# CHAPTER IV

# RESULTS AND DISCUSSION

## 4.1 Characterization of the Functional Groups of the Copolymers by FTIR

The synthesized copolymers were characterized of the functional groups using FTIR technique. The FTIR spectra of cassava starch, and the graft copolymer before extraction, after extraction, and after acid hydrolysis are shown in Figures 4.1-4.7 and demonstrated in Tables 4.1-4.2 [28, 29].

The IR spectrum of cassava starch is shown in Figure 4.1. The spectra display a broad, intense O-H stretching absorption in the region of 3550-3200 $cm^{-1}$, medium intensity of the C-H stretching at 2930 $cm^{-1}$ , and the wave number of 1158, 1081, and 1015 $cm^{-1}$ are very strong bands of the C-O stretching.

The IR spectra of grafting of acrylamide onto starch backbone before extraction, and after extraction are shown in Figures 4.2-4.3. All the characteristic absorption peaks of cassava starch still exist. Additional peaks at 3400, 1650, and 1600 $cm^{-1}$ indicate the N-H stretching, C=O stretching, and N-H bending, respectively, which are the characteristics of the $-CONH_2$ group containing in the acrylamide.

In the case of starch-*g*-poly[acrylamide-co-(itaconic acid)], IR spectra in both before and after extraction (Figures 4.5-4.6) give all the absorption peaks of cassava starch, acrylamide, and itaconic acid. It is therefore confirmed that both acrylamide and itaconic acid have been grafted onto the cassava starch.

