รายงานผลการวิจัย

เงินทุนวิจัยรัชดาภิเษกสมโภช

การสังเคราะห์โพลิเมอร์ดูดซึมน้ำจากแป้งมันสำปะหลัง เพื่อใช้ในการเกษตร

โดย

สุดา เกียรติกำจรวงศ์

2532

จุฬาลงกรณ์มหาวิทยาลัย

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Acknowledgement

The authors gratefully acknowledge the support of this research by a grant from the Ratchadapisak Sompoch Research Fund. We also wish to thank the Polymer Research Laboratory, Faculty of Science, for the provision of facilities during the entire research period from June 1988 through January 1989.

The authors thanks are due to Songsak Chaisukkanont and Narimol Rungsriwong for their help in the experimental work.

Last but not least, special thanks are expressed to Thai Wah Co., Ltd. for the provision of the Cassava Starch; and to Siam Resin & Chemical Co., Ltd. for donating acrylonitrile for this research.

Research Title : Synthesis of Cassava Starch-Based Water-Absorbing Polymer for Agricultural Application
Principal Investigator : Suda Kiatkamjornwong
Coinvestigator : Jean G. Faullimmel
Date of Research Completion : February 1989

Abstract

Native Cassava starch was chemically modified into poly (starch-g-acrylonitrile) under a grafting copolymerization of acrylonitrile onto the 80°C gelatinized starch via a redox initiation mechanism using Ce(IV) as initiator in an acid medium.

In addition to the Cassava starch-g-acrylonitrile, a homopolymer of polyacrylonitrile (PAN) was a byproduct which was later removed by extraction with dimethylformamide. The purified graft copolymer was subsequently saponified with an 8.5% aqueous solution of potassium hydroxide at 85°C to convert the nitrile groups into a mixture of acrylamide and carboxylate groups which were responsible for water absorbency.

Infrared spectrometer was used as a tool to follow up the chemical changes of grafting and saponification. The saponified starch-g-PAN was then characterized in terms of grafting efficiency, percent add-on, the amount of polyacrylonitrile formation and percent conversion of the polymerization. These information provided a guideline to judge an optimum ratio between starch/acrylonitrile.

Water absorption of the newly synthesized copolymer was carried out in deionized water and in $MgCl_2$ solutions. The water absorption capacity in pure water was ranged from 120 to 270 times their original dried weight. Water absorption capacity in saline solutions decreased dramatically with increasing the salt concentrations. Water retention in sand only and in mixed sand-copolymer at different copolymer concentrations were also performed. Increasing the concentrations of the copolymer in sand increased the water retention capacity.

These findings suggested that the development of Green E-sarn might be achieved partly by the aids of the Cassava starch graft polyacrylonitrile.

ชื่อโครงการวิจัย การสังเคราะห์โพลิเมอร์ดูดซึมน้ำจากแป้งมันสำปะหลังเพื่อใช้ในเกษตรกรรม
ชื่อผู้วิจัย สุดา เกียรติกำจรวงศ์
ฌอง ฟอลลีเมล
เดือนและปีที่ทำวิจัยเสร็จ กุมภาพันธ์ 2532

บทคัดย่อ

แป้งมันสำปะหลังที่มีในท้องถิ่นได้รับการดัดแปลงโครงสร้างไปเป็นแป้งที่มีโพลิอะคริโลไนทริลโดยผ่านปฏิกิริยากราฟโคโพลิเมอไรเซชันของอะคริโลไนทริลในแป้งที่ผ่านการทำเจลาทิไนที่อุณหภูมิ 80 °ซ ด้วยสารเริ่มปฏิกิริยาของซีเรียม (IV) ในสารละลายกรด

นอกเหนือจากได้กราฟโคโพลิเมอร์แล้ว ยังได้โฮโมโพลิเมอร์ของโพลิอะคริโลไนทริล (PAN) เป็นสารพลอยได้ ซึ่งจะต้องขจัดออกไปได้ด้วยการสกัดด้วยไดเมทิลฟอร์มาไมด์ นำสารโคโพลิเมอร์ที่บริสุทธิ์แล้วมาทำเซฟพอนิฟิเคชันด้วยสารละลายด่างโพแทสเซียมไฮดรอกไซด์ร้อยละ 8.5 ที่อุณหภูมิ 85 °ซ โดยเปลี่ยนหมู่ไนทริลไปเป็นสารผสมของอะคริละไมด์และคาร์บอซิเลตซึ่งเป็นส่วนที่กำหนดความสามารถในการดูดน้ำ

อินฟราเรดสเปกโทรมิเตอร์ใช้เป็นเครื่องมือสำหรับติดตามการเปลี่ยนแปลงทางเคมีของการเกิดกราฟทิงและการเกิดเซฟพอนิฟีเคชัน โคโพลิเมอร์ที่ผ่านการทำเซฟพอนิฟีเคชันแล้ว นำมาหาประสิทธิภาพในการเกิดกราฟทิง ร้อยละของแอดออน ปริมาณการเกิดโฮโมโพลิเมอร์ของโพลิอะคริโลไนทริลและร้อยละของการเกิดเป็นโพลิเมอร์ ผลที่ได้เหล่านี้ใช้เป็นบรรทัดฐานในการตัดสินหาอัตราส่วนที่เหมาะสมระหว่างแป้งและอะคริโลไนทริล

การกักเก็บน้ำของสารโคโพลิเมอร์ที่สังเคราะห์ได้ใหม่นี้ในน้ำกลั่นและในแมกนิเซียมคลอไรด์ให้ผลดังนี้ ความสามารถในการดูดน้ำกลั่นมีค่าตั้งแต่ 120 ถึง 270 เท่าของน้ำหนักสารโพลิเมอร์แห้ง ในขณะที่การอมน้ำในสารละลายด่างลดลงอย่างเด่นชัดเมื่อเพิ่มปริมาณของเกลือ การอมน้ำในทรายเพียงชนิดเดียวและทรายที่ผสมสารโพลิ

เมอร์นี้ในอัตราส่วนต่าง ๆ กัน ให้ผลว่าเมื่อเพิ่มปริมาณสารโคโพลิเมอร์ในทรายเพิ่มความสามารถในการกักน้ำ

การค้นพบเหล่านี้ให้ข้อแนะนำเกี่ยวกับการนำสารโคโพลิเมอร์นี้ไปพัฒนาอีสานให้เขียวขจีได้

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°C	degree Celsius
°ซ	องศาเซลเซียส
Ce(IV)	cerium ion
PAN	Polyacrylonitrile
%	percent
Mn^{+3}	manganese (III)
AN	acrylonitrile
AGU	anhydroglucose unit
α	alpha
D.P.	degree of polymerization
BU	bushel unit
g	gram
ml	milliliter
N	normality
mmole	millimole
cm^{-1}	unit of wavenumber
cm	centimeter
microns	micrometers
$C\equiv N$	nitrile group
W/V	weight by volume
Eur. Polym. J.	European Polymers Journal
Makromol. Chem.	Makromolekulare Chemie
Cereal Chem	Cereal Chemistry
J. Polymer Sci. A	Journal of Polymer Science, part A
J. Appl. Polym. Sci	Journal Applied Polymer Science
J. Macromol. Sci. Chem.	Journal of Macromolecular Science and Chemistry

Chapter 1

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-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 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 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 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 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 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, previously grew abundently in south-eastern region of Thailand. At present, cassava starch grows throughout the country, particularly 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.

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 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.

1.1.2 Geographical and Economical Background Leading to This Research

The Northeast of Thailand is the largest 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 17 million constituting over one-third of the total population. It is surrounded by hills of approximately 400 meter high in the south and by mountains of 1,300 meter high 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 is drained by the major rivers, the Chi and Mun.

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

a) Rainfall

The rainfall characteristics are dominated by the southwest moonsoon 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 soil 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 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. The soils on the rice are mostly Paleustults and are suitable for field crops. 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 positions in the Northeast, the properties of soil can be divided into the following categories:-

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

Farmings in the Northeast are crops based on rice as the subsistence and field crops as cash crops. Soils 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,·revolve. The four most important crops are cassava (10%), corn (6%), kenaf (3%), and sugarcane (1%). Rice is grown mostly on the so-callecd "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 rices 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 incorporating field crops into the system before and after rice plantation.

e) Crop yield and improvement

The average rice yield in the 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 increases 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 the sandy soil. The utilizations of chemical fertilizers and high water-absorbing polymer totally depend on import of these two types of materials. The construction of chemical fertilizer plant is under the authorities dicision while the latter is still under intensive research by some researchers in Faculty of Science and the Petroleum and Petrochemical College at Chulalongkorn University. It is about time that Thailand should have its own chemical fertilizer and high water-absorbing polymer plants to support the development and expansion of the agricultural sector and agroindustries, which are the backbone of the Country.

1.1.3 Objective

The objective of this research is to develop a cheap and reliable process for manufacturing high water-absorbing polymer, based on cassava starch, which can be transferred to industry for a large scale production; to use the Country's surplus and unused cassava starch; and to improve farm productivity in the Northeastern region during the dry season.

1.1.4 Survey of Related Literature

Extensive studies on the preparation, properties and applications of cellulose graft copolymers have been carried out since 1952. Graft polymerizations onto starch are carried out in much the same way as graft polymerization onto cellulose. A recent review on the synthesis and properties of starch graft copolymers has been compiled (2). Corn starch is most often used as the substrate for graft polymerization, however, starch from wheat, sorghum, rice, and potato will give hydrolyzed starch-g-polyacrylonitrile copolymers with similar properties. The grafting monomers used cover a very wide variety of vinyl monomers. Acrylonitrile, acrylamide, acrylic acid, monomers with amino substituents, acrylic acid esters, vinyl acetate, styrene, butadiene, vinyl chloride, and N-vinyl-2-pyrrolidone have been used in the synthesis of starch graft copolymer. The development of grafted starch products, essentially involving acrylic acid grafted side chains, immediately attracted worldwide attention because of their tremendous water sorbing and retention properties. Fanta, G. F. (1) is the pioneer among the researchers in this field, who has intensively investigated graft copolymerization of acrylonitrile and the relevant vinyl monomers onto several starch substrates. Ranby and coworkers at Department of Polymer Technology in Sweden have been actively involved in synthesis of water absorbing polymers both from cellulose and starch based materials (3-4). Other researchers elsewhere in Asia have just started the research for a decade (5).

1.2 Theoretical Background

1.2.1 Chemistry of Starch (6)

Starch is composed of carbon, hydrogen and oxygen in the ratio of 6:10:5 as an empirical formula of $C_6H_{10}O_5$, placing it in the class of carbohydrate. It is a condensation polymer of glucose. The glucose units in the starch are present as anhydroglucose units (AGU), the linkage between the glucose units being formed as if a molecule of water is removed during a step polymerization. The linkage of one glucose to another through the C-1 oxygen is normally known as a glucoside bond. The glucoside linkage is an acetal, stable under alkaline conditions and hydrolyzable under acid conditions. The hydroxyl groups can react to form ethers and esters and can be oxidized to aldehyde, ketone, and carboxyl groups.

1.2.2 Molecular Structure

Most starches consist of a mixture of two polysaccharide types: amylose, an essentially linear polymer; and amylopectin, a highly branched polymer. The relative amounts of these starch fractions in a particular starch are a major factor in determining the properties of that starch.

a) Amylose

The linear polymer consists of a chain of glucose units connected to each other by 1-4 linkages. These glucose units are in the 'α-D-glucopyranose" form (Figure 1.1). The amylose polymer fraction of a starch will show a distribution of molecular sizes, and the average degree of polymerization will vary with plant variety from which the starch is obtained. Depending upon the type of starch, the D.P. will range from about 250 to 4000 AGU per amylose molecule, corresponding to a molecular weight of approximately 40,000 to 650,000. Most starch such as regular corn, wheat, potato, and cassava contain approximately 28% amylose (7). For cassava starch, the amylose content is about 16.5-22.2 (8).

Starch molecules have a multitude of hydroxyl groups which impart hydrophilic to the starch. In addition to their affinity for water, these hydroxyl groups also tend to attract each other, forming hydrogen bonds. The linear amylose molecules can readily align themselves next to each other and form interchain hydrogen bonds through the hydroxyl groups. When sufficient interchain hydrogen bonds are formed, the individual amylose molecules are associated to form molecular aggregates with reduced hydration capacity and hence, lower solubility.

b) Amylopectin (1)

Amylopectin has a highly branched structure consisting of short linear amylose chains with a D.P. ranging from 12 to 50 AGU and an average chain length of about 20 AGU, connected to each other by alpha-1, 6-linkage (Figure 1.2)

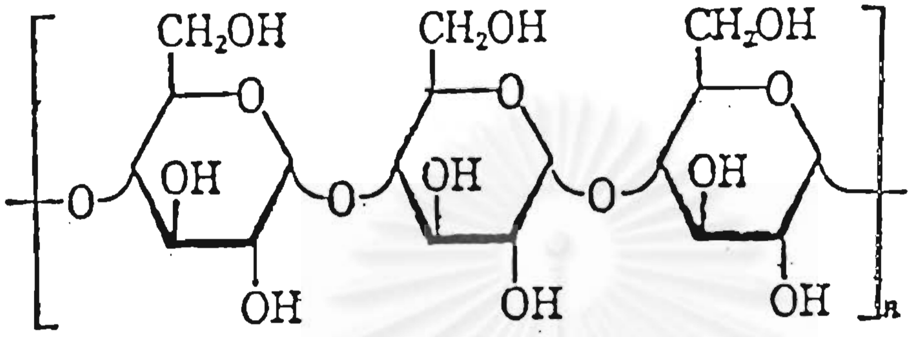


Figure 1.1 Chemical structure of amylose chain

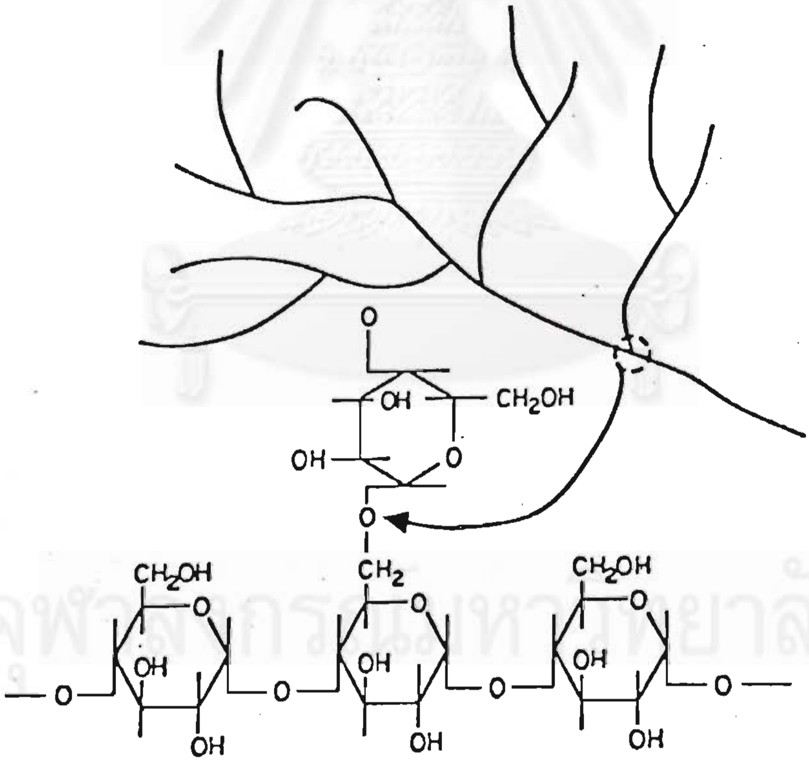


Figure 1.2 Branched structure of amylopectin and chemical configuration at the branch point.

