions

Perhaps the most widely used method of chemical initiation is the reaction of starch with ceric salts, such as ceric ammonium nitrate (CAN). In 1997, Athawale and Rathi [19] performed graft copolymerization of methacrylic acid onto starch using Ce^{4+} initiator in aqueous medium. They pointed out that methacrylic acid can be easily graft polymerized onto starch. The dependence of grafting on the reaction variables, such as monomer and initiator concentrations, reaction time, reaction temperature, was studied in detail. Acid hydrolysis and infrared spectroscopy were used for the confirmation of graft copolymer formation. Further, a representative graft copolymer was characterized by x-ray diffraction, thermogravimetric analysis, and differential scanning calorimetry. They also reported the solubility/swellability and the gelatinization characteristics of the copolymers. In addition, they also studied the effect of alkyl group chain length of alkyl methacrylates on graft copolymerization using CAN as an initiator. They grafted methyl methacrylate (MMA), ethyl methacrylate (EMA), and *n*-butyl methacrylate (BMA) onto starch. They found that as alkyl group chain length increased from MMA to BMA, relative reactivity was found to be in the order of: MMA > EMA > BMA [20]. Moreover, they studied the role and relevance of polarity and solubility of vinyl monomers. They reported that the grafting efficiency decreased with decreasing monomer polarity in the following order: acrylonitrile > acrylic acid > methyl methacrylate > vinyl acetate > styrene [21].

Choi et al. (1998) [22] examined the photodegradation properties of graft copolymers of vinyl ketones and starch. They synthesized starch-g-poly(methyl vinyl ketone) and starch-g-poly(phenyl vinyl ketone) by using CAN as an initiator.

In 1998, Athawale and Lele [23] studied the grafting of acrylic acid (AA) onto granular maize starch in aqueous medium initiated by ceric ions. They expressed the effect of concentration of ceric ion, concentration of AA, reaction temperature, polymerization time, and material-to-liquid ratio on the grafting in terms of %grafting efficiency and %add-on. They found that the crystallinity of starch decrease owing to grafting, and grafting of AA also affected the thermal stability of starch. From scanning electron micrographs, they concluded that grafting is essentially a surface phenomenon.

In 2000, Lutfor et al. [24] used CAN as an initiator in graft copolymerization of methyl acrylate (MA) onto sago starch. They found that the rates of graft copolymerization reaction and grafting efficiency were depended upon the concentration of CAN, MA monomer, sago starch, mineral acid (H_2SO_4), and as well as reaction temperature and time. They proposed a rate equation of polymerization which was the first-order dependence of the MA monomer concentration and square root of the CAN concentration.

Also in 2000, Athawale and Lele [25] used CAN as an initiator once again. This time they grafted methacrylonitrile (MAN) onto dried maize starch in aqueous medium. They studied this graft copolymerization reaction gravimetrically under nitrogen atmosphere, and found that the percentage of grafting was favored by increasing monomer concentration and reaction time, but was affected by higher concentration of initiator and high temperature. No grafting was observed beyond $45^\circ C$. The graft copolymers were analyzed by infrared spectroscopy. The grafting of MAN onto starch does not alter the thermal stability of starch. The crystalline region of starch was also involved in grafting. Scanning electron micrographs showed a thick polymer coating of grafted PMAN on the starch surface.

The work of Sugahara and Ohta in 2001 [26] also used ceric salt as an initiator in the graft copolymerization of three vinyl monomer species, acrylonitrile (AN), acrylamide (AM), and acrylic acid (AA) onto starch. With the constant concentration of ceric salt, the vinyl monomer activity onto starch decreased in the following order: $AN > AM > AA$.

On the basis of available evidence, one reaction path for ceric ions initiated graft copolymerization is diagrammed in Figure 2.5. After initial formation of 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 initiating graft copolymerization or may loose through further reaction with ceric ion [10].

