CHAPTER I

INTRODUCTION

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 scarcely 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 improving root development.

Besides, the removal of suspended water from organic solvents is an important potential use for hydrolyzed starch-g-polyacrylonitrile. It is used 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. It can also be used to absorb water from aqueous solution of polymers, 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 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 the 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 separations.

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 feminime 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. Scientific and Technological Rationale

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

1.1. 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.

1.2. 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.

1.3. 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 as described above 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), manganese (III), ferric (III), etc; or by radical initiators such as benzoyl peroxide; or by radiation from Co^{60} source.

Polysaccharide is mainly found in potato, corn, wheat, and tapioca. Starch, in the form of minute granules ranging from 1 to 1,000 micrometers, is mainly reserved in seeds, tubers, roots of plants. Cassava starch, a native natural reserve carbohydrate, grows abundantly throughout Thailand. 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, in paper and adhesive industries. To the minor industrial use, it is used as a thickening agent in construction, mining and petroleum exploration.

The production of cassava starch in Thailand exceeds the export and consumption scale which cause 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. Extensive work has been reported for the chemical copolymerization of monomers to starch. However, less data are available for the corresponding radiation induced process, particularly the effect of additives on the efficiency of the reaction. It is the purpose of this thesis to discuss the effect of additives in this radiation induced grafting on enhancing graft and minimizing homopolymer.

Objectives

The objectives of this research are the following:

1. To develop a suitable synthesis technique of high-water absorbing polymer (HWAP) in a form of hydrolyzed starch-g-polyacrylonitile by making use of nuclear technology.
2. To decrease a large amount of homopolymer to an acceptable level.
3. To study the effect of additives on radiation grafting and water absorption capacity.
4. To develope degree of wicking (absorption rapidly) of hydrolyzed starch-g-polyacrylonitrile.

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. 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 organic/chemical fertilizers to improve the water holding and fertilizer retention capacities of sandy soils. The benefits for the future development can be:

1. To transfer, possibly, the further developed technology to local industry for a large scale production of cassava starch based high-water absorbing polymer.

2. To decrease the import of this material.

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

Preparing Scheme

In order to ease understanding of the entire synthesis precess, Figure 1.1 reveals the preparation of saponified starch-g-polyacrylonitrile, high- water absorbing polymer. Further details of which is covered in Chapter III.

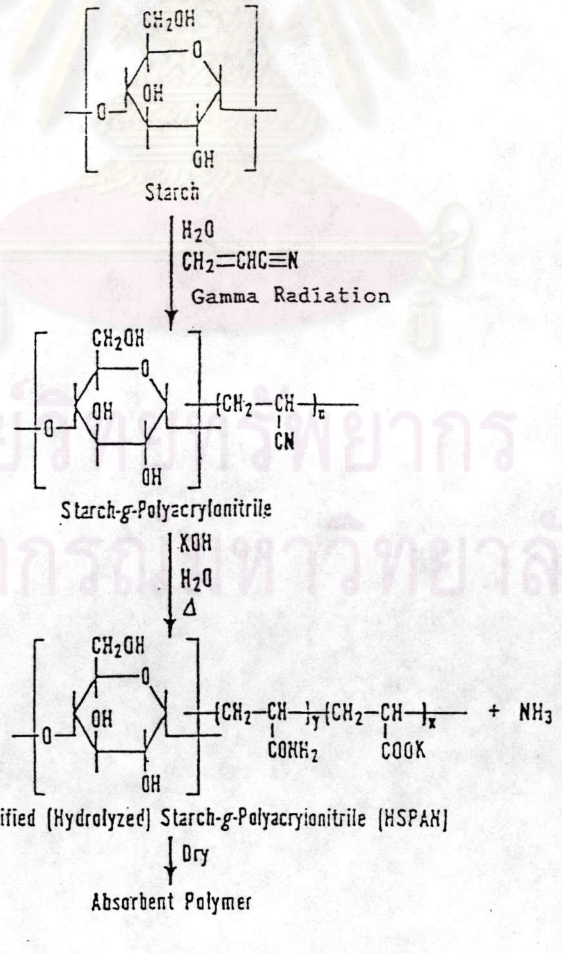

Figure 1.1 Preparation of saponified starch-g-polyacrylonitrile

Scopes of the Investigation

In this research, the necessary procedures of graft copolymerization of acrylonitrile onto cassava starch via gamma radiation to achieve the best product is as follows:

1. Literature survey and in-depth study of this research work.
2. Preparing graft copolymer of acrylonitrile onto cassava starch via gamma radiation by simultaneous irradiation method, by studying the following parameters so as to select the suitable technique and to attain the appropriate reaction conditions:
    a) The optimum quantity of total dose (kGy);
    b) 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 as follows:
        - the different kind of metal sheets such as aluminium foil, copper sheet, zinc and lead plates
        - the inhibitor such as methyl ether hydroquinone
        - nitric acid
        - comonomer such as styrene
    c) The optimum ratios of starch(g)/AN(ml)
    d) The technique of drying the final product
3. Extracting the homopolymer (polyacrylonitrile) of the crude product.
4. Bringing the graft copolymer obtained from section 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_V) of the grafted polyacrylonitrile;

g) Determination of grafting frequency (AGUs/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, simulated urine; and this graft copolymer mixed with sand.

j) Studying the effect of aluminium trichloride hexahydrate on degree of wicking and water absorption capacity of the saponified starch-g-polyacrylonitrile.

k) Studying the effect of drying method for enhancing the water absorption capacity.

5. Summerizing the result and preparing the report.