CHAPTER I

INTRODUCTION

1.1 Introduction

In recent years, a considerable amount of research by polymer scientists has focused on the development of high-water absorbing polymers for their applications to agriculture, horticulture, and arboriculture. Also termed superabsorbents, these materials can be starch-based which is biodegradable and lasts only about one year. They can also be synthetic-based from petrochemicals which is non-biodegradable and has an absorption efficiency of four years or even longer.

The application of superabsorbent polymers to agricultural development especially in the arid rural areas where water is scarely available, has provided a very strong impact on the socioeconomic revolution. In fact, the physical properties of such superabsorbents are indeed very attractive to farmers and reforesters. When sufficient water is in contact with the superabsorbent granules, they transform themselves into water-laden gel chunks. These gels act then as a local reservoir, releasing water vapor into the soil and plants as needed and also maintaining an even moisture balance. These materials improve the available water holding capacity by up to 50%, thus reducing water consumption in an ordinary way. In addition, these superabsorbents also prevent the leaching of nutrients as well as generate more nutrients within the soil to seeds which make them the faster germination, promote earlier emergence, improve stand and give greater crop yield. In transplanting applications, coatings of superabsorbents to bare roots of vegetables, trees, ornamentals, seedings and so on, prior to transplanting help prevent roots from drying, reduce wilting, prevent transplant shock, increase plant survival by decreasing recovery time and improve root development.

Besides, the removal of suspended water from organic solvents is an important potential use for superabsorbent polymers. Its uses as a dehydrating agent for ethanol-gasoline mixture to avoid the azeotropic distillation step that is necessary to remove final traces of water from ethanol has been carried out. It can also be used to absorb water from aqueous solution of polymer, such as proteins, in order to concentrate the polymers under mild concentrations.

In coal mining, the addition of high water-absorbing polymer will wet powdered coal to improve its flow by absorbing water and eliminating moisture-induced blockages. To wet fuel oil, it stabilizes the mixture and retards settling until it can be burned.

High-water absorbing polymers are now being sold as a thickener for water that is dropped by air onto forest fires, since thickened water clings more tenaciously to the combustible foliage and is held above ground where it can do the most good. It is also used as a thickening agent for electrolyte system in alkaline-type batteries.

It is being marketed as an agar substitute for the propagation of plants by tissue culture procedures. Films made from mixtures of this compound and poly(vinyl alcohol) have been tested as composite membranes for molecular separation.

For personal care and medical application, the largest volume use of starch-based superabsorbents is in disposable soft goods designed to absorb body fluids such as adult incontinent pads, hospital underpads, and feminine napkins. In wound dressing, it readily absorbs blood, serum and pus and thus helps promote wound healing and develop a cleaner bed of granulation tissue (1).

1.1.1 Scientific and Technological Rationale

To function as a high-water absorbing polymer for aqueous fluids, a polymer must have certain properties (2):

(1) It must be hydrophilic.

This is a primary prerequisite for water absorption. For example, many, if not most of the superabsorbents reported in the patent literature, contain polymerized acrylamide, acrylic acid, or acrylic acid salts.

(2) The polymer must swell in aqueous fluids, but must not dissolve.

In most instances, this requirement dictates that some crosslinkings take place either during polymerization or after the polymer is prepared. In the preparation of polysaccharide grafted copolymers, crosslinker, can in many cases, excluded because:

a) Some crosslinking often occurs naturally during the graft copolymerization process.

b) Hydrogen bonding between polysaccharide chains prevents the graft copolymer from dissolving.

Crosslink density is a critical factor in determining properties of the superabsorbent. Too little crosslinking will produce a soft, loose gel and excessive water solubility, whereas too much crosslinking reduces polymer swelling to the point where little fluid is absorbed.

(3) Although it is not a steric requirement, absorbents should have some ionic character, since charge repulsion is an important factor in promoting polymer swelling in aqueous fluids.

Superabsorbents or high-water absorbing polymers are those derived from biomaterials which can be made from starch and cellulose. The alteration of the structure of polysaccharides has been extensively investigated which has led to copolymers with novel properties. They can be prepared by graft copolymerization of vinyl monomers initiated either by certain metal ions such as salts of cerium (IV), magnesium (III), ferric (III), etc; or by radical initiators such as benzoyl peroxide, ferrous ammonium sulphate-hydrogen peroxide, hydrogen peroxide-ascorbic acid; or by gamma radiation.

