การเตรียมซุปเปอร์แอบซอร์แบนต์ที่สลายตัวได้ทางชีวภาพของ แป้งมันสำปะหลัง-อะคริลาไมด์/โพแทสเซียมอะคริเลต

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PREPARATION OF BIODEGRADABLE SUPERABSORBENT OF CASSAVA STARCH-ACRYLAMIDE/POTASSIUM ACRYLATE

Miss Piyaporn Limworanusorn

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Petrochemistry and Polymer Science
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บทคัดย่อวิทยานิพนธ์

ปิยพร ลิมวรนุสรณ์ : การเตรียมซุปเปอร์แอบซอร์แบนต์ที่สลายตัวได้ทางชีวภาพของแป้งมันสำปะหลัง-อะคริลาไมด์/โพแทสเซียมอะคริเลต. (Preparation of Biodegradable Superabsorbent of Cassava Starch-Acrylamide/Potassium Acrylate) อ. ที่ปรึกษา : ศาสตราจารย์ ดร.สุดา เกียรติกำจรวงศ์, 112 หน้า. ISBN 974-346-515-4.

ได้เตรียมพอลิเมอร์ซุปเปอร์แอบซอร์แบนต์ที่สลายตัวได้ทางชีวภาพจากปฏิกิริยากราฟต์โคพอลิเมอไรเซชันของกรดอะคริลิก/อะคริลาไมด์ลงบนแป้งมันสำปะหลัง โดยใช้ระบบตัวริเริ่มแบบรีดอกซ์ของไฮโดรเจนเพอร์ออกไซด์และกรดแอสคอร์บิก พารามิเตอร์สำคัญที่ศึกษาเพื่อให้ได้ผลิตภัณฑ์ที่สามารถดูดซึมน้ำได้สูงได้แก่ อัตราส่วนระหว่างแป้งต่อมอนอเมอร์, อัตราส่วนระหว่างกรดอะคริลิกต่ออะคริลาไมด์ และความเข้มข้นของระบบริเริ่มและสารเชื่อมขวาง (เอ็น,เอ็น-เมทิลีนบิสอะคริลาไมด์)ที่ใช้ในระบบ ผลพลอยได้ของปฏิกิริยาคือพอลิเมอร์อิสระของโฮโมพอลิเมอร์ทั้งสองชนิดและโคพอลิเมอร์ซึ่งได้ถูกสกัดออกโดยใช้น้ำเป็นตัวทำละลาย จากนั้นนำกราฟต์โคพอลิเมอร์ที่ได้มาผ่านกระบวนการสะพอนิฟายด์ด้วยสารละลายโพแทสเซียมไฮดรอกไซด์ความเข้มข้นร้อยละ 5 % ที่อุณหภูมิห้อง เป็นเวลา 1 ชั่วโมง เพื่อเปลี่ยนหมู่คาร์บอกซิลิกเป็นหมู่คาร์บอกซิเลต วัดหาความสามารถในการดูดซึมน้ำของผลิตภัณฑ์ที่ได้ นำกราฟต์โคพอลิเมอร์ที่ได้มาพิสูจน์เอกลักษณ์โดยใช้เทคนิคอินฟราเรดสเปกโทรสโคปี เพื่อพิสูจน์หาหลักฐานการเกิดกราฟต์ เปรียบเทียบกราฟต์โคพอลิเมอร์ที่ได้จากระบบที่มีการปรับสภาพให้เป็นกลางก่อนกับหลังเกิดปฏิกิริยากราฟต์โคพอลิเมอไรเซชัน กราฟต์โคพอลิเมอร์ที่ได้นำมาย่อยสลายทางชีวภาพโดยใช้เอนไซม์ α-อะไมเลส และทำการทดสอบผลของการย่อยสลายด้วยวิธีวัดความหนืด และทดสอบด้วยสารละลายไอโอดีนและสารละลายเบเนดิกซ์

ผลิตภัณฑ์ที่ผ่านกระบวนการสะพอนิฟิเคชันแล้วของแป้งที่กราฟต์ด้วยอะคริลาไมด์ (ในภาวะที่มีกรดไนตริกเป็นสารเติมแต่ง) ให้ค่าการดูดซึมน้ำ (270 กรัมต่อกรัมของน้ำหนักพอลิเมอร์แห้ง) สูงกว่าแป้งที่กราฟต์ด้วยกรดอะคริลิก (142 กรัมต่อกรัมของน้ำหนักพอลิเมอร์แห้ง) แต่แป้งที่กราฟต์ด้วยมอนอเมอร์ทั้งสองชนิดนี้ให้ค่าการดูดน้ำที่ดีกว่า โดยเฉพาะอย่างยิ่งที่อัตราส่วนของกรดอะคริลิกต่ออะคริลาไมด์ 1:1 ให้ค่าการดูดน้ำสูงที่สุด (312 กรัมต่อกรัมของพอลิเมอร์แห้ง) เนื่องจากแรงดันออสโมติก โดยเตรียมขึ้นในภาวะที่ใช้อัตราส่วนของแป้งต่อมอนอเมอร์ 3:4, ที่ความเข้มข้นของไฮโดรเจนเพอร์ออกไซด์ 5 %, กรดแอสคอร์บิก 0.5 % และสารเชื่อมขวาง 5 % โดยน้ำหนักของมอนอเมอร์ทั้งหมด นอกจากนี้ยังพบว่า ระบบที่มีการปรับสภาพให้เป็นกลางหลังการเกิดปฏิกิริยาให้ผลิตภัณฑ์ที่ดูดซึมน้ำดีกว่าระบบที่มีการปรับสภาพให้เป็นกลางก่อนเกิดปฏิกิริยา เนื่องจากค่าการละลายของมอนอเมอร์ที่แตกต่างกัน หลังจากทำการย่อยสลายด้วยเอนไซม์พบว่าโครงสร้างของแป้งในกราฟต์โคพอลิเมอร์ถูกย่อยเป็นกลูโคส ทำให้ความหนืดของสารลดลง และไม่เปลี่ยนสีสารละลายไอโอดีน แต่เปลี่ยนสีสารละลายเบเนดิกซ์จากสีน้ำเงินเป็นสีเหลือง แสดงว่ามีกลูโคส นอกจากนี้ทำการศึกษาความสามารถในการดูดซึมน้ำของกราฟต์โคพอลิเมอร์ในสารละลายเกลือและสารละลายบัฟเฟอร์ และทำการตรวจสอบลักษณะพื้นผิวของผลิตภัณฑ์โดยใช้เทคนิค SEM ซึ่งพบว่าพื้นผิวของผลิตภัณฑ์ที่สามารถดูดซึมน้ำสูงมีโครงสร้างเป็นรูอยู่จำนวนมาก งานวิจัยนี้อธิบายผลและปรากฏการณ์ของตัวแปรทางปฏิกิริยาการเกิดกราฟต์และค่าการดูดซึมน้ำ

ภาควิชา ....—......... ลายมือชื่อนิสิต ....
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ปีการศึกษา 2543 ลายมือชื่ออาจารย์ที่ปรึกษาร่วม ....—.........

AN ABSTRACT

4072313423 : MAJOR POLYMER SCIENCE

KEY WORD: BIODEGRADABLE SUPERABSORBENT / CASSAVA STARCH / ACRYLIC ACID / ACRYLAMIDE / REDOX SYSTEM

PIYAPORN LIMWORANUSORN : PREPARATION OF BIODEGRADABLE SUPERABSORBENT OF CASSAVA STARCH-ACRYLAMIDE/POTASSIUM ACRYLATE. THESIS ADVISOR : PROFESSOR SUDA KIATKAMJORNWONG, Ph.D., 112 pp. ISBN 974-346-515-4.

Preparation of a new type of biodegradable superabsorbent polymer by graft copolymerization of acrylic acid/acrylamide onto cassava starch via redox initiator system of hydrogen peroxide-ascorbic acid was investigated. Several important parameters were studied: starch-to-monomer ratio, acrylic acid-to-acrylamide ratio, concentrations of H_2O_2-ascorbic acid initiating system, and crosslinking agent of *N,N′*-MBA to produce the highest water absorption of the product. By-products of the reaction, the free polymers of the homopolymer and the copolymer, were removed by water extraction. Subsequently, the purified graft copolymer was saponified with a 5% aqueous solution of potassium hydroxide at room temperature for 1 hour to change the carboxyl group into the carboxylate group, and thereafter the product was measured for the water absorption capacity. The graft copolymer was characterized by infrared spectroscopy technique for grafting evidences. Comparisons of the graft copolymers between the preneutralized and postneutralized systems (via neutralization) were conducted. Biodegradation of the polymers was carried out using α-*amylase* to degrade the grafted copolymer. Viscosity measurement, iodine and Benedict's solution tests for the biodegraded grafted copolymers were conducted.

The saponified cassava starch-*g*-polyacrylamide (in nitric acid additive) gave the higher water absorbency (270 g/g dry weight) than that of the saponified cassava starch-*g*-poly(acrylic acid) (142 g/g dry weight). However, the saponified cassava starch-*g*-poly(acrylic acid-*co*-acrylamide) provided the increased water absorbency, especially at the ratio of acrylic acid-to-acrylamide of 1:1, gave the highest water absorbency due to osmotic pressure. The highest water absorbency (312 g/g dry weight) grafted copolymer was produced by the starch-to-monomer ratio of 3:4, acrylic acid-to-acrylamide ratio of 1:1, 5% wt of hydrogen peroxide, 0.5% wt of ascorbic acid, and 0.5% wt *N,N′*-MBA based on the total of monomers. The postneutralized system provided the grafted copolymer having the higher water absorbency than those of the preneutralized system because of the different dissociation of the monomers. After the α-*amylase* hydrolysis of the graft copolymers, the viscosity decreased because the graft copolymers were hydrolyzed into the glucose units. The hydrolyzed solution gave a negative test with the iodine solution and a positive test by the Benedict's solution, an indication of the existence of glucose units. The water absorptions of the product in salt and buffered (pH) solutions were measured. Moreover, the surface morphologies of the products were revealed by SEM technique, which indicated that highly porous structure was found in the graft copolymers with the higher water absorption. This research explains effects and phenomena of the reaction parameters on grafting parameters and water absorption.

Department ....—.............. Student's signature ....
Field of study ....Petrochemistry and Polymer Science.... Advisor's signature ....
Acadamic year ....2000.............. Co-advisor's signature ....—..............

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ABBREVIATIONS

SAPs	superabsorption polymers
WAC	water absorption capacity
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscopy
AA	acrylic acid
AM	acrylamide
N,N′-MBA	*N,N*′-methylenebisacrylamide
T_m	melting temperature
^{o}C	degree of celsius
g	gram
wt	weight
w/v	weight by volume
KNU/g	kilo novo unit per gram
cm^3	cubic centimeter
cm^{-1}	reciprocal centimeter, wave number
h	hour
min	minute
kPa	kilopascal
kCal	kilocalory
kGy	kilogray
M	Molarity
N	Normaliy
%T	Transmittance

CHAPTER 1

INTRODUCTION

1.1 Introduction

Superabsorbent polymers (SAPs) are polymers which can absorb water and salt solution, like urine, have many applications including the personal care industry. SAPs help stop water leaking into buried communication cables, make food packaging less messy by preventing fluids from leaking, and help control the moisture available in soil [1]. SAPs, used in infant diapers to absorb body fluids, are prepared from acrylic acid and a crosslinker, in aqueous solution or in a suspension of the aqueous solution in a hydrocarbon. The product is partially neutralized either before or after the polymerization step. Combinations of redox and thermal free-radical initiators, chelating agents, chain-transfer agents, and grafting agents are used to control the polymerization kinetics and molecular characteristics of the network [2]. There are two types of SAPs existing as natural or biodegradable SAPs which is biodegradable and petroleum-based SAPs which is non-biodegradable.

Biodegradable SAPs, the generally occurring resources for this type of polymer are of starch- and cellulose-base. Starch or cellulose is grafted by vinyl monomer in a form of carboxylated product to produce SAPs. Thailand is the great 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 scales that make the country too much surplus and unused cassava products. So it is appropriate to develop a cheap and reliable process to use the surplus cassava starch to increase its commercial value by modifying its chemical structure to produce a SAPs for various applications.

Biodegradable SAPs can be degraded by the microorganism produced enzyme “∝-*amylase*” to fragment a long-chain of starch into a short-chain of glucose. The measurement of biodegradation of SAPs can use various available methods such as viscosity test, benedict’s test, and iodine test.

1.2 Objectives

The objectives of this research are the following

1. To determine the optimum condition for the synthesis of the new superabsorbent polymers based on cassava starch as a grafting substrate, using a chemical initiation.

2. To study influences of reaction parameters on water absorption of the newly synthesized superabsorbent polymers.

3. To study biodegradation of the new superabsorbent polymers.

1.3 Expected Benefits Obtainable for Development of the Research

The benefits for the development can be:

1. To obtain a technique for the synthesis of cassava starch-*g*-poly(acrylic acid-*co*-acrylamide), which can be modified for a production of cassava starch-based SAP.

2. To investigate some influences of the reaction parameters which could improve water absorption of the superabsorbent polymers.

1.4 Scope of the Investigation

In this research, the necessary procedure of graft copolymerization of acrylic acid and acrylamide onto cassava starch via a chemical initiation to achieve the best product is as follows:

1. Preparing graft copolymers of acrylic acid and acrylamide onto cassava starch via a chemical method using a redox initiation, by studying the following parameters so as to select the suitable technique and to attain the appropriate reaction conditions:

    a) The optimum ratio of acrylic acid (g) to acrylamide (g).

    b) The optimum ratio of cassava starch (g) to monomer (g).

    c) The optimum quantity of ascorbic acid (% based on the total of monomers)

    d) The optimum quantity of hydrogen peroxide (% based on the total of monomers)

    e) The optimum quantity of crosslinking agent (% based on the total of monomers)

2. Extracting the homopolymer [poly(acrylic acid), polyacrylamide] and free copolymer [poly(acrylic acid-*co*-acrylamide)] of the crude product.

3. Bringing the obtained graft copolymer to further characterization steps:

    a) Determination of the free polymers formation.

    b) Determination of the percent add-on of the grafted copolymer.

    c) Determination of grafting ratio of the grafted copolymer.

    d) Determination of grafting efficiency of the grafted copolymer.

5. Saponification of starch graft copolymer.

6. Studying the absorption capacity of the saponified starch-*g*-poly(acrylic acid-*co*-acrylamide) in distilled water, sodium chloride, magnesium chloride, calcium chloride, and pH buffer solutions.

7. Investigating the biodegradation of the saponified starch-*g*-poly(acrylic acid-*co*-acrylamide) via the *amylase* enzyme and evaluated by a viscometry method.

8. Summarizing the result and preparing the report.

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 Superabsorbent Polymers (SAPs)

Superabsorbent polymers are three-dimensional polymer networks of flexible polymer chains that swell in aqueous solutions while maintaining their structural integrity. The polymer chains that make up the network do not dissolve in water because they are connected to each other through either covalent or non-covalent bonds. SAPs are the polymers of which absorbing capacity is higher than 15 times their dry weight in the aqueous fluids and liberate the retained fluid out via the diffusion through the gel membrane in the form of moisture.

Classification of SAPs from composition and preparation methods (networks formation, introduction of hydrophilic groups and product form) is indicated in Table 2.1 [3].

Table 2.1 Four Classifications of Superabsorbent Polymers

A. Polymer composition	
a) Starch	Graft polymerization
	Carboxymethylation
b) Cellulose	Graft polymerization
	Carboxymethylation

Table 2.1 (continued) Four Classifications of Superabsorbent Polymers

A. Polymer composition	
c) Synthetic polymer	Poly(acrylic acid)
	Poly(vinyl alcohol)
	Polyacrylamide
	Polyoxyethylene
B. Network formation	
a) Graft polymerization	
b) Crosslinked copolymerization	
c) Network forming reaction of water-soluble polymer	
d) Self-crosslinked polymerization	
e) Radiation crosslinking	
f) Introduction of crystal structure	
C. Hydrophilic groups	
a) Polymerization of hydrophilic monomers	
b) Carboxymethylation of hydrophilic monomers	
c) Graft polymerization of hydrophobic polymers with hydrophilic monomers	
d) Hydrolysis of nitrile or ester group	
D. Product form	
a) Powder	Globular
	Amorphous
b) Film	
c) Fiber	Short fiber
	Long fiber
	Non-woven fiber

2.1.1 Physical Behavior of Superabsorbents

SAPs swell remarkably well to form hydrogel structures with absorbed water. The most efficient water absorbers are polymer networks that carry dissociated, ionic functional groups. The factors that supply absorbing power to polymers are osmotic pressure based on movable counter-ions, and affinity between the polymer electrolyte and water. The factor that suppresses absorbing power, in contrast, is found in the elasticity of the gel resulting from its network structure.

Figures 2.1 and 2.2 show the absorption mechanism of an example of a superabsorptive resin, in the case a crosslinking polymer with sodium carboxylate groups. Before absorption, long chains of polymers are interwoven and polymers make a three-dimensional structure by crosslinking between the chains to make a dense phase. These SAPs instantaneously absorb water and swell with dissolution of Na^+, owing to the hydrophilic ionic groups, and becoming a gel [3]. In contact with water, the hydrophilic polymer backbone containing hydrophilic functional groups, interacts with the solvent accompanied by energy decrease and entropy increase. Hydration and the formation of hydrogen bonds are two sources for such polymer/solvent interactions. The polymer chains also tend to disperse in the given volume of solvent. This leads to a higher number of allowed configurations for the system, which is equivalent to a higher degree of entropy.

Due to the presence of the crosslinks, the polymer chains are restricted in swelling by elastic retraction forces of the network. The more the chains separate from each other, the more stiffness the originally coiled polymer chains become. This decreases the entropy of the chains. Finally there is a balance between the infinite dilution of the chains and the retractive forces. Higher cross-link densities give networks with stronger retractive forces and SAPs with lower degrees of swelling at equilibrium.

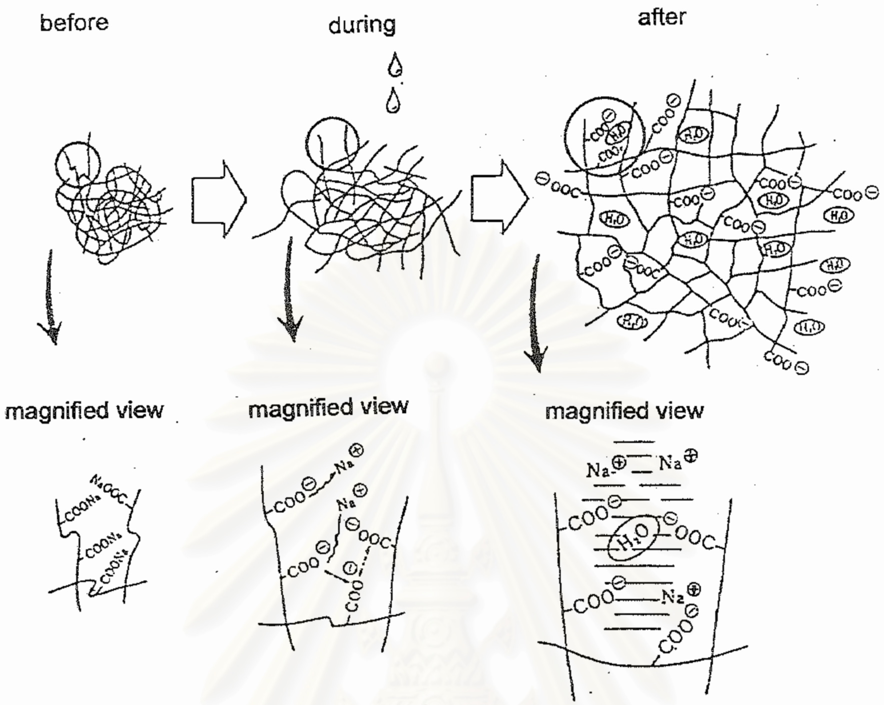


Figure 2.1 Water absorption in ionic polymer network. Sodium carboxylate groups are present in a stable salt form (before). Sodium cations (Na^+) leave carboxylate anions ($-COO^-$) bound to polymer chains, which then extend as a result of repulsion between anionic charge (during). Water molecules are taken in and retained in the polymer network (after).

For ionic polymers the solvent/polymer interactions include more than a simple mixing term. These gels bear electrical charges along the polymer chains. The negative charges of the carboxyl groups repel one another and are compensated for by the positive charges of the sodium ions, in order to maintain electrical neutrality. When the polymer comes into contact with water, the solvent diffuses into the polymer network and solvates the sodium ions. Water with its high dielectric constant lowers the attractive forces between the sodium ions and the negatively charged carboxylate groups. As in solutions of simple salts, the sodium ions are released and become freely moveable within the gel. Hence they contribute to the osmotic pressure. But for them it is impossible to leave the gel region due to the attraction forces of the negative charges, which are fixed along the polymer backbones. The driving force for swelling is then the difference between the osmotic pressure inside and outside of the gel. Increasing the salinity and the attraction force, the osmotic pressure of any external aqueous solution lowers the absorption capacity of the gel for that fluid [4].

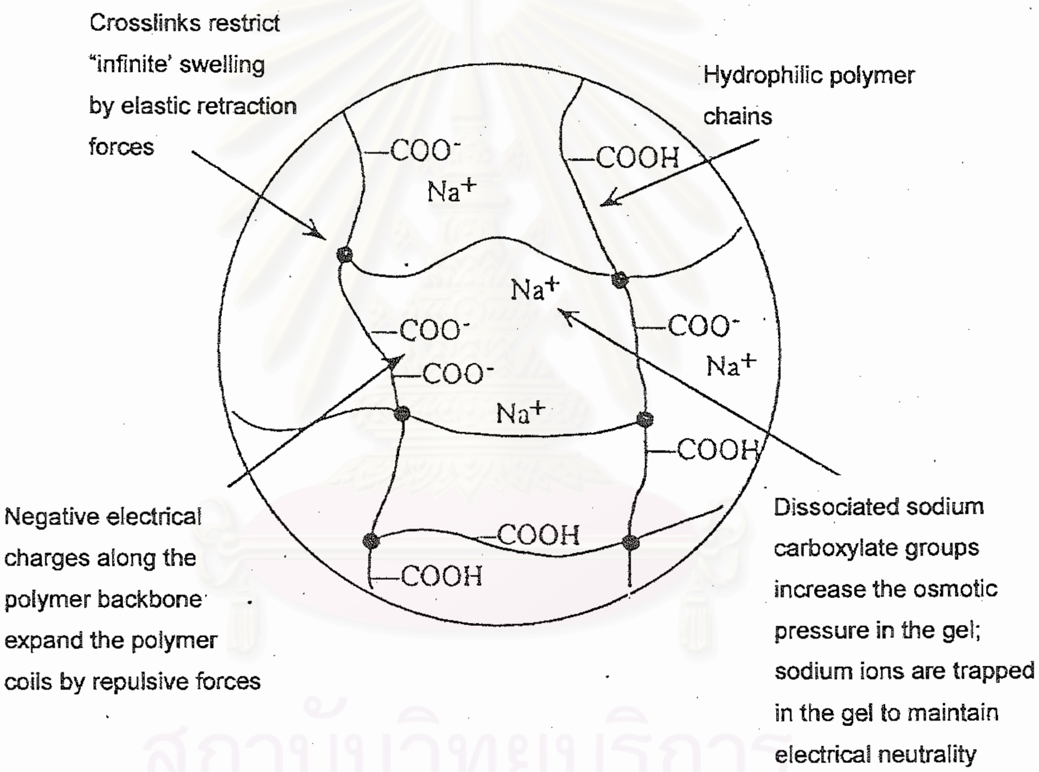


Figure 2.2 Mechanisms of swelling of superabsorbent polymers

The principal structural factors contributing to the properties of superabsorbent polymers are the crosslink density and the charge density. Numerous structural features of the polymer system and the magnitude of their interaction, however, govern how the crosslink density and charge density affect the macroscopic properties. Key parameters that are involved in how the crosslink density and charge density interact to yield macroscopic properties are: [5]

1) The molecular weight of the polymer chain between crosslinks, $\overline{M}_c$

2) The molecular weight of polymer chain if no crosslinks were present, $\overline{M}_n$

3) The amount of uncrosslinked polymer present (the extractable fraction of polymer)

4) The extent of entangling of the chains

5) The volume of the polymer system during preparation

6) The spacing of the charges along the chain

7) The thermodynamic interaction of the solvent with the polymer chains

8) The number of polymer strands that meet at a crosslink point, f

The Flory-Erman description of how these factors affect the swelling and modulus is given in Equation 2.1, which describes polymers swollen to their maximum with a solvent.

$$ln(1-\nu_{2,s})+\nu_{2,s}+\chi_1\nu^2_{2,s} = -(\xi / V_0)V_1\nu_{2,s}^{1/3}[1+(\mu/\xi)K\nu_{2,s}^{-2/3}] \qquad (2.1)$$

The left hand side of Equation 2.1 represents the swelling extent of the polymer and the right hand side represents the elastic retraction of the polymer as it swells. At some point, the two come into balance and maximum swelling is obtained.

The equilibrium swelling capacity of polyacrylate gels is commonly taken as the mass of liquid absorbed per unit mass of dry polymer; it is the weight swelling ratio, q. It is related to the volume fraction of polymer in the gel, $\nu_{2,s}$, and the density of polymer and liquid, $\rho_{polymer}$ and ρ_{liquid}, respectively, by

$$1+q(\rho_{polymer}/\rho_{liquid}) = 1/\nu_{2,s} \tag{2.2}$$

For very high values of swelling capacity, the polymer volume fraction is closely approximated by the reciprocal of the swelling capacity. The polymer-solvent interaction parameter is χ_1; the molar volume of solvent is V_1; the number (moles) of crosslinks is μ; the cycle rank of the network is ξ; and K is a complex function of the constraints of junctions or entanglements.

In the Flory-Erman treatment, polymer networks are fully characterized by their “cycle rank”, ξ. The cycle rank incorporates the crosslink density and all other structural features of the crosslinked polymer. That is convenient mathematically, but it would be synthetically more useful if the term is broken out into conventional structural parameters. For a random network such as that obtained in copolymerizations of vinyl and divinyl monomers, with crosslink functionality of four, the cycle rank density, ξ / V_0 is

$$(\xi / V_0) = (\rho N_a / 2\bar{M}_c)(1-(3\bar{M}_c / \bar{M}_n)) \tag{2.3}$$

where ρ is the density of the polymer as prepared and N_a is Avogadro’s number. The number density of effective crosslinks, μ / V_0 is

$$\mu / V_0 = (\rho N_a/2\bar{M}_c)(1-(\bar{M}_c/\bar{M}_n)) \tag{2.4}$$

and the shear modulus, G is

$$G = (\xi RT/N_aV_0)(\nu_2/\nu_{2,r})^{1/3} \tag{2.5}$$

where R is the gas constant, T is absolute temperature, $\nu_{2,r}$ is the volume fraction of polymer during network formation and ν_2 is the volume fraction of polymer at which the measurement of shear modulus is made. In summary, Equations 2.1–2.5 provide the fundamental relationships among swelling capacity, modulus and the crosslink density.