Amylopectin has a molecular weight average ranging from 50 million to over 100 million. Due to its large size and branched nature, the mobility of the polymers reduces and dictates the tendency to orient and pack themselves close enough to permit significant levels of hydrogen bonding.

1.2.3 Graft copolymerization of vinyl monomer onto starch via radical initiation of cerium (IV) ion

As mentioned previously that high water-absorbing polymer can be made by modification of starch and cellulose by grafting with a petroleum derived monomer to form a graft copolymer. The grafted material can either be synthesized by a free-radical or anionic process with some vinyl monomers such as acrylonitrile, acrylamide, acrylic acid and so on.

The most widely used method of free radical initiation of starch is the reaction with cerium(IV) formed by dissolving ceric ammonium nitrate or ceric ammomium sulphate in dilute nitric acid. The entire free radical graft copoymerization involved the mechanism of initiation, propagation, and termination by the ceric ion is depicted in Figure 1.3

The reactions of ceric salts with alcohols have been studied and research has also been carried out on model compounds to determine the chemistry involved when a glucopyranosyl unit is attacked by the ceric ion. Based on available evidence, the most important reaction path for ceric-initiated graft copolymerization starts with the initial formation of a starch-ceric complex, ceric (IV) ion is consequently reduced to cerous (III) ion, a hydrogen atom is oxidized, and a free radical is formed on starch, while the bond between carbon atoms 2 and 3 of the glucopyranosyl unit is broken. The polymeric starch free radical so formed may then react with the vinyl monomer to initiate graft copolymerization or may be lost through further reaction with ceric salt. The presence of free radicals in ceric treated starch has been confirmed by electron spin resonance (9), and the technique has also been used to study free radicals formed in ceric-treated cellulose. (10)

Evidence also shows that free radicals are formed on starch by chain transfer reactions, significant amounts of homopolymer are often formed by reaction of the initially formed radical with monomer before chain transfer to starch can occur.

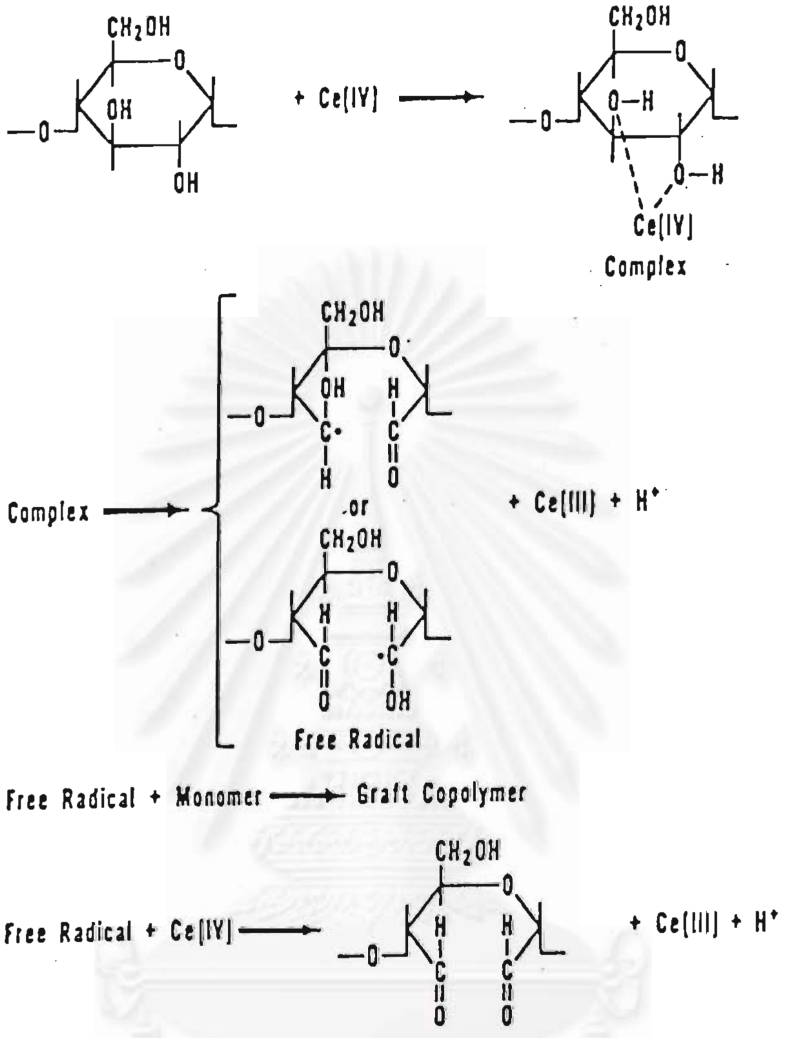


Figure 1.3 Free radical graft copolymerization of vinyl monomer onto starch by cerium (IV) initiator.

1.2.4 Saponification of the graft copolymer of starch-g-polyacrylonitrile

Since the synthesis of high water-absorbing polymer involves simultaneously graft-copolymerization and homopolymerization, it is of great essential to remove the useless part, polyacrylonitrile, which does not contribute to water absorption, if a substantial amount is present. Dimethylformamide is used to extract the homopolymer while the grafted copolymer remains solid.

To enhance the hydrophilic character of the starch-g-polyacrylonitrile, it will be hydrolyzed with an 8.5% potassium hydroxide. One usually observes color changes from initially a deep red solution which is due to the formation of naphthyridine intermediate structure from the adjacent nitrile groups. The intermediate rings are consequently hydrolyzed which causes changes in color from red to light yellow. Saponification is another step to convert the polyacrylonitrile chains in the graft copolymer to a mixture of polycarboxamide and polycarboxylate. The resulting dry copolymer is responsible for high water absorption which may take up water several hundred times its dry weight. The following reaction in Figure 1.4 elucidates the saponification procedure:

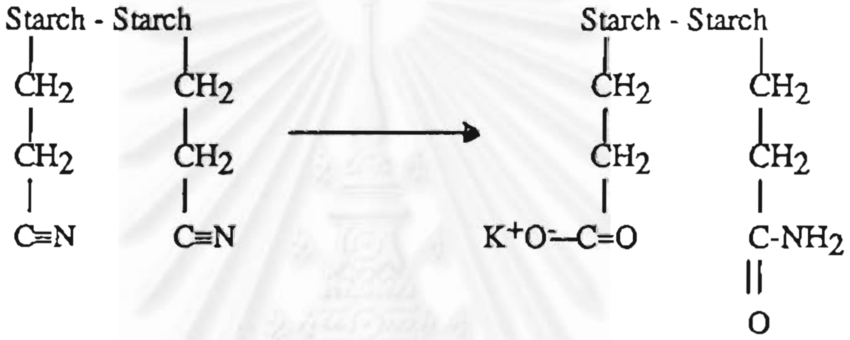


Figure 1.4 Saponification of the starch-g-polyacrylonitrile.

1.3 Terminology and Definition

Before proceeding to the experimental part, several technical terms are needed to be clarified for the better understanding of readers.

1.3.1 Gelatinization

The properties of the starch granule in water are the major factors in its commercial utility. The granule is insoluble in water below about 50°C and form an aqueous slurry. This slurry is heated to a temperature about 55° to 80°C where, depending on the type of starch and concentration, the intermolecular hydrogen bonds holding the granule together are weakened and the granule undergoes a rapid, irreversible swelling. The critical temperature at which this occurs is known as the pasting or gelatinization temperature.

Rodehed, C and B. Ranby (11) studied the grafting of acrylonitrile with granular and gelatinized starch. It was found that the efficiency of the grafting was higher with gelatinized starch rather than with granular one. The accessibility of starch for grafting is enhanced, which will increase conversion. The resulting starch-g-polyacrylonitrile from gelatinized starch gave about eight times higher molecular weight than that from granular starch. A higher molecular weight of the graft copolymer has shown to give a higher water absorption.(12)

1.3.2 Percent add-on

It is referred to as the percent of synthetic polymer in the graft copolymer and is determined as follows:-

$$\text{percent add-on} = \frac{\text{Polymer in grafts}}{\text{weight of the grafted sample}} \times 100$$

Usually, one has to cleave the polymer attached from the starch matrix by acid hydrolysis. The graft copolymer is under reflux in dilute acid solution in which the grafted polymers are separated from the starch backbone.

1.3.3 Grafting efficiency

It is a term used to describe graft copolymerization which is defined as the percentage of the total synthetic polymer formed that has been grafted to starch. High grafting efficiencies are desirable since a polymerization of low grafting efficiency would afford mainly a physical mixture of starch and homopolymer. The grafting efficiency can be calculated as follows:

$$\text{grafting efficiency (\%)} = 100 - \text{\% homopolymer formed.}$$

1.3.4 Percentage conversion

Conversion of a monomer is defined as the extent of the monomer to which is changed to become a respective polymer (polymers). For this particular case, the conversion of acrylonitrile to be a graft copolymer (starch-g-polyacrylonitrile) and a homopolymer of polyacrylonitrile is referred to as the percentage conversion.

$$\text{\% conversion of monomer} = \frac{\text{(Polymer formed)} \times 100}{\text{monomer charged}}$$

1.4 Preparation Scheme

In order to ease understanding of the entire synthesis process, Figure 1.5 reveals the preparation of saponified starch-g-polyacrylonitrile, high water-absorbing polymer. Further detail of which is covered by the following Chapters.

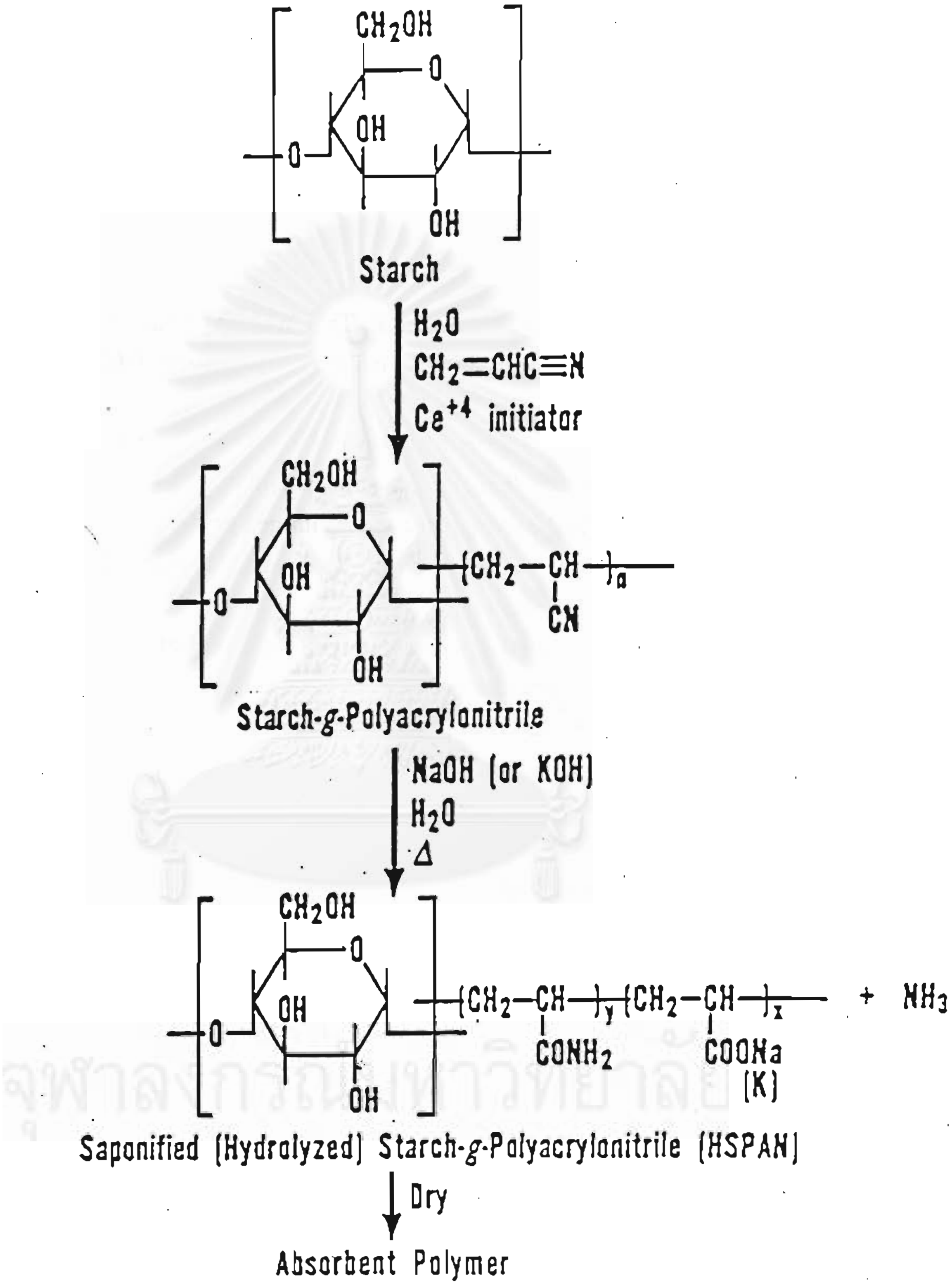


Figure 1.5 Preparation of saponified starch-g-polyacrylonitrile.

Chapter 2

Experimental

2.1 Chemicals, Equipment and Glasswares

2.1.1 Chemicals

Cassava starch was obtained from Thai Wah Co. Ltd. It was produced from tapioca cultivated in summer. It contains 12.80% moisture, 0.07% ash, 32.57 ppm SO_2, pH value of 5.80 and viscosity at 66-77°C of 780 BU.

Acrylonitrile (98.% pure) was provided by Siam Resin & Chemical Co. Ltd. It was puried by fractional distillation at atmospheric pressure through a 14-inch vigreux column and stored in the refrigerator under nitrogen gas.

Methanol, commercial grade from BDH was also purified by fractional distillation at atmospheric pressure.