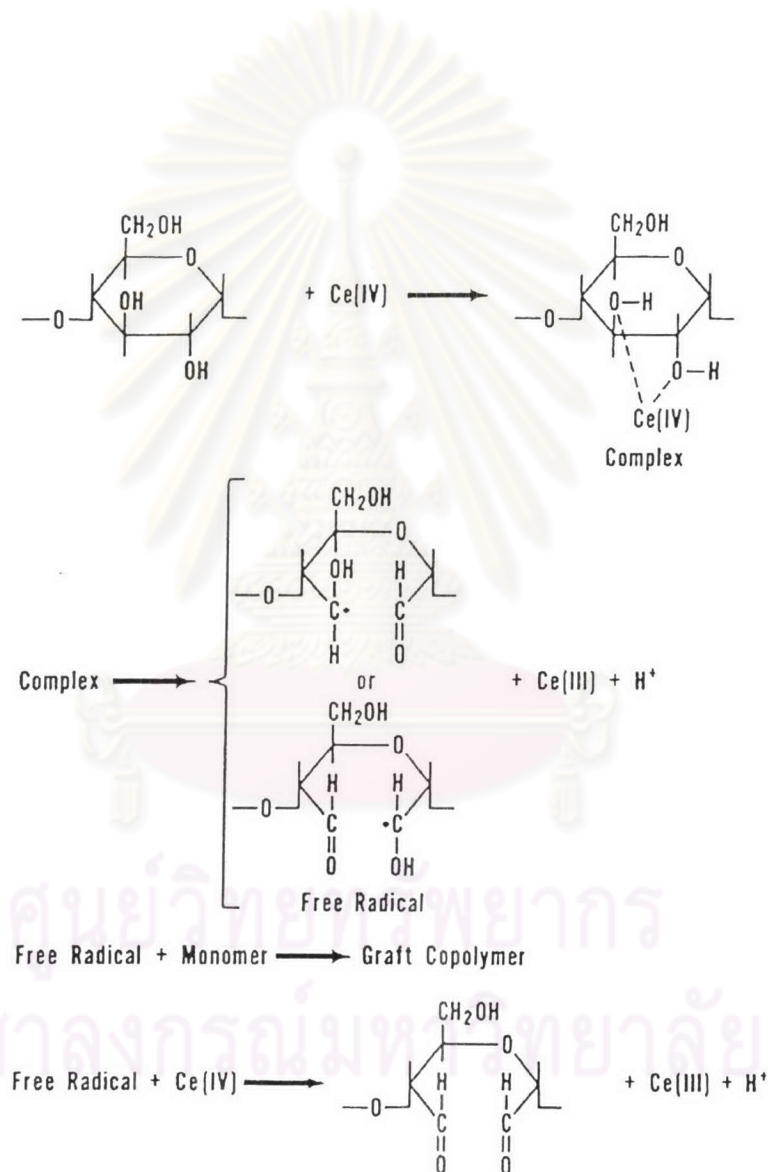
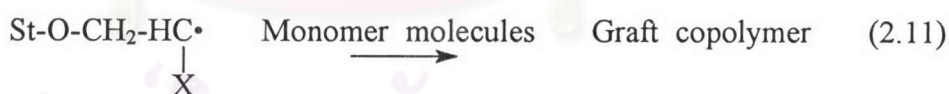
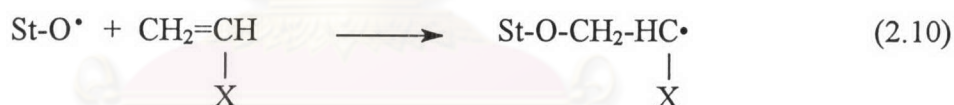
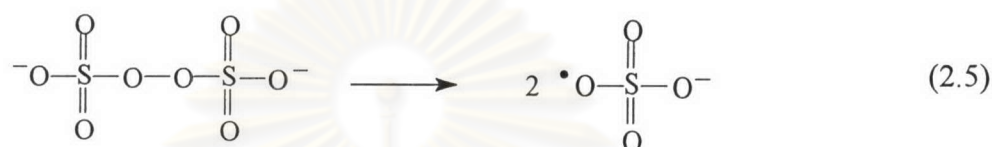


Figure 2.5 Initiation of graft copolymerization by ceric ion [10]

b.) Initiation by Persulfate Groups

Generally, potassium persulfate (PPS) and ammonium persulfate are used as the initiators for graft copolymerization. When an aqueous solution of persulfate is heated, it decomposes to yield sulfate radical anions along with the other free radical species. The mechanism for grafting is as follows [8]:



Where St-OH = starch, R• = HO• and HO₂•

Sago starch-g-PMMA copolymer was prepared by Fakhru'l-razi et al. (2001) [27] in aqueous medium by different initiators of PPS and CAN. When they used PPS as an initiator, the maximum percentage of grafting was 90%. The optimum conditions were at the reaction temperature of 50°C, the reaction time of 1.5 hours, the monomer amount of 47 mmol, and PPS amount of 1.82 mmol. They suggested that this sago starch-g-PMMA may have application as a biodegradable plastic.