2.1.2 Swelling Capacity

From the equations given above based on the Flory-Erman theory, and assuming a randomly crosslinked, four-functional network, typical commercial superabsorbent polymers, an equation can be derived for the swelling capacity in terms of the key polymerization parameters. The theory provides that networks at high extension or in a highly swollen state behave according to the more simple phantom network model. This is obtained from Equation 2.1 by setting the second term in the square brackets on the right hand side (the term providing for the constraints on the crosslinks) to zero. The logarithmic term may be expanded in a series, keeping only the first two terms as an approximation at small $\nu_{2,s}$. Then the terms in $\nu_{2,s}$ are collected, and the volume swelling ratio, $Q=1/\nu_{2,s}$ is substituted for the polymer volume fraction at maximum swelling. The resulting approximation for the volume-swelling ratio in terms of polymerization parameters is given below

$$Q^{5/3} = [(\{1/2\}-\chi_1)2\bar{M}_c\,]/[V_1\rho_0\nu_{2,r}^{\ 2/3}(1-\{3\bar{M}_c/\bar{M}_n\,\})] \qquad (2.6)$$

Therefore, swelling depends on the length of polymeric chain between crosslinks through $\bar{M}_c$ and the kinetic chain length of the polymerization through $\bar{M}_n$. In addition, the concentration of monomer at preparation affects the ultimate swelling through the term $\nu_{2,r}^{\ 2/3}$ [6].

2.1.3 Modulus of Elasticity

The molecular weight of polymer between crosslinks $\overline{M}_c$ in superabsorbent polymers made by a crosslinking co-polymerization depends on the ratio of the concentration of crosslinker to the concentration of monomer (acrylic acid). The value of $\overline{M}_c$ may be approximated by the molecular weight of the extractable polymer fraction, because most of the soluble polymer is made in the polymerization when the molecular weight of the forming chains drops below the molecular weight of chain between crosslinks, as estimated from the stoichiometric crosslink density. This occurs near the completion of the polymerization reaction when the monomer concentration is low, and, as a result, the kinetic chain length is also low. When combined with the molecular weight of the backbone polymer chain (if all the crosslinks are somehow cut), the mole fraction of “dangling chains” is accounted for in Equation 2.3 by a factor of $2\overline{M}_c/\overline{M}_n$ inside the parentheses. The dependence of the modulus on crosslinker concentration is shown in Figure 2.3.

Expressing the shear modulus in terms of polymerization parameters, by inserting the expression for ξ / V_0 obtained from Equation 2.3 into Equation 2.5, yields

$$G = (\rho_0 RT/2\overline{M}_c)(1-(3\overline{M}_c/\overline{M}_n))\nu_2^{1/3}\nu_{2,r}^{2/3} \qquad (2.7)$$

The swollen modulus therefore depends on the molecular weight between crosslinks, $\overline{M}_c$, the backbone molecular weight, $\overline{M}_n$, the concentration during crosslinking, represented by the polymer fraction at crosslinking, $\nu_{2,r}$, and the extent of swelling during measurement as expressed through ν_2. A slightly different form of this equation, and also of Equation 2.6, is given in some of the original literature that describes the properties of rubber. These different forms result from the assumption that the networks are formed in the absence of any solvent, in which case $\nu_{2,r}$ =1, and V_0 contains no contribution from the volume of solvent.

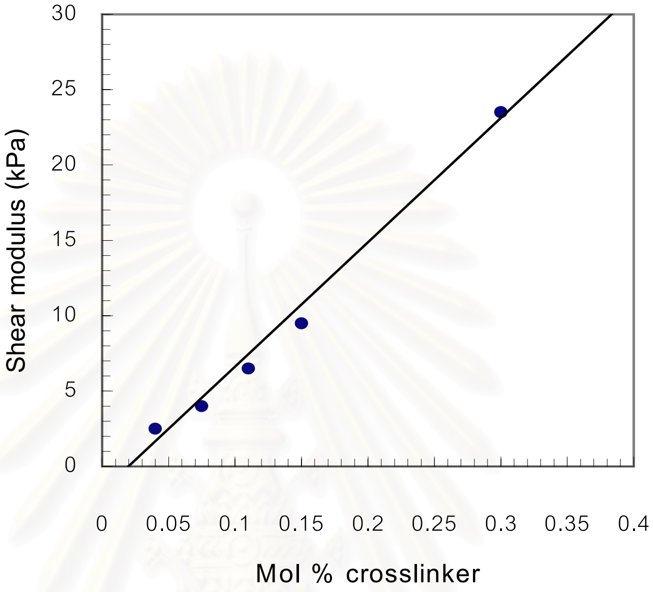


Figure 2.3 The shear modulus of sodium polyacrylate gels as a function of the stoichiometric ratio of crosslinker used in the polymerization, per mole of acrylic acid. The moduli have been normalized to the preparation volume according to Equation 2.5.

The molecular weight between crosslinks and the molecular weight of the polymer backbone together define the amount of "dangling chains" in the network. The fraction of dangling chains, which are network chains having one end attached at a crosslink point and the other unattached to the network, is accounted for in Equation 2.3 by a factor of $2\overline{M}_c/\overline{M}_n$ in the term $(1-3\overline{M}_c/\overline{M}_n)$. The number of elastic chains meeting at a crosslink that also is connected to a dangling chain is a fewer than if all the chains could support stress. This leads to a lower modulus and is accounted for by the extra factor of $\overline{M}_c/\overline{M}_n$ in Equation 2.3. Even though the dangling chains cannot support stress and therefore cannot contribute to the modulus, they do of course contribute to the swelling of the polymer by solvent (controlled by the thermodynamic solvation of the polymer units and the ions). Branching reactions during synthesis are an additional source of dangling chains that is not accounted for in Equation 2.7. These reactions occur by radical chain-transfer to polymer coupled with chain termination to a radical not connected to the network.

The polymer concentration during crosslinking $\nu_{2,r}$ defines the extent of entanglement of the network chains and therefore the number of configurations available to a chain in space. The extent of entanglement is determined by the distance between chains when the crosslinks are formed. The effect of entanglements on properties depends on the ratio of the distance between covalent crosslinks to the distance between entanglements. The concentration of monomer approximately fixes the concentration of chains at crosslinking, although strictly speaking the concentration of elastic chains continuously increases as a free-radical crosslinking copolymerization proceeds. For example, suppose that a certain polymer at some concentration has an entanglement every 300 monomer units. The entanglements will have less effect on properties if the polymer is crosslinked every 250 monomer units than if the crosslinks are every 500 units.

The straightforward effects of concentration, as suggested by theory, are complicated in crosslinking co-polymerizations because many things change in concert with a change in monomer concentration. The solubility of crosslinkers may increase or decrease as the concentration of undissociated acrylic acid increases in the monomer solution, thereby changing the effective concentration of crosslinker. In addition, the molecular weight of the backbone polymer should increase, in general, as the monomer concentration that is loaded initially into the reactor increases, but decreases as the monomer is depleted during polymerization. Also, free-radical degradation of the polymer chains in the sodium persulfate initiator occurs

Table 2.2 The Effect of Monomer Concentration on the Modulus of Swollen Superabsorbent Polymer.[a]

Monomer Concentration (wt%)	Swollen Molulus (kPa)
24	2.65
25	3.04
26	3.26
27	3.46

[a] The networks are all 65 mol% neutralized poly(acrylic acid), swollen in 0.9%NaCl solution to their maximum swelling extent.

after the main polymerization is complete, when the polymer gel is still at elevated temperature. For chains attached to the network at only one place (dangling chains), only a single chain scission is required to cleave it from the network and form a soluble chain. As a result, the amount of extractable polymer increases as reaction time is extended. But for each extractable polymer chain formed, there must be many new dangling chains formed. Because only a small fraction of the network chains are initially dangling chains (most are elastic) and because the degradation process is random, the chains that will be most affected are those chains in largest number. The cleavage of chains during this side reaction affects the magnitude of the entanglement effect and hence the modulus. The general effects of concentration on the elastic shear modulus in the fully swollen state are shown in Table 2.2. In these polymers, the amount of crosslinker added to the polymerization, the amount of soluble polymer, and the equilibrium swelling capacity are all very similar, but the modulus increases as the acrylic acid concentration increases.

The extent of swelling of a crosslinked polymer affects the modulus. An increase in the swollen volume decreases the concentration of elastic chains and therefore decreases the modulus. In Equation 2.7 the modulus of a swollen (non-ionic) polymer is proportional to the cube root of the ratio of the swelling change. The situation is more complex with polyelectrolyte networks. Over a wide range of charge density and ionic strength, the modulus decreases and then increases as swelling progresses. This is thought to be due to the very extended chain configurations that are possible at high charge density and low ionic strength, when the swelling extent is very large. However, for superabsorbent polymers used as liquid absorbents in personal care, the ionic strength of the absorbed fluid usually is sufficiently high that the chain configurations are not greatly extended. The modulus behavior observed for a commercial polyacrylate absorbent polymer with increasing swelling is shown in Figure 2.4. A fit of the data to a power law shows that the modulus (swollen) decreases as the 0.37 power of the change in swelling, very close to the theoretical value of 1/3 shown in Equation 2.7 [7].

2.1.4 Applications of Superabsorbent Polymers

Superabsorbent polymers possess a number of attributes that make them attractive in many different applications. Superabsorbent polymers have supplanted much of the traditional absorbents in infant diapers and have made significant improvements in the performance of feminine hygiene products and adult incontinence products as a result of superior water-absorbing properties. The basic property of water absorption has suggested the use of superabsorbent polymers in many other applications, including paper towels, surgical sponges, meat trays, disposable mats for outside doorways and in bathrooms, and for household pet litter,

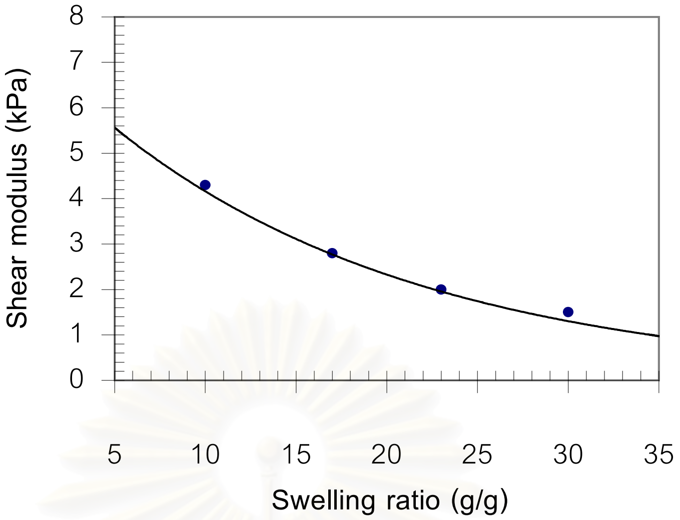


Figure 2.4 The shear modulus dependence on the swelling ratio of the sample. A single sample of superabsorbent polymer was swollen to less than equilibrium by limiting the fluid available. The modulus scales with the –0.37 power of the swelling ratio.

bandages and wound dressings. The ability of the swollen gels to release the absorbed water to the surroundings as vapor has also been used in various ways, for example, as humidity-controlling products or as soil conditioners. Superabsorbent polymers may also be used to release water-soluble substances from within the network structure into the surroundings as a solution. For example, pharmaceuticals and fertilizers may be incorporated into superabsorbent polymers to yield controlled release products. Another characteristic of the swollen polymer is its rubbery nature, which has been used to control the consistency of products as diverse as cosmetics or concrete or to contribute a soft, yet dry, feel to a product like a hot or cold pack for sore muscles. The soft, rubbery nature may also be employed to impart sealing properties to products that are in contact with water or aqueous solutions, for examples, underground wires and cables [8]. Table 2.3 indicates the application of these polymers classified from the market fields and the properties of polymer [3].

Table 2.3 Possible Applications of Superabsorptive Polymers

Properties Fields	Water absorption and retention	Swelling in volume	Gelling ability	Increase in Viscosity
Sanitary Products	-Sanitary napkins -Diapers -Breast pads			
Agriculture Gardening	-Water-retaining agents in soil -Seed coatings -Drying preventives for samplings -Artificial moss		-Cultivation plot for mushroom -Seed beds in fluid	
Civil engineering, architecture	-Dew preventing agents in walls -Water-retaining agents in concretes	-Water sealing agents -Substitutes for sandbags	-Sludge solidification agents -Lubricants in drilling works -Slurry explosives	-Mud shielding works
Cosmetics, Toiletries	-Sweat absorbing and kitchen papers		-Gelaromatics -Pocket warmers -Disposable chamber pots	
Medical	-Wound dressings -Sheets for surgical operation	-Control release agents for drug -Disintegrators in tablets	-Gelation of blood wastes	-Wet plasters

Table 2.3 (continued) Possible Applications of Superabsorptive Polymers

Food industry	-Agents for preservation of freshness		-Gelling agents -Cold keeping hydrogels	-Viscosity enhancing additives
Others	-Fog preventing film -Dehydrating agents in oil -Moisture sensor -Ink jet for printer	-Toys swelling when soaked in water	-Hydrogel for fire fighting -Artificial snow -Water bed	-Emulsion paints

2.2 Polyacrylates by Free-Radical Polymerization

The structure of a polymeric network is ultimately determined by the method of synthesis. The monomer and crosslinker concentrations, the initiator type and concentration, the relative reactivities of the monomers, the specific solvent and reaction temperature are all significant factors. Commercially, the rate of the polymerization reaction is also of importance, since it directly affects the volumetric efficiency of the production equipment. Fortunately, many of the important structural parameters are determined by the polymerization kinetics and by the various stoichiometries of the reaction.

The kinetics of free radical polymerization are well understood. In general, very small concentrations of free radicals are generated by any member of chemical or photochemical reactions, which then initiate the polymerization by reacting with the carbon-carbon double bond present in the monomer. The original radical-containing fragment is added to the double bond, generating a single bond and a new free radical. This radical quickly adds to another monomer molecule, and another, and another, in the propagation step. Finally, the now macromolecular radical reacts with another macromolecular radical to step or terminate the kinetic chains. The entire process is generally complex because many radicals from different sources are present at anytime, giving the possibility of many different termination reactions which affect the polymer structure.

The derivation of the kinetics of individual steps of free radical polymerization is available. Key results give the rate of polymerization in terms of the concentrations of monomers and initiators, for bimolecular termination:

for polymerization with thermal initiator

$$R_p = k_p[M](fk_d[I]/k_t)^{1/2} \tag{2.8}$$

for polymerization with redox initiators

$$R_p = k_p[M](fk_d[oxidant][reductant]/2k_t)^{1/2} \tag{2.9}$$

R_p is the polymerization rate, k_p is the rate constant for the propagation step, k_d is the rate constant for initiator decomposition, k_t is the rate constant for the termination step, $[M]$ is monomer concentration, f is an efficiency factor for the initiators and $[I]$, $[oxidant]$, and $[reductant]$ are concentrations of the initiators. The general first-order dependence of rate on monomer concentration is altered when the macroradicals are terminated by radicals directly formed from the initiator, and when the monomer is involved in the initiation step.

In any free radical polymerization, a given initiator radical will start a polymer chain, which will propagate until it is terminated by another radical. The conditions of solvent, type of monomer, temperature, additives, and impurities will determine how long the chain grows. This length is the kinetic chain length. Derivation of the kinetic chain length in terms of these polymerization conditions yields the following equation where ν is the kinetic chain length.

$$\nu = k_p[M]/2(fk_dk_t[I])^{1/2} \tag{2.10}$$

The dependence of the kinetic chain length on polymerization rate is given by

$$\nu = k_p{}^2[M]^2/2fk_tR_p{}^{1/2} \tag{2.11}$$

The molecular weight of the polymer formed is also derived from the kinetic chain length and the particular termination mechanism. If two macroradicals couple to form a polymer molecule, the number of monomer units is twice the kinetic chain length. If two macroradicals terminate by disproportionation into a molecule with a terminal double bond and another molecule with a hydrogen atom end-group, the number of monomer units in each polymer molecule is equal to the kinetic chain length. The molecular weight of the final molecule is just the monomer molecular weight times the average number of monomers per molecule. For networks formed by free radical, crosslinking copolymerization, this gives the backbone molecular weight or the molecular weight of chains if somehow the crosslinks were removed.

In a free radical polymerization, which leads to ultrahigh molecular weights, such as the polymerization of acrylic acid without crosslinker, chain transfer is a low frequency event and the termination of radical chains is by combination of macroradicals. When this is true, the ends of the polymer chains incorporate the initiator fragment that started the chain. Since these same kinetic events are present in the crosslinking polymerization it seems reasonable to assume that the vast majority of dangling chains come from the chain initiation events rather than from chain transfer reactions.

The kinetic chain length is proportional to the ratio of monomer concentration to the square root of initiator concentration. In a typical polymerization, the initiator concentration remains virtually constant throughout while the monomer concentration changes. This is due to the significant differences in activation energies for the initiator decomposition and the polymerization. As a result, the kinetic chain length decreases with increasing monomer conversion, resulting in increased amount of extractable polymer as the polymerization proceeds to high conversion [9].

2.2.1 Standard Co-Polymerization Kinetics

To be useful as superabsorbent polymers, linear polymers must be crosslinked to form gels. Two general approaches exist for crosslinking. The first method is through co-polymerization of acrylic acid with a second monomer, which has multiple vinyl groups, to form a gel directly during the polymerization process. The second approach is via crosslinking of a polymer by a reaction with a di-functional molecule, similar to a rubber curing reaction. The model is based on the concept of its reactivity. In a simple co-polymerization of two monomers, M_1 and M_2, there are four possible propagation events. The growing chain with a monomer 1 moiety on the end $RM_1^\bullet$ can react with another molecule M_1 with a rate constant k_{p11} or with a molecule M_2 with a rate constant k_{p12}. Likewise, when monomer 2 moiety $RM_2^\bullet$ is at the end of the growing chain, it can add to M_1 with a rate constant k_{p21} or to M_2 with a rate constant k_{p22} as shown in Equations 2.12–2.15.

$$RM_1^\bullet + M_1 \xrightarrow{k_{p11}} RM_1M_1^\bullet \qquad (2.12)$$

$$RM_1^\bullet + M_2 \xrightarrow{k_{p12}} RM_1M_2^\bullet \qquad (2.13)$$

$$RM_2^{\bullet} + M_1 \xrightarrow{k_{p21}} RM_2M_1^{\bullet} \quad (2.14)$$

$$RM_2^{\bullet} + M_2 \xrightarrow{k_{p22}} RM_2M_2^{\bullet} \quad (2.15)$$

The reactivity ratio r_1 and r_2 are defined by Equations 2.16–2.17

$$r_1 = k_{p11}/k_{p12} \quad (2.16)$$

$$r_2 = k_{p22}/k_{p21} \quad (2.17)$$

when $r_1>1$, radical $RM_1^{\bullet}$ preferentially resets with monomer M_1 (i.e., homopolymerizes), instead of monomer M_2. Very frequently $r_1<1$, which indicates $RM_1^{\bullet}$ preferentially reacts with monomer M_2. This latter behavior can lead to alternating co-polymers. The reactivity ratio can also be zero, indicating that a monomer will not homopolymerize.

Consider a co-polymerization of a di-functional vinyl crosslinker; after incorporation of one double bond, a new species form that was not present in the original monomer solution. This species has a pendant double bond, as well as some other unique characteristics that confound the kinetic analysis of a crosslinking co-polymerization. Most obvious is that the new species, which is now a macromolecular reactant, and so its diffusion to the growing radical chain is slowed more by the viscosity increase resulting from polymerization than is the diffusion of monomeric reactant [46].

2.2.2 Monomer Concentration

The acrylic acid concentration in the polymerization mixture is one of the key parameters affecting both the properties of the polymer and the economics of the process. Higher monomer concentrations allow higher throughputs and require less energy for drying the polymer. There are of course some limitations, which restrict the monomer concentration in most of the processes mainly to values below 40 wt%. Higher monomer concentration in the mixture generally affords a gel that is more sticky and tough. This complicates gel handling such as tearing or chopping. High torque of the agitators and high mechanical stress of the equipment is necessary.

The heat of polymerization (18.5 kcal/mol for acrylic acid) heats up the whole reaction mass. The water added to the monomer mix acts as an inert heat absorber and limits the peak temperature of the polymerization. High peak temperatures have a negative impact on the molecular mass of the polymer chains formed and may induce saponification of the cross-links when hydrolytically sensitive cross-linkers are used. The excess heat can be removed readily by evaporating some of the water in the gel under reduced pressure. This technique works best in those processes where the reactor is designed to tear up the gel as the polymerization proceeds. Alternately, in non-agitated reactors the monomer concentration is kept at lower levels and the polymerization can be run adiabatically.

Polymerization at high temperature favors the termination step of the propagation radical chains, which leads to polymer chains of low molecular weight. On the other hand grafting reactions that formally lead to higher crosslink densities in the gel can occur preferably at higher polymer concentrations and at higher reaction temperatures. When the monomer concentration is raised, higher polymer concentration is achieved at lower conversion and the reaction temperature may increase more rapidly due to the lower heat capacity of polymer compared to water. For these reasons, high monomer concentrations provide unfavorable ratios between the centrifuge capacity, which are the most common measure of the swelling capacity in the superabsorbent polymer industry, and the percentage of soluble polymer.

2.2.3 Neutralization

Neutralization can be done either before or after the polymerization. Either the monomeric acrylic acid is neutralized directly (pre-neutralization step) or the poly (acrylic acid) gel is neutralized (post neutralization step). From a technical point of view, pre-neutralization is preferred due to the relative ease of neutralizing the liquid monomer solution. As a drawback, sodium acrylate polymerizes less readily than acrylic acid because ionized monomers react more slowly in the propagation step of polymerization. Higher percentages of soluble polymer and higher residual monomer concentration in the final product can result.

The post neutralization step requires an even distribution of the neutralization agent into the gel mass. Preferably this is done during a chopping step. Either a weak base neutralizing agent or a hydrolytically stable crosslinker have to be used in order to avoid extended cleavage of the ester-containing crosslinks.

The bases applied (mainly sodium carbonate and sodium hydroxide) are less expensive than acrylic acid. From a purely economic point of view, high neutralization degree would therefore be preferred. However there are some limiting factors. The problems encountered in a pre-neutralization process at high neutralization degrees were already described. In addition, the pH of an aqueous solution containing swollen gel is directly related to the degree of neutralization. A pH between 5.5 and 6.5 is desired for use in applications where the product may come into contact with human skin. These factors practically restrict the degree of neutralization to between 60 and 80 mol%.

2.2.4 Free-Radical Initiators

The polymerization in the aqueous phase is initiated by free radicals, which originate from the decay of initiator molecules. The initiator may arise from thermal decay or by means of a reduction-oxidation (redox) reaction, or by a combination of these. Peroxo compounds like hydrogen peroxide, sodium or ammonium peroxodisulfate and water soluble azo-compounds like $2,2'$-azobis(2-amidinopropane)-dihydrochloride or $2,2'$-azobis(4-cyanopentanoic acid) are the preferred radical sources. Examples for redox systems are peroxodisulfate/hydrogen sulfite, peroxodisulfite/thiosulfate, peroxodisulfate/ascorbic acid or iso-ascorbic acid, and hydrogen peroxide/ascorbic acid.

The polymerizations frequently are initiated at room temperature with the aid of redox couple. After the reaction mass is heated up the polymerization proceeds further by the thermal decay of a second initiator. Starting at lower temperature minimizes undesirable high peak temperatures. Initiator concentrations are always adapted to the monomer concentration with particular regard to the decay rates of the initiators. Usually there is a practical balance struck between high conversions (low residual monomer), high conversion rates at high initiator concentrations, and products having low fractions of soluble polymer but high monomer residues at low initiator concentration [10].

2.3 **Biodegradable Superabsorbent**

The term biodegradable describes a polymer that can be reduced to carbon dioxide, methane, water, and biomass under a biochemical action. Based on testings and experiences, several generalizations have been made relating biodegradability to chemical structure:

1. Naturally produced polymers biodegrade.
2. Chemically modified natural polymers may biodegrade, depending on the extent of modification.
3. Synthetic addition polymers with carbon-carbon backbones do not biodegrade.
4. Synthetic addition polymers with heteroatoms in their backbones may biodegrade.
5. Synthetic step-growth or condensation polymers are generally biodegradable to a greater or lesser extent, depending on the chemical nature of the chain coupling, molecular weight, morphology, and hydrophilicity.
6. Water solubility does not guarantee biodegradability.

With these generalities in mind, two approaches to achieving truly biodegradable superabsorbent materials are apparent: modification of a superabsorbent to enhance its biodegradability or modification of a biodegradable polymer (e.g., a natural polymer) to enhance its superabsorbency. The first approach would entail incorporating some nonbiochemical mechanism to degrade the polymer molecular weight to below 1,000-2,000 g/mol. The degraded polymer could then pass the cell membrane where a host of intracellular enzymes could biodegrade it. There are several significant challenges to the success of this approach, though some progress has been made. The latter approach would involve incorporating charged functional groups into a hydrophilic biopolymer to enhance its absorbency, then crosslinking the polymer to achieve desired absorbent properties. These modifications may impact the biodegradability of the polymer. A third approach of mixing biodegradable fillers with nonbiodegradable superabsorbents has also been attempted; however, this approach has not led to a fully biodegradable product [11].

