

Chapter 1

Introduction

1.1 Starch

Starch is the reserve carbohydrate of the plant kingdom, where it generally is deposited in the form of minute granules ranging from 1 up to 1,000 μm or more in diameter [1]. These granules are mainly deposited in the seeds, tubers, or in the roots of plants. Starch is produced commercially from corn, wheat, rice, tapioca (cassava), potato, and other sources. For cassava starch, the size of the granule ranges from 5 to 35 μm [2].

With regard to the cassava plant, it originated in South America where its tubers have been used through the age as a basic food. From there it spread to Asia and Africa, where main areas of cultivation are Brazil, Nigeria, Ivory Coast, Indonesia, Malaysia, Thailand, Philippines, India, and Taiwan. Thailand ranks ninth in the world as a producer of cassava roots and is the world's largest exporter of cassava products [3].

Previously, tapioca grew mainly in south eastern region of Thailand. At present, tapioca grows throughout the country, particularly in Korat and Buri Ram in the

northeastern region; Prachin Buri and Aranpradet in the east; Uttaradit and Phetchabun in the north; Kanchanaburi and Suphanburi in the west; and finally Phetchaburi, Surat Thani, and Songkla in the south [4].

Today, 95% of cassava is used directly as human food, and as animal food as well. To the starch industry, cassava is used as a sizing agent in textile; and in the paper and adhesive industry.

Chemically, starch is a polymeric carbohydrate consisting of α -D-glucopyranosyl units (often called anhydroglucose units, or simply AGU), linked together primarily through α -D-(1-4)glucosidic bonds. Although the detailed fine structure has not been fully elucidated, it has been established that starch is a heterogeneous material consisting of two major types of polymers: amylose and amylopectin.

Amylose is essentially a linear polymer in which the anhydroglucose units are predominantly linked through α -D-(1-4)glucosidic bonds as shown in Figure 1.1. Its molecular size varies depending upon the plant source and processing conditions employed in extracting the starch. It may contain anywhere from about 200 to 2,000 AGU [1]. The average molecular weight (MW) of amylose is about 250,000 [5]. It behaves as a random coil or double helix in aqueous solution. The level of amylose found in starch varies depending upon the starch source and harvesting

period. Most starch such as regular corn, wheat, potato, and cassava contains about 18 to 28% amylose [1]. For cassava starch, the amylose content is about 16.5-22% [6].

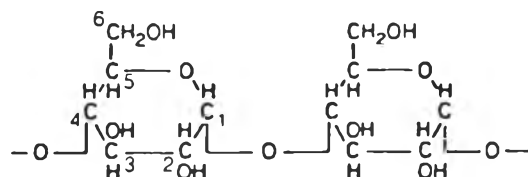


Figure 1.1 Chemical structure of amylose.

Amylopectin, on the other hand, is a branched polymer containing, in addition to AGU linked together as in amylose, periodic branches at the carbon-6 position. These branches are linked to the carbon-6 by the α -D-(1-6) glucosidic bonds. Each branch contains about 20 to 30 anhydroglucose units [1]. A schematic diagram of the amylopectin molecule is shown in Figure 1.2.