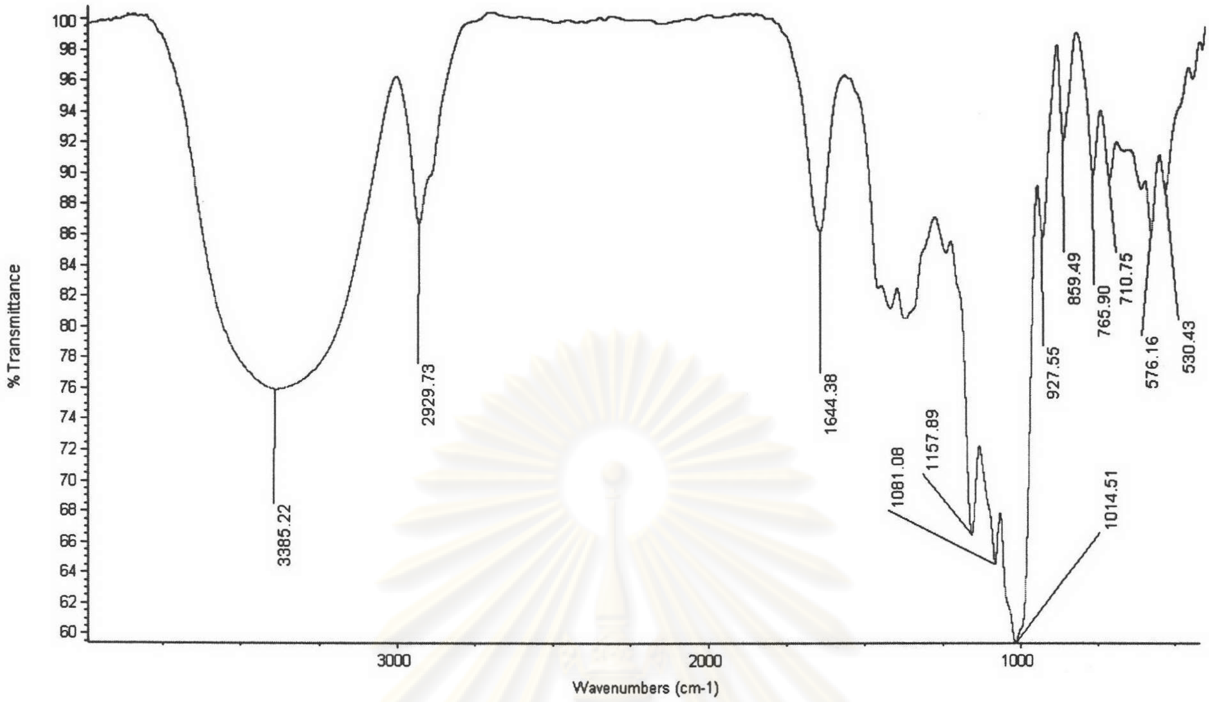


**Figure 4.1** Infrared spectrum of cassava starch

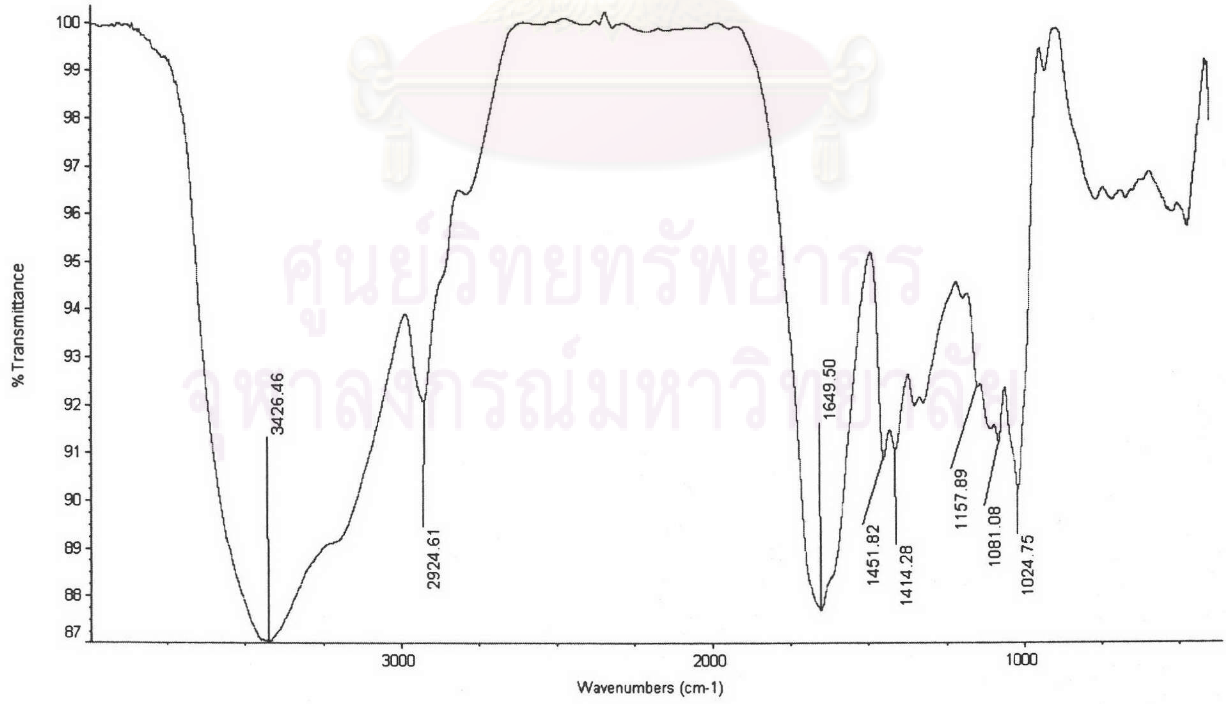


**Figure 4.2** Infrared spectrum of starch-*g*-polyacrylamide before extraction

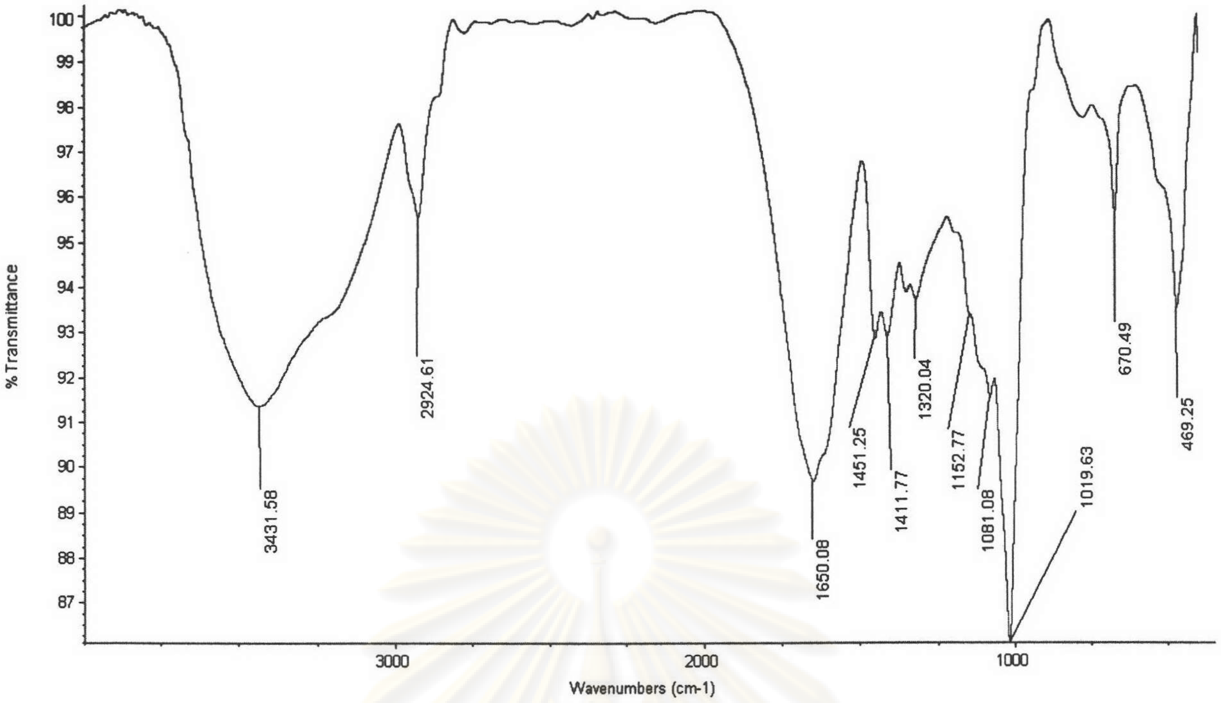


**Figure 4.3** Infrared spectrum of starch-*g*-polyacrylamide after extraction

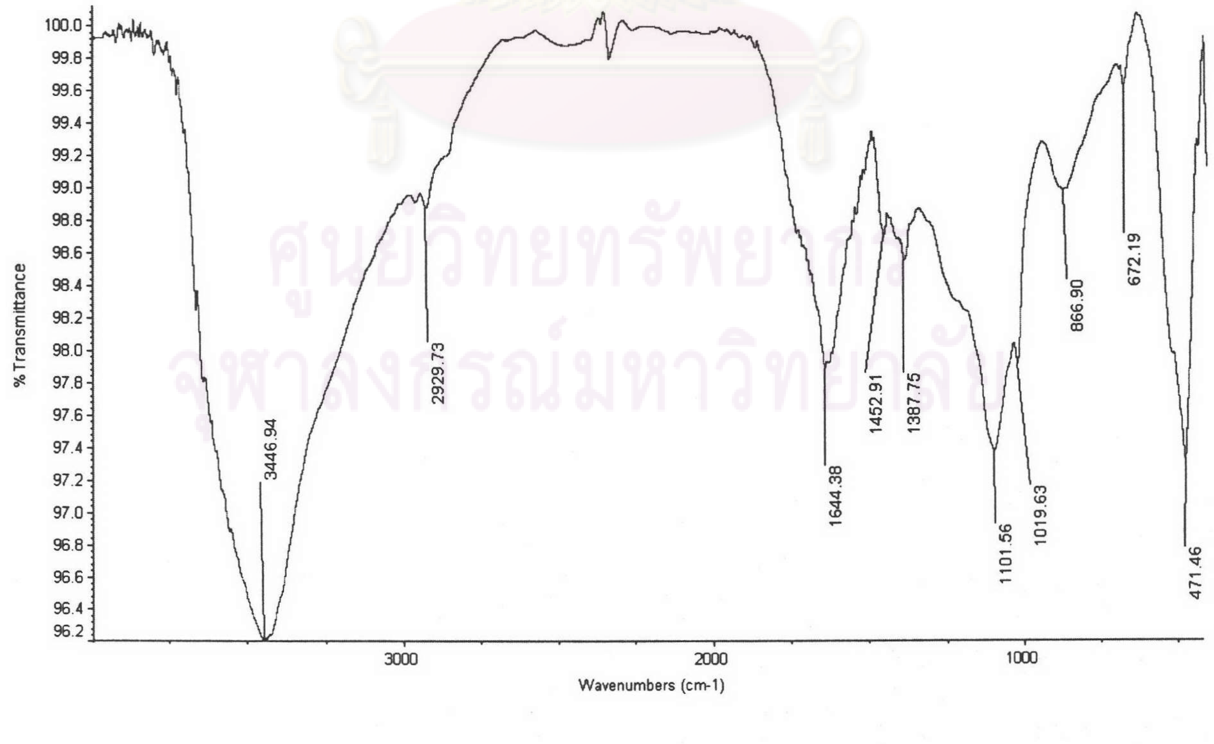