2.3.1 Starch Graft Copolymer

Starch is a polysaccharide composed of repeating *1,4-*α*-D*-glucopyranosyl units (often called anhydroglucose units, or AGU) and is one of the cheapest and most readily available of all natural polymers. Starch is generally a mixture of linear and branched polymers. The linear component, amylose, has a molecular weight of several hundred thousand that consists of α-glucopyranosyl residues linked via *1,4*-glycosidic bonds. While the molecular weight of the branched amylopectin is on the order of several million with α-glucopyranosyl residues linked by *1,4*-glucosidic linkages and by α*-1,6* bonds at branch points. Starch is predominantly hydrophilic in nature owing to the three-hydroxyl groups on each monomeric unit. However, starch forms helical structures where many of the hydroxyl groups are directed outside and the hydrocarbon groups are retained inside of the helix. Therefore, the interior of the helix is rather hydrophobic. Starch tends to absorb moisture from the environment owing to the accessibility of hydroxyls. Starch granules are partially crystalline and are insoluble in water at room temperature. When a water-slurry of starch is heated, hydrogen bonds are broken, a measurable fraction of the starch dissolves, and the granules swell and lose their birefringence. The granules swell owing to increased diffusion and loose crystallinity. The process is called gelatinization or melting (terms are used interchangeably). Near the boiling point of water, starch granules rupture and disintegrate to form a smooth dispersion or paste. Starch gelatinization or melting temperature (T_m) may vary depending on the botanical source and moisture content. As the gelatinized starch cools, the amylose fraction crystallizes rapidly by forming intermolecular hydrogen bonds.

In addition to the α*-1,4* and α*-1,6*-glycosidic linkages in starch, the hydroxyl groups on both the primary and secondary carbon atoms offer the opportunity for chemical modification, incorporating near and useful properties. Graft copolymers have been prepared using starch as a backbone. Grafting synthetic copolymers onto starch often superimposes the physical and chemical characteristics of the copolymer.

Use of starch as an extender and replacement for synthetic polymers is currently an active research area. Incorporation of starch into other polymers not only reduces our dependence on petrochemical-derived monomers but also provides materials in which the starch portion can biodegrade rapidly in the environment. Free-radical graft polymerization is an excellent method for preparing these starch-synthetic composites [12].

Graft copolymerization of vinyl monomers to polysaccharide substrates is used for the preparation of absorbent polymers. The polymerization kinetics are the initiation step and chain transfer reactions. Practical graft polymerization attempts to initiate the polymerization using a redox reaction of an oxidant with oxidizable groups of the polysaccharide. Many of the metal ion systems investigated also initiate polymerization in the absence of the polysaccharide and so contribute to homopolymerization of the monomer with reduction in the amount of graft copolymer. Another complication is the generally observed termination of propagating chains with metal ion. This reduces the backbone molecular weight and hence the modulus of the swollen network. A third complication is chain transfer of propagating chains to polysaccharide, by abstraction of hydrogen atom from polysaccharide. This results in a dangling chain from the polyacrylate chain and a branch point on the polysaccharide, again negatively affecting the swollen modulus [9].

Graft copolymers are prepared by first generating free radicals on the polysaccharide backbone and then allowing these free radicals to serve as macroinitiators for the vinyl or acrylic monomer. Graft polymerizations have usually been carried out in water near room temperature with either granular starch or with starch that has been gelatinized by heating the starch-water slurry to about 70-90^{o}C prior to graft polymerization. Since only a minor fraction of starch dissolves under these gelatinization conditions, graft polymerizations can be viewed as talking place onto a substrate that is largely insoluble [12].

2.3.2 Carbohydrate Hydrolyzing Enzymes

Enzyme: The action of enzymes can be experienced at breakfast time. The physicians tell clients “chew your bread well,” and when they do, they experience a sweet taste. The enzymes in human saliva, the salivic amylases, convert tasteless starch in bread into sweet-tasting sugar. Cooked starch forms rigid gels, which are called *pastes*. A trace amount of salivic amylase converts such a paste into a liquid in seconds. The high molecular weight, hydrophilic starch is hydrolyzed into low molecular weight sugars and dextrins. This hydrolysis is essential for our nutrition because humans, animals, and even microorganisms absorb carbohydrates only in the hydrolyzed form as sugar.

Scientifically, the carbohydrate cleaving enzymes are called glycosidases or more commonly, carbohydrases. The hydrolyze polysaccharides are, such as, starch, cellulose, and pectin. Their action is apparent in lowering the viscosity of watery solutions of carbohydrates such as pectin and carboxymethylcellulose solutions. The activity of the enzyme is determined by the amount of free reducing sugars produced by its action.

Enzyme Specificity: Carbohydrases hydrolyze the specific glycosidic linkages of certain monosaccharide residues. They are able to cleave short chain oligosaccharides as well as polysaccharides with various structures. Table 2.4 depicts some naturally occurring polysaccharides, their monomeric building blocks, their linkages, and the enzymes used for their scission.

Table 2.4 Polysaccharides, their Hydrolyzed Monomer and Enzyme

Polysaccharide	Monomer Unit	Linkage	Enzyme
Starch	Glucose	α-1,4 - α-1,6	α-Amylases β-Amylases Isoamylases
Cellulose	Glucose	β-1,4	Cellulases
Dextran	Glucose	α-1,6	-
Xylan	Xylose	β-1,3; β-1,4	Xylanases
Pectin	Galacturonic acid	α-1,4	Pectinases
Araban	Arabinose	α-1,5; α-1,3	Arabanases
Inulin	Fructose	β-1,2	Inulinase

The specificity of carbohydrases depends on:

1.The configuration of the glycosidic linkage, for example, maltose can be hydrolyzed only by α-glucosidase and not by β-glucosidase.

2. The chemical structure of the monomeric sugars joined by the linkage.

3. The molecular weight of the substrate. α-Amylases are able to hydrolyze high molecular weight amylose very rapidly, but maltose or maltotriose are hydrolyzed only very slowly, if at all. Enzymatic hydrolysis is, by definition, reversible. The aqueous reaction equilibrium favors the hydrolysis products.

Endoamylases (EC 3.2.1.1): The *α-amylase* (*1,4-α-D-glucan glucano-hydrolases*) are endohydrolases, which cleave *1,4-α-D*-glucosidic bonds and can bypass but cannot hydrolyze *1,6-α-D*-glucosidic branchpoints. Commercial enzymes used for the industrial hydrolysis of starch are produced by *Bacillus* *amyloliquefaciens* (Supplied by various manufacturers) and by *Bacillus licheniformis* (supplied by Novo Industry A/S Termamyl). Many *α-amylases* can by produced in a pure crystalline form, such as those from malt, pancreas, *Aspergillus oryzae*, and *Bacillus subitilis*. Their properties have been well investigated. They differ in their molecular weights, temperature stability, optimum-activity pH, and hydrolytic specificity. Because of this specificity, different *α-amylases* produce oligosaccharides of various chain lengths and yields. The fast and complete degradation of starch requires pre-gelatinization of the substrate. Bacterial *α-amylase* degrades gelatinized starch 300 times faster and fungal α-amylase 100,000 times faster than native starch. The rate of hydrolysis depends primarily on the degree of polymerization of the starch, dropping markedly with a lower degree of polymerization. Amylose is hydrolyzed faster than amylopectin. Amylose-induced starch hydrolysis is shown in Figure 2.5 [13].

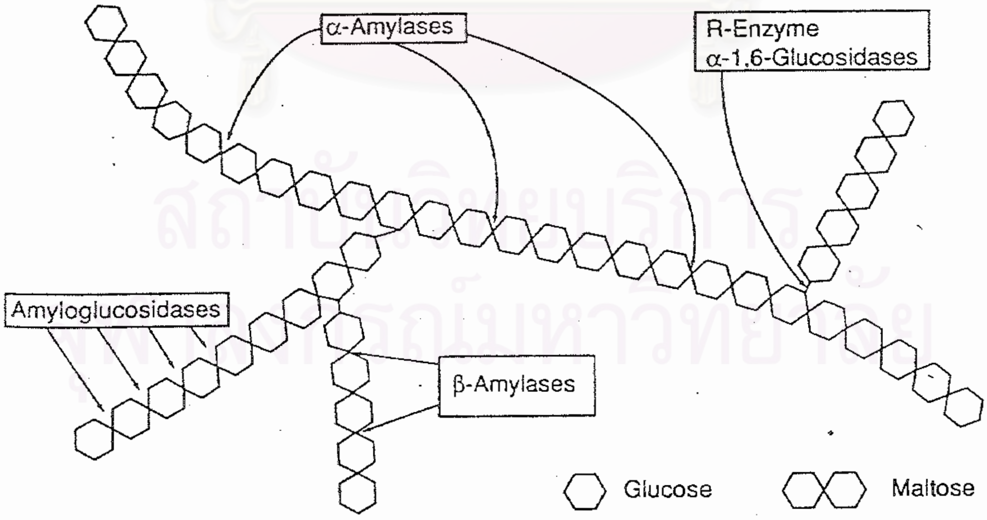


Figure 2.5 Starch hydrolysis by amylases.

2.4 Terminology and Definition

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

1) Grafting Efficiency

It is a term often used to describe graft copolymerization reactions and it 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 the low grafting efficiency would afford mainly a physical mixture of starch and free polymers. It can be calculated as follows:

$$\%\text{grafting efficiency} = \frac{\text{weight of polymer grafted}}{\text{weight of free polymers + weight of polymer grafted}} \times 100 \qquad (2.18)$$

2) Percentage Add-on

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

$$\%\text{add-on} = \frac{\text{weight of polymer grafted}}{\text{weight of the grafted copolymer}} \times 100 \qquad (2.19)$$

It is calculated by the acid hydrolysis method. The grafted polymers are separated from the starch backbone by heating the graft copolymer under reflux in a dilute acid solution.

3) Grafting Ratio

It is a term used to describe graft copolymerization, which is defined as the percentage ratio between the polymer grafted to the cassava starch and it can be calculated by the following expression.

$$\%\text{grafting ratio} = \frac{\text{weight of polymer grafted}}{\text{weight of starch}} \times 100 \qquad (2.20)$$

2.5 Literature Survey

Masuda et al., [14] patented a process for producing a highly water-absorbent resin by grafting at least one monomer having a polymerizable double bond, which is water-soluble or becomes water-soluble by hydrolysis of starch or cellulose. The synthesized polymers have maximum water absorbency of 500 and 90 times its dry weight in deionized water and 0.5% aqueous NaCl, respectively.

Heidel [15] claimed a method of manufacturing polysaccharide graft polymers using the single-stage, batch inverse suspension polymerization. The technique of inverse suspension polymerization has been developed as an improved polymerization method for producing high molecular weight homo- and graft polymers in solid, fine particulate form. The new polymer has a maximum water absorbency of 900 times its dry weight.

Makita and Tanioku [16] stated a method for producing water-absorbent resin having a high water absorbency and a high water absorption rate and capable of forming a gel having a high gel strength and nonstickiness. The newly water-absorbent resin particles consist of water and a crosslinking agent were agitated in the semi-swollen state at an elevated temperature in the presence of an inert inorganic powder to conduct the crosslinking of the resin. While removing water, the water-absorbent resin containing monomer units having carboxyl groups in the form of free acid or metal salt.

Saotome [17] investigated a process for producing water absorbent polymer coated employing a redox initiator system. The system, a peroxide radical initiators, was used in combination with a reducing agent, which promotes decomposition of the peroxide initiator. The said initiator was adapted to decompose at a temperature from about 40^{o}C to about 180^{o}C and acted on the polymer to crosslink. Formation of crosslinking proceeded with the progress of decomposition of the peroxide, and was completed within a short period of several minutes.

Kiatkamjornwong and Faullinmel [18] synthesized a superabsorbent polymer by chemical modification of cassava starch to poly(starch-*g*-acrylonitrile) via a redox initiation mechanism using Ce(IV) as initiator in acid medium. The purified graft copolymer was subsequently saponified with an 8.5%KOH solution at 85^{o}C to convert the nitrile groups into a mixture of carboxamide and carboxylate groups, which were responsible for water absorbency. The water absorption capacity in pure water of the new graft copolymer was ranged from 120 to 270 times its original dried weight. Water absorption capacity decreased dramatically in saline with increasing the salt concentrations.

Okieimen et al., [19] disclosed graft copolymers of acrylonitrile and of acrylic acid monomers on cellulosic materials using ceric ion initiator in aqueous medium at a 50%w/w cellulose-monomer ratio. They studied the variations of polyacrylonitrile grafts and of the efficiency of grafting reaction with ceric ion concentration, and of poly(acrylic acid) grafts with temperature. They also founded that the water retention capacity of the grafted fiber depends on the graft level.

Gurdag et al., [20] studied the reaction kinetics of graft copolymerization of acrylic acid on cellulose using ceric ammonium nitrate initiator in aqueous nitric acid solution at 30, 50, 70, and 90^{o}C during reaction periods of 30 to 180 minutes. They observed that poly(acrylic acid) grafted cellulose produced at 30^{o}C for 150 minutes had the highest water retention capacity. The time dependence of acrylic acid conversion allowed a calculation of first-order reaction rate constants. These rate constants were then used to determine apparent activation energies. They found that high temperature favor homopolymerization more than grafting reaction.

Joseph et al., [21] investigated the kinetics of grafting of poly(butyl acrylate) onto gelatin using H_2O_2-ascorbic acid redox system. They reported that the grafted copolymer as functions of reaction temperature, time, initiator, monomer, and backbone concentrations and found that rate of graft copolymerization depends on first power of monomer concentration and 0.5 power to the initiator concentrations.

Kiatkamjornwong and Phunchareon [22] synthesized high water-absorbing copolymers of poly(potassium acrylate-*co*-acrylamide) by an inverse suspension copolymerization. Potassium acrylate and acrylamide were used as comonomers, and *N,N′*-methylenebisacrylamide as a crosslinker polymerized by ammonium persulfate in *n*-hexane, each was emulsified by a series of sorbitan surfactants with a relatively lower concentration of 1.0%w/v at 60^{o}C for 2 hours. The effects of influential reaction parameters on the water absorption of the newly synthesized copolymers were investigated. The obtained copolymer had the high water absorption (775 g/g of dry weight) and liquid sorption rate (21.41 seconds). The water absorption depended highly on the pH of the buffer solution and the type and concentration of the saline solution. The copolymers exhibited a shear-thinning behavior at both low and high shear rates.

Kiatkamjornwong et al., [23] studied graft copolymerization of acrylamide and/or acrylic acid onto cassava starch by a simultaneous irradiation technique using gamma rays as an initiator. The extracted graft copolymers were subsequently saponified with a 5% aqueous solution of potassium hydroxide at room temperature to convert the carboxylic group of acrylic acid to carboxylate group. Cassava starch ratio 2:1, total dose 6.04 kGy, dose rate 2.24 kGy/hr, and acrylamide-to-acrylic acid ratio 70:30 gave the saponified copolymer having the highest water absorption in distilled water as high as 1142 g/g its dry weight.

Kurita et al., [24] proposed a graft copolymerization of vinyl compounds onto chitin using cerium(IV) as the initiator. The reactions with acrylamide and acrylic acid onto powdery chitin were carried out under various conditions to elucidate the polymerization behavior in terms of grafting percentage. They achieved high grafting percentages under appropriate conditions in spite of the heterogeneous reaction. The resulting graft copolymers showed improved affinity for solvents and hygroscopicity compared to the original chitin, indicating graft copolymerization to be effective for chitin modifications.

Mostafa [25] reported the graft copolymer of acrylic acid onto rice starch using potassium permanganate/acid redox system as initiator. When starch was reacted with $KMnO_4$ solution, MnO_2 was deposited onto starch. He founded that the highest graft yield was obtained with citric acid and the least with hydrochloric acid, with tartaric and oxalic acid in between. The graft yield increased by increasing the concentration of acid to a certain concentration beyond which grafting leveled off. A similar trend was observed when the magnitude of grafting was related to the amount of MnO_4 deposited. The graft yield increased by increasing the polymerization temperature from 30 to 50^{o}C.

Liu and Rempel [26] prepared the high water-absorbent copolymer comprising acrylic acid and acrylamide in the presence of a crosslinking agent, monofunctional aldehyde, by a solution polymerization technique via potassium persulfite-potassium metabisulfite a redox initiation system. The copolymer formed absorbed about 900 g water/g dry copolymer. They found that the absorption behavior of superabsorbents related to their chemical composition and the nature of the solvent.

Rangaraj et al., [27] synthesized homopolymers and copolymers of acrylamide and acrylic acid by the free radical solution polymerization technique using hydrogen peroxide, potassium persulfate, and benzoyl peroxide as initiators. The copolymers were purified by removing homopolymers. The homopolymers and copolymers were characterized by infrared (IR), ^{13}C-nuclear magnetic resonance (NMR), ^{1}H-NMR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and viscosity measurements.

Deo and Gotmare [28] grafted acrylonitrile monomer onto gray cotton yarn using a $KMnO_4$-HNO_3 redox system by a chemical initiation technique. They studied the major factors affecting polymerization of acrylonitrile, such as $KMnO_4$, nitric acid, and acrylonitrile concentration as well as the reaction time and temperature of the polymerization. They found that the water absorbency of grafted fibers depends strongly on their post-treatment.

Rath and Singh [29] reported the proof of grafting by a combined use of viscometry and enzyme hydrolysis. Two series of graft copolymers of amylopectin with polyacrylamide were synthesized using ceric ion-induced redox initiation technique. In the first series, a variation of ceric ion concentration at fixed acrylamide concentration and in the second series, a variation of acrylamide concentration at fixed ceric ion concentration were undertaken to effect a variation in the number and length of polyacrylamide chains by evidencing from their intrinsic viscosity. Comparison between the flow times of a solution of each of the graft copolymers both before and after hydrolysis with α-*amylase* indicated that the products are free graft copolymers.

CHAPTER 3

EXPERIMENTAL

3.1 Chemicals, Equipment, Glassware, and Apparatus

3.1.1 Chemicals

Cassava starch was obtained from Thai Wah Co., Ltd. It was product from topioca cultivated in summer. It contained 13.5% moisture, 0.20% ash, pH range 4.00-7.00 and viscosity 550 B.U.

Acrylic acid, AA, and acrylamide, AM, were provided by Siam Resin & Chemical Co., Ltd. They were used as received.

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

Termamyl SC, *1,4-α-D*-glucan glucanohydrolase *(EC 3.2.1.1)*, was obtained from EAC Thailand. It is available with a standard strength of 120 KNU/g.

Other chemicals of analytical grade, as shown in Table 3.1, were used without further purification.

3.1.2 Equipment and Glassware

Four-necked round bottom flask, condenser, mechanical stirrer, thermometer, water bath circulator, hot plate and magnetic stirrer, flat bottom flask, desiccator, reduced pressure filtering system, steel wire filtering, 100-mesh aluminium screen, analytical balance, oven, and other general laboratory glassware and equipment.

3.1.3 Apparatus

Fourier Transform Infrared Spectrophotometer, Perkin Elmer 1760X, USA.

Scanning Electron Microscope, JEOL, JSM-6400, Japan

Viscometer, model DV-III, Brookfield, USA.

Table 3.1 Chemicals

Chemicals	Source
Hydrogen peroxide 35%, H_2O_2	Peroxythai, Rayong, Thailand
L(+)Ascorbic acid, $C_6H_8O_6$	Ajax Chemicals, Auburn, Australia
Potassium hydroxide, KOH	Merck, Hohenbrunn, Germany
Calcium oxide, CaO	Ajax Chemicals, Auburn, Australia
N,N′-Methylenebisacrylamide, *N,N′*-MBA	Nacalai Tesque Inc, Kyoto, Japan
Hydrochloric acid, HCl	J.T.Baker Inc, Phillipsburg, USA.
Nitric acid, HNO_3	J.T.Baker Inc, Phillipsburg, USA.
Sodium chloride, NaCl	Merck, Darmstadt, Germany
Magnesium chloride, $MgCl_2{\cdot}6H_2O$	Carlo Erba, Milan, Italy
Calcium chloride, $CaCl_2$	Fluka, Buchs, Switzerland
Boric acid, H_3BO_3	Merck, Hohenbrunn, Germany
Citric acid monohydrate, $H_3C_6H_5O_7{\cdot}H_2O$	Merck, Hohenbrunn, Germany
Tri-sodium phosphate, $Na_3PO_4{\cdot}12H_2O$	J.S.Chemical, Bangkok, Thailand
Tri-sodium citrate, $Na_3C_6H_5O_7{\cdot}2H_2O$	Chemikit, Bangkok, Thailand
Cupric sulfate, $CuSO_4{\cdot}5H_2O$	BDH, Poole, England
Anhydrous Sodium Carbonate, Na_2CO_3	Merck, Hohenbrunn, Germany

3.2 Procedure

3.2.1 Gelatinization of Cassava Starch

Cassava starch 24 g was mixed with 160 cm^3 of distilled water in a 1,000 cm^3 4-necked round bottom flask. The system was stirred mechanically at 360 rpm under heating within the temperature range of 80 ± 2^oC for thirty minutes under the nitrogen atmosphere to form a slurry-paste.

3.2.2 Graft Copolymerization of Acrylic Acid and Acrylamide onto Cassava Starch

The gelatinized starch was then cooled to 32^oC; 0.4 g of calcium oxide, 0.16 g of ascorbic acid, 0.16 g of *N,N*$^/$-MBA, 16 g of acrylamide and a mixture of 1.6 cm^3 of hydrogen peroxide and 16 g of acrylic acid were added into the reaction. The reaction mixture was stirred under the nitrogen atmosphere for 10 minutes. The reaction product was precipitated with acetone and dried at 65^oC in an oven for 24 hours.

A product with the highest water absorption capacity could be obtained by investigation of the influential effects on graft copolymerization. Various reaction parameters of grafting characteristics and water absorption were investigated as shown in Table 3.2.

3.2.2.1) Effect of Acrylic Acid-to-Acrylamide Ratio on Graft Copolymerization

The amount of starch remained constant for each experiment while the AA-to-AM ratios were varied as 100:0, 75:25, 50:50, 25:75, and 0:100.

In the case of 100%AM, 20 cm^3 of 1N HNO_3 was added into the reaction and the reaction time was 1 hour.

Table 3.2 Parameters for Graft Copolymerization of Cassava Starch and Acrylic Acid/Acrylamide

Starch (g)	24
Weight ratio of the monomer, AA:AM	100:0-0:100
Weight ratio of starch -to- monomers	24:8-24:64
Ascorbic acid, % weight of monomers	0.25-2.0
Hydrogen peroxide, %volume by weight of monomers	0.16-20.0
Crosslinking agent, *N,N′*-MBA, %weight of monomers	0-0.7

3.2.2.2) Effect of Starch-to-Monomer Ratio on Graft Copolymerization

The same reaction procedure as describe above was carried out. The amount of starch remained constant for each experiment while one of the monomer mixtures was varied. The different starch-to-monomer ratios to be investigated were 24:8, 24:16, 24:32, and 24:64. Each batch of the reaction mixture was conducted at the optimum acrylic acid-to-acrylamide ratio (Section 3.2.2.1).

3.2.2.3) Effect of Ascorbic Acid on Graft Copolymerization

From the experimental data gained, the optimum ratios of the AA-to-AM (Section 3.2.2.1) and starch-to-monomer (Section 3.2.2.2) were fixed. Concentrations of ascorbic acid of 0.25, 0.5, 1.0, and 2.0% weight based on the monomer mixture were added to each batch of the gelatinized starch.

3.2.2.4) Effect of Hydrogen Peroxide on Graft Copolymerization

The concentrations of hydrogen peroxide used were 0.16, 1.0, 5.0,10.0, and 20.0%volume by weight based on the monomer mixture. Each batch of the reaction mixture was carried out at the optimum ratio of the AA-to-AM (Section 3.2.2.1), starch/monomer (Section 3.2.2.2), and ascorbic acid (Section 3.2.2.3).

3.2.2.5) Effect of the Crosslinking Agent on Graft Copolymerization

The crosslinking agent was added in each batch of the gelatinized starch-monomer mixture with the optimum AA-to-AM ratio (Section 3.2.2.1) and the optimum starch-to-monomer ratio (Section 3.2.2.2), ascorbic acid (Section 3.2.2.3), and hydrogen peroxide (Section 3.2.2.4). The concentration of crosslinking agent was varied from 0-0.7%weight based on the monomer mixture.

3.2.2.6) Effect of Neutralization of Acrylic Acid on Graft Copolymerization

A predetermined amount of aqueous potassium hydroxide solution was carefully added to the acrylic acid, which was thermally controlled and was not overheated than 40^{o}C in order to obtain a 100% neutralized acrylic acid. The neutralized acrylic acid was mixed with hydrogen peroxide and then was added by dropwise into the cooled gelatinized starch with an exact amount of ascorbic acid and acrylamide, which were dissolved in there.

For comparison of the influence of adding initiator, the another approach was added rapidly by pouring.

3.2.3 Removal of Free Polymers

The dried product derived from the above sections that was ground previously into a powder form was stirred in distilled water (about 1 g to 100 cm^3 of distilled water) at room temperature for 24 hours. The mixture was centrifuged to separate the graft copolymer. The graft copolymer was washed with distilled water and centrifuged to allow another separation of the grafted copolymer. Then it was dehydrated with acetone to give fine precipitate, dried in the oven at 65^{o}C for 24 hours and it was weighed to examine the amount of the free polymers.

3.2.4 Saponification of the Graft Copolymer

A suspension of 5 g of graft copolymer in 125 cm^3 of 5% potassium hydroxide solution was stirred with a magnetic stirrer at room temperature and the saponification reaction was carried out for 1 hour. The reaction product was washed with water, until pH 7 was reached, and dehydrated with acetone to give fine precipitated. It was dried at 65^{o}C for 24 hours and ground into a powder form.

3.3 Characterization of the Copolymers

The synthesized copolymers were characterized as follows:

3.3.1 Proof of Functionalities by FTIR Spectroscopy

The functional groups of the copolymers were examined by a Fourier-Transform Infrared Spectrophotometry (FTIR), Perkin-Elmer Infrared Spectrophotometer, model 1760X, using a KBr pellet.

3.3.2 Determination of Percentage Free Polymers

The weights obtained from Section 3.2.3 were the amount of free polyacrylamide, poly(acrylic acid), and poly(acrylic acid-*co*-acrylamide) produced as by product, which were then calculated.

3.3.3 Determination of Percentage Grafting Efficiency

Percentage grafting efficiency is the percentage of the total synthetic polymer formed that had been grafted to starch, which was computed as follows:

$$\%\text{ grafting efficiency} = \frac{\text{weight of polymer grafted}}{\text{weight of free polymers + weight of polymer grafted}} \times 100 \tag{2.18}$$

3.3.4 Determination of Percentage Add-on

In a 125-cm^3 Erlenmeyer flask mounted with a condenser, 0.5 g of the graft copolymer was refluxed in 50 cm^3 of 1N HCl for 2 hours. The polymer was filtered and washed with distilled water until pH 7 was reached and then it was dried.

The weight percentages of polymers in the graft copolymer or the so called “percentage add-on” were calculated from the weight of the remaining polymer.

3.3.5 Determination of Percentage Grafting Ratio

The experimental procedure of Section 3.3.4 also gave the weights of the polymer in grafts and the substrate (starch), which was considered as the percentage grafting ratio as computed in Section 2.4.