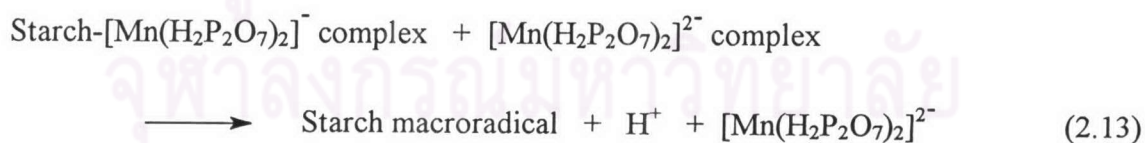
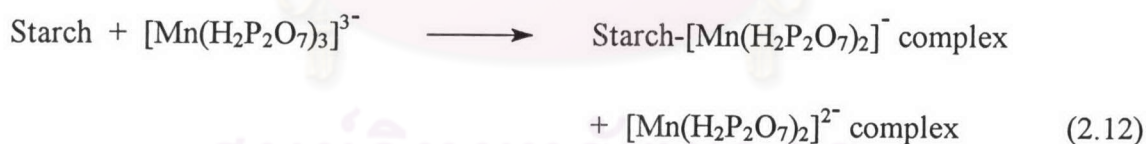
Recently, in the year 2002, PPS was used by Cho and Lee [28]. In their research, they grafted styrene onto native corn starch by emulsion polymerization, using PPS as an initiator, sodium dodecylbenzenesulfonate as an emulsifier, and tetraethylthiuram disulfide as a chain transfer agent. They found that, when the reaction time and the emulsifier concentration increased, the graft percent increased, but when the concentration of chain transfer agent increased, the graft percent decreased. The molecular weight of the grafted polystyrene showed a certain relationship with the variation of the graft percent.

c.) Initiation by Manganese Ions

Mn^{3+} (as manganic pyrophosphate) and Mn^{4+} (as MnO_2 from a $KMnO_4$ -acid system) have been employed for graft copolymerization of vinyl monomers onto starch.

The following reaction mechanism has been presented to account for the synthesis of starch graft copolymers initiated by manganese ions [8].

Initiation



Propagation



Termination

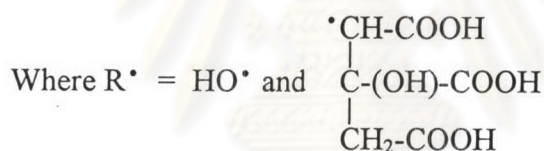
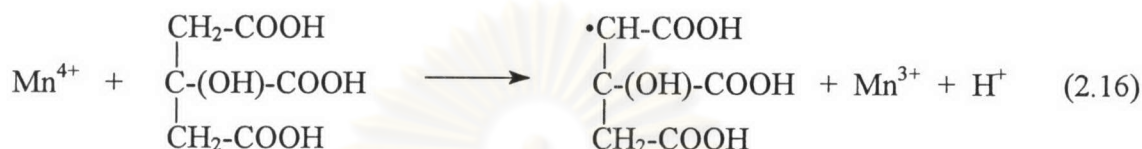


Gao et al. (1994) [29] investigated graft copolymerization of canna starch and MMA monomer initiated by manganic pyrophosphate. They found that manganic pyrophosphate can initiate the reaction efficiently. The percentage of grafting, grafting efficiency, and rate of grafting were all depended on the concentration of the initiator, monomer and starch, as well as reaction time and temperature. From the characteristics of starch-g-PMMA showed that not only the amorphous, but also the crystal phase of starch was involved in graft copolymerization.

For the Mn^{4+} initiator, starch is generally immersed in potassium permanganate ($KMnO_4$) 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 initiation system is to produce starch macroradicals by direct abstraction of hydrogen atom from the hydroxyl groups of starch molecules. In the presence of vinyl monomers, starch macroradicals are added to the double bonds of vinyl monomers, resulting in covalent bonds between the monomers and starch and the creation of free radicals on the monomers (i.e., the chains are initiated). Subsequent addition of monomer molecules to the initiated chains propagates the grafting onto starch. The termination of the growing grafted chains may occur by coupling (combination), disproportionation, reaction with the initiator, and/or chain transfer.