**Figure 4.4** Infrared spectrum of starch-*g*-polyacrylamide after acid hydrolysis

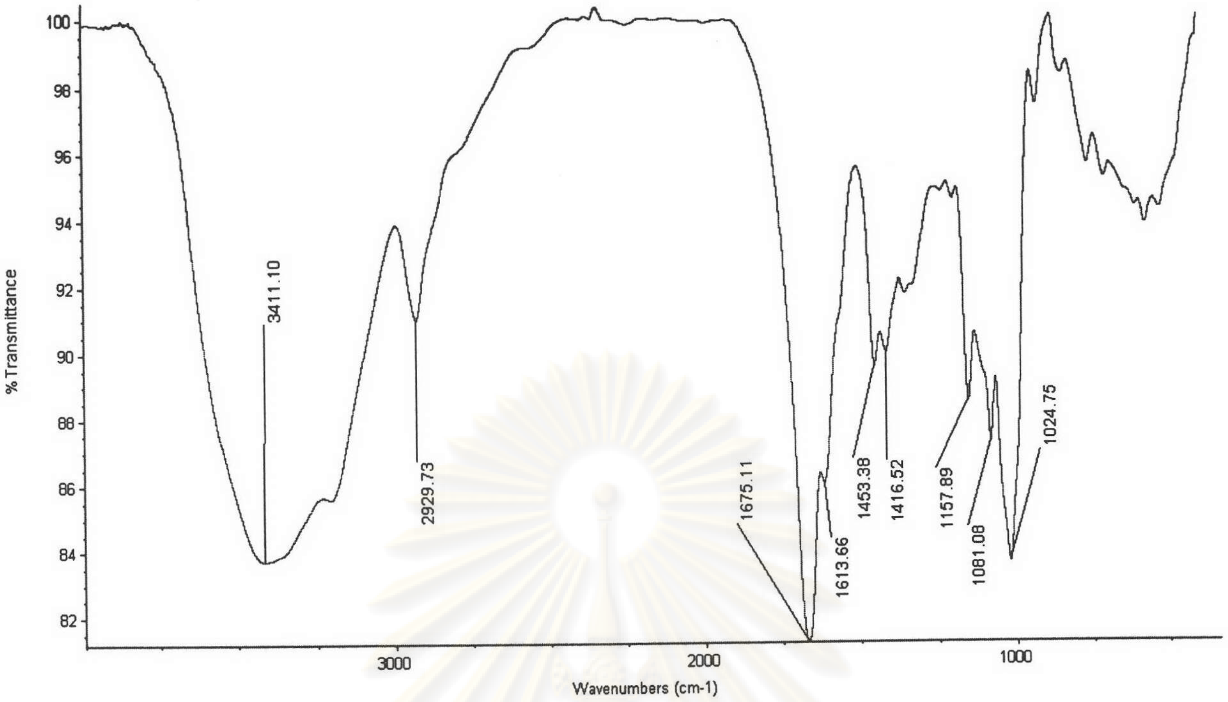


**Figure 4.5** Infrared spectrum of starch-*g*-poly[acrylamide-*co*-(itaconic acid)] before extraction

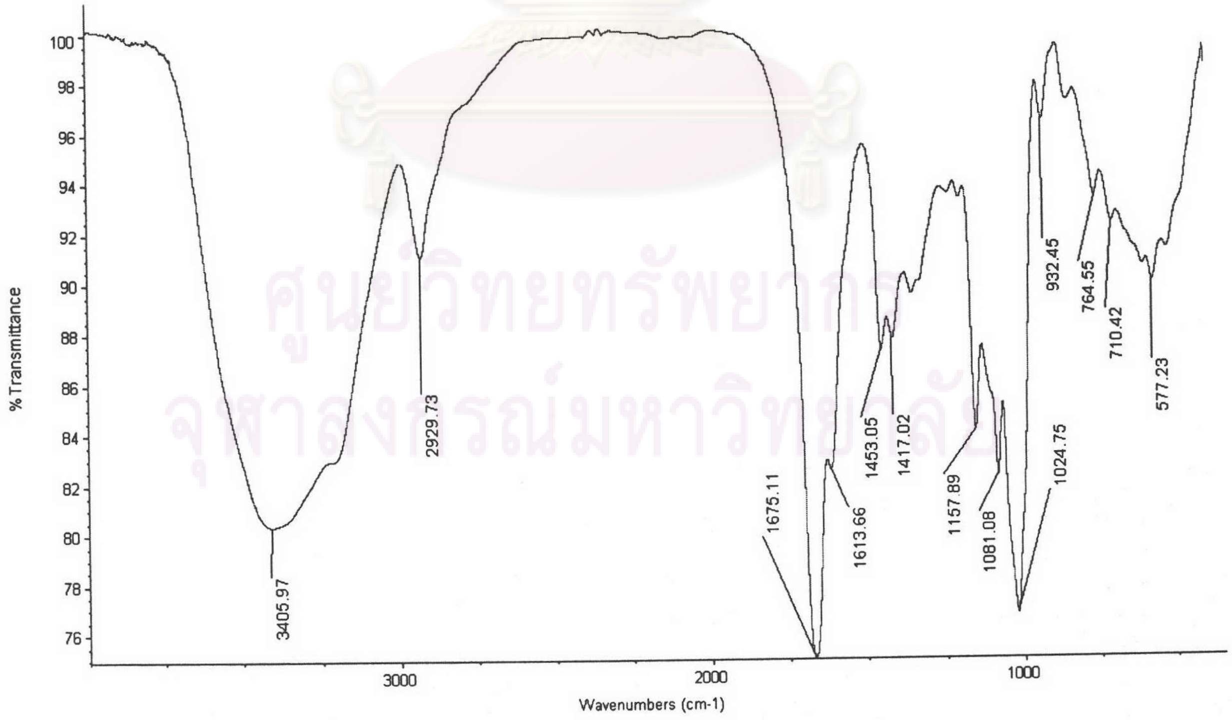


**Figure 4.6** Infrared spectrum of starch-*g*-poly[acrylamide-*co*-(itaconic