3.3.6 Determination of Surface Morphology of the Copolymer

The surface morphology of the copolymers was investigated using a scanning electron microscope (SEM), Joel, model JSM-6400, Japan.

3.4 Water Absorption/Retention Capacities of the Copolymers

3.4.1 In Distilled Water

The dried, saponified graft copolymer of 0.10 g was soaked in 75 cm^3 of distilled water for 1 hour. The swollen copolymer was filtered through a weighed 100-mesh aluminium screen and allowed to drain for 2 hours. Then it was weighed to determine the weight of the water-swollen gel.

The water absorption capacity was calculated in g/g of the dried polymer as follows:

$$\text{Water Absorption Capacity (g/g)} = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \qquad (3.1)$$

3.4.2 In Salt Solutions

The same experimental procedure as described in Section 3.4.1 was carried out, except for that a series of sodium chloride, magnesium chloride, and calcium chloride solutions of 0.1, 0.5, and 0.9% weight by volume were used instead of distilled water.

3.4.3 In Buffer Solutions

The same experimental procedure as described in Section 3.4.1 was carried out, except for that a series of buffer solutions of pH 3 to 11 were prepared by mixing of 0.20M boric acid, 0.05M citric acid, and 0.10M tri-sodium phosphate [30].

3.5 Enzyme Hydrolysis of the Copolymers

The dried and saponified graft copolymer of 0.35 g was swollen in 100 cm^3 of distilled water for 1 hour at room temperature and filtered through a 100-mesh aluminium screen and then allowed to drain for 2 hours. The water-swollen gel was added with 1%enzyme solution and stirred with a magnetic stirrer for 1 hour at ambient temperature. The degraded copolymer was heated to destroy the enzyme, cooled at room temperature and investigated using chemical test [31], iodine and Benedict’s test, and physical test, viscometry. In comparison, the control copolymer was tested by adding the determined amount of distilled water instead of the enzyme solution.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization the Functional Groups of the Copolymers by FTIR

The synthesized copolymers were characterized of the functional groups using FTIR technique, which reference peak of styrene spectrum is at 2000 cm^{-1} as shown in Figure A-1 of Appendix A. The FTIR spectra of cassava starch, and the synthesized copolymers are shown in Figures 4.1–4.9 and demonstrated in Tables 4.1–4.3 [32,44].

The IR spectra of cassava starch are shown in Figure 4.1. The spectra display a very broad, intense O-H stretching absorption in the region of 3550-3200 cm^{-1}; a medium intensity of the C-H stretching at 2932 cm^{-1}; and the wave number of 1158, 1083, and 1020 cm^{-1} are many very strong bands of the C-O stretching.

IR spectrum of the starch-*g*-polymer contains absorption bands of functional groups of cassava starch and the grafted. The IR spectra of starch-*g*-poly(acrylic acid) (Figures 4.2–4.4) give absorption peaks of the carboxylic acid groups in addition to O-H stretching, C-H stretching, and C-O stretching in cassava starch. The spectra of carboxylic acid group show a medium broad band of the O-H stretching, a strong C=O stretching absorption band, a moderate intensity of the C-O-H in-plane bending and C-O stretching in the region of 3428, 1724, 1417, and 1245 cm^{-1}, respectively.

In the case of saponified cassava starch-*g*-poly(acrylic acid) and cassava starch-*g*-poly(potassium acrylate), the carboxylic group was changed to the

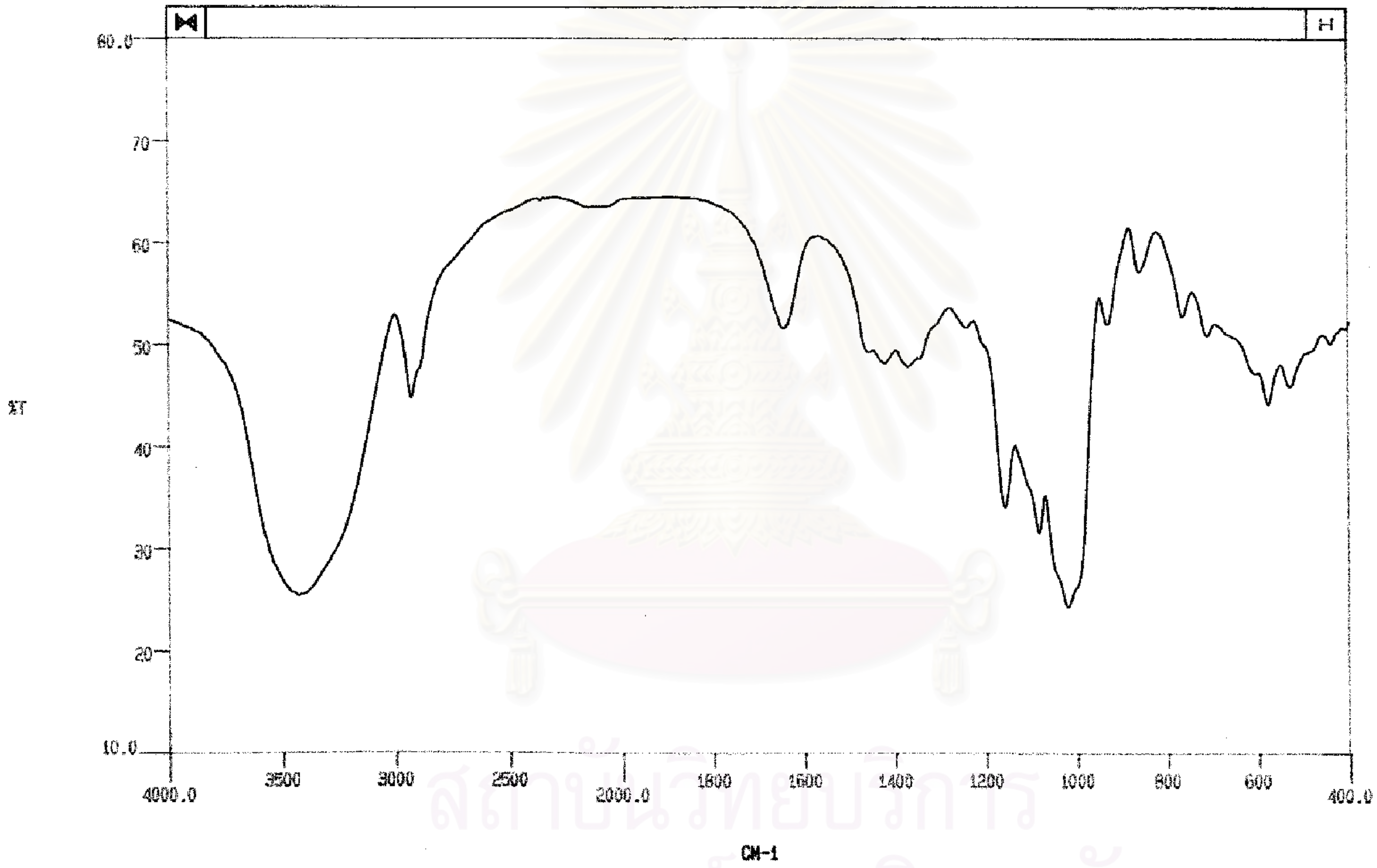


Figure 4.1 Infrared spectrum of cassava starch

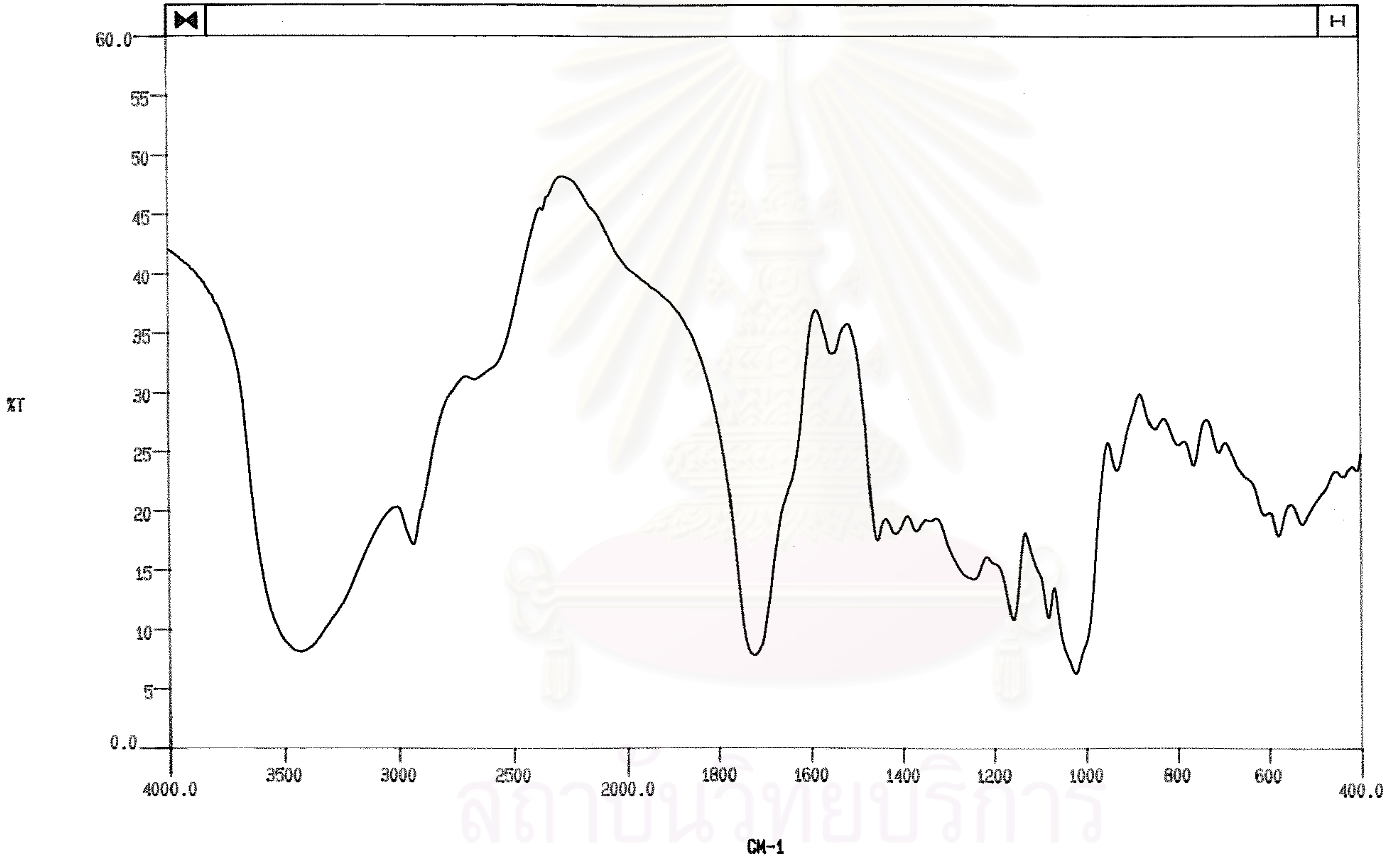


Figure 4.2 Infrared spectrum of cassava starch-*g*-poly(acrylic acid)

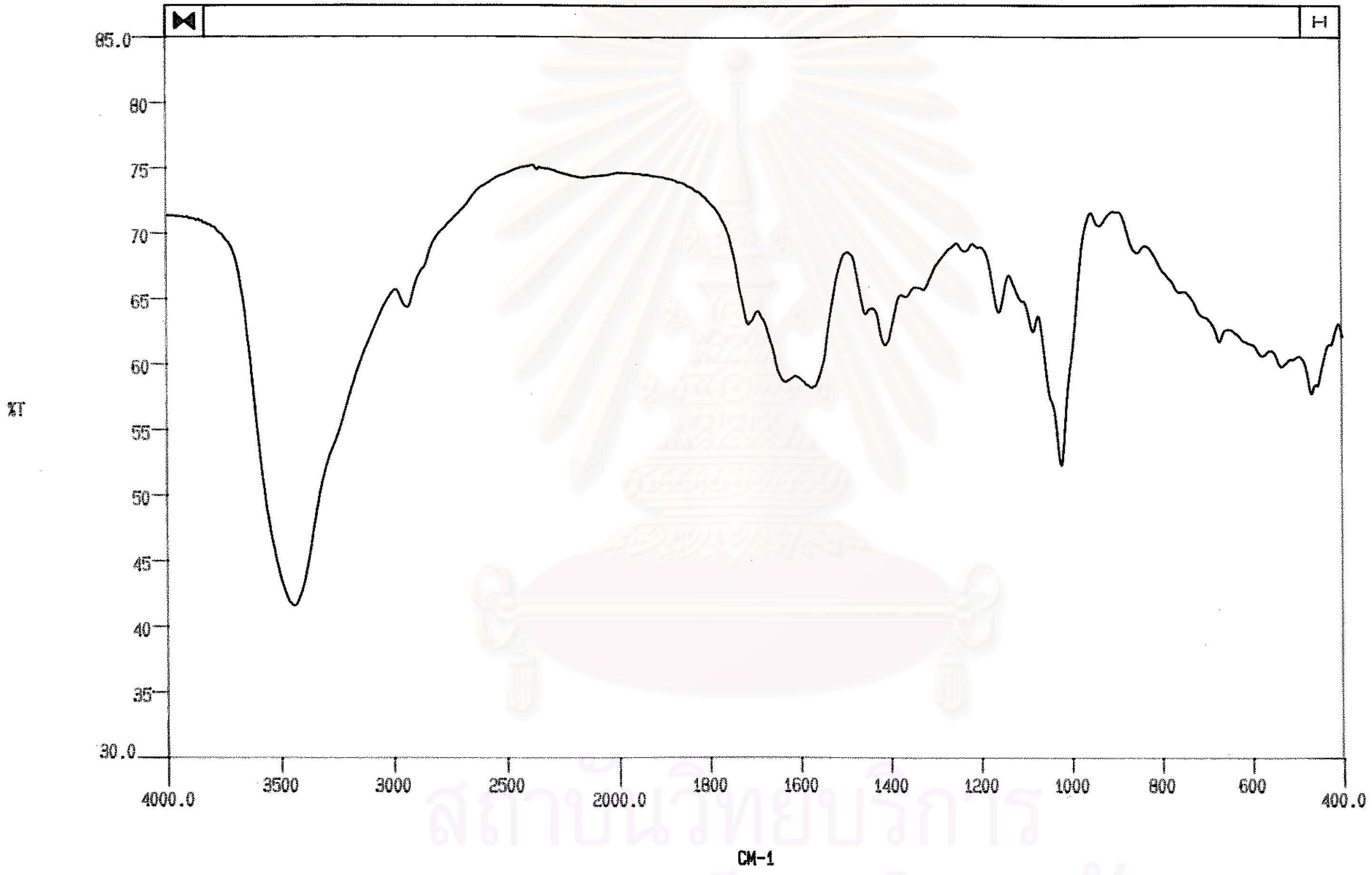


Figure 4.3 Infrared spectrum of cassava starch-*g*-poly(acrylic acid) after saponification

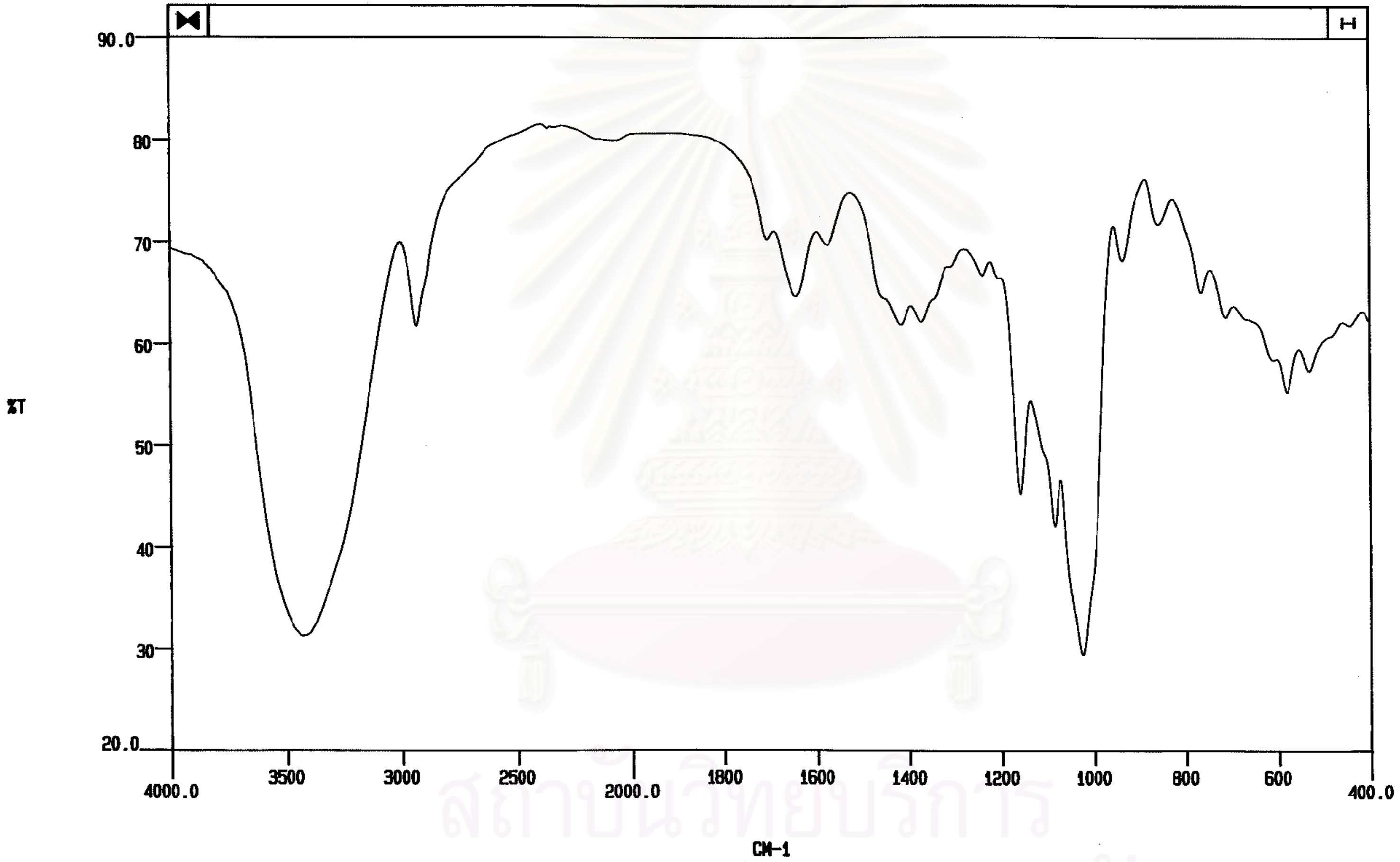


Figure 4.4 Infrared spectrum of cassava starch-*g*-poly(potassium acrylate)

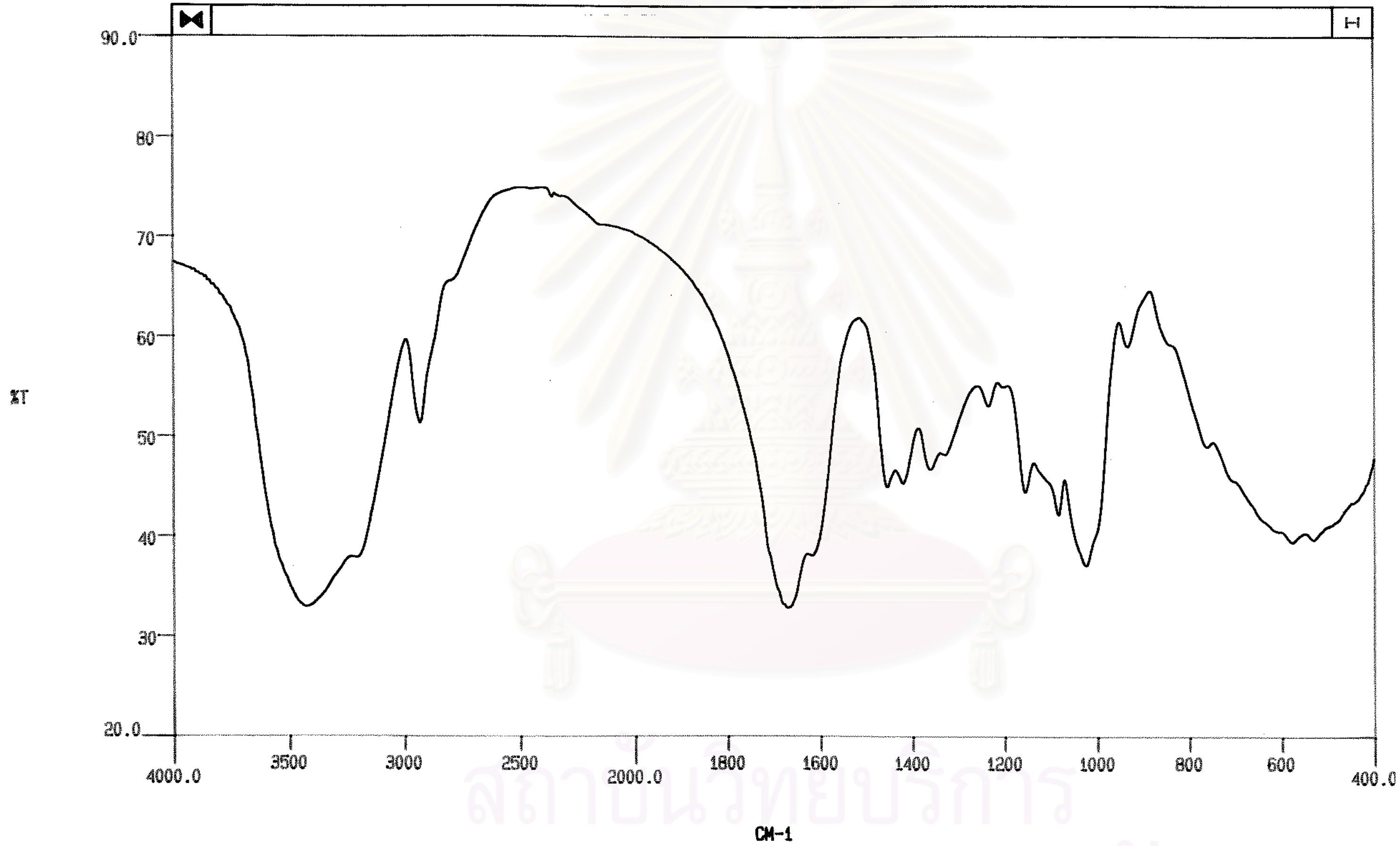


Figure 4.5 Infrared spectrum of cassava starch-*g*-polyacrylamide

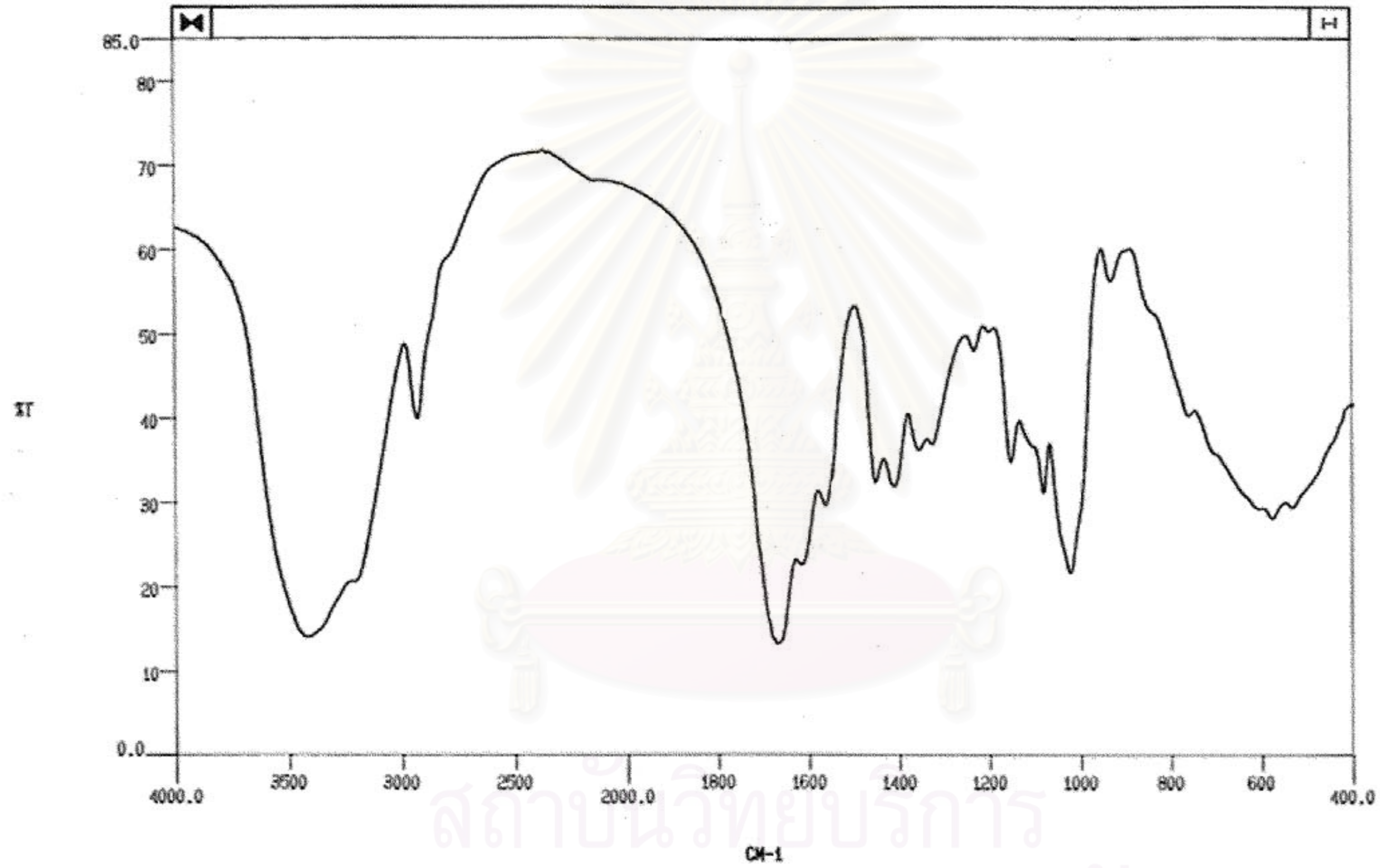


Figure 4.6 Infrared spectrum of cassava starch-*g*-polyacrylamide after saponification