Other chemicals used as shown below which were of analar grade, were employed without further purification:

analar grade ceric ammonium sulphate
analar dimethylformamide (DMF)
sodium free potassium hydroxide
triply-distilled water
analar grade nitric acid

2.1.2 Equipment and Glasswares

4-necked round bottom flask, hot plate and magnetic stirrer, heating mentle, beakers, motar and pestle, filtering system, analytical balances and other general laboratory glasswares and equipment.

2.2 Procedure

2.2.1 Gelatinization of Cassava Starch

Into a 1,000 ml 4-necked round bottom flask, 10 g of cassava starch was mixed with 292 ml of triply distilled water. The system was heated at around 80° ± 3°C for one hour under the nitrogen atmosphere to form a paste-like slurry.

2.2.2 Grafting of Acrylonitrile onto Cassava Starch

The gelatinized starch was then cooled to about 40°C. Two portions of 5 g of acrylonitrile were added into the gelatinized starch containing 0.55 mmole of 8.0 ml ceric ammonium sulphate in 0.5 and 1.0 N HNO_3, respectively. The mixture was stirred under nitrogen atmosphere at 40°C for 3 hours. The reaction product was subsequently precipitated with methanol, filtered, and washed with methanol again before being dried at 65°C for 3 hours.

The dried samples were investigated its acidic activity under infrared spectrometer. Measure the length of the $C \equiv N$ peak at 2,243 cm^{-1}. The better acidic activity based on the length of the $C \equiv N$ peaks was used to determine the effect of starch (g) /AN(g) ratios on grafting and water absorption.

2.2.2.1 Effect of starch/AN ratios on grafting

Various amounts of acrylonitrile (g) of 5, 10, 15, 20, 25 and 30 were added to each of 10 g of the cool gelatinized starch in the presence of 8.0 ml solution of 0.55 mmole cerium ammonium sulphate and the chosen acidity of nitric acid (found 1.0 N). The reaction steps were repeated as mentioned above. The dried samples were inspected with an IR spectrometer.

2.2.3 Homopolymer Extraction by N,N-Dimethylformamide (DMF)

In a 500-ml erlenmeyer flask, 5.0 g of the dried starch-g-polyacrylonitrile, ground into a powder form, was stirred in 250 ml of DMF at room temperature for 24 hours.

The extracted product was filtered, washed with methanol, and dried for 30 hours at 65°C. Then 100 ml of the clear extract was precipitated in an excess amount of methanol, then filtered and washed again with methanol. The precipitate was dried for 3 hours at 65°C and weighed to determine the amount of the homopolymer, polyacrylonitrile. All products were detected with the IR spectrometer. The IR analyses were carried out with 0.04 gm of dried product mixed with 2.00 g dried analar KBr. Calibration of the spectrometer was held constant for all analyses.

2.2.4 Copolymer Characterization

2.2.4.1 Saponification of Starch-g-Polyacrylonitrile

A suspension of 10 g DMF- extracted starch-g-polyacrylonitrile was added to 200 ml of an 8.5% potassium hydroxide solution. The mixture was stirred with a magnetic stirrer and the saponification was carried out at 85°C for 2 hours. One could observe a deep red solution developed and changed to light yellow at the later stage. It was then allowed to cool to room temperature and precipitated with alcohol. The product was then filtered and washed thorougly with methanol until pH 7 was reached. It was dried in the 65°C oven for 30 hours to remove any residual methanol. The dried product was ground into a powder form.

2.2.4.2 Determination of Percent Add-On

In a 250-ml erlenmeyer flask equipped with a condenser, 1.00 g DMF-extracted polymer was stirred in 100 ml of 1 N H_2SO_4 and the mixture was refluxed for 60 minutes. Filtered the water-insoluble polymer, then washed until pH of the washed solution was 7, and then dried. The weighed percentage polyacrylonitrile in the graft copolymer or so called "percentage add-on" was computed from the weight difference between the graft copolymer and the soluble starch which was removed by acid hydrolysis.

2.2.4.3 Determination of Percentage Conversion

The experimental procedure described in sections 2.2.1 through 2.2.2 were carried out. The weight of the grafted copolymer and homopolymer was regarded as the total amount of polymer obtained from the weight of monomer charged.

2.2.4.4 Determination of Homopolymer Formation

The weight obtained from section 2.2.3 was the amount of polyacrylonitrile produced as a by-product.

2.2.4.5 Determination of Grafting Efficiency

The experimental procedures of sections 2.2.2 through 2.2.3, gave the weight difference between the total weight of polymer and the weight of homopolymer produced were regarded as the percentage grafting efficiency.

2.3 Water Absorption/Retention Capacities of the Copolymer

2.3.1 In Deionized Water

A 0.1 g of dried and saponified starch-g-polyacrylonitrile was immersed in a weighed amount of triply-distilled water. After one hour, the slurry was filtered through a wetted and weighed No. 41 filter paper in a funnel by normal gravity force. Corrections were made for the water retention of the filter paper, i.e., the wetted filter paper will reduce, to a certain extent, the capillary effect of the filter paper. The amount of water retained by the starch-g-polyacrylonitrile was calculated as in gram per gram of dry modified starch.

2.3.2 In Magnesium Chloride Solutions

The same experimental procedure as described in section 2.5.1 was carried out, except a series of magnesium chloride solutions of 0.5 and 1% W/V was used instead of deionized water.

2.3.3 In Sand Alone and Sand with Saponified Starch-g-polyacrylonitrile

To determine the water retention capacity of the river sand itself, a known quantity of water was drained at approximately rate of 2 ml/min to a layer of 20 g river sand. Then drained away any excess unabsorbed water and weighted.

A sandwich comprising 10 g of the river sand, 0.1 g of the starch-g-polyacrylonitrile and another 10 g of the sand was made in a sequential order to observe the water retention capacity of sand in the presence of the super-absorbent. The experiment was then carried out exactly the same technique as the determination of water retention capacity of the sand alone.

Likewise, 0.2, 0.3, and 0.4 g of the starch-g-polyacrylonitrile were mixed with the sand by repeating the above experimental procedure.

The weight difference between the two experiments indicates the efficiency of water retention capacity of the sand by incorporating the starch-g-polyacrylonitrile.

2.4 Scanning Electron Microscopy of the Copolymer

The dry and ground copolymers synthesized with various ratios of starch(g)/AN (g) were investigated by the simple technique of scanning electron microscopy and x-ray microanalysis to observe the morphology of the superabsorbent and the elements left from the reaction steps, such as the potassium cation from the saponification and the cerium ion from the grafting copolymerization.

It must be noted that all the experiments mentioned above were carried out at least duplicately to check their reproducibility.

Chapter 3

Results and Discussion

3.1 Infrared Analyses

At present, IR spectroscopy was used as a tool to follow up changes in graft copolymerization. The IR spectra of Cassava starch, and the copolymers after grafting, after extraction, and after saponification are given in Figures 3.1 through 3.4, respectively. The IR specetrum of Cassava starch in Figure 3.1 gave absorption bands at 3,400 and 1,000-1,100 cm^{-1}, characteristics of amylose containing in the starch.

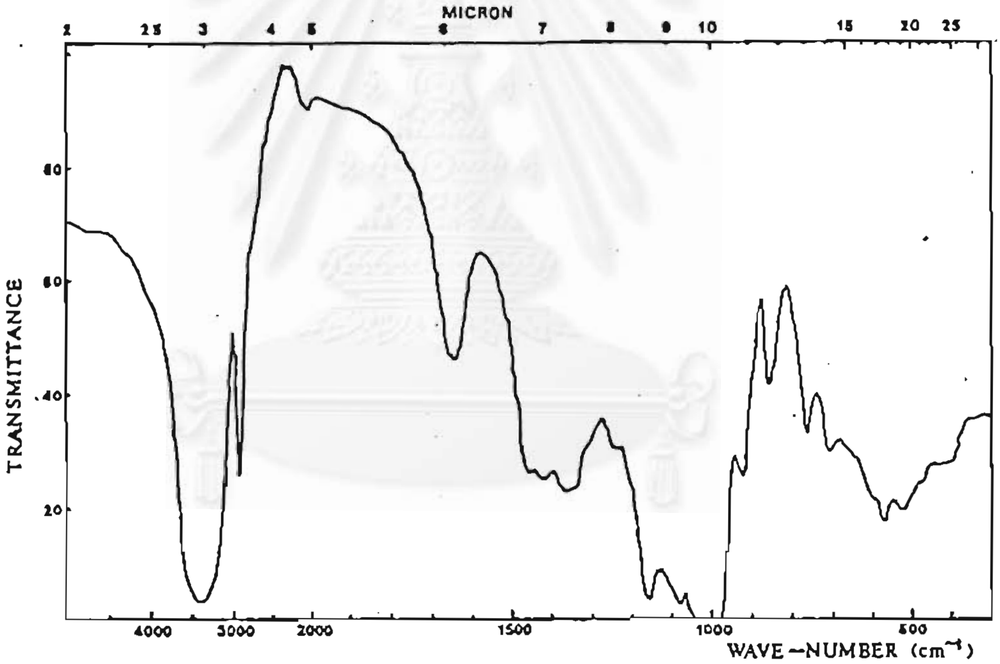


Figure 3.1 Infrared spectrum of dried Cassava starch.

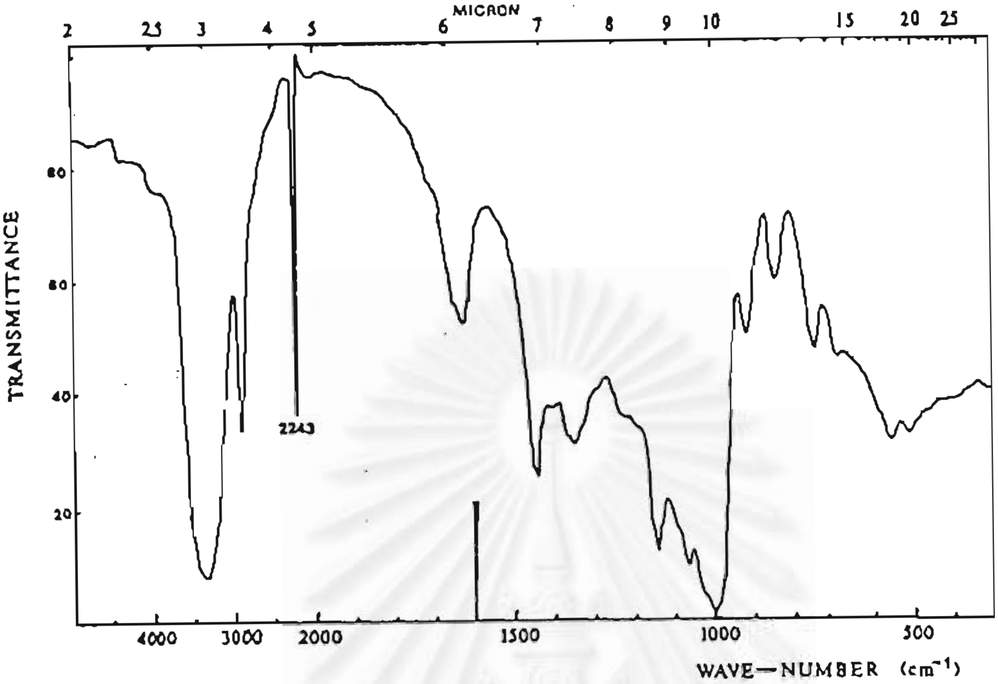


Figure 3.2 Infrared spectrum of the graft copolymer after grafting. One can observe the stretching absorption peak of the C≡N group at 2,243 cm^{-1}.

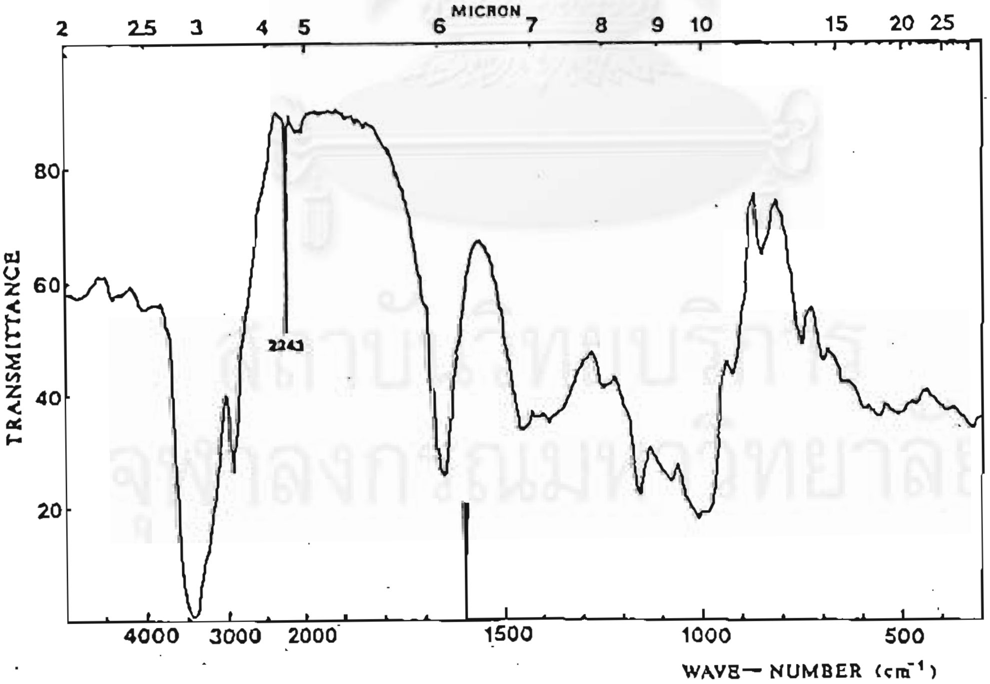


Figure 3.3 Infrared spectrum of the graft copolymer after DMF extract. One can observe the decrease in the stretching absorption peak of the C≡N group at 2,243 cm^{-1}.