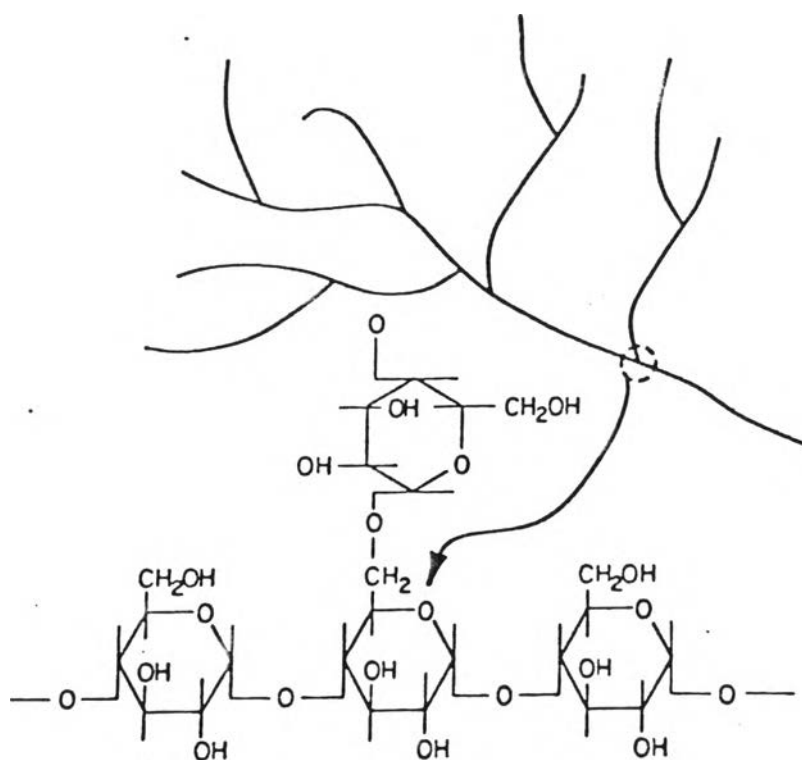


Figure 1.2 Chemical structure of amylopectin

Amylopectin is a large branched molecule, ranging from 50 million to over 100 million in MW [5]. In most cases it is much larger than amylose. The large size and branched nature of amylopectin reduce the mobility of the polymers and interfere with any tendency for them to become oriented and packed closely enough to permit significant levels of hydrogen bonding.

1.2 Gelatinization Phenomena

Starch in the granule state is virtually insoluble in water at ambient temperature. When an aqueous starch suspension is heated, the granules first slowly and reversibly take up water with limited swelling, and then they lose their birefringence and undergo irreversibly a sudden rapid swelling, as hydrogen bonds between individual starch molecules are broken. As a result, starch forms a continuous system, referred to as starch paste. In this paste there is a mixture of hydrated and swollen granules, and granule particles, held together by a typical maze of associative forces [7]. The temperature at which the granules lose their birefringence is known as the gelatinization temperature [8]. The gelatinization temperature varies with the type of starch. It can vary between 40 to 75 °C.

1.3 High water-absorbing polymer

In recent years, considerable research has focused on the development of high water-absorbing polymers (HWAP or superabsorbents) for agricultural applications [8-12]. These materials can be a synthetic copolymer, or a biodegradable starch-based graft copolymer. In deionized water, 1 g of dry HWAP will absorb several hundred grams of water within a few minutes. The polymer does not dissolve, but remains as a highly swollen gel. They have already been used as soil additives or ameliorants and as seed and root coating

material. For example, when a seed is coated with HWAP, the particles stick to the seed wall. These particles then absorb water in the liquid or moisture form, a few hundred times their dry weight and form a gel at the surface which softens the seed wall and accelerates germination. Virtually all water held in the swollen gel is available to the seed and emerging root plant, and the holding water is released into the soil as a function of water stress. Ready availability of water further acts to promote optimum growth since the water is available to the emerging seedling as needed. Accelerated emergence minimizes the possibility of the plant being entrapped by crusting, roots grow rapidly, penetrating into deeper soil where moisture stress is less likely than at the surface. Root coating, on the other hand, is a means to prevent transplant shock after the seedling is taken out of the soil, The roots are dipped into a gel solution before being transited to the planting site.

HWAP can also be mixed with soil. Once the growing medium and the correct quantity of copolymer have been mixed and sufficiently watered, the polymer granules transform themselves into water-laden gel chunks. These gels then act as local reservoir, releasing water to the soil and plants as needed and maintaining an even moisture balance. This prevents over-watering because excess of water can be absorbed for later use. Similarly, the danger of too little watering is reduced since the available water capacity of the growing medium is increased. HWAP increases the

available water holding capacity by more than 50%. Water consumption is therefore reduced as less water percolates through the soil and evaporation losses are drastically lowered. Thus the soil quality is improved and watering frequency is reduced. HWAP does not only protect plants against water stress but also helps improve air capacity of the growing media and produces healthier root systems. In summary, these superabsorbents have been proven to retain soil nutrients, promote germination, speed up emergence, provide more uniform stands, and increase the yields of crops such as wheat, oats, sunflower beans and soybeans. Their attractive properties make them excellent materials for agriculture, arboriculture and horticulture in the semi-arid region of the northeast of Thailand.

Other important applications of HWAP is in disposable soft goods designed to absorb body fluids such as adult incontinent pads, hospital underpads, feminine and sanitary napkins and baby diapers. They have also been used as a thickener as investigated by Taylor and Bagley et al. [13].