Polysaccharides are mainly found in potato, corn, wheat, and tapioca. Starch, in the form of minute granules ranging from 1 to 1,000 micrometres, are mainly reserved in seeds, tubers, roots of plants. Cassava starch is a native natural reserve carbohydrate, previously grew abundantly in South-eastern region of Thailand. At present, cassava has been grown throughout the country, particulaly in Korat and Buri Ram provinces in the northeastern region; Prachin Buri and Aranpradet in the east. In the northern region, it is found in Uttaradit and Phetchabun provinces; and Kanchanaburi and Suphan Buri in the west. It is also found in the South mostly in Phetchaburi, Surat Thani and Songkla provinces (3).

1.1.2 Cassava Production in Thailand

Cassava, a tropical root crop, ranks as the seventh largest staple food in the world. The crop is called by various common names in different parts of the world, but all apply to the one species, Manihot esculenta

Crantz. The names most frequently encountered are "cassava" in English-speaking tropical areas, "yuca" in Spainish-speaking areas, and "manioc" among French-speaking peoples. Tapioca, one of the products manufactured from the roots, is sometimes used as a common name.

Cassava was first grown in Southern Thailand some time around 1850, primarily for human consumption. It has become quite popular in the Eastern Seaboard provinces only during the past 40 years. Cassava growing has spread during the past fifteen years to provinces in the Northeastern, Western and upper Central parts of Thailand (4). The total area planted has increased from 240,000 rais (384 millions metre square) in 1957 to 10.1 million rais (16,160 million metre square) in 1989 (5). Output increased from 420,000 tons in 1957 to 24.2 million tons in 1989. The rapid expansion was due to the increasing demand for tapioca pellet exports and the advantages in cassava production. The main attributes which favor the production of cassava are as follows :

1. It is easily and cheaply propagated. Seeds or roots are not required; propagation is simply a matter of planting stalk cuttings, which have no other economic value.

2. It is relatively high-yielding.

3. It is relatively inexpensive to produce. It is easily planted and harvested and requires little or no weeding because of its leafy canopy. It does not have a critical planting or harvesting time; hence, it is not

season-bound.

4. It is a good risk-aversion crop; its hydrocyanic acid content makes it subject to minimal animal and pest attacks; it is capable of growing on soils often considered too poor for other crops.

5. It is a reliable staple and an excellent producer of carbohydrates.

The local cassava market is relatively simple. The cassava growers sell their cassava roots either to tapioca factories or to middlemen. The tapioca factories can be divided into 2 categories: those processing tapioca products for animal feed and those producing tapioca products for human consumption and industrial use.

The first category processes fresh roots into chips, meal, and pellets. Among these, the chips factories are numerous because their operation needs only simple machinery, mainly cutters. This machinery is mostly made locally. After cutting, the only process left is sun drying. The dried chips are sold to pellet factories, where they are ground and further processed into pellets by either local- or foreign-made pelletizing machines. Pellets are sold to exporters in Bangkok.

The second category of factories processes fresh roots into tapioca starch or flour. This involves grinding fresh roots and then separating sap from the dregs (waste). Sap is then further separated into fluid and wet starch.

The wet starch is dried and then ground finely once more before being packed. The starch or flour is sold to exporters or wholesalers in Bangkok. The waste is dried and sold to animal feed factories (pelletizers).

Most of the flour factories and chip producers are scattered throughout the cassava production area, while the pelletizing factories are mostly close to large towns. However, some big chip producers in production areas are installing small, locally-made pelletizing machines in their plants.

Cassava production initially was for domestic consumption. Shortly after the Second World War, modern processing machinery became available to process cassava into tapioca starch or flour. Tapioca flour was then exported to the United States for use in the paper and textile industry, with a small proportion going to human consumption. Tapioca flour competes with maize or corn starch in the U.S. market.

After 1973, Japan became the most important importer of Thai tapioca flour. Of the total volume of Thai tapioca flour exported, 42 percent in 1973 and 47 percent in 1977 were exported to Japan.

In 1956, Thai tapioca products for animal feed were introduced into the European animal feed market by European importers. This market developed rapidly and successfully into a very important market for Thai tapioca products. The trade started with the export of tapioca waste from starch manufacturing, shifted to tapioca chips and then after 1967 shifted to pellets. The pellet manufacturing followed the introduction of a German pelletizing plant in Thailand. Ease in handling, and shiping of pellets compared to chips and waste facilitated the rapid growth in pellet production. This coincided with the growth in the EEC animal feed market. The animal feed export market of Thailand expanded from 17.7 percent of total value of Thai tapioca export to 89.49 percent in 1976. Out of the total quantity of tapioca products imported into the EEC, 76 percent in 1962 and 81 percent in 1975 were imported from Thailand.