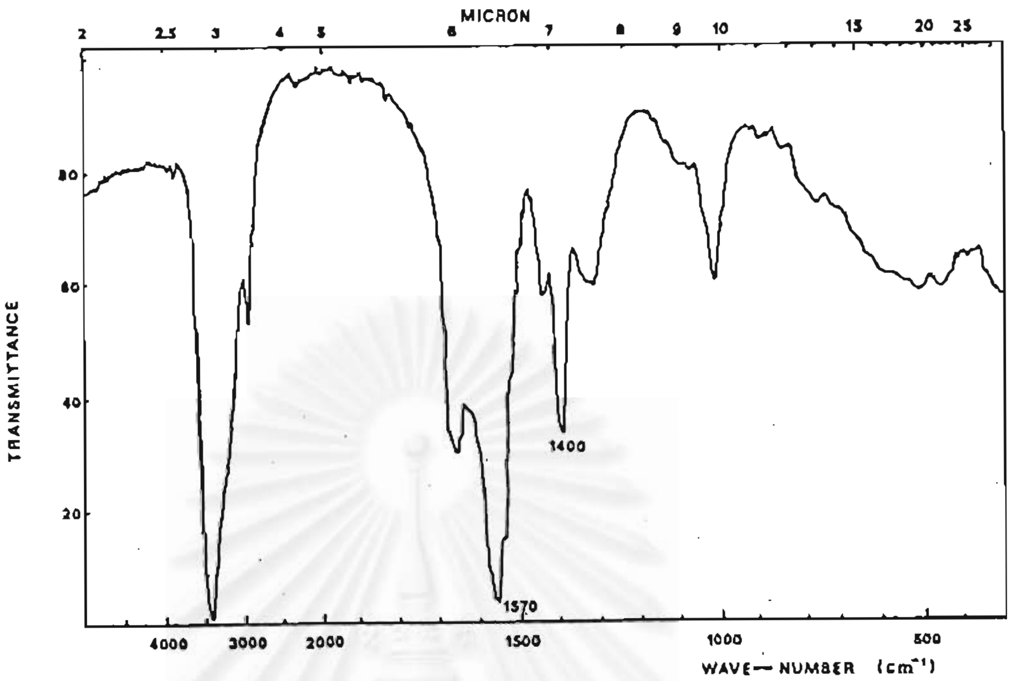


Figure 3.4 Infrared spectrum of the saponified graft copolymer.

The absence of the C≡N group at 2,243 cm^{-1} and the strong asymmetrical stretching band at 1,570 cm^{-1}, and a weak symmetrical stretching band 1,430-1,390 cm^{-1}, characteristics of the -c=o^{-} group indicated the occurrence of grafting. The absence of the primary amine may be due to a relatively low concentration, and/or the usually low intensity of the NH stretching band and overlapping with the existing one (s) of the starting materials.

3.2 Grafting of Acrylonitrile onto Cassava Starch

3.2.1 Effect of Nitric Acid Normality on Grafting Efficiency.

Since 0.5 and 1.0 N HNO$_3$ were used as a medium for ceric ammonium sulfate for grafting acrylonitrile onto Cassava starch. The IR spectra of the graft copolymer indicated that the acid normality of 1.0 N HNO$_3$ catalyst solution gave a relatively high C≡N stretching peak at 2,243 cm^{-1} as shown in Table 3.1

Table 3.1 The Peak Length of the C≡N Streching Bank.

Normality of acidic solution (N)	Peak length (cm)
0.5	3.0
1.0	3.9

According to the result, the subsequent experiments were carried out in a reaction medium of 1.0 N HNO_3. The higher acidity of nitric acid activates the activity of the catalyst which enhances the complex formation between the Ce(IV) and the Cassava starch. Higher acidity than 1 N is not needed since the acid is produced stoichiometrically under the cleavage of glycolic C_2 and C_3. Too high an acid content is undesirable due to the interference of the excess anions on water absorption. That is the overall glycol cleaving rate is governed by the concentration of Ce(IV), the amount of nitric acid and the glycol concentration(12).

3.2.2 Effect of Starch/Acrylonitrile Ratios on Grafting

Upon investigation of the IR spectra of the starch-g-polyacrylonitrile by the ratios of starch (g)/acrylonitrile (g) with the following amounts: 10:5, 10:10, 10:15, 10:20, 10:25 and 10:30, it was found that the peak lengths of the nitrile stretching absorption at the wavelength of 2,243 cm^{-1} were increased with increasing the acrylonitrile concentrations. Since the preparation of the pellets from these samples were carefully made, and the condition of the IR spectrometer was kept constant. After the DMF extraction of the products, the peak lengths of all ratios were decreased which indicated of the removal of the homopolymer, polyacrylonitrile. All the nitrile peaks disappeared after saponification which means that these peaks were converted into the carboxamide and carboxylate groups which are capable of high water absorption. The proportional increase of the $C \equiv N$ stretching absorption peak at 2,243 cm^{-1} after grafting as the acrylonitrile content increased is illustrated in Figure 3.5. Table 3.2 shows the change in peak lengths of the nitrile stretching absorption due to grafting, extraction, and saponification of the polymers.

3.2.2.1 Determination of Homopolymer Content and Percentage Grafting Efficiency

Although the synthesis of starch-g-polyacrylonitrile involves a free-radical pathway, contributed by the redox initiator, free radicals formed on starch caused by chain transfer reactions produce a significant amount of homopolymer which is removable by dimethylformamide. Polyacrylonitrile is soluble in such a solvent while the starch-g-polyacrylonitrile remains unchanged. This renders the decrease in the peak lengths of nitrile groups of the graft copolymer as shown in Table 3.2.

Table 3.2 The Change in Peak Lengths of the Nitrile Stretching Absorption Due to Grafting, Extraction, and Saponification of the Polymers.

Amount of acrylonitrile added (g)	Peak length of the C≡N peak		
	After grafting (cm)	After DMF extract (cm)	After saponification (cm)
5	3.9	1.9	0
10	5.2	5.0	0
15	6.7	5.0	0
20	7.5	7.4	0
25	7.4	6.8	0
30	9.4	8.1	0

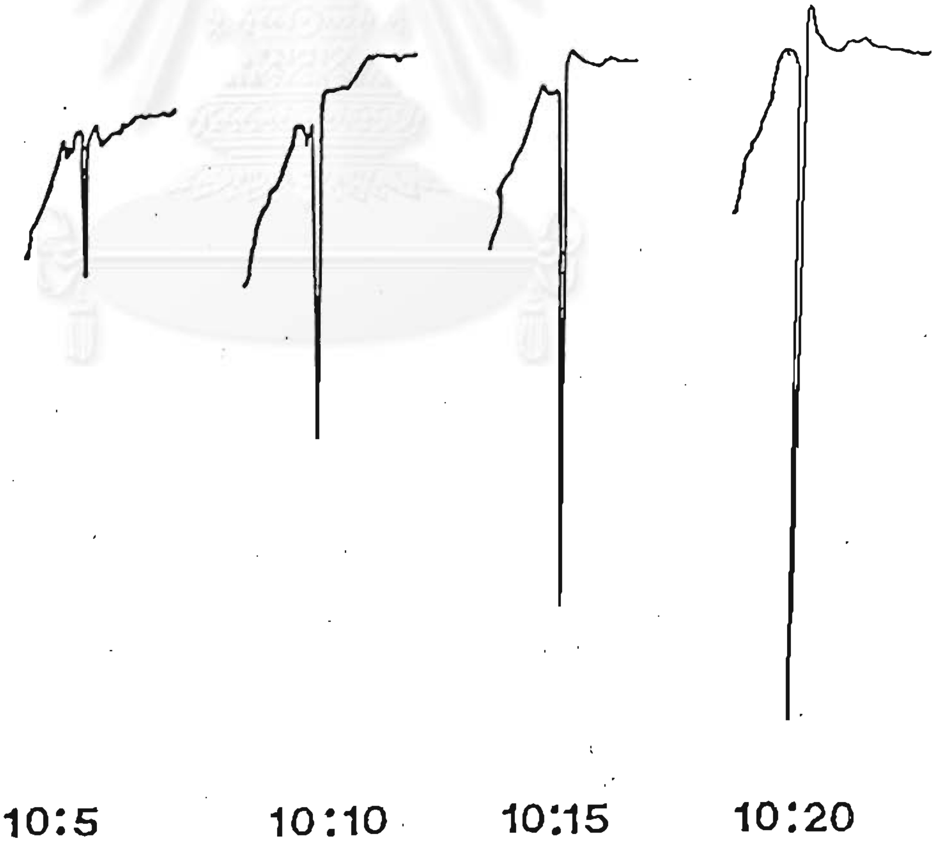


Figure 3.5 The proportional increase of the C≡N stretching absorption peak at 2,243 cm^{-1} after grafting as the acrylonitrile content increased.

Grafting efficiency is a term used to explain the extent of graft copolymerization. Usually, high grafting efficiencies are desirable since a highly grafted copolymer will ultimately yield a material with a higher water absorption efficiency. The amounts of polyacrylonitrile and grafting efficiency of the experiment were presented as follows:

Table 3.3 The Amounts of Polyacrylonitrile and the Grafting Efficiency of Acrylonitrile onto Cassava Starch.

Starch (g)/ Acrylonitrile(g)	Percent of Poly-acrylonitrile	Percent grafting efficiency
10/5	5.51	94.45
10/10	6.61	93.39
10/15	11.67	88.33
10/20	15.27	84.73
10/25	18.00	82.00
10/30	19.4	80.60

Figures 3.6 and 3.7 illustrate the relationship between starch/ acrylonitrile and the amount of homopolymer, polyacrylonitrile, and percent grafting efficiency, respectively.

The data in Table 3.3 and Figures 3.6 and 3.7 elucidate the following:

1) The higher the acrylonitrile content, the greater the homopolymer produced.

2) Grafting efficiency decreased with increasing the concentrations of acrylonitrile. This is because less initiator is available to the polysaccharide chain and thus becomes more favorable to chain transfer to the increasing amount of acrylonitrile.

It is noted that increasing viscosity of the medium causes the stirring problem. The efficiency of the stirring system such as the stirring rate, the geometry of the propeller should be seriously taken into account for effective stirring.

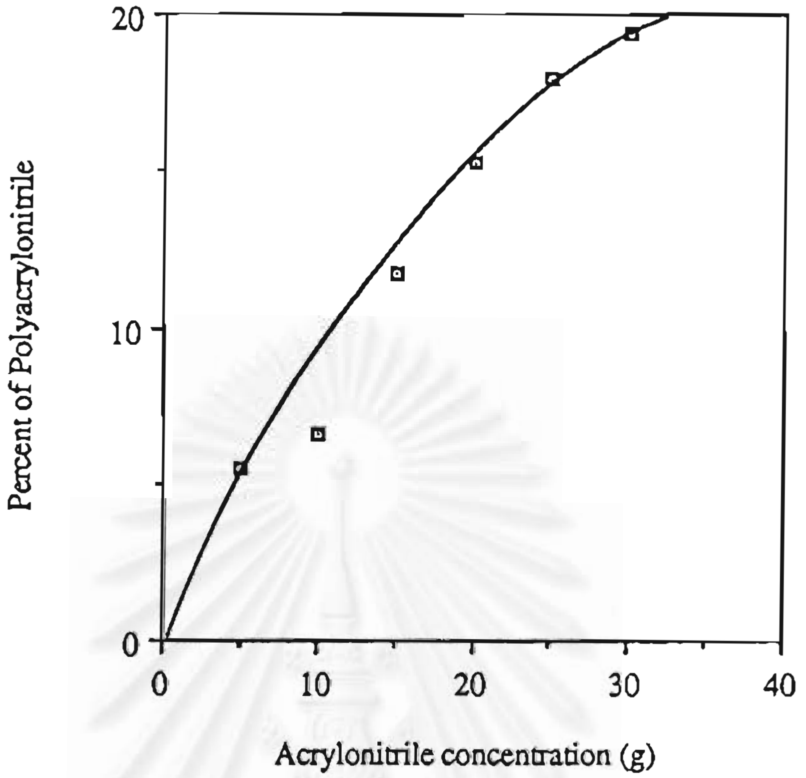


Figure 3.6 Effect of the Concentration of Acrylonitrile on the Amount of Homopolymer, Polyacrylonitrile, Produced.

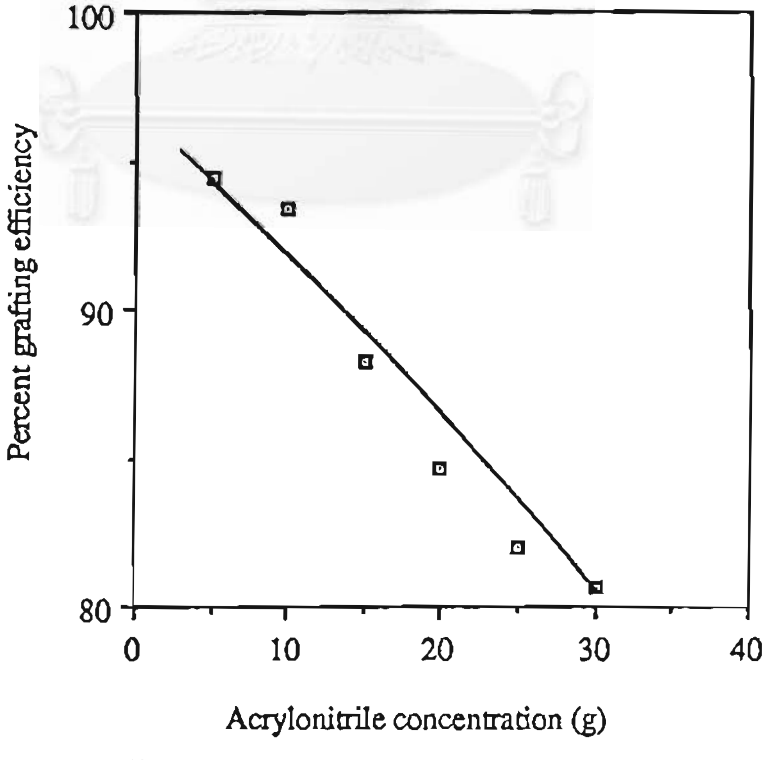


Figure 3.7 Effect of the Concentration of Acrylonitrile on the Percentage Grafting Efficiency.

In this experiment, especially at high acrylonitrile content, the stirrer could only move at the center bottom of the reaction flask, due to gel effect or Trommsdorf-Norrish effect. Under this situation, the diffusion efficiency of radicals to the reactive grafting sites would surely be reduced. This behavior allows the polymer growing chains become larger which eventually will decrease the number of chain terminations. Thus, the viscosity increased which was accompanied by the higher molecular weight.

In addition, the data presented in Table 3.3 should be treated only as a guideline for the polyacrylonitrile formation as the technique for filtering the very viscous and sticky polymers, especially at a high acrylonitrile content, caused a material loss due to very strong adhesion with the filter paper. One comment needs to be mentioned here is although the polyacrylonitrile produced as a byproduct may not be desirable for water absorption, it is indeed a very good packaging film with high barrier effects such as moisture protection, the applications of which should not be overlooked in the future for the agroindustry of Thailand.

3.2.2.2 Determination of Percent Conversion of Monomer and Percent Add-On

Table 3.4 and Figures 3.8 through 3.9 gave the result of a series of graftings of the native gelatinized Cassava starch with different amounts of acrylonitrile.

Table 3.4 Effect of Starch/Acrylonitrile Ratio on Percent Conversion and Percent add-on.