acid)] after extraction

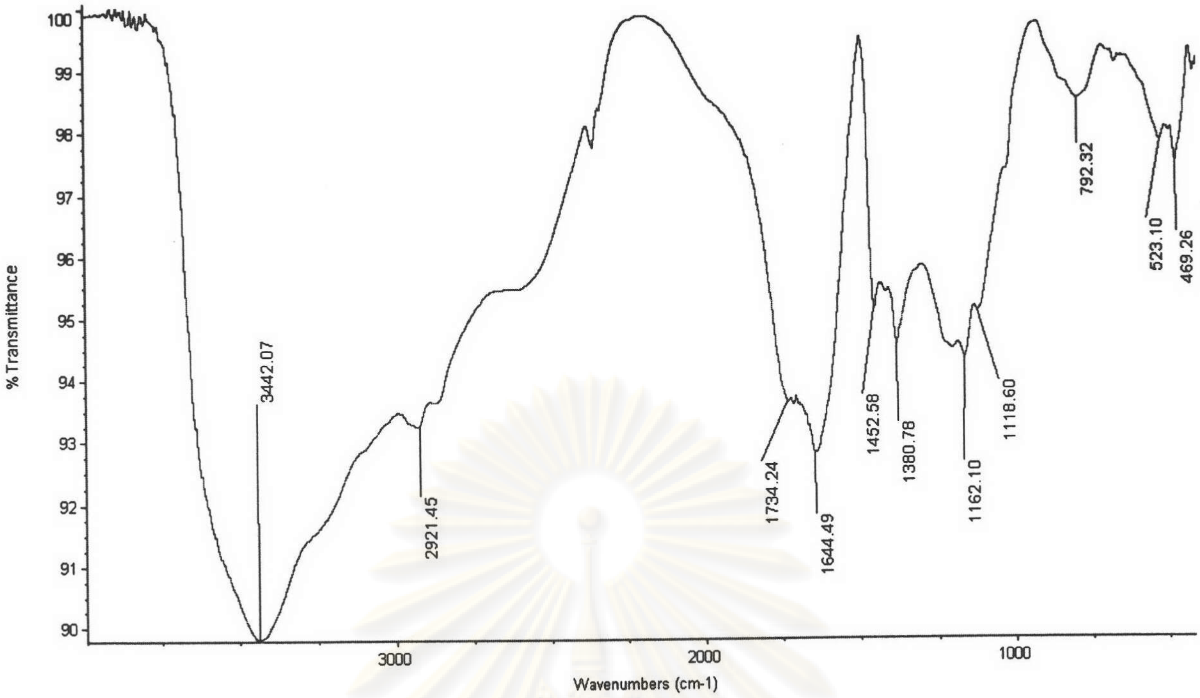


**Figure 4.7** Infrared spectrum of starch-*g*-poly[acrylamide-*co*-(itaconic acid)] after acid hydrolysis

**Table 4.1** The Infrared Absorption of Functional Groups in Cassava Starch and Starch-*g*-polyacrylamide Before Extraction, After Extraction, and After acid hydrolysis