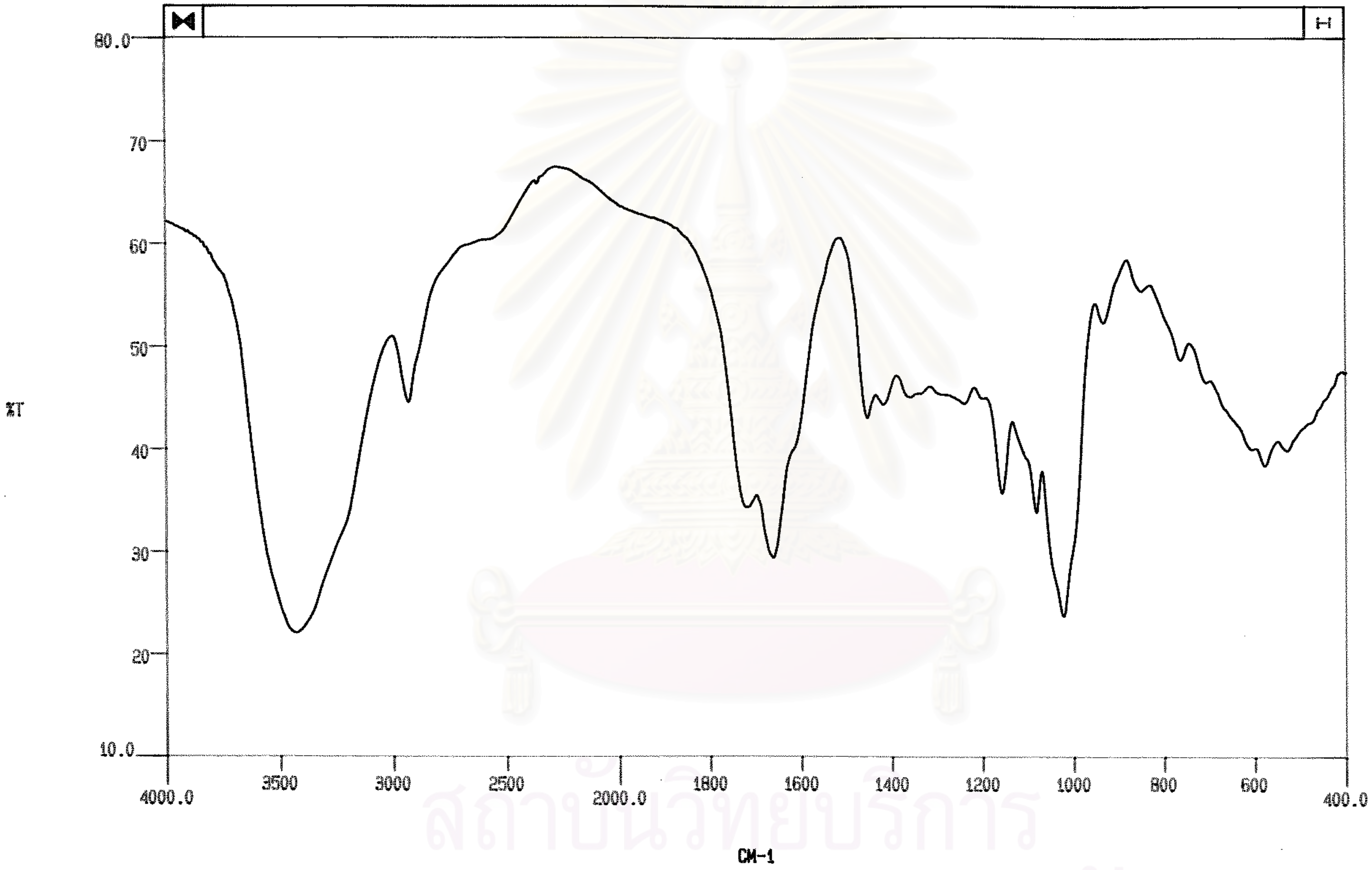


Figure 4.7 Infrared spectrum of cassava starch-*g*-poly(acrylic acid-*co*-acrylamide)

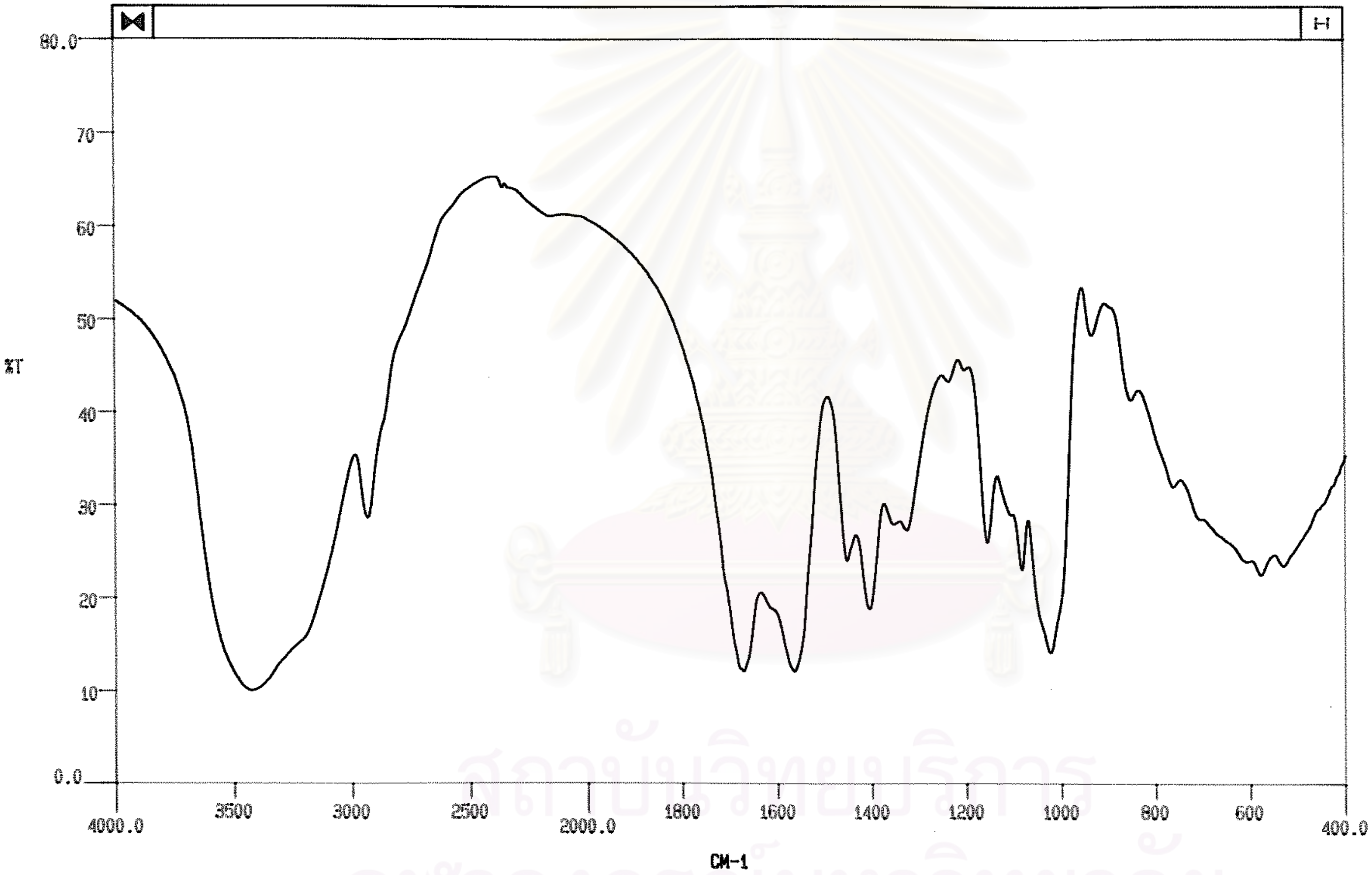


Figure 4.8 Infrared spectrum of cassava starch-*g*-poly(acrylic acid-*co*-acrylamide) after saponification

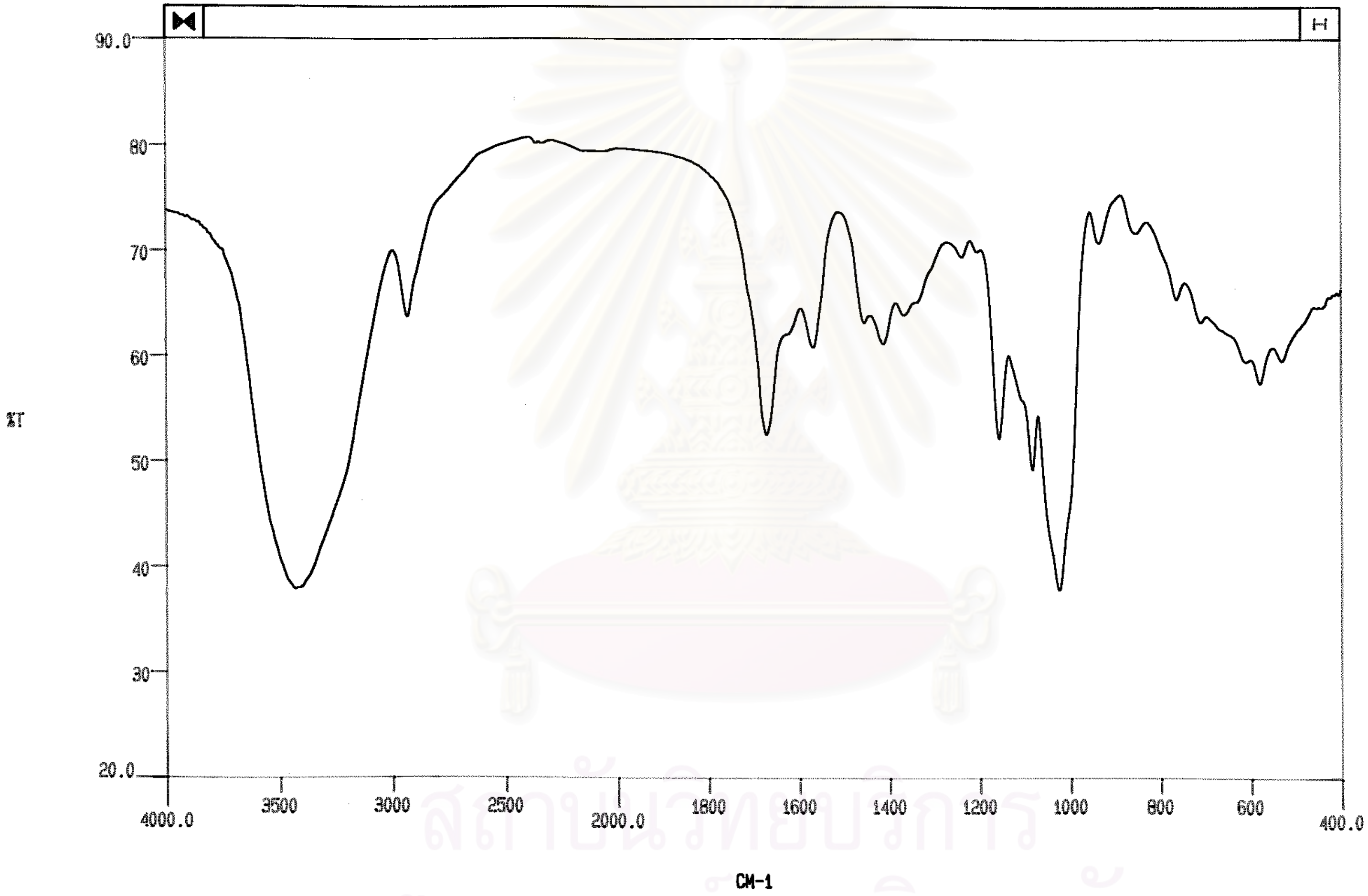


Figure 4.9 Infrared spectrum of cassava starch-*g*-poly(potassium acrylate-*co*-acrylamide)

Table 4.1 The Infrared Absorption of Functional Groups in Cassava Starch, Starch-*g*-poly(acrylic acid), Starch-*g*-poly(acrylic acid) After Saponification, and Starch-*g*-poly(potassium acrylate)

Starch			Starch-*g*-poly(acrylic acid)			Starch-*g*-poly(acrylic acid) after saponification			Starch-*g*-poly(potassium acrylate)		
wave number (cm^{-1})	I	assignment	wave number (cm^{-1})	I	assignment	wave number (cm^{-1})	I	assignment	wave number (cm^{-1})	I	assignment
3550-3200	s, vb	O-H stretching	3550-3200	s, vb	O-H stretching	3550-3200	s, vb	O-H stretching	3550-3200	s, vb	O-H stretching
2932	m	C-H stretching	2936	m	C-H stretching	2933	m	C-H stretching	2931	m	C-H stretching
1158, 1083, 1020	s	C-O stretching	1158, 1082, 1023	s	C-O stretching	1158, 1083, 1022	s	C-O stretching	1156, 1082, 1023	s	C-O stretching
			3428	m, b	O-H stretching of COOH	1575	s	C=O stretching of COO$^-$	1574	s	C=O stretching of COO$^-$
			1724	s	C=O stretching of COOH						
			1417	m	O-H bending of COOH						
			1245	s	C-O stretching of COOH						

I = intensity: vb = very broad, b = broad, s = strong, and m = medium

Table 4.2 The Infrared Absorption of Functional Groups in Cassava Starch, Starch-*g*-polyacrylamide, and Starch-*g*-polyacrylamide After Saponification

Starch			Starch-*g*-polyacrylamide			Starch-*g*-polyacrylamide after saponification		
wave number (cm^{-1})	intensity	assignment	wave number (cm^{-1})	intensity	Assignment	wave number (cm^{-1})	intensity	assignment
3550-3200	s, vb	O-H stretching	3550-3200	s, vb	O-H stretching	3550-3200	s, vb	O-H stretching
2932	m	C-H stretching	2931	m	C-H stretching	2932	m	C-H stretching
1158, 1083, 1020	s	C-O stretching	1155, 1083, 1023	s	C-O stretching	1154, 1083, 1024	s	C-O stretching
			3432	m	N-H stretching	3427	m	N-H stretching
			1690-1650	s	C=O stretching of $CONH_2$	1690-1650	s	C=O stretching of $CONH_2$
			1671	s	N-H bending	1672	s	N-H bending

intensity: vb = very broad, b = broad, s = strong, and m = medium

Table 4.3 The Infrared Absorption of Functional Groups in Cassava Starch, Starch-*g*-poly(acrylic acid-*co*-acrylamide), Starch-*g*-poly(acrylic acid-*co*-acrylamide) After Saponification, and Starch-*g*-poly(potassium acrylate-*co*-acrylamide)

starch			starch-*g*-poly(acrylic acid-*co*-acrylamide)			starch-*g*-poly(acrylic acid-*co*-acrylamide) after saponification			starch-*g*-poly(potassium acrylate-*co*-acrylamide)		
wave number (cm^{-1})	I	assignment	wave number (cm^{-1})	I	assignment	wave number (cm^{-1})	I	assignment	wave number (cm^{-1})	I	assignment
3550-3200	s, vb	O-H stretching	3550-3200	s, vb	O-H stretching	3550-3200	s, vb	O-H stretching	3550-3200	s, vb	O-H stretching
2932	m	C-H stretching	2934	m	C-H stretching	2934	m	C-H stretching	2931	m	C-H stretching
1158, 1083, 1020	s	C-O stretching	1157, 1082, 1023	s	C-O stretching	1156, 1083, 1024	s	C-O stretching	1156, 1082, 1024	s	C-O stretching
			3300-2500	m, b	O-H stretching of COOH	3300-2500	m, b	O-H stretching of COOH	3300-2500	m, b	O-H stretching of COOH
			1722	s	C=O stretching of COOH	1565	s	C=O stretching of COO^-	1567	s	C=O stretching of COO^-
			1419	m	O-H bending of COOH	1406	m	O-H bending of COOH	1412	m	O-H bending of COOH
			1240	s	C-O stretching of COOH	1237	s	C-O stretching of COOH	1237	s	C-O stretching of COOH

I = intensity: vb = very broad, b = broad, s = strong, and m = medium

Table 4.3 (continued) The Infrared Absorption of Functional Groups in Cassava Starch, Starch-*g*-poly(acrylic acid-*co*-acrylamide), Starch-*g*-poly(acrylic acid-*co*-acrylamide) after saponification, and Starch-*g*-poly(potassium acrylate-*co*-acrylamide)

starch			starch-*g*-poly(acrylic acid-*co*-acrylamide)			starch-*g*-poly(acrylic acid-*co*-acrylamide) after saponification			starch-*g*-poly(potassium acrylate-*co*-acrylamide)		
wave number (cm^{-1})	I	assignment	wave number (cm^{-1})	I	assignment	wave number (cm^{-1})	I	assignment	wave number (cm^{-1})	I	assignment
			3500-3300	m	N-H stretching	3500-3300	m	N-H stretching	3500-3300	m	N-H stretching
			1690-1650	s	C=O stretching of $CONH_2$	1690-1650	s	C=O stretching of $CONH_2$	1690-1650	s	C=O stretching of $CONH_2$
			1663	s	N-H bending	1663	s	N-H bending	1663	s	N-H bending

I = intensity: vb = very broad, b = broad, s = strong, and m = medium

carboxylate ion, which displays a strong C=O stretching of the latter in the region of 1575 and 1574 cm^{-1}, respectively.

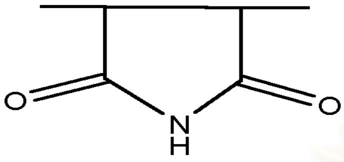
The infrared absorption of starch-*g*-polyacrylamide before and after saponification (Figures 4.5–4.6) give the similar absorption bands, that is, the absorption band of cassava starch and of carboxamide. IR spectra of the carboxamide group show a medium N-H stretching, a strong C=O stretching and a strong N-H bending in the region of 3500-3300, 1690-1650, and 1650-1580 cm^{-1}, respectively. The similar absorption bands of starch-*g*-polyacrylamide before and after saponification indicate that the saponification condition converted a little amount of the acrylamide moiety to the acrylate functional group.

IR spectra of starch-*g*-poly(acrylic acid-*co*-acrylamide) before saponification (Figure 4.7) display all the absorption peaks of cassava starch, acrylic acid and acrylamide. The saponified cassava starch-*g*-poly(acrylic acid-*co*-acrylamide) and cassava starch-*g*-poly(potassium acrylate-*co*-acrylamide) show the similar absorption peaks of cassava starch, acrylate and acrylamide as shown in Figures 4.8–4.9.

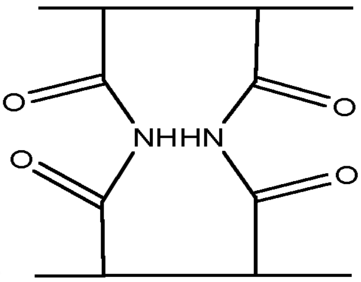
4.2 Graft Copolymerization of Acrylic Acid and Acrylamide onto Cassava Starch

4.2.1 Effect of Acrylic Acid-to-Acrylamide Ratio on Graft Copolymerization

The effect of AA-to-AM ratio is illustrated in Table 4.4 and Figures 4.10–4.14. The copolymerization of either AA or AM presented the lower percentage of free polymers than those of both AA and AM. In the case of AA, an autocrosslinking may occur through a hydrogen abstraction from the polymer backbone resulted from polymerizing the highly concentrated solutions of acrylic acid. The copolymerization of AM may form imidization because the occurrence of imidization that usually takes place in the polymerization of acrylamide in concentrated solutions and at high temperature and pH [45]. The result so obtained is evidenced with a higher gel strength than those with both AA and AM because of cyclic imide structures (I-II).



I



II

Table 4.4 Effect of Acrylic Acid-to-Acrylamide Ratio on Graft Copolymerization

AA : AM	FP (%)	GE (%)	Add-on (%)	GR (%)	WAC (g/g)
100 : 0	15.5	61.1	28.8	40.5	142±3
75 : 25	28.0	49.3	37.8	60.9	157±3
50 : 50	30.8	52.8	49.8	99.2	312±4
25 : 75	29.1	52.1	44.7	80.8	289±2
0 :100[a]	9.7	80.1	43.3	76.4	270±10

FP = Free Polymers; GE = Grafting Efficiency; GR = Grafting Ratio; WAC = Water Absorption Capacity; Starch:Monomer = 3:4, *N,N′*-MBA 0.5%wt, Ascorbic acid 0.5%wt, HOOH 5.0%wt, [a]1N HNO_3 as additive.

When the starch-*g*-poly(AA-*co*-AM) was saponified with KOH solution then the functional groups of carboxylic acid and carboxamide were partially altered to the carboxylate group, which consists of mobile K^+ ions. The water absorbency increases with increasing number of hydrophilic and ionic functional groups (Figure 4.14). The reactivity ratios of AA and AM, 1.43 and 0.60, respectively [33], render that the structure of the copolymer should contain more AA units than AM units,

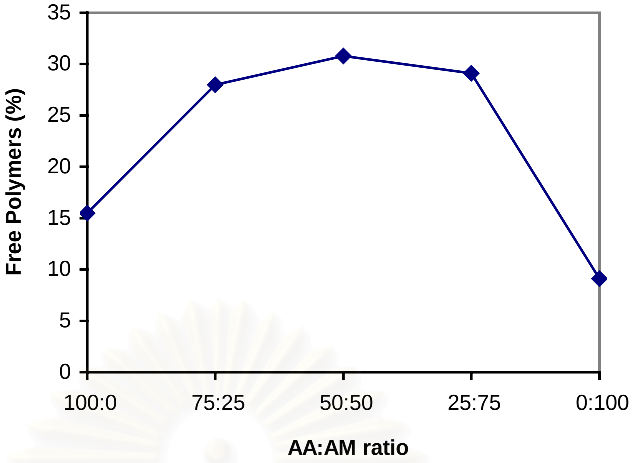


Figure 4.10 Effect of AA-to-AM ratio on percentage free polymers

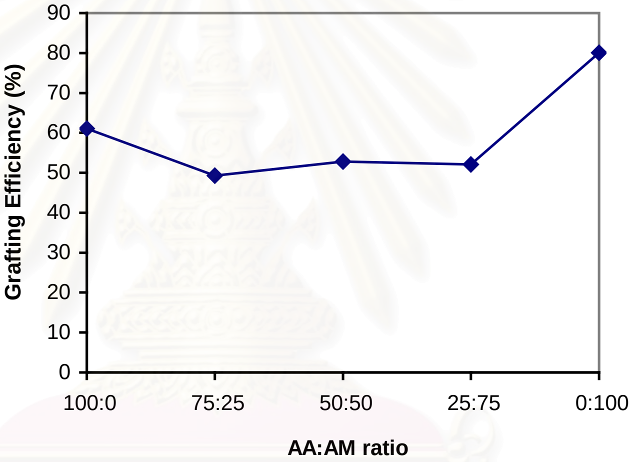


Figure 4.11 Effect of AA-to-AM ratio on percentage grafting efficiency

which produce the saponified graft copolymer with high ionic functional group upon saponification. However, if the flexibility of polymer chains was a significant parameter, the water absorption capacity should increase with decreasing concentration of acrylate unit in the polymer chain owing to the glass transition temperature (T_g) of potassium acrylate is higher than of acrylamide, i.e., 194^{o}C and 165^{o}C, respectively [33,34]. Therefore, the optimum ratio of AA-to-AM is a key factor, which can produce the saponified graft copolymer with the highest water absorbency. From the obtained water absorbency, the AA-to-AM ratio of 50:50 can produce polymer, which can absorb distilled water at the highest value of 312±4 g/g its dry weight.

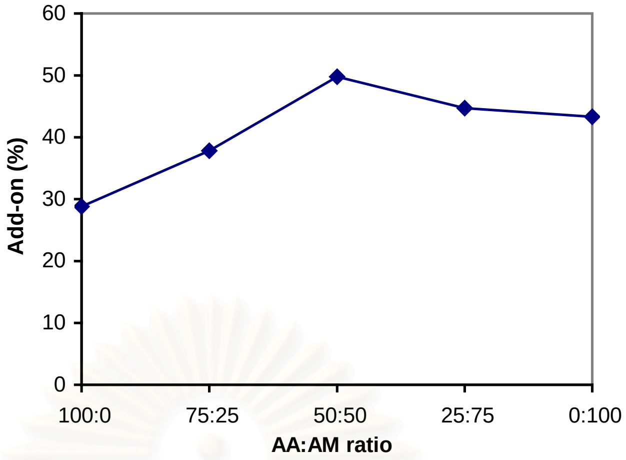


Figure 4.12 Effect of AA-to-AM ratio on percentage add-on

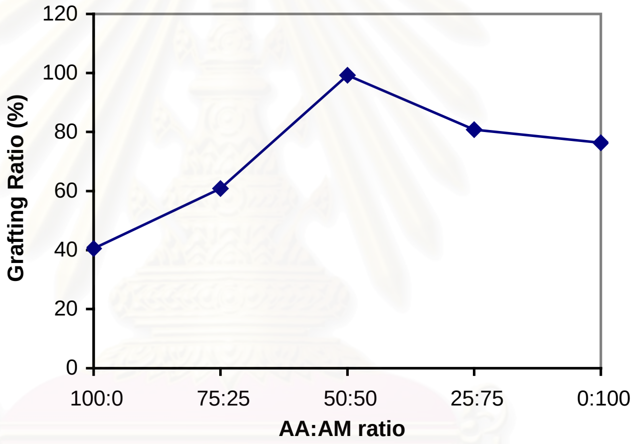


Figure 4.13 Effect of AA-to-AM ratio on percentage grafting ratio

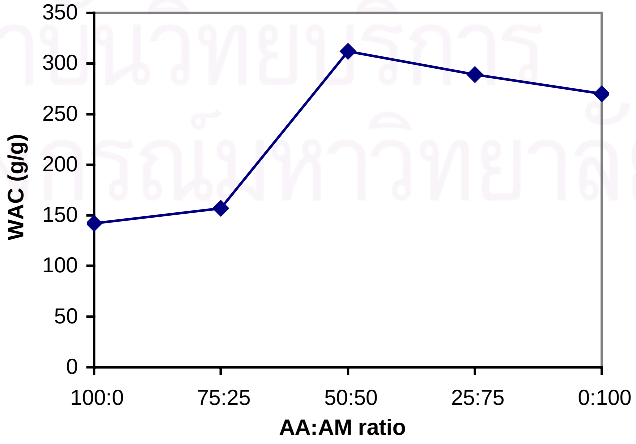


Figure 4.14 Effect of AA-to-AM ratio on water absorption capacity

4.2.2 Effect of Starch-to-Monomer Ratio on Graft Copolymerization

The effect of starch-to-monomer ratio is shown in Table 4.5 and Figures 4.15–4.19. The percent free polymer varies between 28-30%, which may be caused by the short reaction time that induces variation of the free polymers contents. Generally, free-radical degradation of the polymer chains occurs after the main polymerization is complete, when the polymer gel is still at elevated temperature. For chains attached to the dangling chains, only a single chain scission is required to cleave it from the network and form a soluble chain. As a result, the amount of extractable polymer increases as reaction time is extended [7].