Starch (g)/ Acrylonitrile (g) Ratio	Conversion of Monomer (%)	Percent Add-on (%)
10/5	40	8.5
10/10	44	36.5
10/15	60.8	42.8
10/20	64.5	50.5
10/25	66.4	69.0
10/30	77.8	75.0

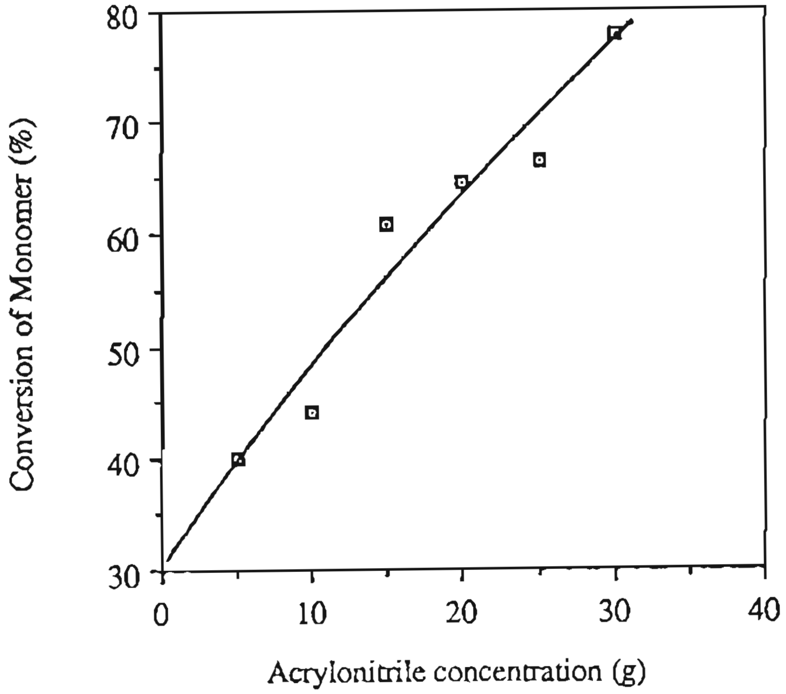


Figure 3.8 Effect of the Starch/Acrylonitrile Ratios on Percent Conversion of Monomer.

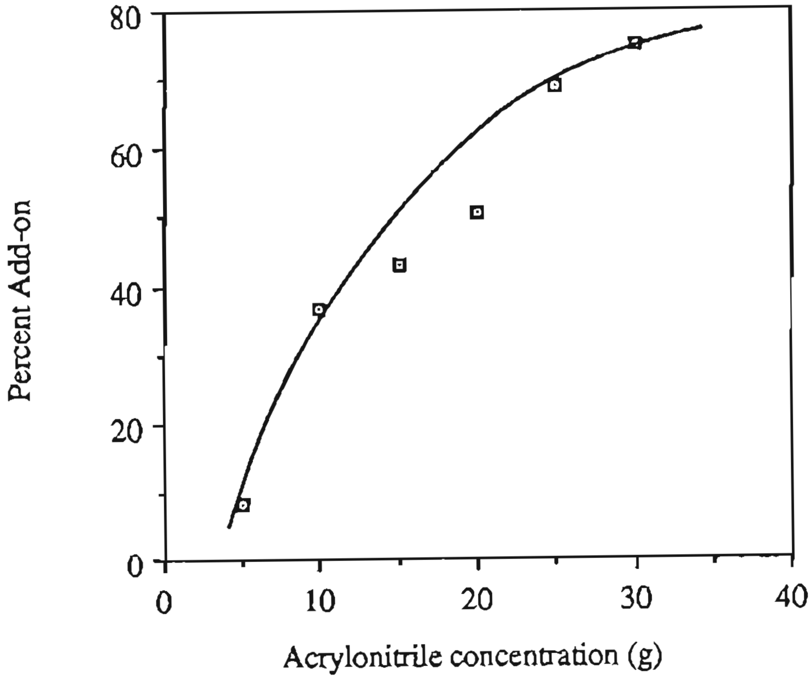


Figure 3.9 Effect of the Starch/Acrylonitrile Ratios on Percent Add-On.

The conversion of acrylonitrile and the percent add-on increased with increasing the amounts of acrylonitrile charged

The results indicated that the more concentrate the monomer, the more it could react with the starch substrate free radicals as well as could polymerize via chain transfer reaction to form polyacrylonitrile. The 10/10 ratio of starch(g)/ acrylonitrile (g) gave a very interesting indication of economical and practical viewpoints in that only increasing the acrylonitrile content by 5 g, the amount of percent add-on increased by more than 4 times and the amount of homopolymer produced as a byproduct was only 6.6% (see Table 3.3); while the conversion of polymerization was as high as 41%, the amount of which was normally expected for the radical chain polymerization. It is of great interest to see the extent of water absorption capacity of the copolymer itself and in the soil, and chemical environments.

3.3 Water Absorption

3.3.1 In Deionized Water

Table 3.5 and Figure 3.10 illustrate the water absorption capacity of starch-g-polyacrlonitrile in deionized water.

Table 3.5 Water Absorption Capacity of Starch-g-Polyacrylonitrile in Deionized Water.

Starch(g)/Acrylonitrile (g) Ratio	Water Absorption Capacity (g/g)
10/5	118
10/10	172
10/15	194
10/20	234
10/25	264
10/30	264

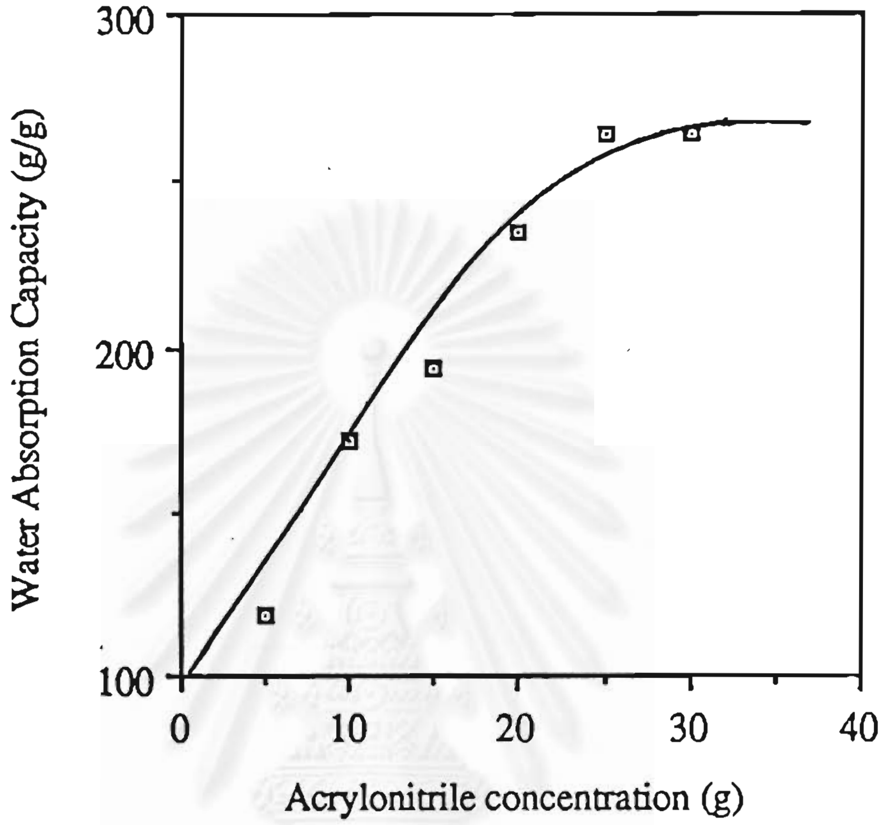


Figure 3.10 **Water Absorption Capacity of Starch-g-Polyacrylonitrile in Deionized Water.**

As shown in Table 3.5 and Figure 3.10, water absorption capacity of the starch-g-polyacrylonitrile increased with the acrylonitrile contents. Water absorption capacity of the copolymer was in the same trend as the percent add-on and grafting efficiency. A linear relationship between water absorption and the amount of acrylonitrile was observed at the low acrylonitrile contents from 5% to 20%. The absorption curve reached a plateau when the acrylonitrile concentrations exceeded 20%. Similar trend of water absorption and percent add-on is observed which is showed in Figure 3.11.

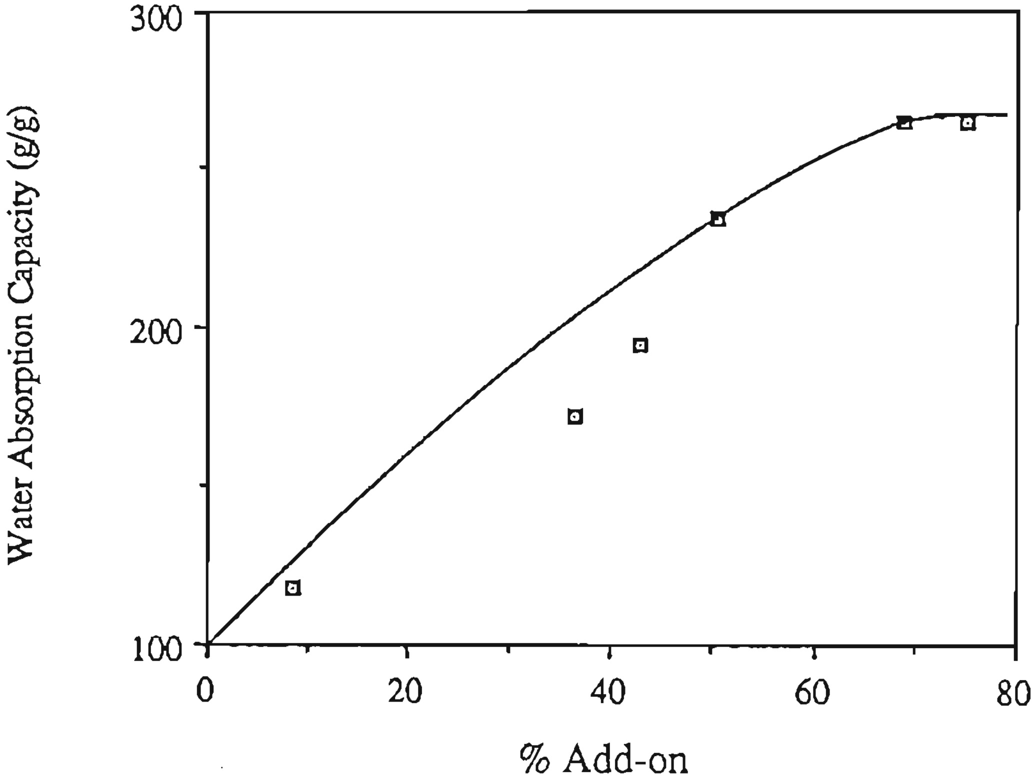


Figure 3.11 Effect of Percent Add-On on Water Absorption Capacity of Starch-g-Polyacrylonitrile in Deionized Water.

These results correlate quite well with the mechanistic model of the enhanced water absorbency of acrylate-grafted polysaccharides (13) that is identical to the same as that described by Grignon and Scallman for the swelling of cellulose gels (14). The swelling is considered to be caused by osmotic pressure differential resulting from a difference in concentration of mobile ions between the interior of the gel and the external solution. Figure 3.12 elucidates a schematic representation of a starch graft copolymer which is responsible of osmotic pressure for water intake.

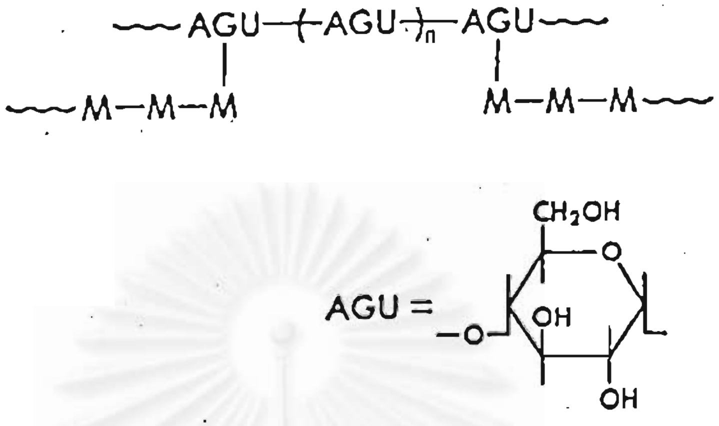


Figure 3.12 Schematic Representation of a Starch Graft Copolymer.

In this case, the concentration of mobile K^+ ions in the polymer gel, resulting from the saponification step, is higher than those in deionized water which comprises only hydrogen and oxygen atoms. As the ionic groups cannot move out of the gel, the solution within the gel is regarded as separated from the external solution by a semipermeable membrane which confines to the potassium carboxylate and carboxamide groups, but gives free passage of water. The gel swells as a result of the entry of water in an attempt to reduce the osmotic pressure differential due to the difference in ion concentrations. Swelling continues until the osmotic pressure differential is equal to the resistance to further expansion, i.e., when the ion concentration between inside and outside the gel has reached equilibrium.

Okieimen and Ebhoaye (15) suggested that the water absorption properties of cellulosic materials are thought to result from interaction through hydrogen bonding of the hydroxyl groups on the cellulose with water molecules.

In conclusion, the effect of water absorption depends on the frequency of interposition of the grafted polymer chains on the cellulosic starch backbone, and the nature of the grafted polymer. In other words, the amount of grafting chain or acrylonitrile is one of the determining factors which is indicated in Table 3.5

It must be noted that the figures of water absorption capacity of the graft copolymer in deionized water change with multiple wetting-drying cycles. The loss of absorbency is probably due to a condensation type of crosslinking reaction occurring between hydroxyl, carboxamide or carboxyl substituents at the drying temperature(15).

3.3.2 In Magnesium Chloride Solutions

Table 3.6 and Figure 3.13 present the result of water absorbency of starch-g-polyacrylonitrile in 0.50 and 1.0% $MgCl_2$ solutions as follows:

Table 3.6 Results of Water Absorption of Starch-g-Polyacrylonitrile in Saline Solutions.

Starch(g)/Acrylonitrile(g)	Water absorption (g/g) in Percent $MgCl_2$ solutions	
	0.5	1.0
10/5	9.8	11.1
10/10	17.1	14.0
10/15	19.0	14.5
10/20	19.6	14.4
10/25	19.4	14.3
10/30	19.0	14.4

In magnesium chloride solutions, a plateau indicating an osmotic pressure differential of zero, was reached with a maximum water absorption of only 19.6 g/g with 0.5% solution of magnesium chloride at 20% acrylonitrile content. The 1% solution gave similar result with the maximum water absorption of only 14 g/g.