| Starch | | Starch-*g*-polyacrylamide before extraction | | Starch-*g*-polyacrylamide after extraction | | Starch-*g*-polyacrylamide after acid hydrolysis | |
|---|---|---|---|---|---|---|---|
| wavenumber ($cm^{-1}$) | assignment | wavenumber ($cm^{-1}$) | assignment | wavenumber ($cm^{-1}$) | assignment | wavenumber ($cm^{-1}$) | assignment |
| 3385 (s,b) | O-H stretching | 3385 (s,b) | O-H stretching | 3385 (s,b) | O-H stretching | - | O-H stretching |
| 2930 (m) | C-H stretching | 2925 (m) | C-H stretching | 2925 (m) | C-H stretching | 2930 (w) | C-H stretching |
| 1158, 1081, 1015 (s) | C-O stretching | 1158, 1081, 1025 (s) | C-O stretching | 1081, 1020 (s) | C-O stretching | 1102, 1020 (m) | C-O stretching |
| | | 3427 (m) | N-H stretching | 3432 (m) | N-H stretching | 3447 (s) | N-H stretching |
| | | 1650 (s) | C=O stretching of $CONH_2$ | 1650 (s) | C=O stretching of $CONH_2$ | 1645 (s) | C=O stretching of $CONH_2$ |
| | | 1614 (w) | N-H bending | 1614 (w) | N-H bending | | |

b = broad, s = strong, and m = medium

**Table 4.2** The Infrared Absorption of Functional Groups in Cassava Starch and Starch-g-poly[acrylamide-co-(itaconic acid)] Before Extraction, After Extraction, and After acid hydrolysis

| Starch | | Starch-g-poly[acrylamide-*co*-(itaconic acid)] before extraction | | Starch-g-poly[acrylamide-*co*-(itaconic acid)] after extraction | | Starch-g-poly[acrylamide-*co*-(itaconic acid)] after acid hydrolysis | |
|---|---|---|---|---|---|---|---|
| wavenumber ($cm^{-1}$) | assignment | wavenumber ($cm^{-1}$) | assignment | wavenumber ($cm^{-1}$) | assignment | wavenumber ($cm^{-1}$) | assignment |
| 3385 (s,b) | O-H stretching | 3385 (s,b) | O-H stretching | 3385 (s,b) | O-H stretching | - | O-H stretching |
| 2930 (m) | C-H stretching | 2930 (m) | C-H stretching | 2930 (m) | C-H stretching | 2921 (w) | C-H stretching |
| 1158, 1081, 1015 (s) | C-O stretching | 1158, 1081, 1025 (s) | C-O stretching | 1158, 1081, 1025 (s) | C-O stretching | 1162, 1110 (s) | C-O stretching |
| | | 2500-3300 (m,b) | O-H stretching of COOH | 2500-3300 (m,b) | O-H stretching of COOH | 2500-3300 (m,b) | O-H stretching of COOH |
| | | 3411 (m) | N-H stretching | 3406 (m) | N-H stretching | 3442 (m) | N-H stretching |
| | | 1675 (s) | C=O stretching of $CONH_2$ | 1675 (s) | C=O stretching of $CONH_2$ | 1645 (s) | C=O stretching of $CONH_2$ |

b = broad, s = strong, and m = medium

**Table 4.2** (continued) The Infrared Absorption of Functional Groups in Cassava Starch and Starch-g-poly[acrylamide-co-(itaconic acid)] Before Extraction, After Extraction, and After acid hydrolysis

| Starch | | Starch-g-poly[acrylamide-*co*-(itaconic acid)] before extraction | | Starch-g-poly[acrylamide-*co*-(itaconic acid)] after extraction | | Starch-g-poly[acrylamide-*co*-(itaconic acid)] after acid hydrolysis | |
|---|---|---|---|---|---|---|---|
| wavenumber ($cm^{-1}$) | assignment | wavenumber ($cm^{-1}$) | assignment | wavenumber ($cm^{-1}$) | assignment | wavenumber ($cm^{-1}$) | assignment |
| | | 1614 (w) | N-H bending | 1614 (w) | N-H bending | 1734 (m) | C=O stretching of COOH |

b = broad, s = strong, and m = medium

## 4.2 Graft Copolymerization of Acrylamide and Itaconic Acid onto Cassava Starch

### 4.2.1. Effect of Mole Percent of Acrylamide-to-Itaconic Acid Ratios on Graft Copolymerization

The effect of acrylamide-to-itaconic acid ratio on starch-*g*-poly [acrylamide-*co*-(itaconic acid)] is shown in Table 4.3 and Figures 4.8 - 4.12. The free polymer contents increase with increasing amount of itaconic acid.

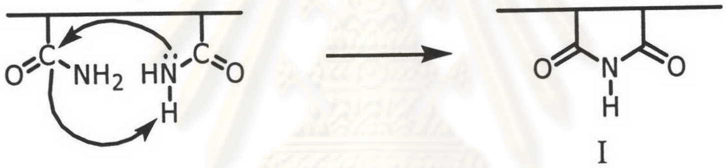
**Table 4.3** Effect of Acrylamide-to-Itaconic Acid Ratio on Graft Copolymerization

| AM:IA ratio | FP (%) | GE (%) | Add-on (%) | GR (%) | WA (g $g^{-1}$) |
|---|---|---|---|---|---|
| 100:0 | 11.0 | 84.4 | 59.9 | 149.5 | 39±1 |
| 98:2 | 11.9 | 82.3 | 55.6 | 125.2 | 70±2 |
| 96:4 | 10.4 | 83.3 | 51.8 | 107.3 | 115±0 |
| 94:6 | 17.1 | 74.5 | 49.8 | 99.2 | 249±1 |
| 92:8 | 23.2 | 68.3 | 49.9 | 99.6 | 264±6 |
| 90:10 | 25.0 | 66.8 | 50.3 | 101.4 | 379±10 |
| 85:15 | 39.0 | 55.1 | 47.7 | 91.4 | 222±4 |

FP = Free Polymers; GE = Grafting Efficiency; GR = Grafting Ratio; WA = Water Absorption; Starch-to-monomer ratio = 1:2; APS = 1.0 % wt, N-MBA = 2.0 %wt, at 45°C, 250 rpm, 30 min.

This result indicates that itaconic acid does not behave as a crosslinking agent and both monomers prefer to copolymerizing as an ungrafted free copolymer rather than becoming a grafted copolymer onto the starch backbone, indicated by the decreasing grafting efficiency.

The copolymerization of acrylamide presented the lower percentage of free polymer than those of both AM and IA. The copolymeriztion of AM may form imidization because the occurrence of imidization that usually takes place in polymerization of acrylamide in concentrated solutions and at high temperatures or very long reaction times [30]. The result so obtained is evidenced with a higher gel strength than those with AM and IA because of cyclic imide structure (I-II).



