#### 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 polymer for their applications to agriculture, horticulture, and arboriculture. Also termed superabsorbents, these materials can be starch-besed 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 capecity 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 hydrolyzed starch-g-polyacrylonitrile. 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 waterabsorbing 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 polymer is 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

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 copolymer 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; 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 micrometers, are mainly reserved in seeds, tubers, roots of plants. Cassava starch, a native natural reserve carbohydrate, previously grew abundantly in South-eastern region of Thailand. At present, cassava has been grown thoughout the country, particulally 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 (2).

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. 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 (3).

# 1.1.2 Geographical and Economical Background Leading to This Research

The Northeast of Thailand is the region of the Country covering about 170,000 square kilometers which is one-third of the Country. It comprises 17 provinces with a population of 19 million constituting over one-third of the total population. It is surounded by hills of approximately 400 meter high in the south and by mountains of 1,300 meter hight in the west with the Mekong River as a border with Laos in the north and east. The Korat Triangle, an area in the center of the region, is a plateau which slopes gently to the southeast and drained by the major rivers, the Chi and Mun (4).

The main problems in this region are rainfall, land form and soil.

#### a) Rainfall

The rainfall characteristics are dominated by the southwest monsoon from the Indian Ocean and tropical cyclones from the South China Sea. The rainy season normally starts from May to October with a maximum annual rainfall about 1,400 millimeters. The distribution of

rainfall varies from above 1,400 millimeters to the north and east, below 1,200 millimeters to the west, and between 1,200 to 1,400 millimeters within the central area. These zones suffer from quite a large number of drought days on an average of 80-100 days. More importance of the main characteristics of rainfall in the Northeast is its high irregularity.

#### b) Landform

There are 5 types of landform: flood plain, low terrace, middle terrace, high terrace, and hill. The flood plains occur along the river each year by the overflowing of the river banks. Most of the soils belongs to the great group Ustifluvents and Tropaquepts. The low terraces are at a slightly elevation than the flood plains so they are rarely flooded. These soils are at mostly Paleaquults, which are poorly drained and only suitable for rice production. The middle and high terraces are also known as non-flood plains which are undulating areas. The soils in the depression usually belong to the great group Paleaquults and are used for rice crop. These soils usually have low fertility and low water holding capacity. Hills of the Northeast are protected as forest reserves.

#### c) Soils

According to the important physiographic position in the Northeast, the properties of soil can be

divided into the following categories:-

- 1) Phimai soil represents soil on the flood plains.
  - 2) Roi Et soil represents the low terrace.
  - 3) Korat soil represent the middle terrace.

Phimai soil has very high clay content while the terrace soils are extremely sandy. Due to its high clay content, Phimai soil has a higher cation exchange capacity (CEC) and also higher base saturation than the terrace soils. Soils are usually acidic with pH about 5 or less, so aluminium toxicity is a common problem. In general, soils in the Northeast are not fertile partly due to their parent materials being sandstone which has low inherent fertility.

The water holding capacity of soils in the Northeast is generally low because the organic matter and clay contents are very low. Erratic rainfall together with low water holding capacity of soils often creates water stress affecting the stability of rice production as well as other crops.

#### d) Farming in the Northeast

Farming in the Northeast are crops based on rice as the subsistence and field crops as cash crops. Soil have profound effects on the productivity or crop yield, and stability of the Northeast farming systems. The generally low fertility of the soils results in low crop productivity

while the erratic rainfall leads to the instability of rice fields.

Rice production is the center of the Northeast farming systems around which other activities, such as field-crops and animal production and various social activities, revole. The four most important crops are cassava (10%), corn (6%), kenaf (3%), and sugarcane (1%). Rice is grown mostly on the so-called "low land" which are flood plains and low terrace because water accumulation in paddy field is required for rice growth. Field crops generally occupy the upland areas to paddy fields, the so-called "upper paddy field", apparently because of increasing population pressure.

In an attempt to adapt to unfavorable growing conditions of upper paddy land, farmers grow short-duration varieties of rice in order to fully utilize the short period of water accumulation in the upper paddy fields. Some farmers try to improve their rice-based cropping system by incoporating field crops into system before and after rice plantation.

# e) Crop Yield and Improvement

The average rice yield in Northeast is less than 2 tons a hectare, which is the lowest in the Country. Farmers use very little chemical fertilizers because of the expensive price relative to the income from their crops. Animal manure, and other organic residues such as rice

straw, ash from rice husks, and corn stover are normally applied to soil so as to maintain and increase the soil fertility. Wherever crops are grown in rotation, fertilizer are applied to the high-value cash crops such as water melon and tobacco.

In conclusions, 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. 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.

## 1.2 Objectives

The objectives of this research are the following:

1.2.1 To develope a suitable synthesis technique of HWAP in a form of hydrolyzed starch-g-polyacrylonitrile by

making use of nuclear technology.

- 1.2.2 To decrease a large amount of homopolymer to a acceptable level.
- 1.2.3 To study and develope 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
- 1.3.1 To transfer, possibly, this technology (further developed) to local industry for a large scale production of cassava starch based high-water absorbing polymer.
- 1.3.2 To obtain low cost and applicable cassava starch based high-water absorbing polymer uses in agricultural and other purposes.
- 1.3.3 To decrease the import of this material so as to save the Country's foreign currencies.
- 1.3.4 To use the surplus cassava starch to save the pricing of the crop and to add more values to this croup as well.

## 1.3 Scopes of the Investigation

Graft copolymerization of acrylonitrile onto cassava starch via gamma radiation is a relatively new idea, the appropriate parameters are theoretically not thoroughly known in the field. The necessary procedures to achieve the best product may be as follows:-

- 1.3.1 Literature survey and in-depth study of this research work.
- 1.3.2 Preparing graft copolymer of acrylonitrile onto cassava starch via gamma radiation by 2 techniques, simultaneous radiation, and preirradiation techniques by changing the following parameters so as to selection the suitable radiation technique and to attain the appropriate reaction condition:
- a) Investigation of a suitable materials to be used in the presence of gamma irradiation to reduce the homopolymer formation: several of which would be tried such as Mohr's salts, lead nitrate, and a thin piece of aluminium foil, etc.;
  - b) The optimum quantity of total dose (kgy);
- c) The optimum quantity of dose rate (gray/min);
  - d) The optimum ratios of starch(g)/AN(ml);
- 1.3.3 Extracting the homopolymer (polyacrylonitrile) of the crude product.

- 1.3.4 Bringing the graft copolymer obtained from section 1.3.3 to further characterization steps:
  - a) Saponification of starch graft copolymer;
- b) Determination of percent add-on of the graft copolymer;
- c) Determination of percent conversion of the monomer;
  - d) Determination of the homopolymer formation;
- e) Determination of grafting efficiency of the grafted polyacrylonitrile;
- f) Determination of the viscosity average molecular weight ( $M_{
  m V}$ ) of the grafted polyacrylonitrile;
- g) Determination of grafting frequency (AGU/chain) of the graft copolymer;
- h) Determination of grafting ratio of graft copolymer;
- i) Studying the absorption capacity of the saponified starch-g-polyacrylonitrile in distilled water and selected solutions: sodium chloride, magnesium chloride, ammonium chloride, dibasic ammonium phosphate, potassium chloride, potassium phosphate tri-hydrate; and this graft copolymer mixed with sand.
  - 1.3.5 Summerizing the result and preparing the report.