In 1995, Mostafa [30] used $KMnO_4$ /citric acid as the initiators in graft copolymerization of methacrylic acid on starch and hydrolyzed starches. By this system of grafting, he could control the molecular weight of the polymeric backbones of starch and the substituents present on them. The percent solubility of hydrolyzed starches decreased with increasing graft yield. On the other hand, it was found that the copolymers derived from hydrolyzed starches functioned better as the sizing agents than the original starch, hydrolyzed starches lying between the two. So, he suggested that this kind of copolymer could be developed to use for sizing of cotton textiles. Then two years later, in 1997, he used this initiator system again to graft acrylamide onto rice starch and hydrolyzed rice starch on the purpose as a size base material for cotton textiles [31].

The formation of radical in a polymerization system initiated by KMnO_4 in the presence of citric acid seems likely to occur through reduction of Mn^{4+} to Mn^{3+} and/or Mn^{2+} . Thus during grafting of a vinyl monomer such as acrylamide onto starch under the catalytic effect of KMnO_4 in the presence of citric acid, the creation of a primary free radical may be as follows [31]:



The acid and/or hydroxyl radicals attack the starch or hydrolyzed starches to produce starch macroradicals. The latter may also be represented as follows:



Where $\text{St-OH} = \text{starch}$, $\text{St-O}\bullet = \text{starch radical}$

In the work of Gao et al. (1998) [32], they studied the graft copolymerization of starch and AN using KMnO_4 as an initiator. The results indicated that the grafting parameters, such as the concentrations of initiator, monomer, starch, and catalyst acids, all had significant effects on the graft copolymerization and the components of graft copolymers. Moreover, they pointed out that KMnO_4 can be used as a cheap initiator to replace Ce^{4+} salt in manufacturing the starch-g-PAN copolymer, a raw material for water-absorbing materials.

d.) Initiation by Hydrogen Peroxide-Ascorbic Acid

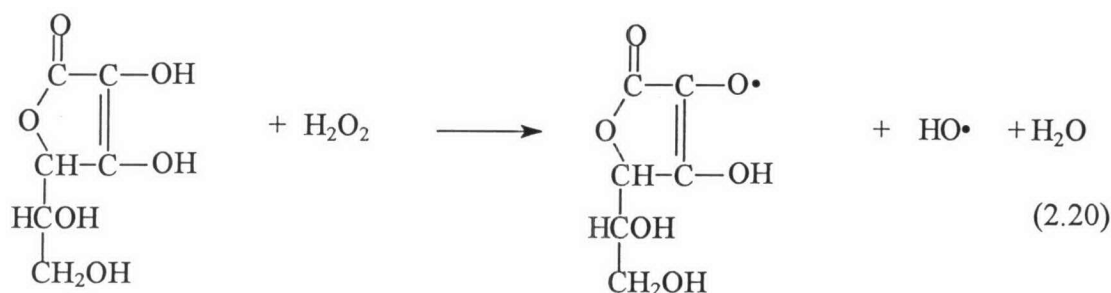
Several researches involving starch graft copolymerization using hydrogen peroxide-ascorbic acid as an initiator system are presented below.

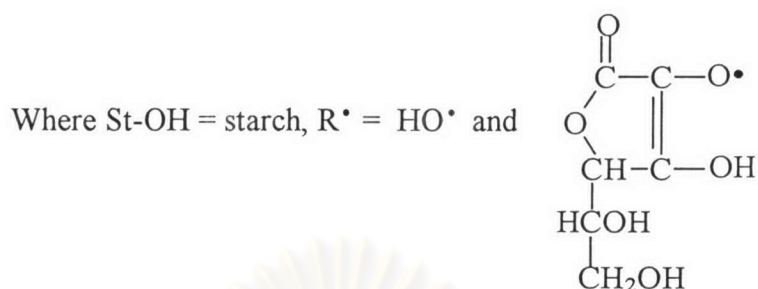
In 1992, Wiwatwarrapan [33] investigated graft copolymerization of acrylic acid onto cassava starch by hydrogen peroxide-ascorbic acid initiation. Prior to the grafting reaction, starch was gelatinized at 80°C. He studied the effects of reaction parameters, such as monomer concentration, initiator concentration, and reaction temperature in the range of 35-65°C. The graft copolymer was then saponified and characterized in terms of weight average molecular weight, and water absorption capacity in distilled water and many types of solutions.

Arayamaythalert (1996) [9] prepared graft copolymers of native cassava starch and acrylic acid. Same as Wiwatwarrapan, Arayamaythalert also used hydrogen peroxide-ascorbic acid as an initiator system. She suggested the application of this starch graft copolymer as a thickener for cotton fabrics printing.

Moreover, in 2000, Limworanusorn [34] prepared a new type of biodegradable superabsorbent polymer by graft copolymerization of acrylic acid/acrylamide onto cassava starch by the initiator system of hydrogen peroxide-ascorbic acid.