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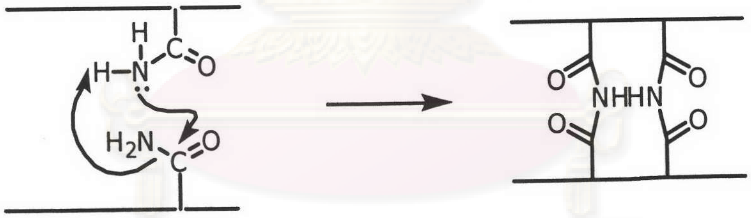
(4.1)



II

(4.2)

The percentages of the homopolymer and free polymer increase when the grafting efficiency and percentage add-on decrease. The increasing homopolymer content may be from the formation of polyacrylamide or the random copolymerization of AM and IA radicals with the monomers, leading to the formation of the ungrafted, free copolymer of AM and IA. The percentage grafting efficiency and percentage add-on thus decrease which could be caused by an increase in the non-grafted polymers in the solution phase, compared with a heterogeneous phase grafting between the two monomers with the gelatinized starch.

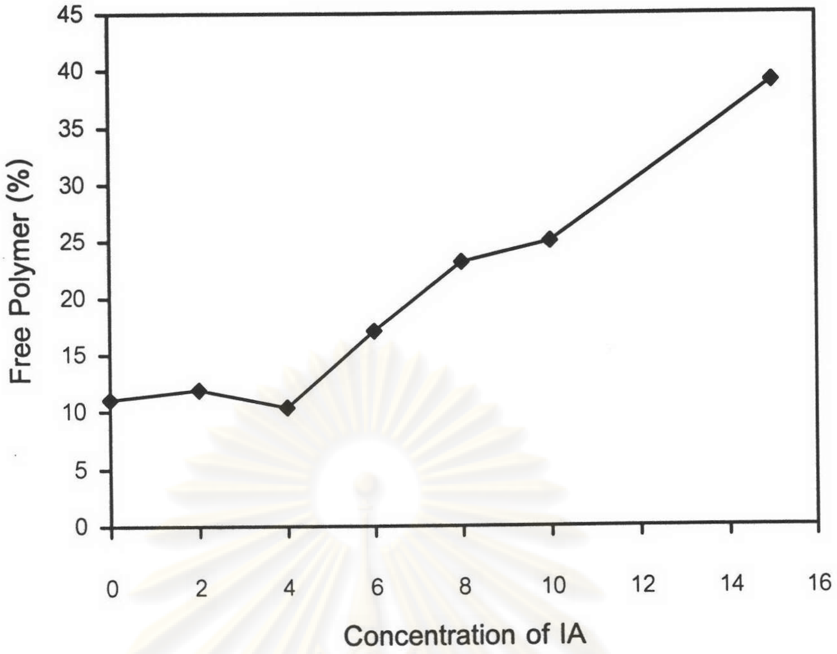


**Figure 4.8** Effect of concentration of itaconic acid (mole percent) on the percentage of free polymers

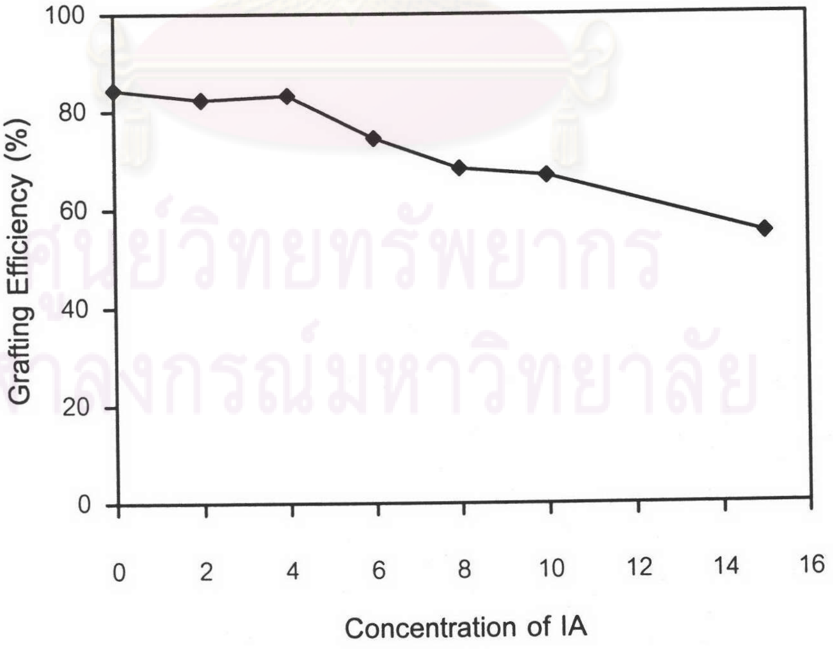


**Figure 4.9** Effect of concentration of itaconic acid (mole percent) on the percentage of grafting efficiency

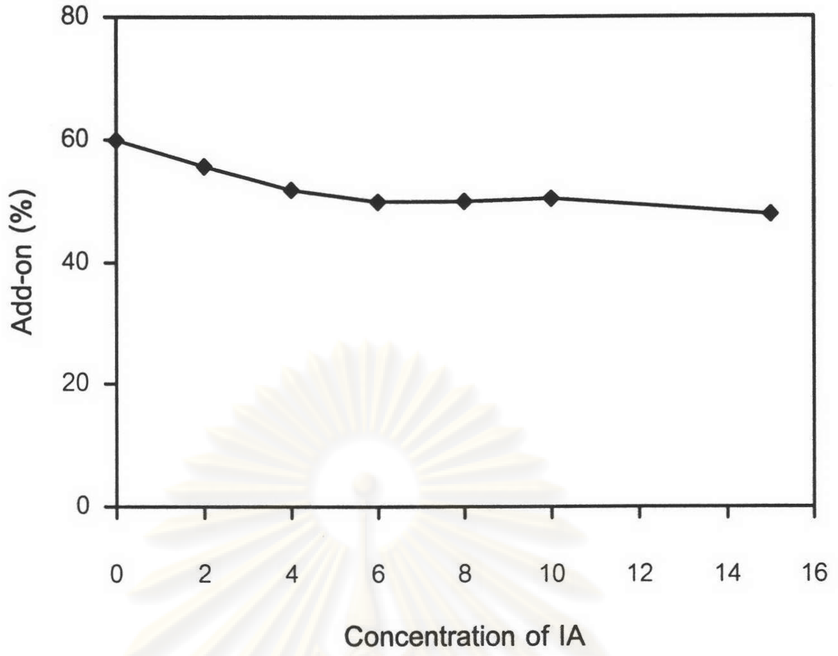


**Figure 4.10** Effect of concentration of itaconic acid (mole percent) on the percentage of add-on

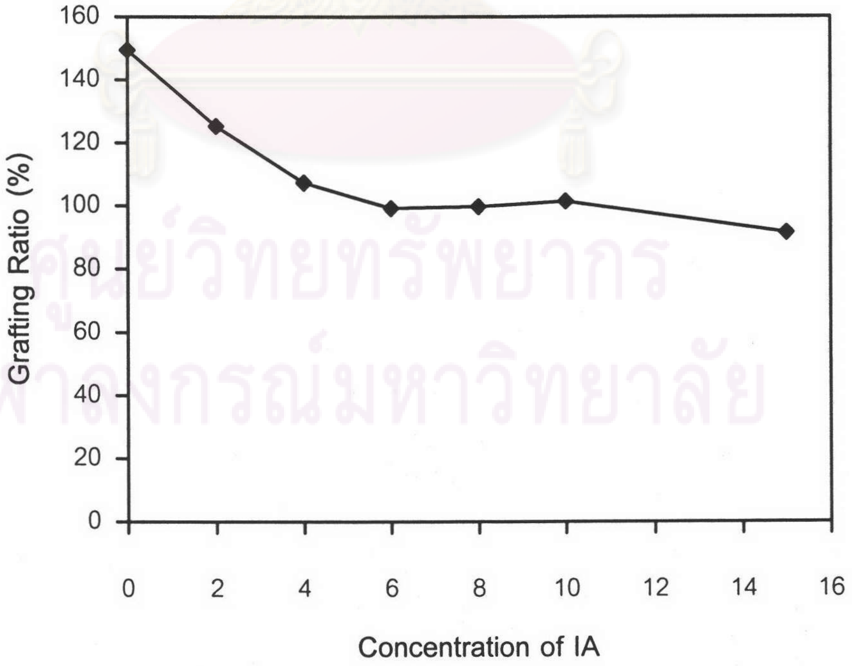


**Figure 4.11** Effect of concentration of itaconic acid (mole percent) on the percentage of grafting ratio

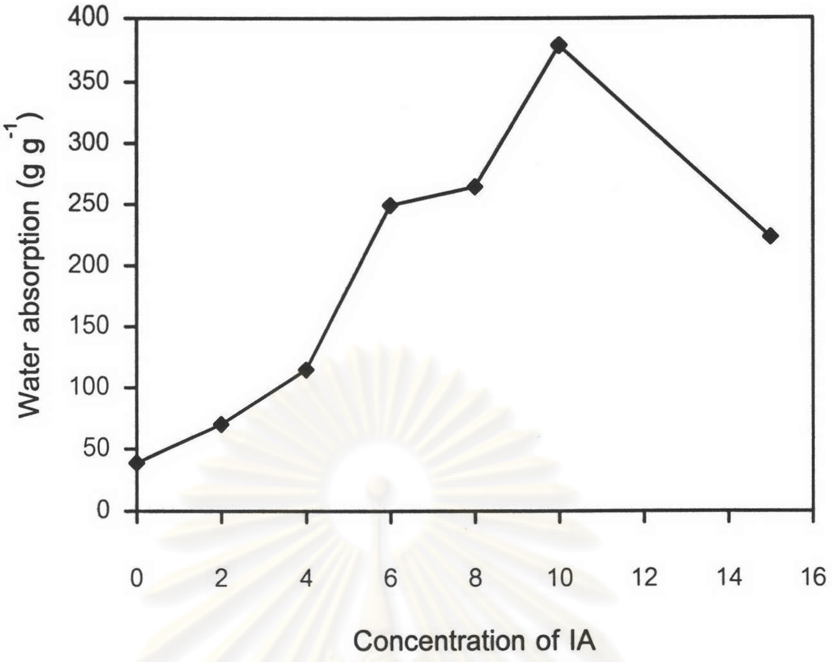


**Figure 4.12** Effect of concentration of itaconic acid (mole percent) on water absorption

The water absorbency increases with increasing number of hydrophilic and ionic functional groups. The reactivity ratios of AM and IA are 0.77 and 1.36, respectively [18], which render that the structure of the copolymer should contain more IA units than AM unit. The structure of the copolymer consisting of more itaconic acid units gives a graft copolymer with more hydrophilic groups. The graft copolymer must have an optimum ratio of AM-to-IA in order to have balance of hydrophilic or ionic functional groups and chain flexibility to produce the graft copolymer with highest water absorption capacity. The highest water absorption occurs at the ratio of AM:IA of 90:10, which can absorb distilled water at the highest value of 379±10 g $g^{-1}$. However, at the AM-to-IA ratio higher than 90:10, the water absorption decreases. The lower water absorption may be due to a predominant role of the hydrophobic character of the unionized itaconic acid, leading to the increase in homopolymer and decreases in grafting efficiency and percentage add-on [31].

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

The effect of the starch-to-monomer ratio on the grafting of acrylamide and itaconic acid onto cassava starch is presented in terms of homopolymer formed, grafting efficiency, percentage add-on, grafting ratio, and water absorption as shown in Table 4.4 and Figures 4.13 – 4.17.

**Table 4.4** Effect of the Starch-to-Monomer Ratio on the Graft Copolymerization

| Starch: Monomer | FP (%) | GE (%) | Add-on (%) | GR (%) | WA ($g\ g^{-1}$) |
|---|---|---|---|---|---|
| 1:2 | 25.0 | 66.8 | 50.3 | 101.4 | 379±10 |
| 1.5:2 | 28.1 | 64.5 | 51.1 | 104.5 | 237±2 |
| 2:2 | 28.6 | 53.5 | 33.0 | 49.2 | 209±7 |
| 2.5:2 | 28.7 | 47.12 | 25.7 | 34.7 | 170±2 |
| 3:2 | 33.5 | 31.7 | 15.5 | 18.4 | 118±9 |
| 3.5:2 | 47.2 | 13.8 | 7.6 | 8.2 | 114±3 |

FP = Free Polymers; GE = Grafting Efficiency; GR = Grafting Ratio; WA = Water Absorption; AM-to-IA ratio = 90:10; APS = 1.0 % wt, N-MBA = 2.0 %wt, at 45°C, 250 rpm, 30 min.

When increasing the quantity of the starch mixture, the percentage of homopolymer formed increases but the grafting efficiency, the percentage of add-on, and grafting ratio decrease with an increasing in the starch-to-monomer ratio.