In generalization, the decrease in water absorption of starch-g-polyacrylonitrile in the presence of salt solutions, such as Ca^{+2}, Mg^{+2}, and fertilizers is mainly due to the fast approaching of zero osmotic pressure differential of the potassium carboxylate and carboxamide semipermeable membrane. It is also interpreted as due to the ionic strength resulted from electronic configuration on one hand, and on the other hand for divalent cations such as Mg^{+2} ions, the less absorption of the copolymer probable is the consequence of crosslinking by salt formation of carboxyl groups on adjacent chain or chain segments. In addition, it has been suggested that the presence of sodium chloride, a monovalent cation, causes the grafted polyion chain to undergo configurational changes, resulting in the reduction of the swelling forces(15). By far, the sound explanation for water absorption is the osmotic pressure differential concept. It is suggested, therefore, that more superabsorbent be incorporated in the saline or fertilized soil, the amount of which to be added needs more experimental works to indicate.

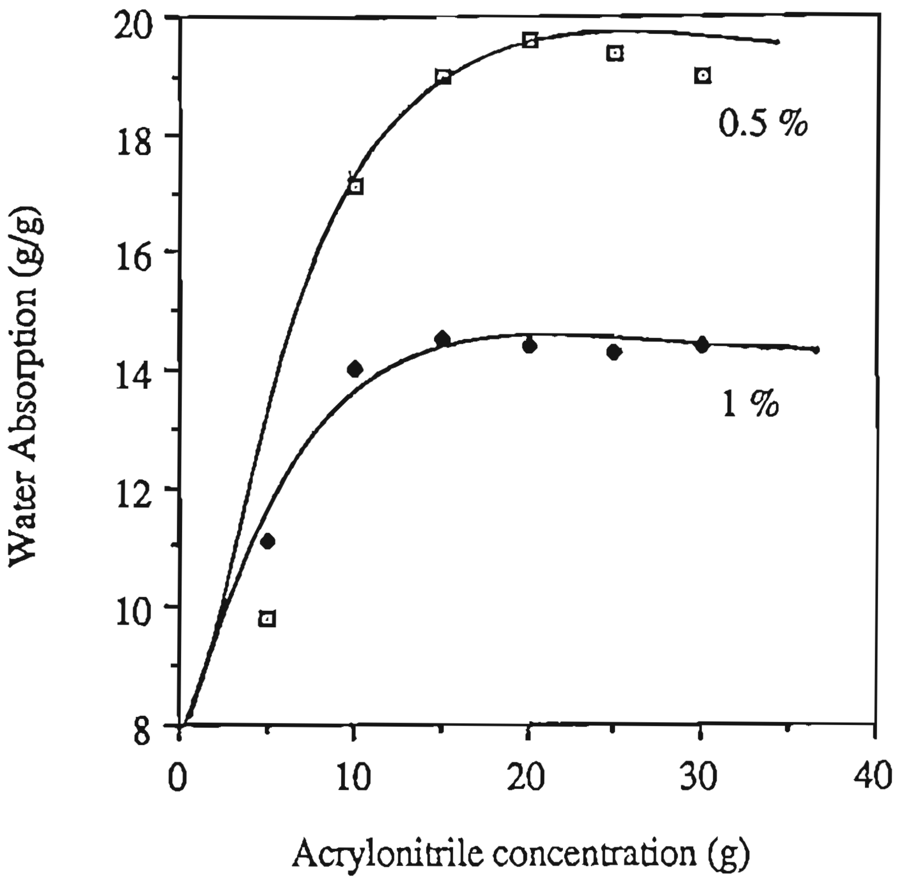


Figure 3.13 Results of Water Absorption of Starch-g-Polyacrylonitrile in the Presence of Magnesium Chloride Solutions.

3.3.3 In Sand Alone and Sand with Saponified Starch-g-Polyacrylonitrile

The results of water retention capacity in sand are given in Table 3.7 and illustrated in Figures 3.14 through 3.15. They clearly indicate that the water retention capacity is definitely depend on the amount of starch-g-polyacrylonitrile used. The water retention of the medium increased dramatically, since that of sand was only 36.5 g/g.

Table 3.7 Water Retention Capacity of Sand Mixed with Various Concentrations of Saponified Starch-g-Polyacrylonitrile.

Starch(g)/ Acrylonictrile(g)	Water retention Capacity (%) on polymer added in sand			
	0.5%	1.0%	1.5%	2.0%
10/5	50	68.2	81.3	96.8
10/10	60	85.8	93.3	109.1
10/15	66.4	100.3	122.3	137
10/20	68.5	102.8	158.2	186
10/25	81.2	130.0	174.6	220
10/30	85.2	135.8	182.7	232

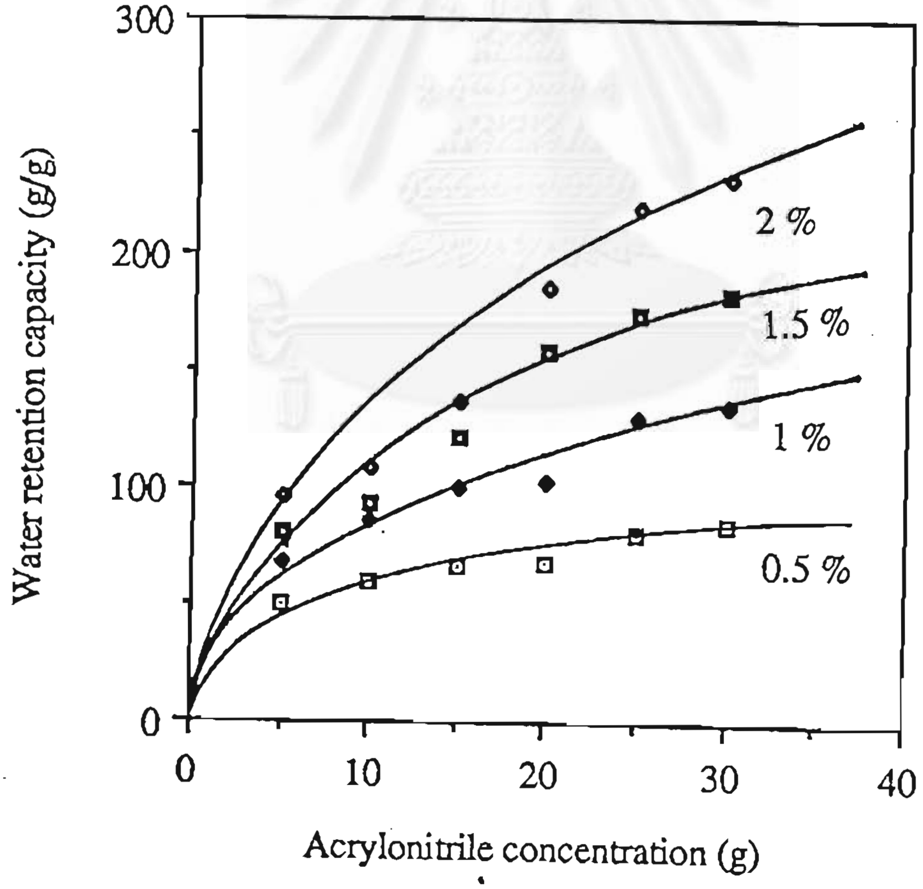


Figure 3.14 Water Retention Capacity of Sand Mixed with Various Amounts of Cassava Starch-g-Polyacrylonitrile at Various Acrylonitrile Contents.

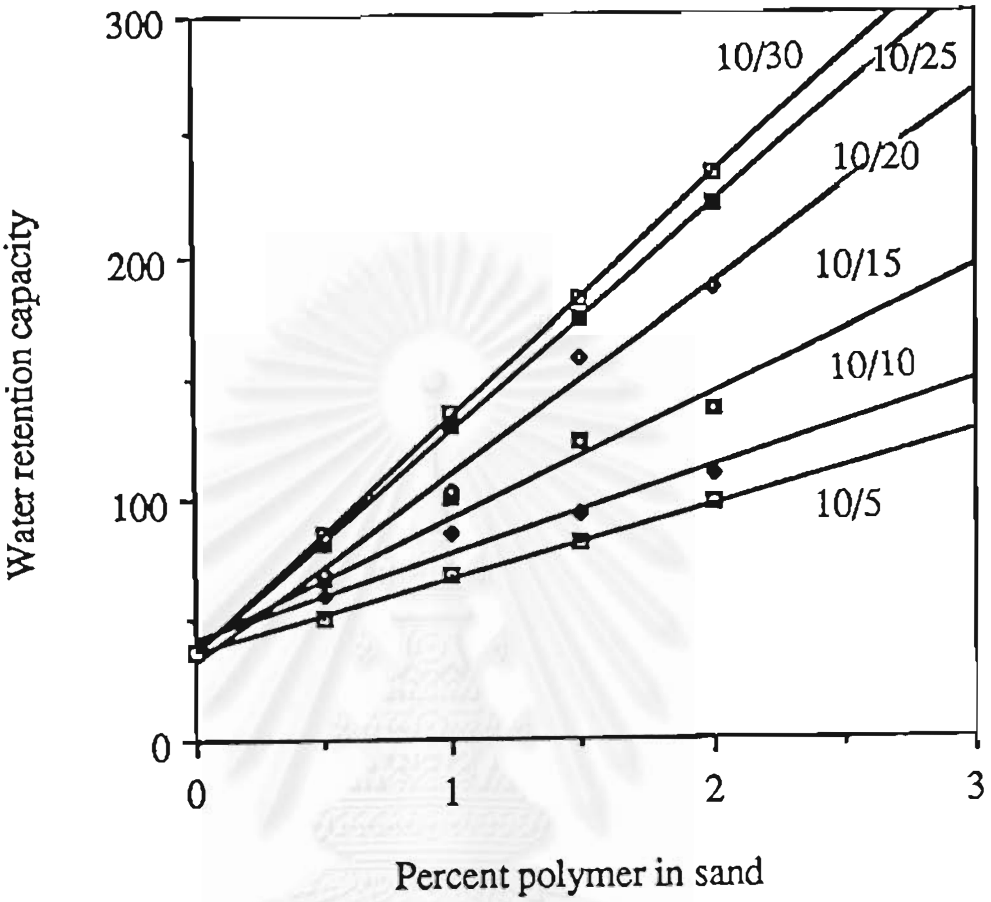


Figure 3.15 **Water Retention Capacity of Sand Mixed with Cassava Starch-g-Polyacrylonitrile Containing Various Acrylonitrile Contents at Different Amounts of the Copolymer Added.**

Figures 3.14 and 3.15 show a linear relationship between water retention and polymer concentration. As the concentration increases, so does the water retention capacity. In the case of increasing the starch/acrylonitrile ratios, going from 10:5 to 10:30, water retention capacity increased accordingly to the increasing amounts of acrylonitrile and the amounts of the copolymer added.

3.4 Scanning Electron Microscopy of Saponified Cassava Starch-g-Polyacrylonitrile

In order to observe the changes in particle size and shape of the graft copolymer, Cassava starch was investigated under a Fritsch Laser Particle Sizer, model

Analysette 22. It is very unfortunate that under all the available techniques of this equipment, the graft copolymer cannot be investigated which is due to its absorptivity causing itself stickiness and coalescence, and finally becoming an aggregate center. The aggregator then adhered to parts of the unit which ceased the measurement. Therefore, only the particle size distribution of the starch could be illustrated in Figure 3.16. It was found that the average size was 16.8 micrometers with a mean square diviation of 11.91 micrometers at the measure reliability of 98.1%. Truncated, round and oval like are the shapes of this Cassava starch viewed under a light microscope(16).

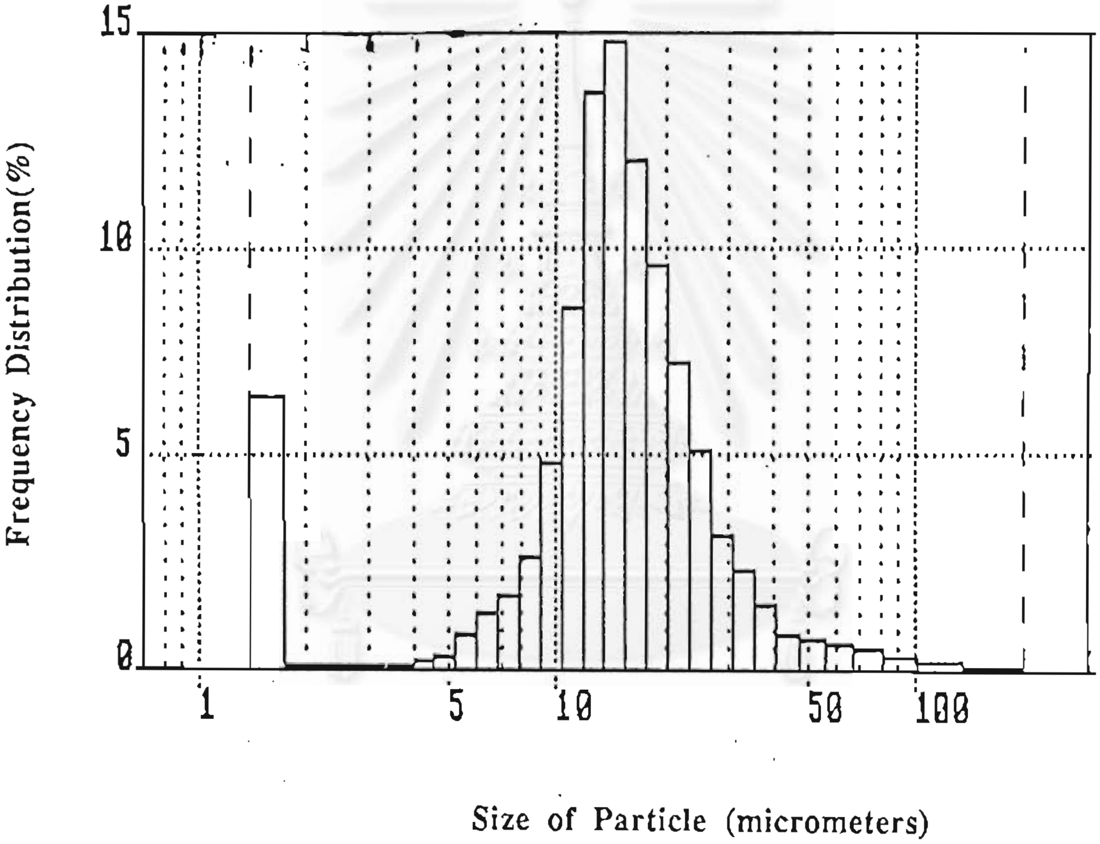


Figure 3.16 Freguency Distribution of Cassava Starch.

The electron micrographs of all ratios of cassava starch/acrylonitrile gave identical surface characteristic and pore structure. These micrographs in Figure A-1 indicated a very soft, sticky and porous surface. The distributions of pores were very irregular and so did the depth of the pores. These pores, indeed, could accommodate huge amounts of water and solutions. Since the particle shapes of the starch-g-polyacrylonitrile were changed through the grinding process, therefore, no correlation between the pore size distribution and absorptivity can be deduced. X-ray microanalysis indicated the presence of huge amount of the potassium ion and very minute amount of the sodium, iron and cerium ions. However, the reliability of tracer element analysis should be performed by X-ray fluorescence technique. The electron micrographs were presented in Appendix 1.