This method used ascorbic acid as an accelerator for hydrogen peroxide. The mechanisms of this initiator system are showed below [9]:





Then propagation and termination reactions occur respectively.

e.) Initiation by Benzoyl Peroxide

Benzoyl peroxide (BPO) is one of the initiators which initiation mechanism involving thermal homolytic dissociation. This kind of initiators is widely used as mode of radical generation for initiation. Only few classes of compounds, including those with O-O, S-S, and N-O bonds, possess the desired range of dissociation energies. However, it is only peroxide which are extensively used as radical sources. The other classes of compounds are usually either not readily available or not stable enough.

BPO 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 slightly dissolves in water and dissolves in organic solvents. BPO can be used as a bleaching agent and a drying agent; however, it is usually used as an initiator or catalyst in free radical polymerization [35]. BPO is one type of diacylperoxide, RC(O)OO(O)CR , which decomposes by an initial cleavage of oxygen-oxygen bond. BPO undergoes the initial bond scission (β -scission) as shown in Figure 2.6 with a first order rate constant of $1 \times 10^{14} e^{-29,900/RT} \text{ s}^{-1}$ [36].

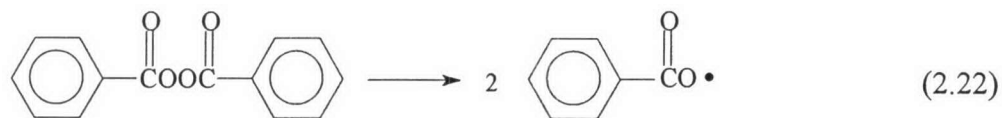


Figure 2.6 Dissociation of benzoyl peroxide [36]

This rate constant indicates the BPO is a useful thermal initiator in the temperature range of 60 to 80°C. Despite the relative low temperature at which this initiator is useful, the benzoyloxy radicals formed by the initial bond rupture may further decompose as shown in reaction 2.23 before they can react with monomer. However, the occurrence of reaction 2.23 has slightly effect on the overall rate of initiation, because the phenyl radicals formed in reaction 2.23 can add themselves to the monomer to bring about the initiation. So that, both benzoyloxy and phenyl radicals are important as initiating species. In solution, there is a small possibility for reformation of BPO (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 reactions of benzoyl peroxide [6].

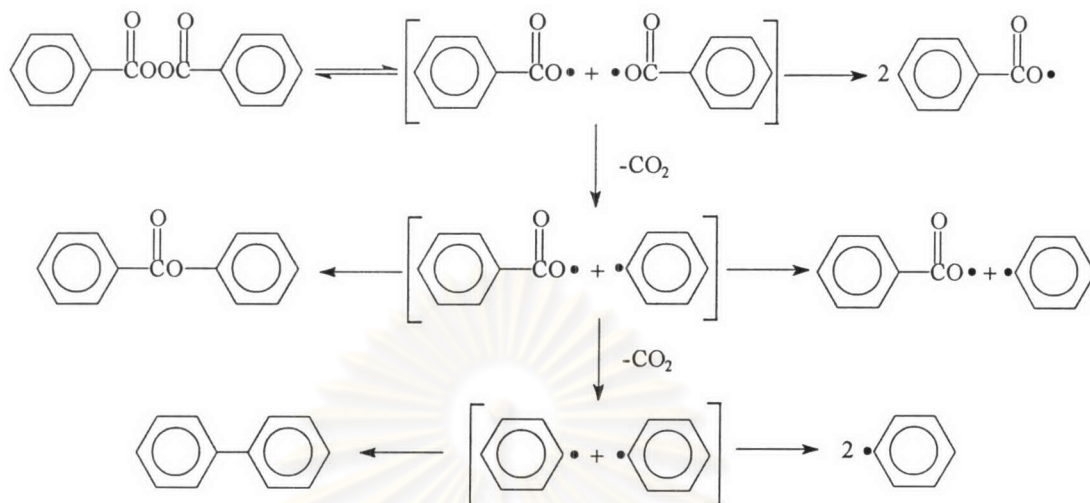


Figure 2.7 Overall dissociation reactions of benzoyl peroxide [6]

Since this work has been focused on graft copolymerization of cassava starch initiated by BPO. Therefore, the research related to this work is reported below.