High water-absorbing polymers can be made by modification of starch and cellulose [14-18]. The alteration of the chemical and physical structure of these compounds can be done by grafting a petroleum derived monomer onto the polysaccharide chains to form a graft copolymer. The grafted material can either be synthesized by a free-radical or anionic reaction process, with

monomers such as acrylonitrile, acrylamide, acrylic acid and vinyl acetate. For example, acrylonitrile graft copolymerizes readily to starch at a high grafting efficiency in the presence of a free radical initiator.

The most widely used method of free radical initiation of starch is the reaction with cerium (IV) formed by dissolving ceric ammonium nitrate in dilute nitric acid. This method has been widely used to graft copolymerize a number of monomers onto polysaccharides [8, 14, 16, 17]. The initiation, propagation, and termination mechanism by the ceric ion [8] is illustrated in Figure 1.3.

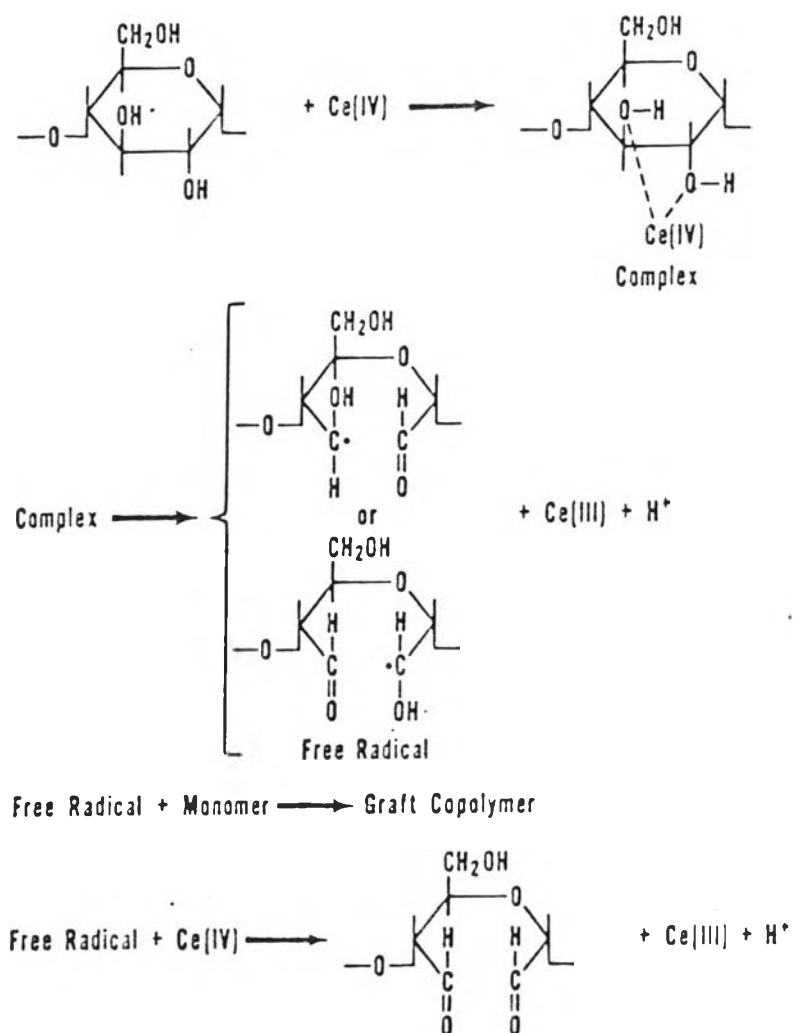
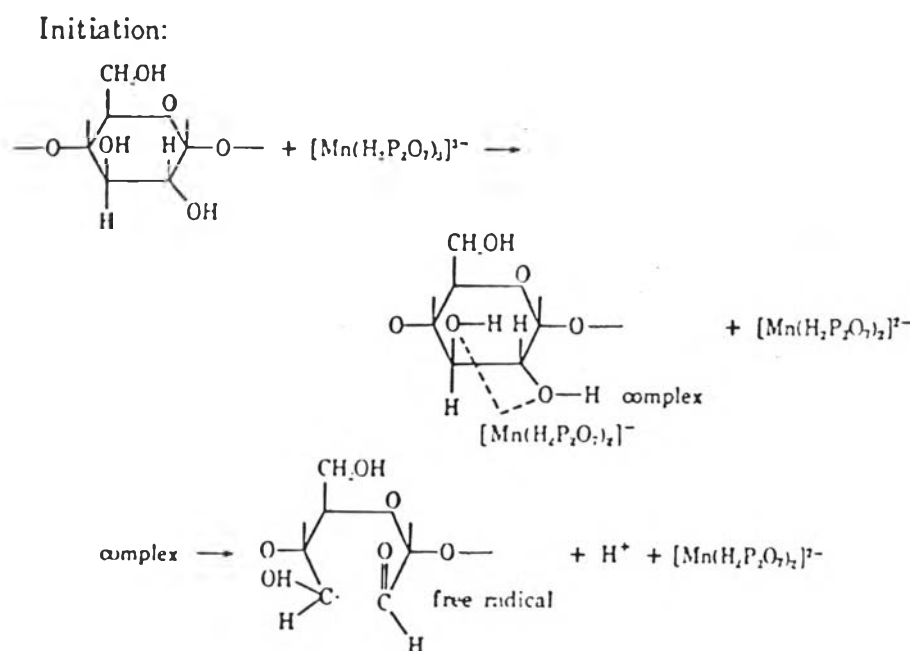