In terms of the percent grafting efficiency, add-on, and grafting ratio, they can be explained in the same way. They increased with increasing the concentration of monomer because the starch free radicals could react with a lot of macroradicals (Equation 2.11), the molecular weights of the resulting polymer increase with increasing monomer concentration.

Table 4.5 Effect of Starch-to-Monomer Ratio on Graft Copolymerization

Monomer (g)	Starch : Monomer	FP (%)	GE (%)	Add-on (%)	GR (%)	WAC (g/g)
8	3 : 1	30.7	14.5	7.5	8.1	ND
16	3 : 2	28.5	35.3	21.7	27.8	230±8
32	3 : 4	30.8	52.8	49.8	99.2	312±4
64	3 : 8	28.5	59.3	58.1	138.5	300±6

FP = Free Polymers; GE = Grafting Efficiency; GR = Grafting Ratio; WAC = Water Absorption Capacity; AA:AM = 50:50, *N,N*′-MBA 0.5%wt, Ascorbic acid 0.5%wt, HOOH 5.0%wt, ND = Not Detected

The quantity of starch to monomer ratio of 3:4 is the optimum condition, which provides the highest water absorption. Water absorption increases with increasing the monomer content until the starch to monomer ratio exceeds 3:4, the water absorption starts to decline. The starch/monomer ratio of 3:8 gives the highest percent grafting efficiency, add-on, and grafting ratio, but the water absorbency shown the opposite director. This result may be due to chain transfer to polymer, which leads to the production of a branched polymer, and increases the self-crosslink of polymer that renders the gel strength of the polymer gel become higher than those of 3:4 ratio [43]. The extent of entanglement of the network chains, which is responsible for much of the increase in modulus with increasing monomer concentration, may be accounted for by the entanglement parameter of the Flory-Erman theory [35]. The smallest amount of monomer cannot give a water absorption because the most of the grafted copolymer was dissolved in the saponification process. The lower the monomer concentration, the shorter the kinetic chain length [7].

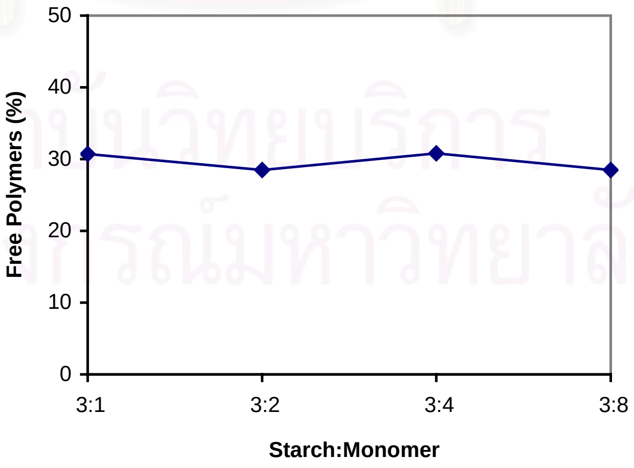


Figure 4.15 Effect of starch-to-monomer ratio on percentage free polymers

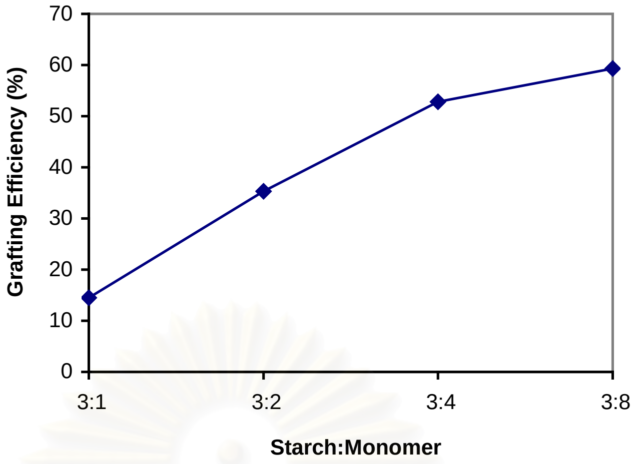


Figure 4.16 Effect of starch-to-monomer ratio on percentage grafting efficiency

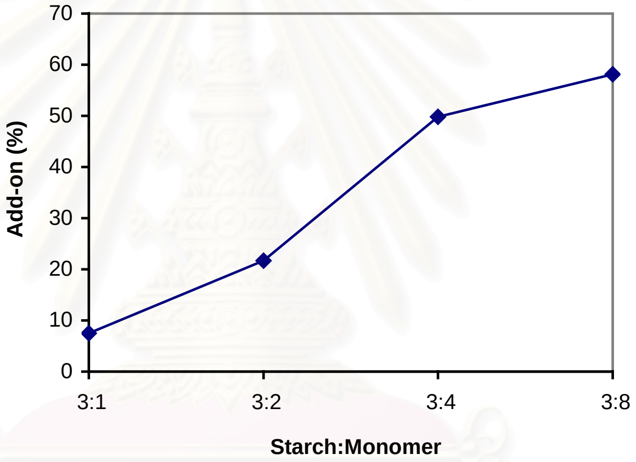


Figure 4.17 Effect of starch-to-monomer ratio on percentage add-on

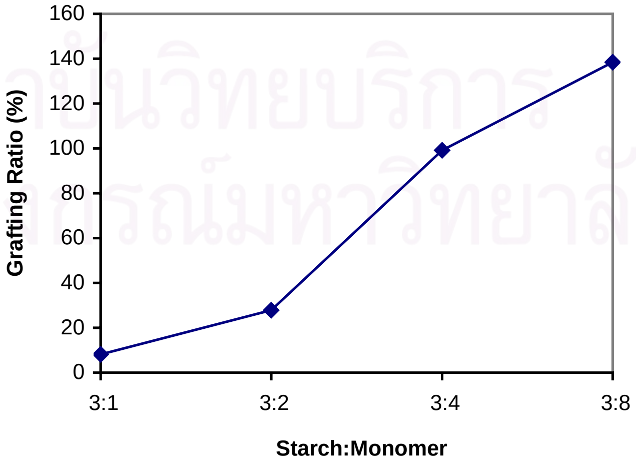


Figure 4.18 Effect of starch-to-monomer ratio on percentage grafting ratio

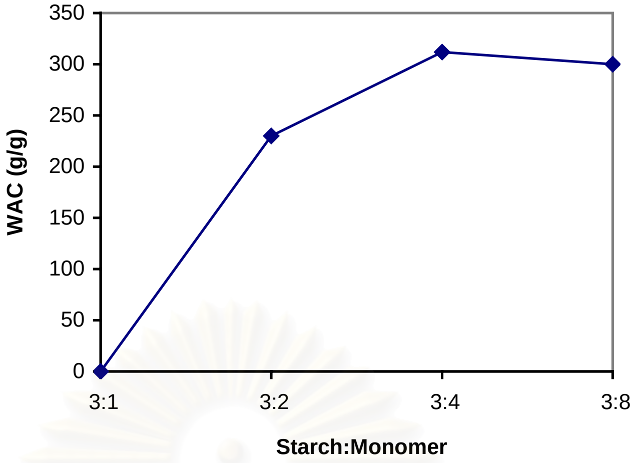


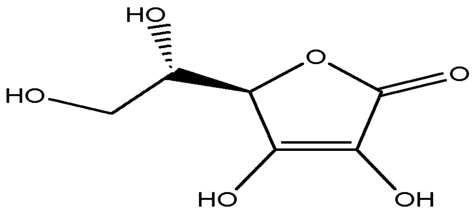
Figure 4.19 Effect of starch-to-monomer ratio on water absorption capacity

4.2.3 Effect of the Redox Initiator on Graft Copolymerization

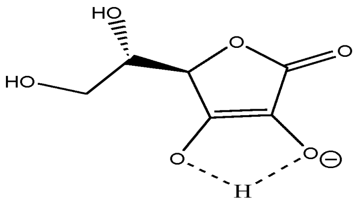
Hydrogen peroxide and ascorbic acid were used as the redox initiating system. The reaction between HOOH and ascorbic acid produces the charge-transfer complexes, which eventually dissociates to give the hydroxyl radical and ascorbate free radical as shown in Equation 4.1 [21,36]. Since free radicals on starch are not formed initially, but they are produced through the chain transfer reaction with an existing free radical, significant amounts of homopolymer are often formed by the reaction of initially formed radicals with a monomer before chain transfer to starch can occur [37]. Therefore, the percentage of free polymers increases with increasing the redox initiator.

$$AH_2 \ + \ HOOH \longrightarrow {}^{\bullet}AH \ + \ {}^{\bullet}OH \ + \ H_2O \qquad (4.1)$$

where AH_2 is ascorbic acid (structure III) and ${}^{\bullet}AH$ is ascorbate radical (structure IV).



III



IV

From Equation 2.10, the kinetic chain length decreases with increasing initiator concentration, which directly affect the molecular weight of the polymer. The mechanisms of the graft copolymerization via the redox system involve the chain transfer reaction shown in Equations 4.1–4.8 [38].

Initiation:

$$\mathrm{AH_2} + \mathrm{HOOH} \longrightarrow {}^{\bullet}\mathrm{AH} + {}^{\bullet}\mathrm{OH} + \mathrm{H_2O} \qquad (4.1)$$

$$\mathrm{M} + {}^{\bullet}\mathrm{OH} \text{ or } {}^{\bullet}\mathrm{AH} \longrightarrow {}^{\bullet}\mathrm{M} \qquad (4.2)$$

Propagation:

$${}^{\bullet}\mathrm{M} + \mathrm{M} \longrightarrow {}^{\bullet}\mathrm{M}_1 \qquad (4.3)$$

$${}^{\bullet}\mathrm{M}_{n-1} + \mathrm{M} \longrightarrow {}^{\bullet}\mathrm{M}_n \qquad (4.4)$$

Termination:

$${}^{\bullet}\mathrm{M}_x + {}^{\bullet}\mathrm{M}_y \longrightarrow \text{Homopolymer} \qquad (4.5)$$

$${}^{\bullet}\mathrm{M}_x + {}^{\bullet}\text{Starch} \longrightarrow \text{Starch-}\mathrm{M}_x \qquad (4.6)$$

Chain Transfer Reaction:

$${}^{\bullet}\mathrm{R} + \text{Starch} \longrightarrow {}^{\bullet}\text{Starch} \qquad (4.7)$$

$${}^{\bullet}\text{Starch} + {}^{\bullet}\mathrm{M}_n \longrightarrow \text{Graft copolymer} \qquad (4.8)$$

4.2.3.1 Effect of Ascorbic Acid on Graft Copolymerization

The effect of ascorbic acid concentration is indicated in Table 4.6 and Figures 4.20–4.24.

Table 4.6 Effect of Ascorbic Acid Concentration on Graft Copolymerization

Ascorbic acid (%)	FP (%)	GE (%)	Add-on (%)	GR (%)	WAC (g/g)
0.25	27.5	54.8	46.0	85.2	240±10
0.5	30.8	52.8	49.8	99.2	312±4
1.0	33.7	44.9	41.4	70.6	209±4
2.0	32.1	46.8	41.6	71.3	179±10

FP = Free Polymers; GE = Grafting Efficiency; GR = Grafting Ratio; WAC = Water Absorption Capacity; AA:AM = 50:50, Starch:Monomer = 3:4, N,N'-MBA 0.5%wt, HOOH 5.0%wt.

At the minimum of ascorbic acid concentration (0.25% wt), the percentage of free polymers is lowest and the percentage of grafting efficiency is highest. Because the reaction is an exothermic reaction, which the increase of the reaction temperature renders the increasing rate of hydrogen peroxide decomposition to water and oxygen gas. Subsequently, ascorbic acid is oxidized to dehydroascorbic acid (DHA) which is a non-reactive species for the graft polymerization as shown in Equations 4.9–4.10 [38]. The percentage of add-on and grafting ratio at 0.5% wt of ascorbic acid are the highest values which may give the optimum chain transfer reaction, because at a high concentration of HOOH and ascorbic acid favor frequent grafting of low-molecular weight branches [39].

The water absorbency of the grafted copolymer, synthesized with various ascorbic acid concentrations is shown in Figure 4.24. The optimum product properties at 0.5% wt ascorbic acid give the highest water absorbency of 312±4 g/g. Considering the characteristics of swollen gel, size and flexibility of the swollen gel decreased with increasing ascorbic acid concentration. When ascorbic acid concentrations are more than 0.5% wt, the gel strength is reduced because the low-molecular weight branches are grafted on starch backbone.

$$AH_2 \xrightarrow[\text{slow}]{O_2} {}^{\bullet}AH + {}^{\bullet}OH_2 \xrightarrow[\text{fast}]{O_2} A + H_2O_2 \qquad (4.9)$$

$$AH_2 + A \xleftrightarrow{\text{very fast}} 2\,{}^{\bullet}AH \qquad (4.10)$$

where AH_2, ${}^{\bullet}AH$, and A represent ascorbic acid, ascorbate radical, and dehydroascorbic acid, respectively.

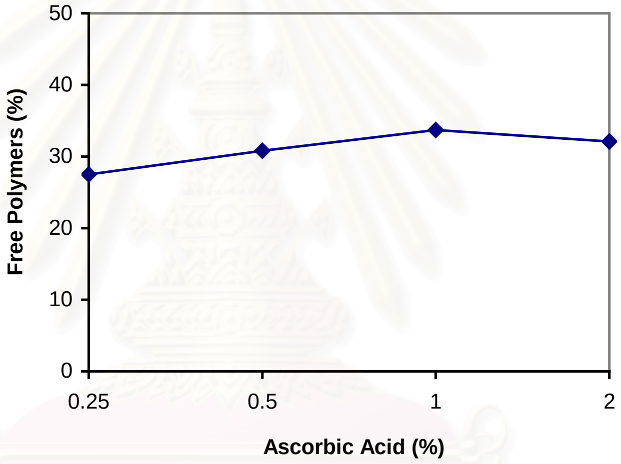


Figure 4.20 Effect of ascorbic acid concentration (%) on percentage free polymers

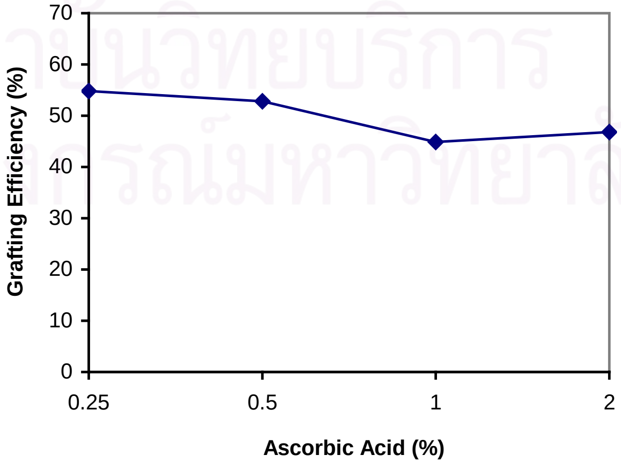


Figure 4.21 Effect of ascorbic acid concentration (%) on percentage grafting efficiency

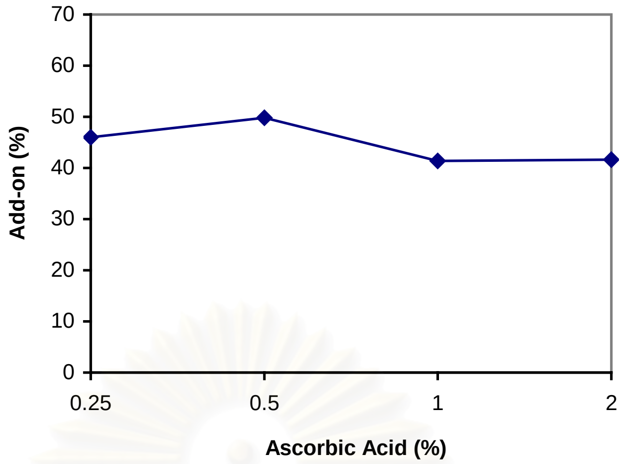


Figure 4.22 Effect of ascorbic acid concentration (%) on percentage add-on

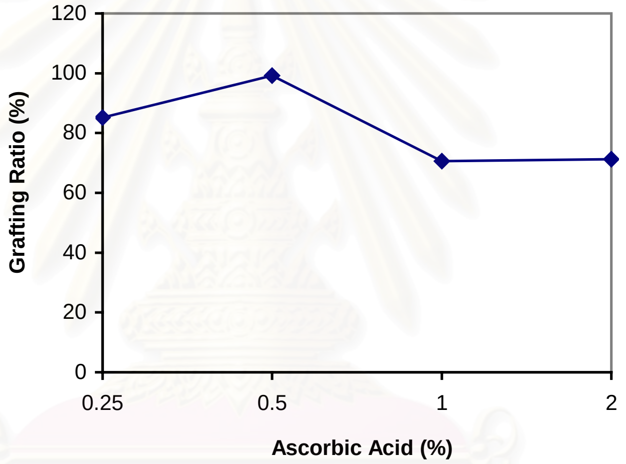


Figure 4.23 Effect of ascorbic acid concentration (%) on percentage grafting ratio

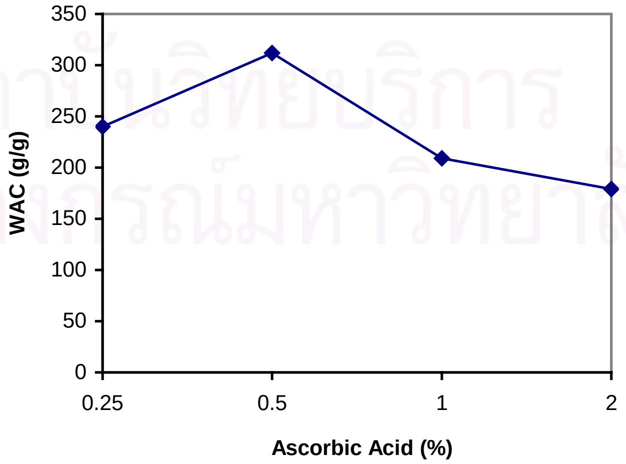


Figure 4.24 Effect of ascorbic acid concentration (%) on water absorption capacity

4.2.3.2 Effect of Hydrogen Peroxide on Graft Copolymerization

The influence of hydrogen peroxide concentration (%weight based on the total monomers) on graft copolymerization is given in Table 4.7 and Figures 4.25–4.29. The concentration of HOOH of 0.16%wt produced 23% of free polymers, which was the lowest amount, but HOOH concentrations of 1.0-20.0%wt gave approximately 30% of free polymers. In addition, the percentage of grafting efficiency, add-on, and grafting ratio decreased with increasing HOOH concentration. From Equation 2.9, the polymerization rate increases with increasing redox initiator concentrations. However, the free radicals on starch are not formed initially, they are produced through chain transfer with an existing free radical bringing about the high percentage of free polymers and the low percent of grafting efficiency. Furthermore, high concentration of the redox initiator renders the grafted copolymers with low-molecular weight branches as a result of the low percent add-on and grafting ratio. The water absorbency increases with increasing HOOH concentration from 0.16-5.0%wt because of the increased polymerization rate and chain transfer reaction of macroradicals to starch radicals. At the excess HOOH concentration (10-20%wt), the water absorbency decreases, which is caused by the deactivation of HOOH to form water and oxygen as shown in Equation 4.11 and forming short branches of the grafted copolymer with decreasing gel strength.

$$\mathrm{HOOH} \longrightarrow {}^{\bullet}\mathrm{OH} \xrightarrow{\text{deactivation}} \mathrm{H_2O} + 1/2\mathrm{O_2} \qquad (4.11)$$

Table 4.7 Effect of Hydrogen Peroxide Concentration on Graft Copolymerization

HOOH (%)	FP (%)	GE (%)	Add-on (%)	GR (%)	WAC (g/g)
0.16	22.9	64.2	53.4	114.5	235±6
1.0	30.1	54.0	50.6	102.5	288±2
5.0	30.8	52.8	49.8	99.2	312±4
10.0	29.7	52.9	47.6	90.9	241±10
20.0	30.6	48.5	41.6	71.3	242±4

FP = Free Polymers; GE = Grafting Efficiency; GR = Grafting Ratio; WAC = Water Absorption Capacity; AA:AM = 50:50, Starch:Monomer = 3:4, *N,N*′-MBA 0.5%wt, Ascorbic acid 0.5%wt.

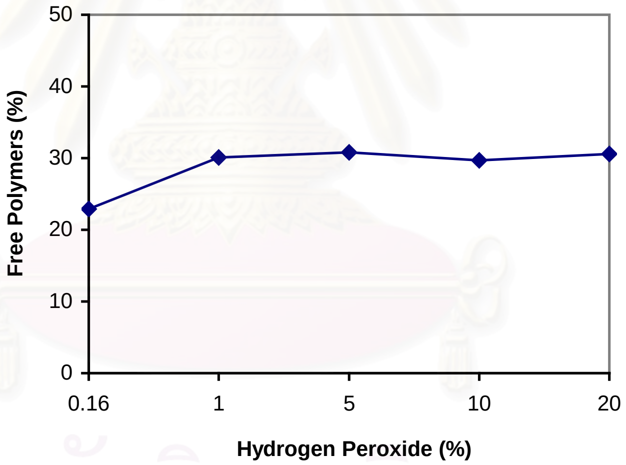


Figure 4.25 Effect of hydrogen peroxide concentration (%) on percentage free polymers

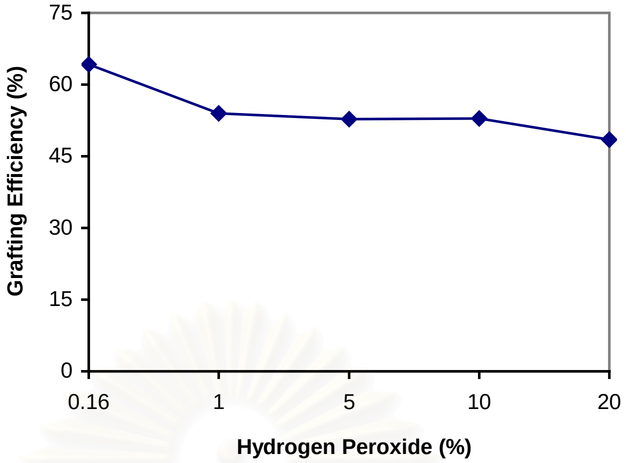


Figure 4.26 Effect of hydrogen peroxide concentration (%) on percentage grafting efficiency

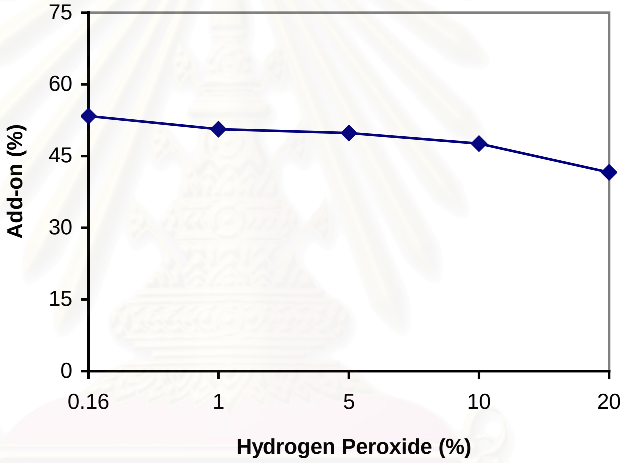


Figure 4.27 Effect of hydrogen peroxide concentration (%) on percentage add-on

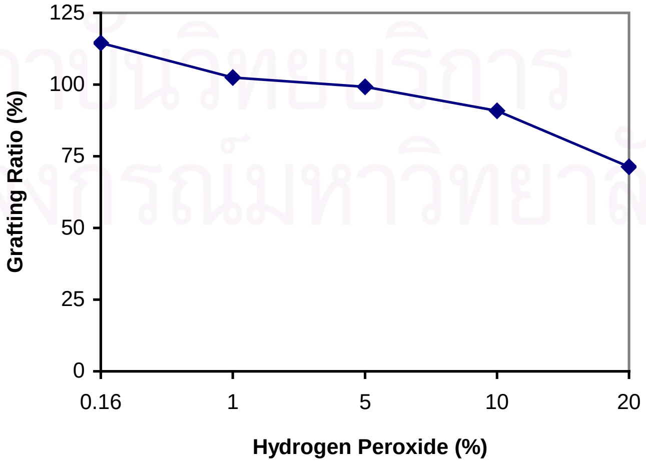


Figure 4.28 Effect of hydrogen peroxide concentration (%) on percentage grafting ratio

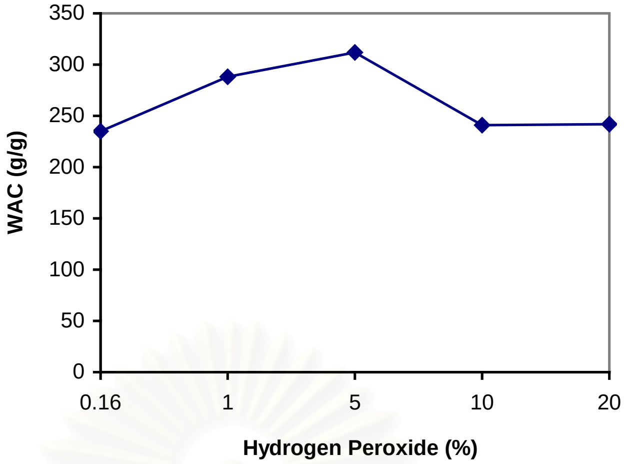


Figure 4.29 Effect of hydrogen peroxide concentration (%) on water absorption capacity

4.2.4 Effect of the Crosslinking Agent Concentration on Graft Copolymerization

The effect of the crosslinker, *N,N*$^{/}$-MBA, concentration (%weight based on the total monomers) on the grafted copolymer is presented in Table 4.8 and Figures 4.30–4.34. The free polymer contents decrease with increasing the amount of crosslinker because majority of the monomers was used in a crosslinking copolymerization, which decreases the residue monomer concentration, the extent of which depends on the concentration ratio, of the crosslinker to the monomer.