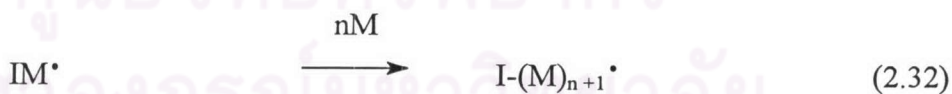
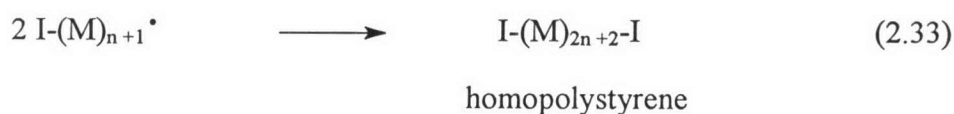
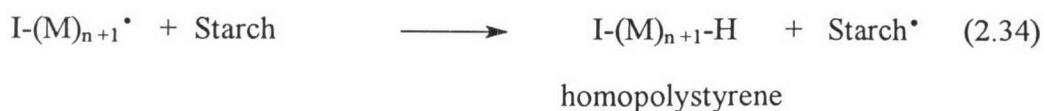
In 2001, Kiratitanavit [37] studied graft copolymerization of cassava starch and styrene monomer using BPO as an initiator in aqueous medium. The influence of the ratio of starch and styrene monomer, the amount and purity of BPO, the mixing method, the reaction temperature and time were studied. As results, the optimum reaction temperature and time were 80°C and 2 hours, respectively. In his report, he suggested the following reaction mechanisms of which starch-g-PS obtained.

Initiation:



Propagation:**Termination:****Chain Transfer Reaction:**

However, the following reactions can occur and this results in the formation of homopolystyrene.

Initiation:**Propagation:****Termination:****Chain Transfer Reaction:**

The crosslinked starch may be possibly formed from termination by combination as showed below.

Termination:



2.3.3 Grafting of PMMA onto Various Polymers

PMMA is general used as a vinyl monomer in graft copolymerizations onto various polymers. Besides this research, some studies about graft copolymerization in which PMMA was grafted onto polymers are reported as follows.

In 1996, Okieimen and Ogbeifun [38] examined graft copolymerization of methyl methacrylate (MMA), acrylonitrile (ACN), and their mixture on carboxy methyl cellulose (CMC). They found that at comparable reaction conditions, the molecular weight of the grafted polymer chains and the frequency of grafting were not of the same order of magnitude. For the monomer mixtures, the copolymer compositions obtained from the total nitrogen contents of the copolymer samples showed that a disproportionately low amount of ACN monomer units were incorporated into the graft copolymer, even at high ACN content of the feed.

Afterwards, in 1999, Thiraphattaraphun [39] studied the grafting of MMA monomer onto natural rubber using potassium persulfate as an initiator. The effects of the initiator concentration, reaction temperature, monomer concentration, and reaction time on the monomer conversion and grafting efficiency were investigated. The grafting efficiency reached a maximum value at initiator concentration of 0.75 phr, reaction temperature was 55°C, and 8 hours reaction time. The morphology of the grafted natural rubber was determined by transmission electron microscopy and confirmed that the graft copolymerization was a surface-controlled process.

Also in 1999, Keles et al. [40] studied the graft copolymerization of MMA upon gelatin using BPO as an organic initiator in aqueous medium. The grafting reactions were carried out within the 65-90°C temperature range, and the effect of monomer and initiator concentrations on the graft yield were also investigated. They found that the maximum graft yield was obtained at a BPO concentration of 0.20×10^{-2} mol/L and the optimum temperature was 80°C. Thermogravimetric analysis showed that the thermal stability of gelatin increased as a result of grafting. Furthermore, such changes in the properties of gelatin-g-PMMA as a density, moisture regain, and water uptake were also determined.

Moreover, in 2000, Bianchi et al. [41] studied the homogeneous grafting of MMA onto methacrylate-modified cellulose (CEMA) using azobisisobutyronitrile (AIBN) as an initiator. Graft copolymerization was achieved by a two-step process at three different reaction temperatures in the range 40-70°C. Grafting yield and grafting efficiency percentage were determined, related to the conditions of synthesis. The role of various reaction parameters on grafting yield and grafting efficiency was also evaluated. They also determined molecular weights of graft PMMA, homoPMMA, and grafted chain of CEMA, utilized to interpret the effect of reaction temperature on grafting yield.

As described earlier, it can be seen that graft copolymerizations have been previously carried out in considerable ways. In this present work, graft copolymerization of MMA onto cassava starch has been studied, using BPO as an initiator. The experiment and the results are reported in the following chapters.