3.5 General Discussion

There were two points proposed to be run in the proposal submitted to the Ratchadapisak Sompoch Research Fund that the graft copolymer could be investigated by nuclear magnetic resonance and the laboratory test on plant's utilization of the graft copolymer.

3.5.1 NMR Spectroscopy

After investigations it was found that: The graft copolymers do not dissolve in any solvent due to the relatively highly crosslinked nature within the gel. This speculation was supported by the work of Fanta and coworkers(17). They pointed out that crosslinking could occur during graft copolymerization, during alkaline saponification, and during drying in which heat induced crosslinking of dry polymer was observed. Combination of polyacrylonitrile macroradicals during the graft copolymerization of acrylonitrile with starch give a crosslinking behavior. Further crosslinking within the granule structure takes place during alkaline saponification, especially in solvents which contain mainly water. As a result of these crosslinking reactions, individual granules of starch-g-polyacrylonitrile do not disintegrate when saponified with hot alkali, but retain their integrity and exist in water as highly swollen gel particles. Aqueous dispersions of these gels thus have high viscosity, when all the free water has been absorbed and the gel particles are in a closely packed state. Upon drying, individual gel particles of viscous aqueous dispersions of starch-g-polyacrylonitrile knit together to form film and also coalesce to form larger conglomerates. Dry grafted polymer does not redisperse back into gel particles when placed in water but swells as either a continuous film or as macroparticles as it imbibes water. Therefore NMR spectroscopy could not be performed.

3.5.2 Plant's Test on Mixture of Sand and Cassava Starch-g-Polyacrylonitrile

Due to the limited time available for this research, the originally planned procedure of this topic was changed. Instead of mixing sand with Cassava starch-g-polyacrylonitrile for cash crop experiment as proposed which needs at least 6-8 months to record the change, we used an ornamental plant, Bai Plu Dung, a kind of Piperaceae, as an experimental species. The plant was dipped in a glass containing a slurry of 0.3 g graft copolymer in 90 ml water. The glass was placed near the window where sunlight and wind could get on the plant. No further irrigation was provided. The plant could survive for 26 days until the water was nearly dried out. Repeated cycles were continued until the third cycle was reached with a decreasing nonirrigation period. Some leaves turned yellow and then fell away while simultaneously a number of new leaves and branches grew with healthy sign. This illustrates that the graft copolymer helps in maintaining the normal growth and vigor of plantation without wilting symptoms, even when the frequency of irrigation is considerably reduced.

In addition, a substantial amount of the graft polymer was given to one professor at the Department of Botany to carried out further experiments on plants.

Chapter 4

Conclusion and Suggestions

The investigation on the chemical modification of native Cassava starch by a graft copolymerization has led to a new type of polymer with attractive water absorption properties. This novel material is a biodegradable high water-absorbing polymer. The results obtained are very significant in terms of the numerous applications possible: The product has already been used in agricultural, horticultural, silvicultural areas and in industrial goods such as sanitary napkins, baby diapers, etc. Our results match well similar material, synthesized from different sources of substrate, in industrial nations.

4.1 Conclusion

The findings can be summarized as follows:-

1. Cassava starch-g-polyacrylonitrile was synthesized and confirmed by Infrared spectroscopy: The nitrile stretching band appeared at 2,243 cm^{-1} during grafting, and disappeared during saponification; The characteristic bands appeared at 3, 400; 1,000-1,100 cm^{-1} indicated the occurrence of grafting with Cassava starch. The disappearance of all the nitrile groups, on the other hand, resulted in the appearance of carboxylate and carboxamide groups. The formation of two new functional groups resulted also in two new absorption bands. Firstly, the carboxylate group -COOK gave rise to two bands: a strong asymmetrical stretching band at 1570 cm^{-1}, and a weak, symmetrical stretching band at 1400 cm^{-1}. Secondly, the primary amide could not be detected, probably as a result of a relatively low concentration, and/or due to the usually low intensity of the NH stretching band and overlapping with existing ones, the OH stretching bands of the starting material. These two groups are capable of water absorption properties based on the differential in osmotic pressure due to the potassium carboxylate and carboxamide semipermeable membrane.

2. By increasing the acrylonitrile content, an increase of percent homopolymers and percent add-on was observed, while the percent grafting efficiency decreased. The formation of polyacrylonitrile as a byproduct was undesirable in water absorption capacity.

3. Water absorption capacity of Cassava starch-g-poly-acrylonitrile synthesized was in the range of 120 to 270 times their original dried weight depending upon the acrylonitrile contents from 5 g to 30 g based on a 10 g Cassava starch.

4. The starch/acrylonitrile ratio of 10:10 is an attractive figure since it is economical to produce, yet still gives a water absorption value of 170. Most of the commercial available ones have water absorption figures of about 120 to 200.

5. Water absorption capacity of the graft copolymer in 0.5 and 1.0% magnesium chloride solutions gave a maximum value at 20 g/g and 14.5 g/g respectively. An increase in ion content in water reduces the water absorption due to a decrease in the osmotic pressure.

6. Water retention capacity in river sand was 36.5 g/g. Mixtures of sand with 0.5, 1.0, 1.5, and 2.0% Cassava starch-g-polyacrylonitrile could increase water retention gradually upto a maximum of 232 g/g at 2% of the polymer synthesized from 30 g. acrylonitrile.

7. Scanning electron micrographs revealed the soft, sticky and porous surface of the graft copolymer as well as the irregular depth and size of the pores. This characteristic is capable of holding a huge amount of water.

4.2 Suggestion and Further Work

Since this current research is only a guideline of the whole spectrum of this area, further experimental work on a wide range of factors should be proceeded. As the starch-based high water-absorbing polymer can be deteriorated by the following factors:

1. Multiple wetting-drying cycle causes less absorption.
2. Degradation by plants.
3. Decomposition by microorganism.
4. Degradation by ultraviolet radiation and heat.
5. Decrease in water absorption by salt solutions.

To develop a better and new high water-absorbing polymers to be used in agriculture and horticulture, the following properties are to be acquired:

1. Permanent water absorption stability.
2. Stable expanding, wetting, and non-shrinking drying.

However, suggestions so far for the current facilities at Chulalongkorn University, the researchers can only pursue the following aspects:-

1. To improve the water absorption capacity by using either a better catalyst system or crosslinking agents.

2. Instead of using acrylonitrile as a grafting monomer, acrylic acid and/ or methyl methacrylate could also be used.

3. To make the production of Cassava starch-g-polyacrylonitrile economically feasible, an attempt to reduce the quantity of the homopolymer, polyacrylontrile, to an acceptable level so that the cost of N,N-dimethylformamide extraction can be reduced or even eliminated. In addition to this, grafting efficiecy and the water absorption capacity of the copolymer should be high enough to be useful for plants utilization.

4. Thailand, instead of importing these polymers, or buying foreign patents which is very expensive, should develop its own superabsorbents. The country being one of the largest cassava producer in the world, Cassava starch is an excellent raw material for such development. Research in this field should be pursued and manufacturing on an industrial scale should seriously be taken into account.

5. The proper uses of this graft copolymer could help the farming community especially those live in the Northeastern provinces to utilize to its fullest applications this product could provide. Field experiments on farm crops and reforestation should be investigated intensively.

6. Today, in view of the hardship of the people of Esarn and their vulnerability to rain shortage, the challenge to Thailand, by a combined effort between the academia and the chemical industry, is to produce superabsorbents at a cost affordable to farmers and reforesters, and to widen its application to other markets.

References

1. Fanta, G. F., and M. D. William, "Saponified Starch-g-Polyacrylonitrile and Related Absorbents," U.S. Department of Agriculture, 1981.
2. Fanta, G. F., and Bagley, E. B., in "Encyclopedia of Polymer Science and Technology," Supplement, Vol. 2, P. 665, N. M. Bikales, ed., Wiley, New York, 1977.
3. Ranby, B., and H. Sundstorm, "Graft Copolymerization onto Native Cellulosic Fibres using Mn^{+3} Initiation," Eur. Polym. J., 19(10), 1067-1070, 1983.
4. Ranby, B., and C. Rodehed, "Water Vapor Absorption and Aqueous Retention of Hydrolyzed Starch Polyacrylonitrile Graft Copolymer-" Superabsorbent Starch", Makromol. Chem., 182, 87-94, 1981.
5. Patel, A. R., K. C. Patel and R. D. Patel, "Graft Copolymers of Starch and Polyacrylonitrile. I. Effect of Source," Die Angewanate Makromolekulare Chemie, 27, 11-20, 1985.
6. Rutenberg, M. W., "Starch and Its Modification", Handbook of Water - Soluble Gums and Resins (Davidson, R.L. ed), pp. 22-2-22-5., McGraw-Hill Book Company, New York, 1980.
7. Paschall, E. F., "Starch," Encyclopedia of Food Technology, (Johnson, A. H., and M. S. Peterson, eds), Vol. 2, pp. 850-853, The Avi Publishing Company. Inc:, Westport, 1974.
8. Radley, J. A., Examination and Analysis of Starch and Starch Products, pp. 18 - 20, Applied Science Publishers Ltd., London, 1976.
9. Mark, A. M., W. B. Roth, C. L. Mehltretter, and C. E. Rist, Cereal Chem, 41, 197, 1964.
10. Brockway, C. E., J. Polymer Sci. A, 2, 3733, 1964.
11. Rodehed, C., and B. Ranby, "Structure and Molecular Properties of Saponified Starch-g-Polyacrylonitrile," J. Appl. Polym. Sci., 32, 3323-3333, 1986.
12. Mehrotra, R., and B. Ranby, "Graft Copolymerization onto Starch. III. Grafting of Acrylonitrile to Gelatinized Potato Starch by Manganic Pyrophosphate Initiation," J. Appl. Polym. Sci., 22, 2991-3001, 1978.
13. Ziderman, I. I., and J. Belayche, "Role of Polyacrylate Starch Copolymer in Water Sorption," J. Appl. Polym. Sci., 32, 5791-5798, 1986.
14. Grignon, J., and A. M. Scallman, "Effect of pH and Neutral Salts upon the Swelling of Cellulose Gels," J. Appl. Polym. Sci., 25, 2829-2843, 1980.

15. Okieimen, E. F., and J. E. Ebhoaye, "Grafting Acrylic Acid Monomer on Cellulosic Materials," J. Macromol. Sci.-Chem., A23(2), 349-353, 1986.

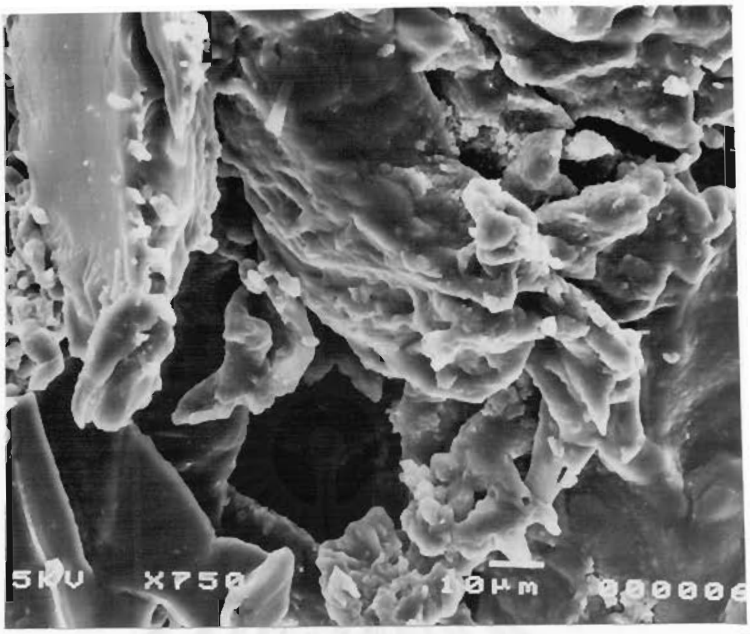
16. Rutenberg, M. W., "Starch and Its Modification," Handbook of Water-Soluble Gums and Resins (Davidson, R.L. ed.) p. 22-12, McGraw-Hill Book Company, Inc., Westport, 1974.

17. Fanta, G. F., B. C. Robert, and M. D. William, "Cross-linking in Saponified Starch-g-Polyacrylonitrile," Graft Copolymerization of Lignocellulose and Fibers, ACS Symp. Ser., pp. 195-215, ACS, Washington, D.C., 1982.