Table 4.8 Effect of the Crosslinker Concentration on Graft Copolymerization

MBA (%)	FP (%)	GE (%)	Add-on (%)	GR (%)	WAC (g/g)
nil	61.5	5.1	8.5	9.3	ND
0.3	35.9	41.8	40.2	67.4	277±10
0.5	30.8	52.8	49.8	99.2	312±4
0.7	20.8	66.9	53.0	113.0	212±10

FP = Free Polymers; GE = Grafting Efficiency; GR = Grafting Ratio; WAC = Water Absorption Capacity; AA:AM = 50:50, Starch:Monomer = 3:4, *N,N*$^{/}$-MBA 0.5%wt, Ascorbic acid 0.5%wt. ND = Not Detected.

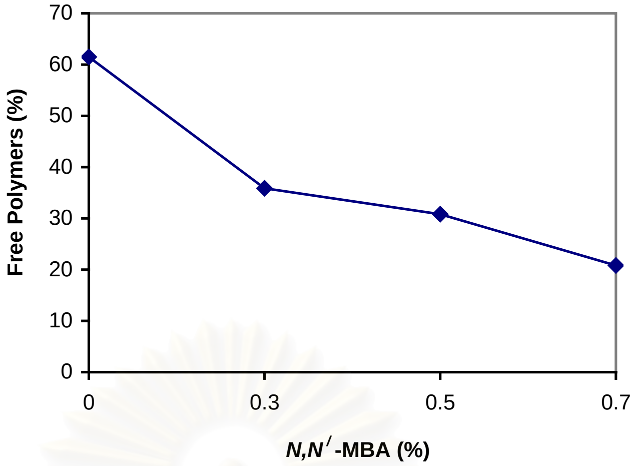


Figure 4.30 Effect of *N,N*′-MBA concentration (%) on percentage free polymers

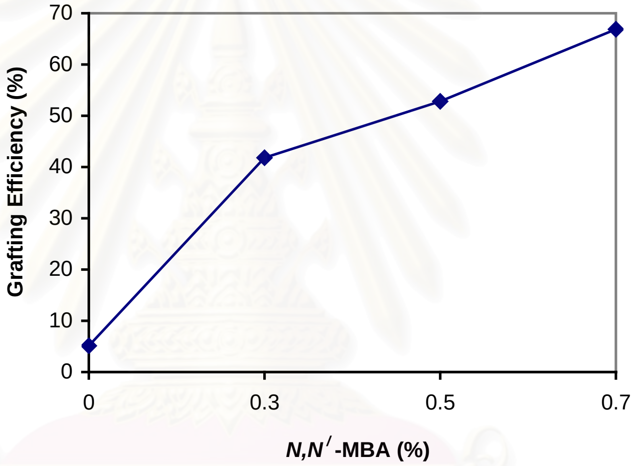


Figure 4.31 Effect of *N,N*′-MBA concentration (%) on percentage grafting efficiency

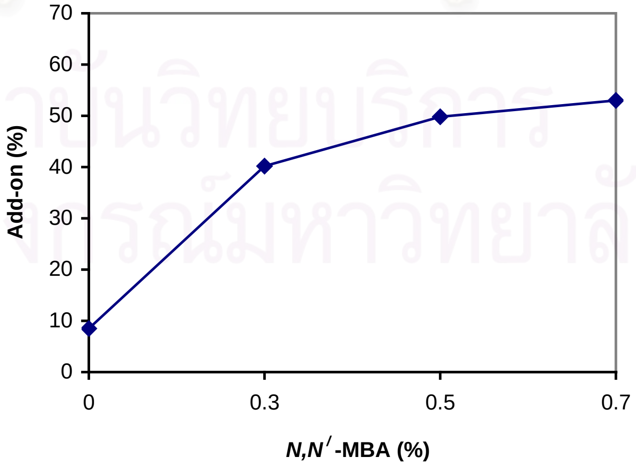


Figure 4.32 Effect of *N,N*′-MBA concentration (%) on percentage add-on

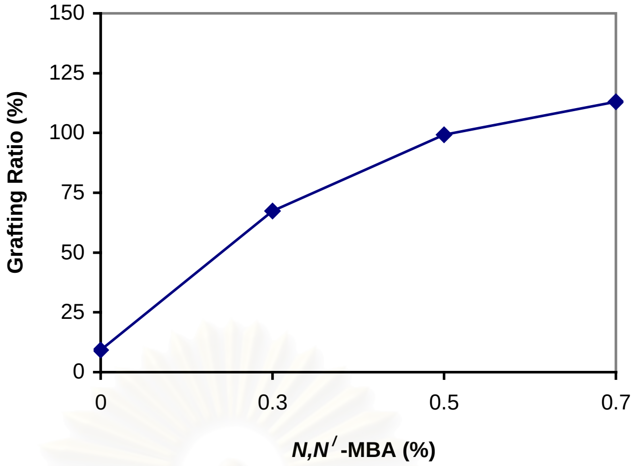


Figure 4.33 Effect of *N,N$^{/}$*-MBA concentration (%) on percentage grafting ratio

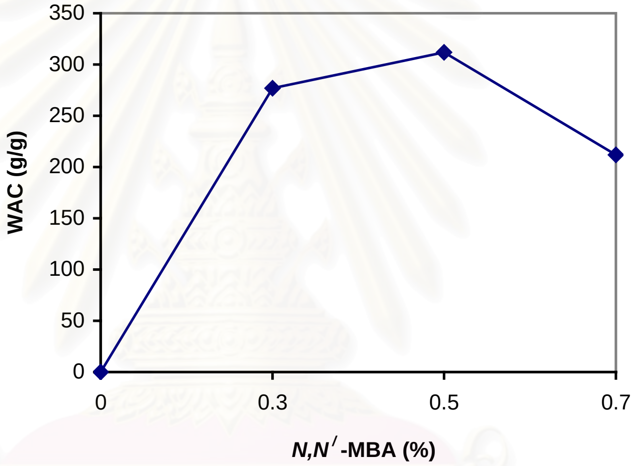


Figure 4.34 Effect of *N,N$^{/}$*-MBA concentration (%) on water absorption capacity

In expression of the percentage of grafting efficiency, add-on, and grafting ratio tend to increase with increasing the percentage of crosslinker since the bifunctionality of crosslinker could be significantly used for reacting with the polymer radicals of the starch substrate.

The grafted copolymer which gave the highest water absorption capacity was synthesized with 0.5%wt of *N,N$^{/}$*-MBA. At 0.7%wt *N,N$^{/}$*-MBA several points of the crosslinking reaction enhanced the higher gel strength and reduced its water absorbency according to Equations 2.6 and 2.7. The grafted copolymer synthesized without the crosslinker cannot be saponified, because the polymer is soluble in the aqueous medium. The crosslinking agent helps reduce the water solubility of the polymer by the crosslinking reaction.

4.2.5 Effect of Neutralization of Acrylic Acid on Graft Copolymerization

The effect of neutralization of acrylic acid is shown in Table 4.9. In series A-1 experiment, the mixture of HOOH with potassium acrylate is added drop by drop at a flow rate of 1 cm^3/min, into the reaction flask containing the starch, co-initiator, and other necessary component. The polymerization temperature must not be higher than the pre-determined reaction temperature. For the series A-2, the mixture of HOOH with potassium acrylate is rapidly poured into the reaction flask. The reaction temperature is raised up to about 40-50^{o}C instantaneously. The different addition technique brings about the interesting results, which may be due to the exothermic reaction of HOOH and its stability.

The results of A-1, A-2 and A-3 indicated that the graft copolymerization of acrylic acid differs greatly from that of potassium acrylate. In conclusion, the unneutralized acrylic acid was much easier to graft copolymerize into gels than the preneutralized systems and the stability of pure HOOH solution is at a maximum between pH 3.5-4.5 [50] thus the percentage of grafting efficiency, add-on, and grafting ratio of A-3 are higher than those of A-1 and A-2. Increasing the monomer concentration lessened this difference, presumably because the higher monomer concentration suppressed dissociation, resulting in a smaller fraction of charged species. These higher monomer concentrations resulted in greater heat release during polymerization, hence, it presented greater difficulty with temperature control [40]. Generally, the monomers and crosslinkers can dissolve in water at a desired concentration, usually from 10%-70%. The acrylic acid family usually is partially neutralized before polymerization, but the crosslinked polymer can be partially neutralized after the completion of polymerization. Degree of neutralization is an important parameter for aqueous acidic monomer, for example, potassium acrylate monomer is more soluble in water than its parent monomer. In addition, the pH of the base solution and the resulting potential for hydrolyzing the water soluble crosslinker. The reactivity ratios for some monomers and crosslinker typically used in making superabsorbent polymers are shown as follows [2]: -

monomer/crosslinker	r_1	r_2
1. Acrylic acid		
acrylamide (bisacrylamides)	2.676	0.324
2. Sodium acrylate		
acrylamide (bisacrylamides)	2.852	0.355

Potassium acrylate is more soluble in water than is sodium acrylate. According to the above reactivity ratios, most of the aqueous monomers are consumed by copolymerization under the influence of bisacrylamide crosslinker. The high reactivity ratios of the crosslinker with acrylic acid or sodium acrylate reflect that the tendency of this crosslinker to be depleted earlier in the copolymerization is higher than graft copolymerization. In a graft copolymerization of a heterogeneous phase such as our case, the availability of the crosslinker between the aqueous phase and the grafting substrate is controlled by the partition ability of the monomers and crosslinker. Otherwise, early depletion of crosslinker and monomer causes higher soluble fraction in the product as homopolymers and free copolymer. In order to achieve some success in graft copolymerization, the high ionic strength of the monomer solution when the acrylic acid is partially neutralized along with its high concentration is definitely needed.

Table 4.9 Effect of Neutralization of Acrylic Acid

Sample	Starch: Monomer	KA:AM	Neutralization	HOOH (%)	Ascorbic acid (%)	Temp. (°c)	Time (min)	FP (%)	GE (%)	Add-on (%)	GR (%)	WAC (g/g)
A-1	Starch 10 g	100:0	100	8	0.8	40	180	36.2	4.1	2.4	2.4	42±10
		75:25						42.4	4.8	3.7	3.7	78±8
		50:50						53.1	5.4	6.4	6.4	91±10
		25:75						64.7	5.7	11.1	11.1	75±10
		0:100						32.2	38.9	30.3	43.8	17±7
	3:1	50:50	100	8	0.8	40	180	25.8	8.4	3.2	3.3	70±3
	2:1							30.1	9.5	4.5	4.8	91±2
	1:1							46.6	4.9	4.5	4.7	94±3
	1:2							64.9	3.3	6.4	7.1	100±3
	1:3							70.6	2.9	7.2	7.8	115±9
	1:6							79.2	2.0	7.7	8.3	130±13
	1:10							89.8	0.7	6.4	6.8	109±15
	2:1	50:50	100	2	0.8	40	180	30.1	15.7	8.0	8.7	84±10
				4				29.7	14.0	6.9	7.4	85±5
				6				28.5	15.3	7.2	7.8	90±7

FP = Free Polymers; GE = Grafting Efficiency; GR = Grafting Ratio; WAC = Water Absorption Capacity;

A-1 : preneutralized system by KOH solution, adding the initiator system by dropwise addition with a rate of 1 cm^3/min

Table 4.9 (continued) Effect of Neutralization of Acrylic Acid

Sample	Starch: Monomer	KA:AM	Neutralization	HOOH (%)	Ascorbic acid (%)	Temp. (^{o}c)	Time (min)	FP (%)	GE (%)	Add-on (%)	GR (%)	WAC (g/g)
A-1	2:1	50:50	100	8	0.2	40	180	22.3	15.8	5.4	5.8	78±4
					0.4			26.4	14.1	5.9	6.3	82±7
					0.6			22.1	18.4	6.4	6.8	76±3
	2:1	50:50	100	8	0.8	30	180	29.7	13.7	6.7	7.1	81±5
						50		35.3	8.1	4.8	5.0	56±5
						60		41.6	3.5	2.6	2.7	40±2
	2:1	50:50	100	8	0.8	40	180	24.5	14.3	5.4	5.7	65±5
			75					16.4	21.6	5.4	5.7	60±5
	2:1	50:50	75	2	0.2	40	120	48.4	7.0	7.1	7.7	107±4
							180	43.1	6.5	5.3	5.5	90±7
							240	40.2	9.1	6.7	7.2	94±6
							300	35.9	16.4	11.0	12.4	94±3
A-2	3:4	50:50	100	5	0.5	35	60	56.9	15.0	23.3	30.4	175±9
A-3	3:4	50:50	-	5	0.5	35	10	30.8	52.8	49.8	99.2	312±4

FP = Free Polymers; GE = Grafting Efficiency; GR = Grafting Ratio; WAC = Water Absorption Capacity;

A-1 : preneutralized system by KOH solution, adding the initiator system by dropwise addition with a rate of 1 cm^3/min

A-2 : preneutralized system by KOH solution, adding the initiator system by rapid pouring

A-3 : unneutralized system with saponification by the KOH solution after graft copolymerization

4.2.6 Influence of Acid on Graft Copolymerization of Acrylamide onto Cassava Starch

The influence of acid on the graft copolymerization of acrylamide onto cassava starch is shown in Table 4.10.

Table 4.10 Effect of acid on graft copolymerization of acrylamide onto cassava starch

Sample	Condition[a]	FP (%)	GE (%)	Add-on (%)	GR (%)	WAC (g/g)
B-1	Neutral	96.9	ND	ND	ND	ND
B-2	Acid	9.7	80.1	43.3	76.4	270±10

FP = Free Polymers; GE = Grafting Efficiency; GR = Grafting Ratio; WAC = Water Absorption Capacity; ND = Not Detected. B-1 = no adding additive; B-2 = add 1N HNO_3 as additive; Parameter control: starch:monomer = 3:4, *N,N′*-MBA 0.5%wt, ascorbic acid 0.5%wt, HOOH 5%wt.

[a] tested by a universal indicator paper after polymerization

The water absroption of grafted copolymer of B-1 is extremely contrast to B-2 in which a strong acid was included during the course of graft copolymerization. Because the acid can partition to the grafting sites of the starch backbone and increase partitioning of monomers, thus increased concentrations of the available monomer enhance the grafting reaction at a particular site. A contributing process involves an increase in hydrogen atom yield from an electron transfer of the redox system shown in Equation 4.12. By the abstraction reactions, these additional atoms can lead to further activation of the backbone polymer. Using starch (StOH) as a backbone polymer, there is an additional mechanism for the hydrogen atom formation. Owing to the presence of the hydroxyl groups in exchangeable positions as shown in Equations 4.13 and 4.14, it may also lead to the creation of further grafting sites on starch backbones as shown in Equation 4.15 [23]. Moreover, the acid additive may bring about charge transfer (CT) monomer complexes with acrylamide, where CT complex can enhance the grafting yield, thus the percentage of grafting efficiency, add-on, and grafting ratio of B-2 are higher and the percentage of the free polymers are lower than those of B-1 [23,51].

$$\mathrm{AH_2} \longrightarrow \mathrm{AH^- + H^+} \tag{4.12}$$

$$\mathrm{StOH + H^+} \longrightarrow \mathrm{StOH_2^+} \tag{4.13}$$

$$\mathrm{StOH_2^+ + e^-} \longrightarrow \mathrm{StOH + H^\bullet} \tag{4.14}$$

$$\mathrm{StOH^\bullet + H^\bullet} \longrightarrow \mathrm{StO^\bullet + H_2} \tag{4.15}$$

4.3 Water Absorption Capacities of the Copolymers in Salt Solutions

4.3.1 Effect of Salt Solution on Water Absorption Capacity

The saponified graft copolymer with the highest water absorbency was chosen to test the salt effect in 0.1%, 0.5%, and 0.9%w/v of NaCl, $MgCl_2$, and $CaCl_2$ solutions. Table 4.11 and Figure 4.35 indicate the water absorbency of the grafted copolymer in salt solutions. The water absorbency decreases with increasing the ionic strength of the saline solutions.

The swelling behavior of superabsorbent gels is resulting from an osmotic pressure differential, that is, the difference in concentration of mobile ions between the interior of the gel and the exterior solution [41]. The gel imbibes in water to reduce the osmotic pressure differential until the ion concentration equilibrium is reached. The forces for the absorption of ionic solutions are attributable to the osmotic pressure based on the movable counter-ions, the polymer-solvent affinity and the rubber elasticity. The effect of the ionic strength to the water absorbency can be expressed by Flory's equation.

$$Q^{5/3} = [(i/2\nu_u S^{*1/2})^2 + (1/2-\chi_1)/\nu_1] / (\nu_e/V_o) \qquad (4.16)$$

where Q is degree of swelling

i/ν_u is charge density of polymer

S^* is ionic strength of solution

$(1/2-\chi_1)/\nu_1$ is polymer-solvent affinity

ν_e/V_o is crosslinking density

Table 4.11 Effect of Different Salt Solution Concentrations on Water Absorption Capacity

Concentration of Salt Solution (%w/v)	NaCl		$MgCl_2$		$CaCl_2$	
	Ionic Strength (mole-ion/dm^3)	WAC (g/g)	Ionic Strength (mole-ion/dm^3)	WAC (g/g)	Ionic Strength (mole-ion/dm^3)	WAC (g/g)
Distilled water	-	312±4	-	312±4	-	312±4
0.1	0.0171	81±1	0.0315	40±3	0.0270	22±1
0.5	0.0856	45±1	0.1575	14±1	0.1351	9±1
0.9	0.1540	28±1	0.2836	6±1	0.2433	1±0.6

$I = ½ \sum(C_iZ_i^2)$; where I, C_i, and Z_i are the ionic strength, the ionic concentration and charge on each individual ion, respectively [47].

WAC = water absorption capacity

The water absorbency increases with increasing number of hydrophilic and ionic functional groups, and with decreases in the crosslinking density of the polymer network and in the concentration of ionic solutions [3]. The ionic strength of the solution depends on both the mobile concentration and their valency on oxidation state. Small quantities of divalent or trivalent ions can decrease drastically the swelling values. This decrease, more significant with Ca^{2+} ions, can be due to the complexing ability of carboxylate groups inducing intramolecular and intermolecular complex formation. Consequently, the crosslink density and modulus of the network increase while water absorption capacity decreases [42].

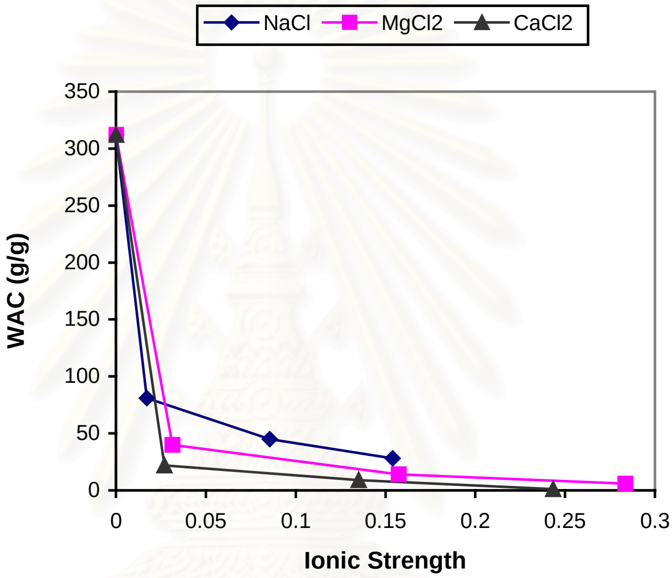


Figure 4.35 Effect of ionic strength of saline solution on water absorption capacity

4.3.2 <u>Effect of the pH Buffer Solution on Water Absorption Capacity</u>

The result of the solution pH 3-11 on the water absorbency of the saponified grafted copolymer is shown in Table 4.12 and Figure 4.36.

The saponified starch-*g*-poly(acrylic acid-*co*-acrylamide) has carboxylate and carboxamide groups which are the majority of anionic-type superabsorbent polymer. An anionic-type superabsorbent polymer normally ionizes at high pH but unionizes at low pH. At high pH where the gel is ionized, the equilibrium degree of swelling increases. At pH 3, the swelling extent of the copolymer decreased so much because acrylic acid has a pK_a value of about 4.25. As the pH is lowered to a strongly

Table 4.12 Effect of pH Buffer Solution on Water Absorption Capacity

pH of Buffer Solution	Ionic Strength (mole-ion/dm^3)	WAC (g/g)
3	0.3607	12±2
5	0.3206	35±3
8	0.2503	40±1
11	0.1804	40±0.6

WAC = water absorption capacity. WAC in distilled water is 312±4 g/g.

$I = ½ \sum(C_iZ_i^2)$; where I,C_i, and Z_i are the ionic strength, the ionic concentration and charge on each individual ion, respectively [47].

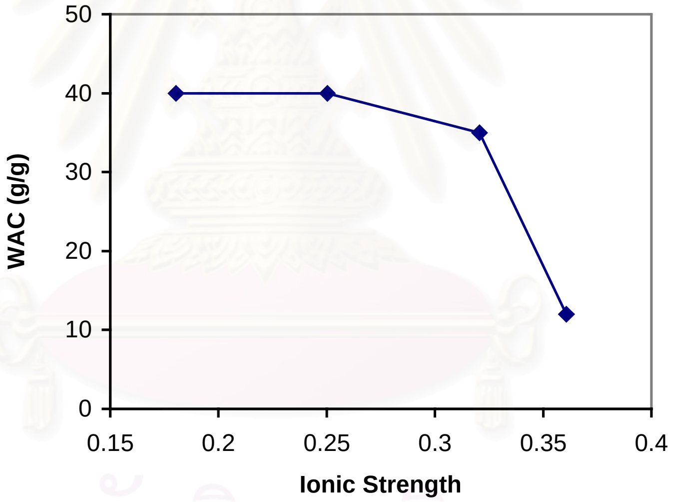


Figure 4.36 Effect of the ionic strength of the pH solution on water absorption capacity

acidic region, the carboxylate side chains of the potassium acrylate moiety become hydrolyzed to be the carboxylic groups, thus decreasing the charge density of anions on the network. The concurrent decreases in mobile counter-ion content of the network sharply reduce the internal osmotic pressure, which retards the observed swelling transitions. As the ionic strength increases, the swelling decreases according to the unionized polymer chain and high ion concentration outside the gel [23].

4.4 Surface Morphology of the Copolymers

The surface appearance of the cassava starch and saponified graft copolymer was viewed by scanning electron microscopy as shown in Figures 4.37–4.41. The characteristic SEM photographs of superabsorbent polymers are porous structure with strong network, which can absorb water substantially. From SEM photographs, the superabsorbents of saponified starch-*g*-poly(acrylic acid-*co*-acrylamide) have many pores and many flexibly cellular structure than that of the saponified starch-*g*-poly(acrylic acid). The surfaces of the saponified starch-*g*-poly (acrylic acid) and the starch-*g*-poly(potassium acrylate-*co*-acrylamide) are relatively rough. Moreover, the water absorbency of the saponified starch-*g*-poly(acrylic acid) is lower than the saponified starch-*g*-poly(acrylic acid-*co*-acrylamide) and the saponified starch-*g*-polyacrylamide with acid addition. The surface characteristic of latter is smooth and flexible.

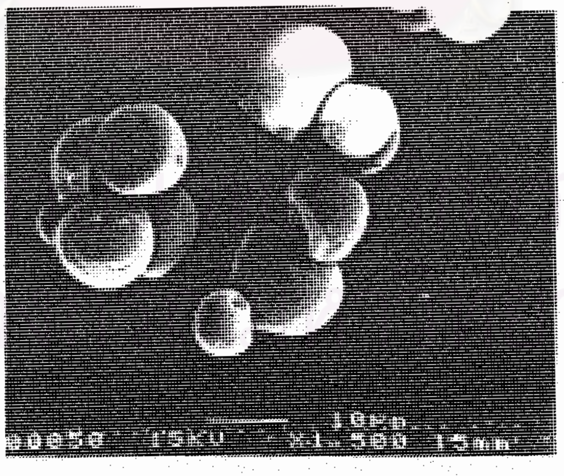


Figure 4.37 SEM photograph of the cassava starch

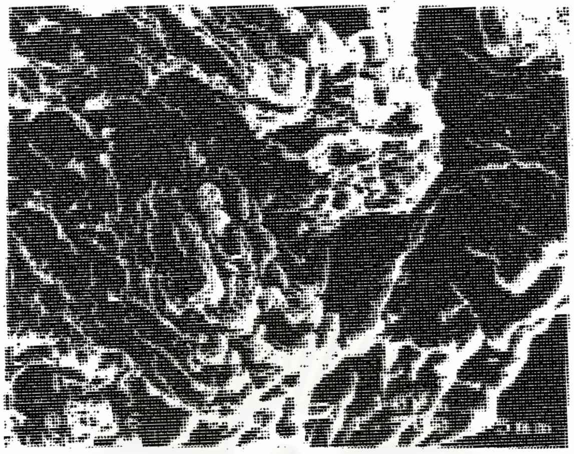


Figure 4.38 SEM photograph of the saponified starch-*g*-poly(acrylic acid)

Figure 4.39 SEM photograph of the saponified starch-*g*-polyacrylamide, with 1N HNO_3

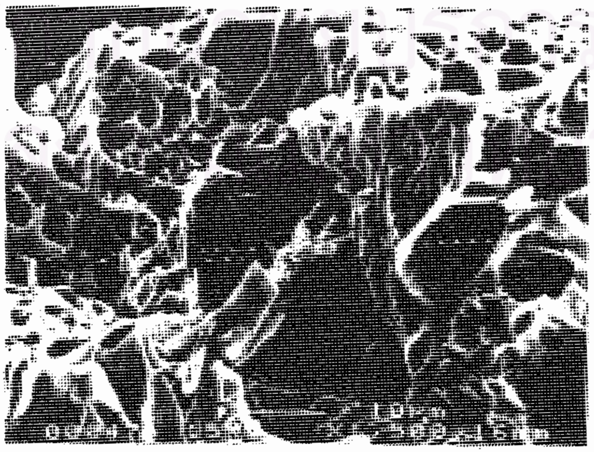


Figure 4.40 SEM photograph of the saponified starch-*g*-poly(acrylic acid-*co*-acrylamide)

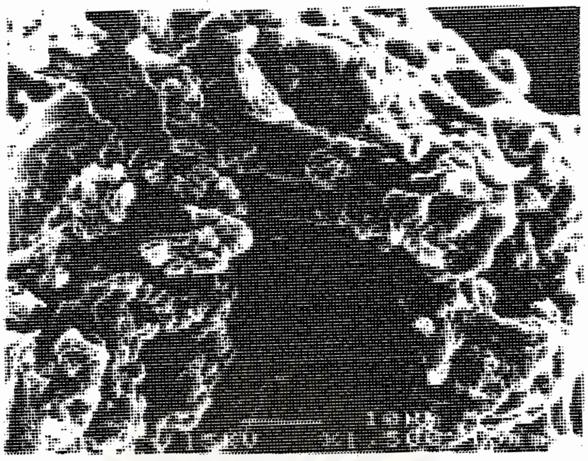


Figure 4.41 SEM photograph of the starch-*g*- poly(potassium acrylate-*co*-acrylamide)

4.5 Enzymes Hydrolysis of the Copolymers

The polyacrylate superabsorbent polymers mixed with a biodegradable microbial nutrient, such as starch, produced a locally high concentration of microbial activity, leading to a degradation of the acrylate polymers [48]. Enzyme, *α-amylase*, was hence used in this experimental biodegradation, because the majority of microbial in our environment provide *α-amylase*, which can easily break down the amylose part of starch (15-22%). The appearance of the hydrolyzed grafted copolymer is rather clearer than that of unhydrolyzed one. The result of the enzyme hydrolysis of the starch-*g*-polymer is presented in Table 4.13.