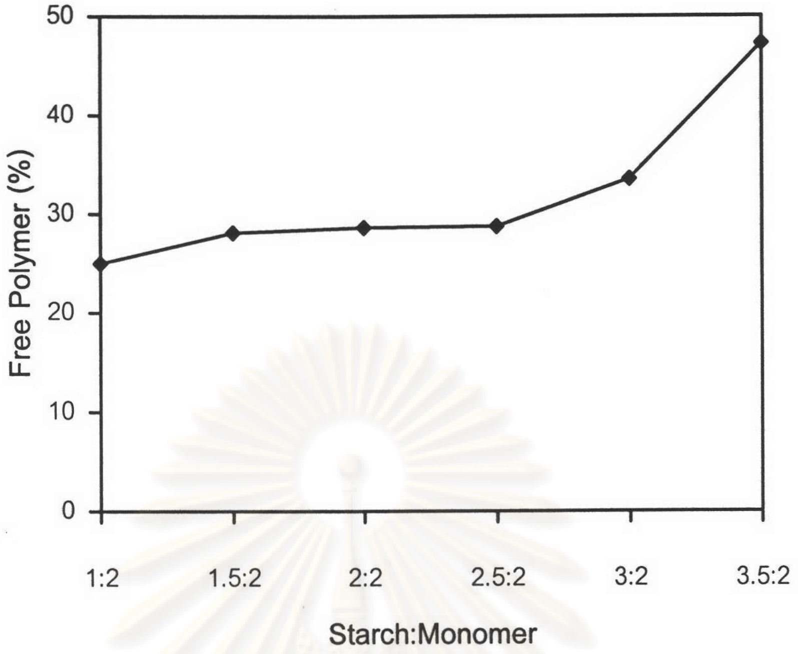


**Figure 4.13** Effect of starch-to-monomer ratio on the percentage of free polymers

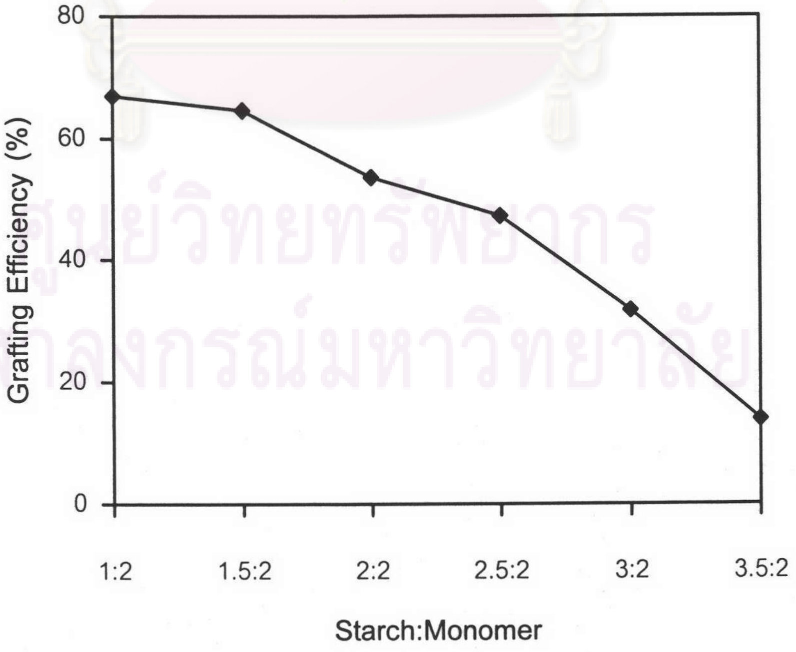


**Figure 4.14** Effect of starch-to-monomer ratio on the percentage of grafting efficiency

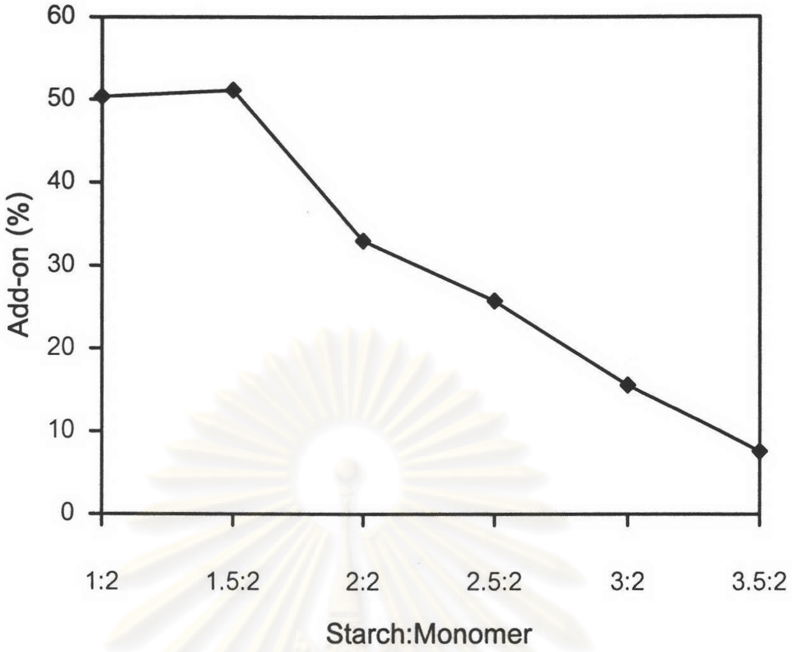


**Figure 4.15** Effect of starch-to-monomer ratio on the percentage of add-on

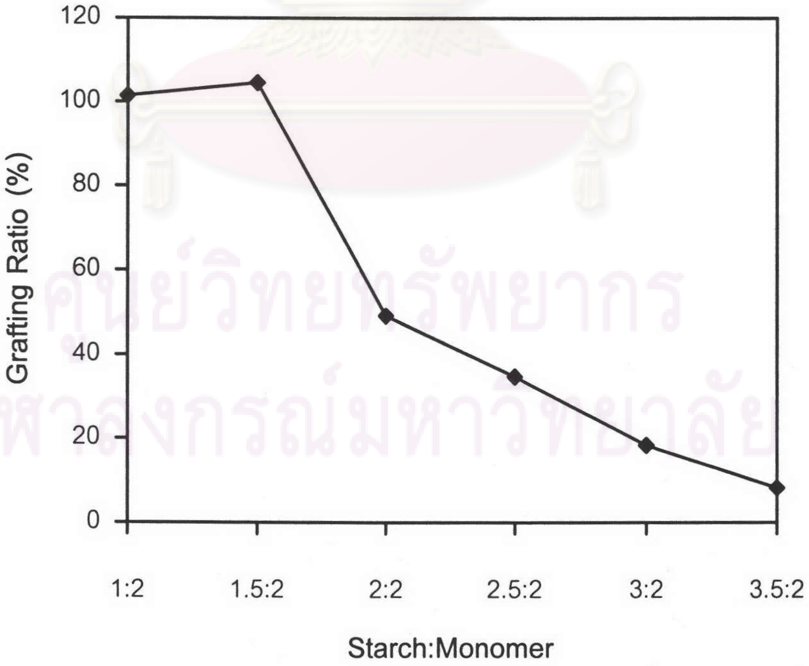


**Figure 4.16** Effect of starch-to-monomer ratio on the percentage of grafting ratio

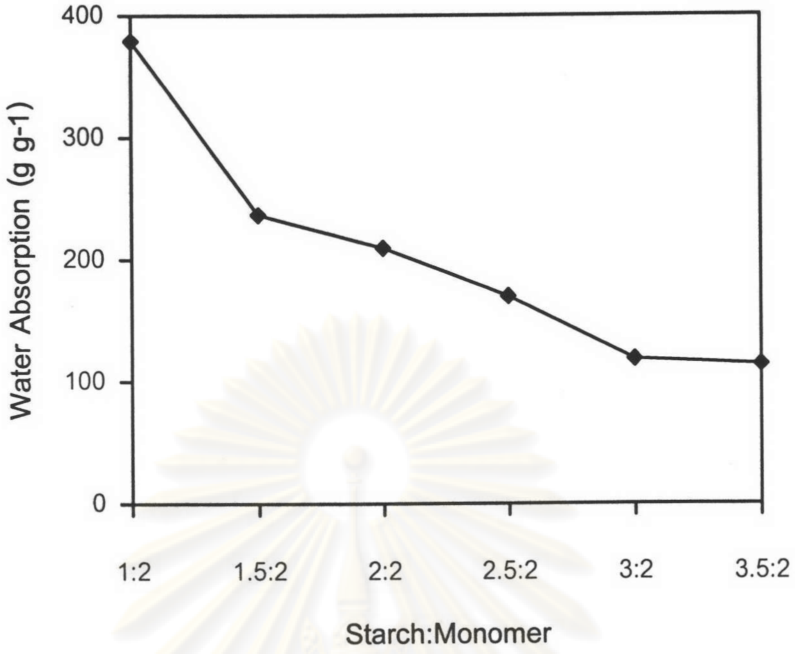


**Figure 4.17** Effect of starch-to-monomer ratio on water absorption

At a higher amount of starch, a small number of monomers can diffuse to graft into the starch backbone. Most of monomers are used for homopolymer formation through collisions due to viscous grafting substrate and the greater bulk volume of the aqueous phase. However, the highest water absorption found in this work occurs at a minimum ratio of 2:1 of monomer (AM/IA) to starch. The graft copolymerization with a higher grafting efficiency gives the graft copolymer containing higher amount of hydrophilic segment. Thus, the swelling increases due to the increase of the differential osmotic pressure between inside and outside the gel. In addition, the swelling also increases because the increasing hydrophilic fraction of the polymer chain tends to disperse better in the solvent.