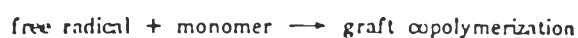
Figure 1.3 Reaction scheme to synthesize starch-g-PAN by Ce (IV)

The use of trivalent manganese as an initiator has also been reported [20-23]. Mehrotra and Rånby [20] have suggested that the mechanism of initiation (similar to that proposed for the ceric ion initiation), is the cleavage of glycol groups of the anhydroglucose units by the manganic pyrophosphate as shown in Figure 1.4. The manganic pyrophosphate ion forms a complex with the starch, probably

at the C_2 and C_3 hydroxyls, which then causes one of the hydrogen atoms on C_2 or C_3 to be oxidized while the manganic pyrophosphate ion is reduced and a free radical is formed on the starch at the C_2 or C_3 carbon atom. The bond between C_2 and C_3 is then broken with the formation of an aldehyde group on the C_2 or C_3 , which does not have the free radical form. It has been concluded that both C_1-C_2 glycol end group and C_2-C_3 glycol groups along the polysaccharide chains form reactive grafting sites [24]. The free radical formed then reacts with the monomer to form a starch grafted copolymer.



Propagation:



Termination:



Figure 1.4 Glycol cleavage mechanism with Mn^{3+} ion leading to initiation of graft copolymerization

Graft copolymerizations have, for the most part, been carried out in water with either granular, unswollen starch or with starch that has been gelatinized by heating [20-23]. Although gelatinization swells and disrupts starch granules, the polysaccharide is still largely insoluble in the aqueous medium, and grafting can thus be viewed as taking place onto an insoluble substrate. Past work by Rånby and coworkers had been done on the dependence of the graft copolymer structure on starch pretreatment [22-23]. They reported that gelatinization gave an increase in the MW of PAN, and a corresponding decrease in the number of grafted branches (larger number of AGU per graft), as compared with the polymerization carried out with granular starch.

If starch-g-PAN is saponified with either NaOH or KOH solutions at temperature near 100°C, nitrile groups are converted into a mixture of carboxamide and alkali metal carboxylate, with ammonia being a by-product. The alkali metal carboxylate to carboxamide ratio will vary depending on saponification conditions, but are typically on the order of 2:1 [25]. These two groups induce an osmotic effect which gives the material water absorbing properties.

1.4 Research abjective

Investigations on grafting of acrylonitrile onto starch have been done by using potato, wheat, rice and corn starch [9, 14, 19-25, 26, 27], but so far no such grafting

reaction has been performed on cassava starch. Thailand being one of the largest cassava producer in the world, her production, however, exceeds the country's consumption and export, thus leaving every year an excess of unused cassava going to waste. In this context, cassava can become an excellent raw material for the development of biodegradable superabsorbent in Thailand. HWAP is no new product and exists already on the market in industrialized nations; but manufacturing it by buying the foreign patent could be very costly. In view of this background the purpose of this research is to develop HWAP in Thailand which could revolutionize the growing industry in the northeastern region, with cassava starch being the raw material for the synthesise of starch-g-PAN.