Area planted and root production of cassava fluctuated from 7.7 million to 10.1 million rais (12,320 million to 16,160 million metre square) and 15.2-24.3 million tons in 1981-1990, respectively. The 10-year average yield was 2.026-2.985 tons per rai. The average cassava production cost fluctuated from 856.71 to 1,041.97 Baht per rai or 0.39 to 0.46 Baht per kg in 1984-1989. The cassava farm price fluctuated from 0.40 to 0.89 baht per kg in 1981-1990.

The main use of cassava is for both human food and animal food. To the major industrial applications, it is used as a sizing agent in textiles, paper and adhesive industries. To the minor industrial uses, it is used as a thickening agent in construction, mining and petroleum exploration.

Thailand ranks ninth in the world's producer of cassava roots and is the world's largest exporter of cassava products. The value of cassava products export is increased from 14,966.9 million Baht in 1985 to 23,974.8 million Baht in 1989. Quite often, the production of cassava starch exceeds the export and consumption scale which make the country too much surplus and unused cassava. This situation forces the cassava starch to go into vain and is usually destroyed in order to keep the stable pricing of the product (6).

1.2 Objectives

The objectives of this research are the following:

1.2.1 To develop a suitable synthesis technique of HWAP in a form of hydrolyzed starch-g-poly(acrylic acid) copolymers by using a hydrogen peroxide-ascorbic acid initiator system.

1.2.2 To study and develop a suitable technique for measuring the water retention capacity of the material, as well as in conjunction with other chemical environments.

1.3 Expected Benifits Obtainable for Future Development of the Research

Most soils in the Northeast are infertile since they produce low crop yields. Furthermore, crop production is unstable because of the erratic nature of the rainfall of the region. On the other hand, one of the major limiting factors of soils in the Northeast is the low water holding capacity which is mainly due to low organic matter and clay contents (see the details in Appendix A). The most practical means to increase water retention capacity is to add organic matter. Because it gives plants nutrients as well as increase soil aeration and water absorption. "Low-input technologies" employed are basically to sustain the soil condition and crop production. Some researchers have been trying to introduce "high-input technologies" such as adding high-water absorbing polymers together with chemical fertilizers to improve the water holding and fertilizer retention capacities of sandy soils. The benefits for the future development are:

1.3.1 To transfer, possibly, this technology (further developed) to some local industry for a large scale production of cassava starch-based high-water absorbing polymer.

1.3.2 To obtain a low cost and applicable cassava starch-based high-water absorbing polymer used in agricultural and other purposes.

1.3.3 To decrease the import of such a type of material so as to save the Country's foreign currencies.

1.3.4 To use the surplus cassava starch as to save the pricing of the crop and to add more values to this crop as well.

1.4 Scope of the Investigation

Graft copolymerization of acrylic acid onto cassava starch via the hydrogen peroxide-ascorbic acid initiation is a relatively low cost procedure and lesser toxic chemicals such as initiator residues are retained. The appropriate techniques is practically not thoroughly known in the field. In order to discover the technology, the necessary procedures to achieve the suitable product for an agricultural application is as follows:-

1.4.1 Literature survey and in-depth study of this research work.

1.4.2 Preparing graft copolymerizations of acrylic acid onto cassava starch via the hydrogen peroxide-ascorbic acid initiation, by studying the following parametres so as to select the suitable technique and to attain the appropriate reaction conditions:

a) The optimum ratio of starch(g)/AA(M);

b) The optimum quantity of hydrogen peroxide concentration (M);

c) The optimum reaction temperature ($^{\circ}$C).

1.4.3 Bringing the graft copolymers obtained from the reaction to further characterization steps:

a) Saponification of the starch graft copolymers;

b) Determination of average-molecular weights of the grafted polyacrylate;

c) Studying the water absorption capacities of the saponified starch-g-poly(acrylic acid) copolymers in deionized distilled water and selected solutions of: sodium chloride, magnesium chloride, ammonium chloride, dibasic ammonium phosphate, potassium chloride, potassium phosphate tri-hydrate.

d) Determination of water retention capacities of sand and the mixture of sand and various amounts of the saponified cassava starch-g-poly(acrylic acid) copolymers obtained.

1.4.5 Summarizing the result and writing up the report.