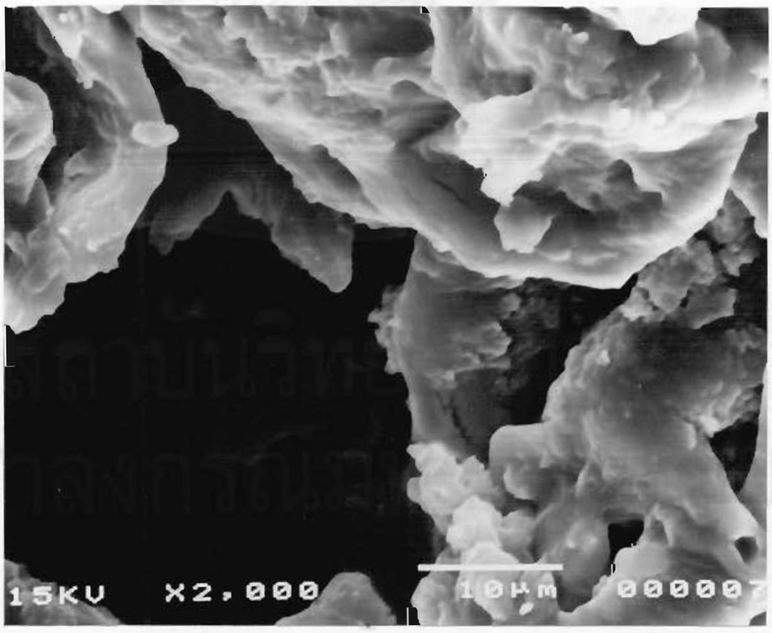
Appendix 1

Electron Micrographs of Cassava Starch-g-Acrylonitrile

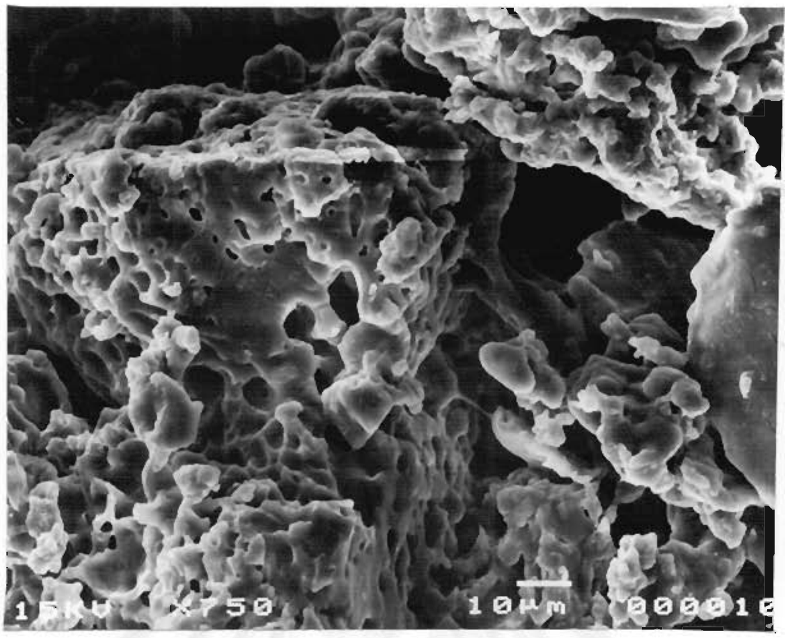
Section 3.4 in Chapter 3 described the characteristics of scanning electron micrographs of the saponified cassava starch-g-polyacrylonitrile, the details of which were presented in Figure A-1. The original average particle size of Cassava starch was 16.8±11.91 micrometers as shown in Figure 3.16. All electron micrographs showed the particle sizes of greater than 134 micrometers. Views of the edge and surface of this ground particle of the copolymer showed that it was composed of closely packed particles. It would therefore seem necessary to propose a crosslink between individual microgel particles to account for the observed macroparticles which could not be ground to their ultimate or primary particle size. This was most probably due to the film formation of the saponified starch-g-polyacrylonitrile on drying. Attempts were applied to grind the film into a powder form by the simple utensils available ,i.e., a motor and a pestle, in the Polymer Laboratory. Therefore, it is not surprising that the electron micrographs of the products synthesized from different concentrations of acrylonitrile gave the same general appearance of sticky and porous surface with various pore diameters and depths. These characteristics are, of course,capable of holding and absorbing a large amount of water and aqueous solutions.



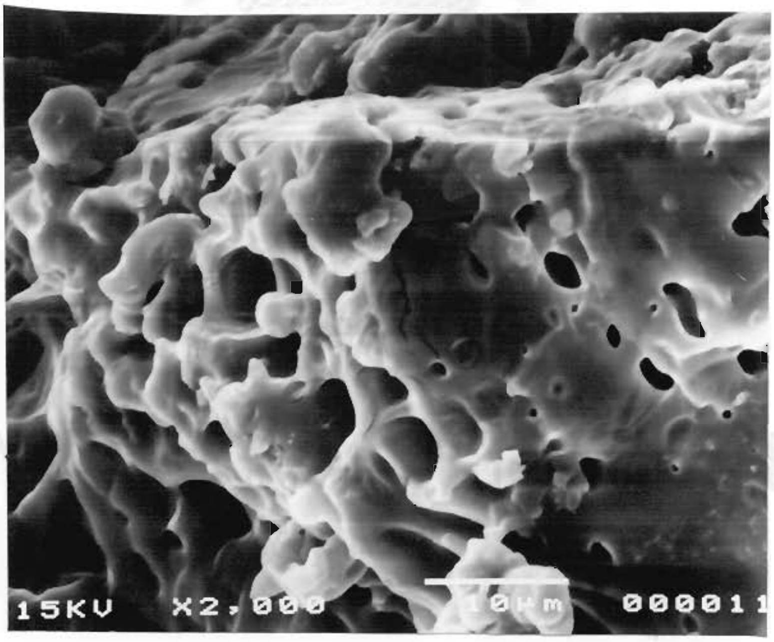
c) Electron micrograph of the copolymer synthesized from 10 g acrylonitrile, magnification at 750 times.



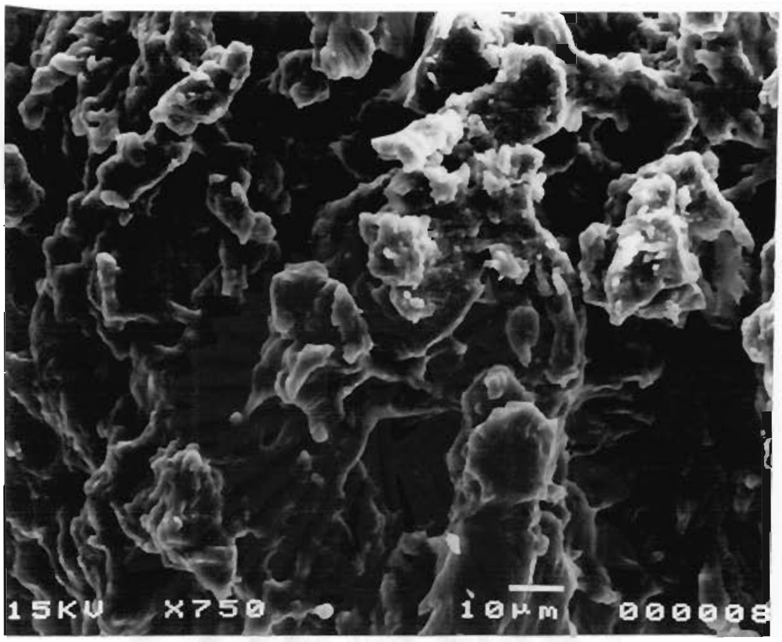
d) Electron micrograph of the copolymer synthesized from 10 g acrylonitrile, magnification at 2,000 times.



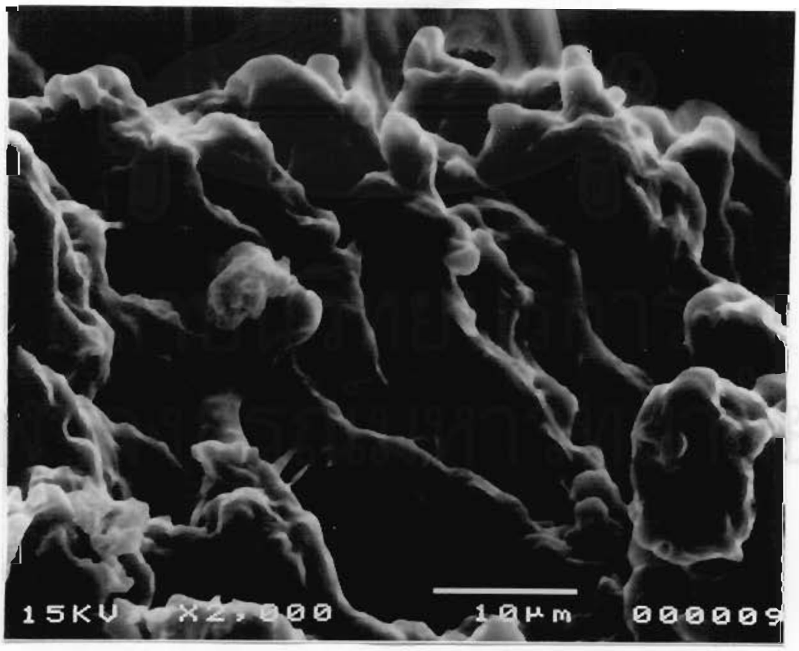
e) Electron micrograph of the copolymer synthesized from 15 g acrylonitrile, magnification at 750 times.



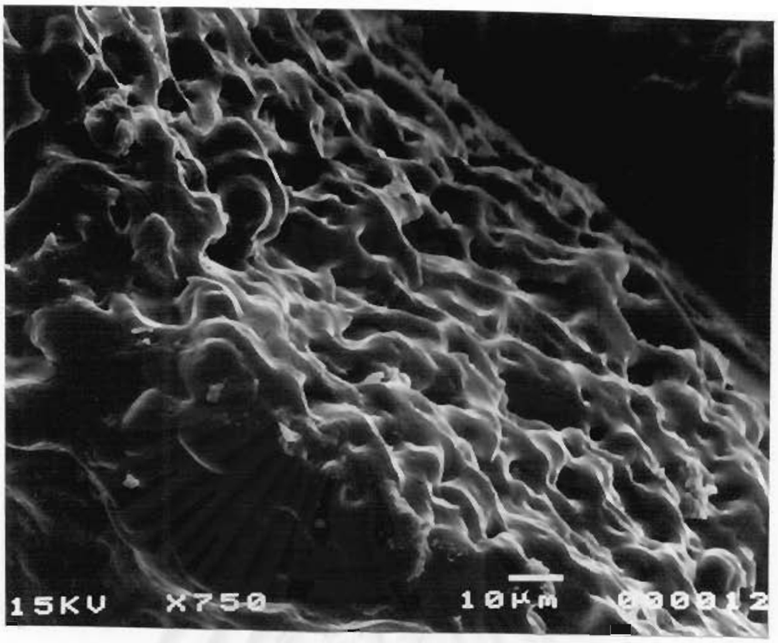
f) Electron micrograph of the copolymer synthesized from 15 g acrylonitrile, magnification at 2,000 times.



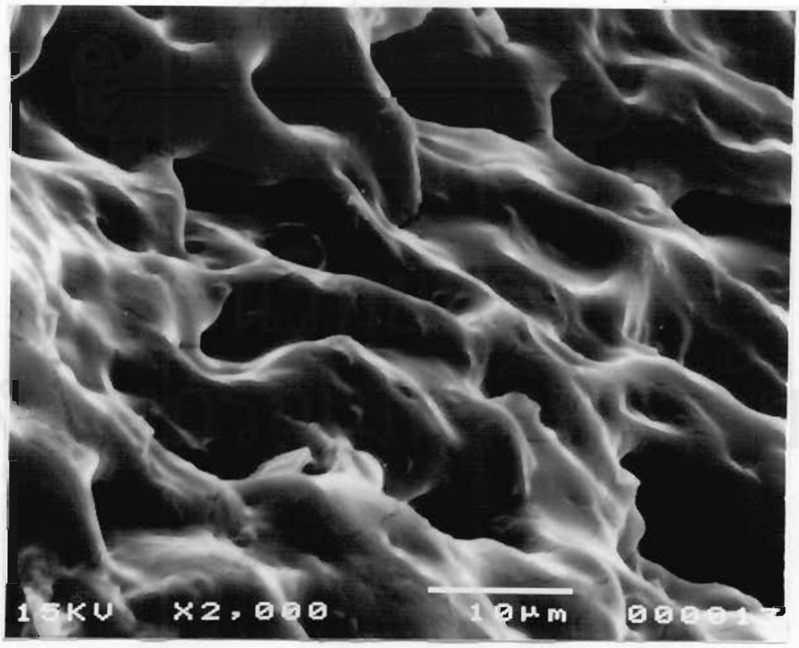
g) Electron micrograph of the copolymer synthesized from 20 g acrylonitrile, magnification at 750 times



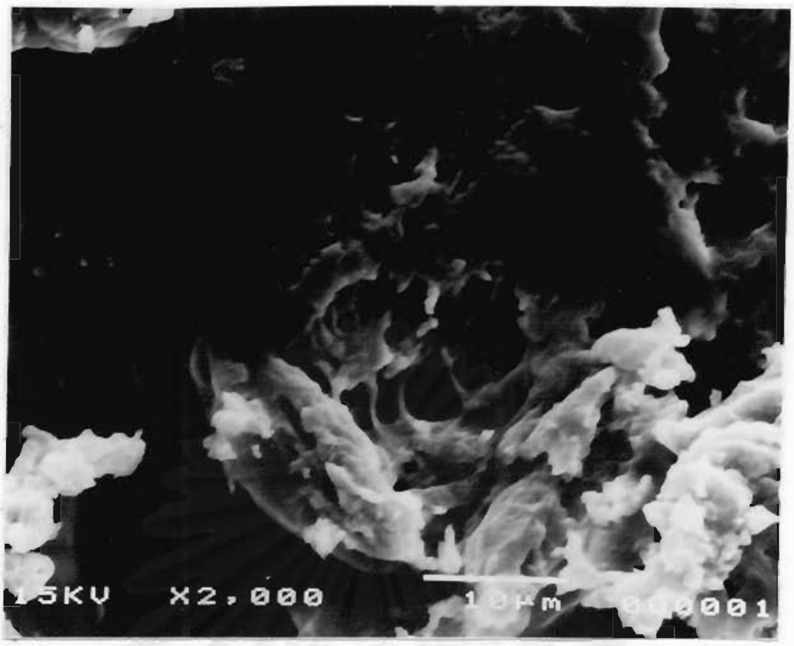
h) Electron micrograph of the copolymer synthesized from 20 g acrylonitrile, magnification at 2,000 times.



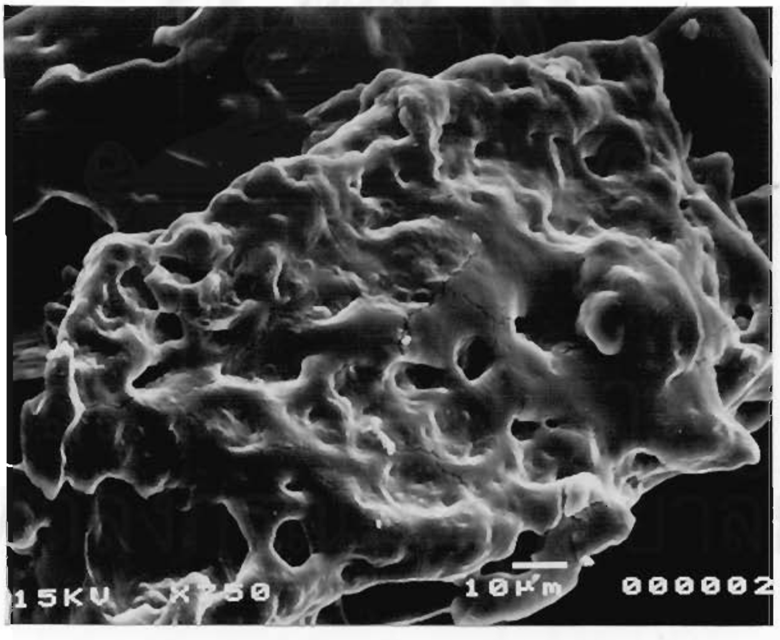
i) Electron micrograph of the copolymer synthesized from 25 g acrylonitrile, magnification at 750 times



j) Electron micrograph of the copolymer synthesized from 25 g acrylonitrile, magnification at 2,000 times.



k) Electron micrograph of the copolymer synthesized from 30 g acrylonitrile, magnification at 750 times.



l) Electron micrograph of the copolymer synthesized from 30 g acrylonitrile, magnification at 2,000 times.

Figure A-1 Electron Micrographs of Saponified Cassava Starch-g-Polyacrlonitrile