Table 4.13 Enzyme hydrolysis of the copolymers

Testing result	saponified starch-*g*-poly (acrylic acid)			saponified starch-*g*-poly (acrylic acid-*co*-acrylamide)			starch-*g*-polyacrylamide		
	nil	1cm^3	3cm^3	nil	1cm^3	3cm^3	nil	1cm^3	3cm^3
Viscosity (mPa s)	14739	17262	6186	16332	18488	11060	15489	5647	562
Shear stress (N/m^2)	29.5	34.5	12.4	32.7	37.0	22.1	31.0	11.3	1.1
%Torque	62.9	73.7	26.4	69.7	78.9	47.2	66.1	24.1	2.4
Iodine test	+ve	-ve	-ve	+ve	-ve	-ve	+ve	-ve	-ve
Benedict's test	-ve	+ve	+ve	-ve	+ve	+ve	-ve	+ve	+ve

Shear rate 2.0 sec^{-1} at 25°C

Iodine test: +ve gives a blue color.

Benedict's test: +ve gives a yellow or red precipitate of cuprous oxide.

Benedict's test: +ve gives a yellow or red precipitate of cuprous oxide.

Basically, when the swollen graft copolymers were hydrolyzed by α-*amylase*, the viscosity of the swollen polymer usually decreased because the enzyme cleaved a long-chain of starch to a short-chain, which rendered the length and entanglement of the polymer chains to decrease. The results in Table 4.13 show the following points:

1. Increasing the amount of enzyme to every superabsorbent polymer, their viscosity eventually decreased. The activity of enzyme amylase on the starch-*g*-polyacrylamide is more effective than on the other two superabsorbent polymers containing the acrylic acid moiety. The acrylated superabsorbent polymers need more enzyme activity to break the glucosidic chains.

2. The increases in the viscosity of saponified starch-*g*-poly(acrylic acid) and saponified starch-*g*-poly(acrylic acid-*co*-acrylamide) could possibly be explained as the dependence of the enzyme activity on the optimum pH and hydrolytic specificity. Because the saponified starch-*g*-poly(acrylic acid) and saponified starch-*g*-poly(acrylic acid-*co*-acrylamide) can form the intermolecular hydrogen bonding between enzyme-substrate complex easier than the cassava starch-*g*-polyacrylamide. Moreover, the complicated α-*amylase* structure (Figure 4.42), which consists of α-helix, parallel and antiparallel β-sheet form, may form disulfide bridge in the structure, leading to the intramolecular complex. This phenomenon may induce an increase in viscosity. When a higher amount of enzyme amylase was added to sacrifice the wastage of complex formation (enzyme poison), the excess, free enzyme (active form) could function its degradation properly in the latter stage. In addition, molecular weight of the polymer is also another parameter; if its molecular weight is very high, the biodegradation is then incomplete [49].

Figure 4.42 The *α-amylase* structure [52].

Another approach, which confirms the existence of a short chain of starch, is the Benedict's test and Iodine test. Benedict's solution is used for checking a reducing sugar. If the sample has a reducing sugar, the solution will give a yellow or red precipitate of cuprous oxide, which is then called a positive test (+ve). Iodine solution is used for checking polysaccharide starch, if the sample contains polysaccharide, the solution will produce a blue color, a blue charge-transfer complex of polysaccharide with iodine, which is called a positive test. For the present research both test solutions gave positive results after the enzyme was added to the superabsorbent polymers. As shown in Table 4.13, after the enzymatic degradation, the iodine test was negative for the existence of starch molecules while the Benedict's test was positive for the occurrence of glucose units.

CHAPTER 5

CONCLUSIONS AND SUGGESTION

5.1 Conclusions

The synthesized biodegradable superabsorbent polymers were made by the grafting copolymerization between the gelatinized starch and acrylic acid/acrylamide via HOOH/ascorbic acid initiation. Subsequently, the saponification was carried out by saponification in potassium hydroxide solution. In this research, the initiator system was a redox initiator system of hydrogen peroxide and ascorbic acid with *N,N′*-methylenebisacrylamide as the crosslinker. The parameter study, of the research consisted of the acrylic acid-to-acrylamide ratio, starch-to-monomer ratio, and the concentration of the redox initiator system and the crosslinker. In addition, the effect of neutralization of acrylic acid, influence of the acid on graft copolymerization of acrylamide onto the starch, the water absorbency of newly synthesized polymers in several ionic strength and enzyme hydrolysis were studied. The results of this research are briefly concluded that the behavior of the superabsorbent polymer is the anionic type. For detailed conclusion, we found the following:

1. The functional groups of synthesized graft copolymer were characterized by FTIR spectroscopy. The infrared absorption spectrum of cassava starch showed the significant absorption peaks at 3550-3200, 3000-2840, and 1260-1000 cm^{-1} demonstrating the O-H stretching, C-H stretching, and C-O stretching, respectively. The starch-*g*-poly(acrylic acid) give the IR spectrum, which contains the characteristic peaks of cassava starch and acrylic acid at 3300-2500, 1720-1706,

1440-1395, and 1320-1210 cm^{-1} for absorption peaks of the O-H stretching, C=O stretching, O-H bending, and C-O stretching, respectively, of carboxylic acid. The IR-spectra of the saponified starch-*g*-poly(acrylic acid) and starch-*g*-poly(potassium acrylate) did not show clearly the absorption peaks of the carboxylic acid; but the absorption peaks of the carboxylate ion at 1650-1550 cm^{-1} were seen, that is, the carboxylic groups were changed to the carboxylate groups. The IR-spectrum of the saponified starch-*g*-polyacrylamide did not differ from that of the starch-*g*-polyacrylamide, which contained the spectra of cassava starch and the N-H stretching, C=O stretching of the carboxamide, and the N-H bending at 3500-3300, 1690-1650, and 1650-1580 cm^{-1}, respectively. This result manifested that the conditions of the saponification for polyacrylamide superabsorbents were not severe to convert the carboxamide group to the carboxylate group.

In case of starch-*g*-poly(acrylic acid-*co*-acrylamide), the saponified starch-*g*-poly(acrylic acid-*co*-acrylamide), and the starch-*g*-poly(potassium acrylate-*co*-acrylamide) gave the identical IR spectra of cassava starch, the absorption peaks of the carboxylic group at 3300-2500, 1440-1395, and 1320-1210 cm^{-1} for the O-H stretching, O-H bending, and C-O stretching, respectively; and the absorption peaks of the carboxamide at 3500-3300, 1690-1650, and 1650-1580 cm^{-1} showing the N-H stretching, C=O stretching, and N-H bending, respectively. The different peaks were at 1720-1706 cm^{-1} of starch-*g*-poly(acrylic acid-*co*-acrylamide), which is the C=O stretching of the carboxylic acid; and at 1650-1550 cm^{-1} of the saponified starch-*g*-poly(acrylic acid-*co*-acrylamide) and the starch-*g*-poly(potassium acrylate-*co*-acrylamide), which is the C=O stretching of the carboxylate ion.

2. The presence of both acrylic acid and acrylamide is essential for the grafting reaction on the gelatinized cassava starch. The saponified graft copolymer,

which gave the highest water absorption of 312±4 g/g could be prepared from the optimum weight ratio of acrylic acid to acrylamide of 50:50. The high percentage add-on was accomplished with this optimal condition.

3. Nitric acid addition as an acid additive enhanced in the graft copolymerization of acrylamide onto starch and the water absorption because of the acid partition phenomena and charge transfer complex between the acid and the monomer of acrylamide.

4. The optimum weight ratio of starch to monomers of 3:4 produced the highest water absorption. The higher amount of monomer was to provide grafting opportunity to the grafting substrate in another phase.

5. The redox initiator system of HOOH-ascorbic acid, the concentration of ascorbic acid of 0.5% wt and HOOH of 5% wt gave the optimum condition of water absorption. Ascorbic acid assisted HOOH initiation needed a non-stoichiometric amount to accelerate the optimum condition for radical generation.

6. Increasing the crosslinking agent concentration in the graft copolymerization enhanced the percentage grafting efficiency, add-on, and grafting ratio. The optimum condition of crosslinking agent, *N,N′*-MBA, is 0.5%wt, which gave the highest water absorption.

7. Comparison between the starch-*g*-poly(potassium acrylate-*co*-acrylamide) of the preneutralized system, and the saponified starch-*g*-poly(acrylic acid-*co*-acrylamide) as the postneutralized stystem, we found that the postneutralized system

gave the higher percentage grafting efficiency, add-on, and grafting ratio than the those of the preneutralized system.

8. Increasing the ionic strength of solution decreased the water absorption capacity of the saponified graft copolymer because of the decrease of the osmotic pressure difference between inside of the gel and the external solution, that is, the concentration of salt solution affected the water absorbency of anionic superabsorbent polymer.

9. The buffer pH solution with the high ionic strength decreased the water absorption of the saponified graft copolymers. The high pH buffered solution gave a constant water absorption when the anionic superabsorbent polymers was immersed.

10. The surface morphology of the cassava starch and saponified graft copolymers by SEM was totally different. The SEM photographs implied that the saponified graft copolymer having the higher water absorbency had many porous structures. The surface morphology of the postneutralized system differed from that of the preneutralized system in roughness and porosity.

11. The starch grafted copolymers could be biodegraded by *∝-amylase* enzyme, which led to the decreased viscosity of the grafted copolymers. In addition, the Benedict’s test and Iodine test after the enzyme hydrolysis confirmed the degraded product of glucose.

5.2 Suggestion for Future Work

Synthesis of superabsorbent polymer of saponified cassava starch-acrylic acid/acrylamide graft copolymers by the redox initiator system should be further investigated as follows:

1. The effects of other kinds and concentrations of mineral acid additive on acrylamide grafting reaction and water absorption could be investigated.

2. The effects of other kinds and concentrations of crosslinking agent on grafting reaction and water absorption should be studied.

3. Other types of the redox initiator system on grafting reaction and water absorption should be investigated.

4. The surface morphology and water absorption capacities of the enzyme-hydrolyzed superabsorbent polymer should be investigated.

REFERENCES

1. Buchholz, F.L. A Swell idea. Chemistry in Britain 30(1994): 652-656.

2. Buchholz, F.L. Preparation methods of superabsorbent polyacrylates. In F.L.Buchholz. and N.A. Peppas (eds.), Superabsorbent Polymers: Science and Technology; ACS Symposium Series#573. pp. 27-38. Washington DC: The American Chemical Society, 1994.

3. Ichikawa, T., and Nakajima, T. Superabsorptive polymers (from natural polysaccharides and peptides). In J.C. Salamone (ed.), Polymeric Materials Encyclopedia (vol. 10). pp. 8051-8059. New York: CRC Press, 1996.

4. Buchholz, F.L., and Burget, J.H. Synthesis and applications of superabsorbent polymers. In C.A. Finch (ed.), Industrial Water Soluble Polymers. pp. 92-93. London: Hartnolls Ltd.,1996.

5. Buchholz, F.L. The structure and properties of superabsorbent polyacrylate. In F.L. Buchholz and A.T. Graham (eds.), Modern Superabsorbent Polymer Technology. pp. 168-169. New York: Wiley-VCH, 1997.

6. Buchholz, F.L. Preparation and structure of polyacrylates. In R.S. Harland (ed.), Absorbency Polymer Technology. pp. 24-27. Amsterdam: Elsevier Science, 1990.

7. Buchholz, F.L. The structure and properties of superabsorbent polyacrylate. In F.L. Buchholz and A.T. Graham (eds.), Modern Superabsorbent Polymer Technology. pp. 171-175. New York: Wiley-VCH, 1997.

8. Buchholz, F.L. Applications of superabsorbent polymers. In F.L. Buchholz, and A.T. Graham (eds.), Modern Superabsorbent Polymer Technology. p. 251. New York: Wiley-VCH, 1997.

9. Buchholz, F.L. Preparation and structure of polyacrylates. In R.S. Harland (ed.), Absorbency Polymer Technology. pp. 29-33. Amsterdam: Elsevier Science, 1990.

10. Buchholz, F.L., and Burget, J.H. Synthesis and applications of superabsorbent polymers. In C.A. Finch (ed.), Industrial Water Soluble Polymers. pp. 97-98. London: Hartnolls Ltd.,1996.

11. Buchholz, F.L. Applications of superabsorbent polymers. In F.L. Buchholz, and A.T. Graham (eds.), Modern Superabsorbent Polymer Technology. pp. 236-238. New York: Wiley-VCH, 1997.

12. Fanta, G.F. Starch graft copolymers. In J.C. Salamone (ed.), Polymeric Materials Encyclopedia (vol. 10). pp. 7901-7902. New York: CRC Press, 1996.

13. Uhlig, H., and Linsmaier-Bednar, E.M. Description of enzymes. Industrial Enzymes and Their Applications. pp. 37-48. New York: John Wiley&Sons, Inc., 1998.

14. Masuda, F., Nishida, K., and Nakamura, A. Water absorbing starch resins. U.S. Pat 4,076,663 (Feb. 28, 1978).

15. Heidel, K. Method of manufacturing polysaccharide graft copolymers which absorb water and are capable of swelling. U.S. Pat 4,777,232 (Feb. 13, 1987).

16. Makita, M., and Tanioku, S. Method for producing improved water-absorbent resins. U.S. Pat 4,587,308 (May 6, 1986).

17. Saotome, K. Water absorbent polymer coated article method of producing same. U.S. Pat 5,026,596 (Jun. 25, 1991).

18. Kiatkamjornwong, S., and Faullimmel, J. Synthesis of cassava starch-based water-absorbing polymer for agricultural application. J. Natl. Res. Council Thailand 23(1)[1991]: 15-35.

19. Okieimen, E.F., and Ebhoaye, J.E. Grafting acrylonitrile and acrylic acid monomers on cellulosic materials. J. Appl. Polym. Sci. 31(1986): 1275-1280.

20. Gurdag, G., Yasar, M., and Gurkaynak, M.A. Graft copolymerization of acrylic acid on cellulose: reaction kinetics of copolymerization. J. Appl. Polym. Sci. 66(1997): 929-934.

21. Joseph, A., Radhakrishnan, G., Joseph, K.T., and Santappa, M. Grafting of polymeric side chains to gelatin. J. Appl. Polym. Sci. 27(1982): 1313-1319.

22. Kiatkamjornwong, S., and Phunchareon, P. Influence of reaction parameters on water sorption of neutralized poly(acrylic acid-co-acrylamide) synthesized by inverse suspension polymerization. J. Appl. Polym. Sci. 72(1999): 1349-1366.

23. Kiatkamjornwong, S. , Chomsaksakul, W., and Sonsuk, M. Radiation modification of water absorption of cassava starch by acrylic acid/acrylamide. Radiant. Phys. Chem. 59(2000): 413-427.

24. Kurita, K., Kawata, M., Koyama, Y., and Nishimura, S. Graft copolymerization of vinyl monomers onto chitin with cerium(IV) ion. J. Appl. Polym. Sci. 42(1991): 2885-2891.

25. Mostafa, KH.M. Graft polymerization of acrylic acid onto starch using potassium permanganate acid (redox system). J. Appl. Polym. Sci. 56(1995): 263-269.

26. Liu, Z.S., and Rempel, G.L. Preparation of superabsorbent polymers by crosslinking acrylic acid and acrylamide copolymers. J. Appl. Polym. Sci. 64(1997): 1345-1353.

27. Ramgaraj, A., Vangani, V., and Rakshit, A.K. Synthesis and characterization of some water soluble polymers. J. Appl. Polym. Sci. 66(1997): 45-56.

28. Deo, H.T., and Gotmare, V.D. Acrylonitrile monomer grafting on gray cotton to impact high water absorbency. J. Appl. Polym. Sci. 72(1999): 887-894.

29. Rath, S.K., and Singh, R.P. Enzyme hydrolysis of grafted amylopectin. J. Appl. Polym. Sci. 70(1998): 2627-2633.

30. Shugar, G.J., Shugar, R.A., Bauman, L., and Bauman, R.S. pH Measurement. Chemical Technicians' Ready Reference Handbook. pp. 536-541. New York: McGraw-Hill, 1981.

31. Wood, A.E., and Aurand, A.W. Carbohydrates. Laboratory Manual in Food Chemistry. pp. 13-14. West Port: AVI Publishing, 1977.

32. Silverstein, R.M., Bassler, C.G., and Morrill, T.C. Infrared spectrometry. Spectrometric Identification of Organic Compounds (6rd ed.). pp. 79-104. New York:: John Wiley &Sons, Inc., 1998.

33. Brandrup, J., and Immergut, E.H. (eds.). Polymer Handbook (2nded.). pp. II-111, III-146. New York: John Wiley&Sons, Inc., 1975.

34. Chang, Y.S., and Dimonie, V.L. Emulsion Polymer Institute Graduate Research Progress Reports, Lehigh University, Pennsylvania, No. 32(1989). pp. 231-241. (unpublished)

35. Buchholz, F.L. The structure and properties of superabsorbent polyacrylate. In F.L. Buchholz and A.T. Graham (eds.), Modern Superabsorbent Polymer Technology. p. 178. New York: Wiley-VCH, 1997.

36. Deutsch, J.C. Ascorbic acid oxidation by hydrogen peroxide. Analytical Biochemistry 255(1998): 1-7.

37. Fanta, G.F. Synthetics of graft and block copolymers of starch. In Ceresa, R.J. Block and Graft Copolymerization (vol.1). pp. 1-4. London: John Wiley&Sons, Inc., 1973.

38. Narain, H., Jagadale, S.M., and Ghatge, N.D. Studies of redox polymerization. I. Aqueous polymerization of acrylamide by an ascorbic acid-peroxydisulfate system. J. Polym. Sci. Polym. Chem. Ed. 19(1981): 1225-1238.

39. Fanta, G.F. Synthetics of graft and block copolymers of starch. In Ceresa, R.J. Block and Graft Copolymerization (vol.1). pp. 16-17. London: John Wiley&Sons, Inc., 1973.

40. Staples, T.L., Henton. D.E., and Buchholz, F.L. Chemistry of superabsorbent polyacrylates. In F.L. Buchholz, and A.T. Graham (eds.) Modern Superabsorbent Polymer Technolygy. pp. 34-36. New York: Wiley-VCH, 1997.

41. Grignon, J., and Scallan, A.M. Effect of pH and neutral salts upon the swelling of cellulose gels. J. Appl. Polym. Sci. 25(1980): 2829-2843.

42. Castel, D., Ricarb, A., and Audebert, R. Swelling of anionic and cationic starch-based superabsorbents in water and saline solutions. J. Appl. Polym. Sci. 39 (1993): 11-29.

43. Odian, G. Radical chain polymerization. Principles of Polymerization (3rd ed.) p. 255. New York: John Wiley&Sons, Inc., 1991.

44. Kemp, W. Infrared spectrum. Qualitative Organic Analysis Spectrochemical Tecniques (2nd ed.). pp. 46-56. London: McGraw-Hill Book Company (UK) Limited, 1986.

45. Bikales, N.M. (ed.), Water-Soluble Polymers, Polymer Science Technolygy. (vol. 2), p 214. New York: Plenum Press, 1973.

46. Staples, T.L., Henton. D.E., and Buchholz, F.L. Chemistry of superabsorbent polyacrylates. In F.L. Buchholz, and A.T. Graham (eds.) Modern Superabsorbent Polymer Technolygy. pp. 47-55. New York: Wiley-VCH, 1997.

47. Christian, G.D. General concepts of chemical equilibrium. Analytical Chemistry (4th ed.) p.108. New York: John Wiley&Sons, Inc., 1986.

48. David, S.A. Other superabsorbent polymer forms and types. In F.L. Buchholz, and A.T. Graham (eds.) Modern Superabsorbent Polymer Technology. pp. 244-245. New York: Wiley-VCH, 1997.

49. Freeman, M.B., et al. Biodegradability of polycarboxylates: structure-activity sudies. In Raphael, M.O., Samuel, J.H., and Kinam, P. Hydrogels and Biodegradable Polymers for Bioapplication; ACS Symposium Series#627. pp.118-136. Washington D.C.: The American Chemical Society, 1996.

50. Kirchner, J.R. Hydrogen peroxide. In Herman, F.M., Donald, F.O., Charles, G.O., and Glenn, T.S. (eds.), Kirk-Otmer Encyclopedia of Chemical Technology (vol. 13). pp.12-38. New York: John Wiley&Sons, Inc., 1983.

51. Garnett, J.L., Ng, L.T., and Viengkhou, V. Grafting of methyl methacrylate to cellulose and polypropylene with UV and ionising radiation in the presence of additives including CT complexes. Radiant. Phys. Chem. 56(1999): 387-403.

52. Wong, Dominic W.S. Amylolytic enzymes. Food Enzymes: structure and mechanism. pp 37-84. New York: Chapman & Hall. 1995.

APPENDICES

APPENDIX A

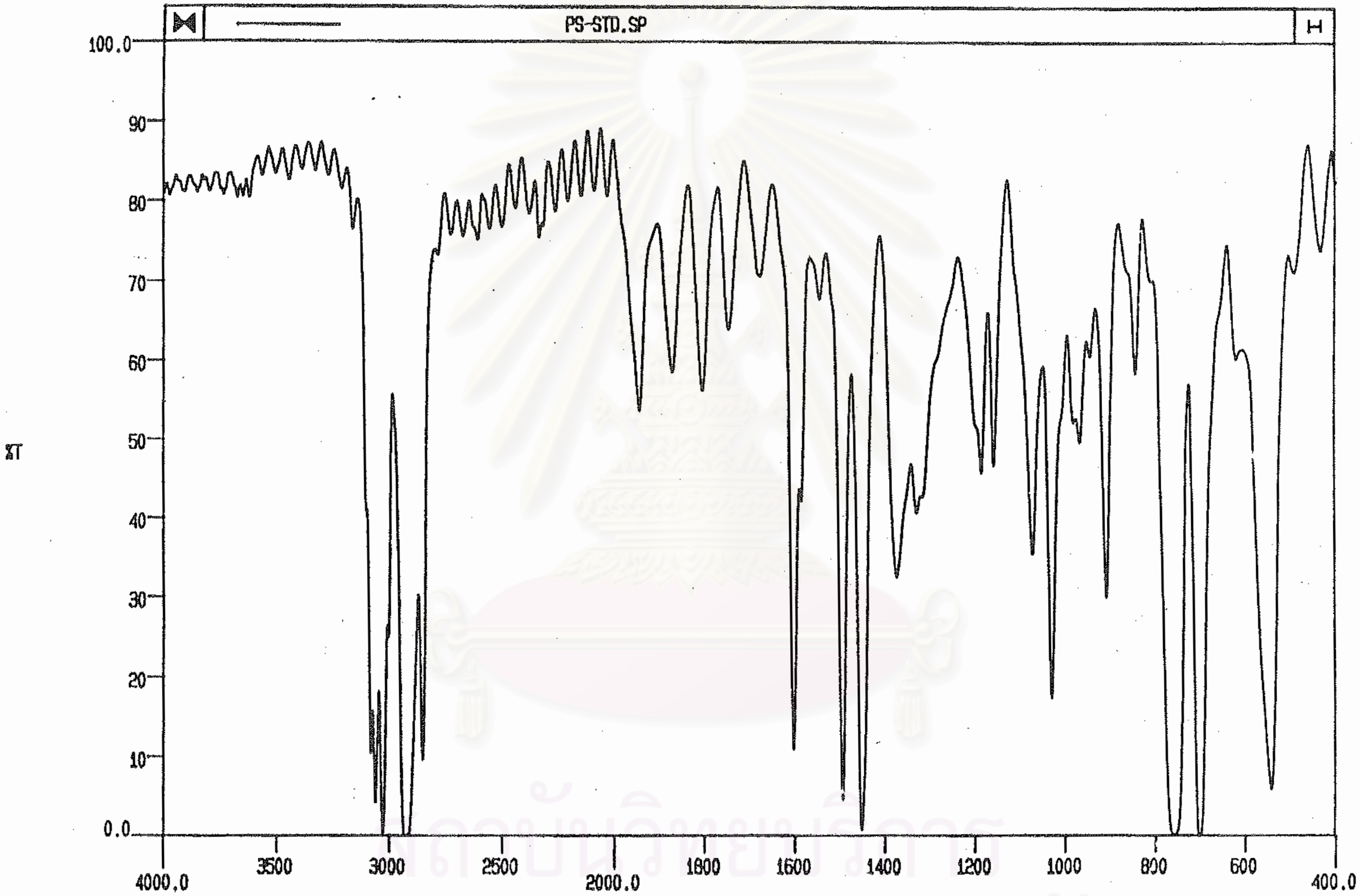


Figure A-1 Infrared reference spectrum of styrene

APPENDIX B

Preparation of Buffer Solutions [30]

Mix the two solutions below according to the instructions indicated in Table B-1 to prepare 1000 cm^3 of a buffer solution of the desired pH.

1. Dissolve 12.37 g of anhydrous boric acid, H_3BO_3, and 10.51 g of citric acid, $H_3C_6H_5O_7 \cdot H_2O$, in distilled water and dilute to 1000 cm^3 in a volumetric flask. This makes a 0.20 M boric acid and a 0.05 M citric acid solution.
2. Dissolve 38.01 g of $Na_3PO_4 \cdot 12H_2O$ in distilled water and dilute to 1000 cm^3 in a volumetric flask. This makes a 0.10 M tertiary sodium phosphate solution.

Table B-1 Preparation of Buffer Solutions

Desired pH	Solution 1, cm^3	Solution 2, cm^3
3.0	880	120
5.0	670	330
8.0	425	575
11.0	220	780

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