### 4.2.3 Effect of Initiator Concentration on Graft Copolymerization

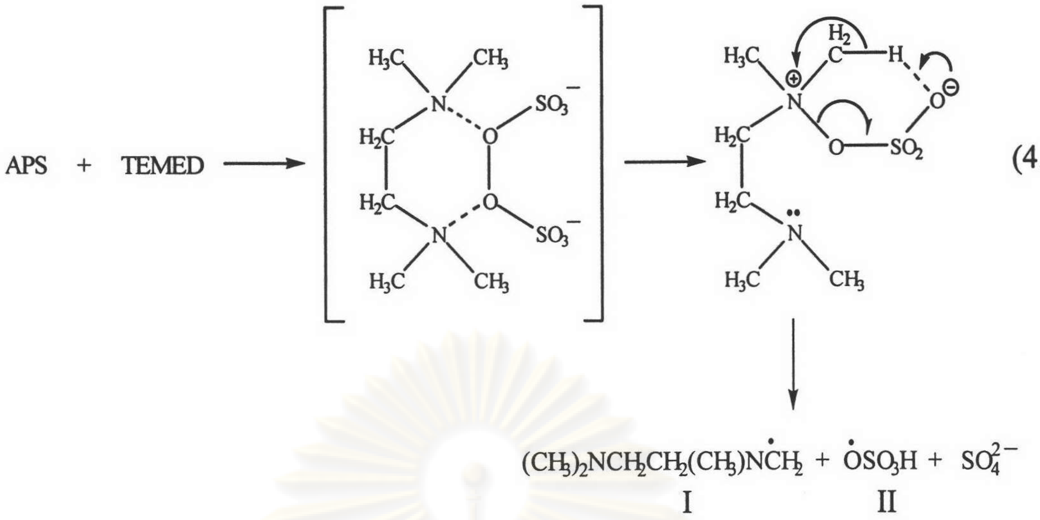
The effect of ammonium persulfate concentration is presented in Table 4.5 and Figures 4.18-4.22.

**Table 4.5** Effect of Ammonium Persulfate on Graft Copolymerization

| APS (%) | FP (%) | GE (%) | Add-on (%) | GR (%) | WA ($g\ g^{-1}$) |
|---|---|---|---|---|---|
| 0.5 | 26.7 | 64.0 | 47.4 | 90.3 | 243±1 |
| 1.0 | 16.9 | 74.2 | 48.9 | 95.5 | 300±2 |
| 1.5 | 29.0 | 58.1 | 40.2 | 67.2 | 230±4 |
| 2.0 | 29.5 | 57.4 | 39.8 | 66.2 | 212±1 |

FP = Free Polymers; GE = Grafting Efficiency; GR = Grafting Ratio; WA = Water Absorption; Starch-to-monomer ratio = 1:2, AM-to-IA ratio = 90:10, N-MBA = 1.0 %wt, at 45°C, 250 rpm, 30 min.

Ammonium persulfate and *N,N,N',N'*-tetramethylethylenediamine were used as the redox initiating system. The reaction between APS and TMED produces the free radical (I) and sulfate free radical (II) as shown in Equation 4.3. The following mechanism represents the production of initial radicals for the polymerization:



(4.3)

The kinetic chain length decreases with increasing initiator concentration, which directly affects the molecular weight of the polymer. The mechanisms of the graft copolymerization via the redox system involved the chain transfer reaction as shown in Equations 4.4-4.10 [32].

Initiation:

$$SO_4^{\bullet -} + M \longrightarrow M^{\bullet} \qquad (4.4)$$

Propagation:

$$M^{\bullet} + M \longrightarrow M_1^{\bullet} \qquad (4.5)$$

$$M_{n-1}^{\bullet} + M \longrightarrow M_n^{\bullet} \qquad (4.6)$$

Termination:

$$M_x^{\bullet} + M_y^{\bullet} \longrightarrow \text{Homopolymer} \qquad (4.7)$$

$$M_x^{\bullet} + \text{Starch}^{\bullet} \longrightarrow \text{Starch-}M_x \qquad (4.8)$$

Chain Transfer:

$$R^{\bullet} + \text{Starch} \longrightarrow \text{Starch}^{\bullet} \qquad (4.9)$$

$$\text{Starch}^{\bullet} + M_n^{\bullet} \longrightarrow \text{Graft copolymer} \qquad (4.10)$$

Since free radicals on the 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 [33]. Therefore, the percentage of free polymers increases with increasing the redox initiator.

In expression of the percentage of grafting efficiency, add-on, and grafting ratio tend to increase with increasing the concentration of initiator, reached a optimum value and then decreased. Free radical occurred as a result of decomposition of APS in various reactions in the polymerization media. An increase in the concentration of the initiator increases the chance of hydrogen abstraction from the starch backbone and chain transfer reaction of the copolymer chain with starch, causes the graft yield to increase. However, the excessive increase in the concentration of APS causes the formation of free radical species (Equation 4.3) from the decomposition of APS and TEMED to give the termination reaction with starch macroradicals (Equation 4.8) or growing polymer chain or a combination reaction between them (Equation 4.7). Consequently, the grafting yield decreases.

The water absorption of the grafted copolymer, synthesized with various ammonium persulfate concentration is shown in Figure 4.22. The optimum product properties at 1.0 % wt APS give highest water absorption of 300±2 g $g^{-1}$. Considering the characteristics of swollen gel, size and flexibility of the swollen gel decreased with increasing ammonium persulfate concentration. When ammonium persulfate concentrations are more than 1.0 % wt, the gel strength is reduced because the low-molecular weight branches are grafted on starch backbone [34].

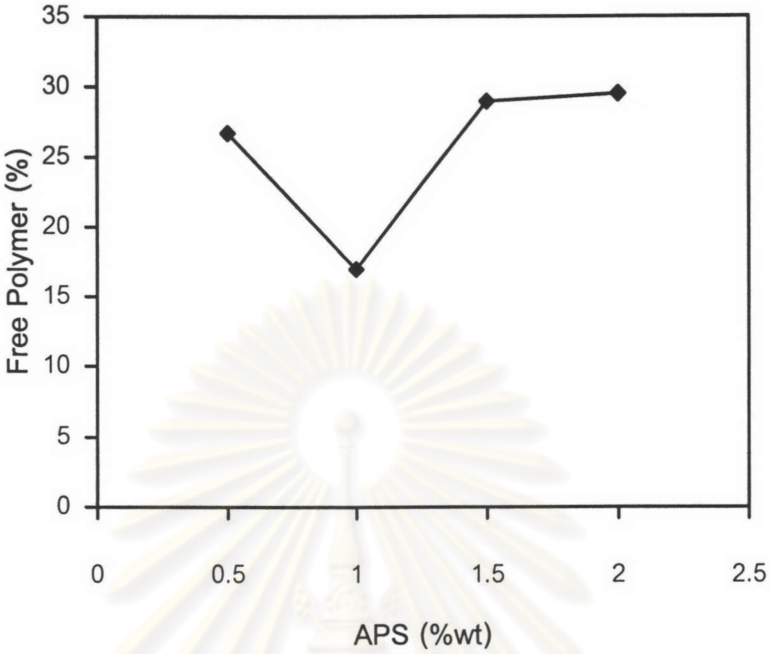


**Figure 4.18** Effect of APS concentration (%) on the percentage of free polymers

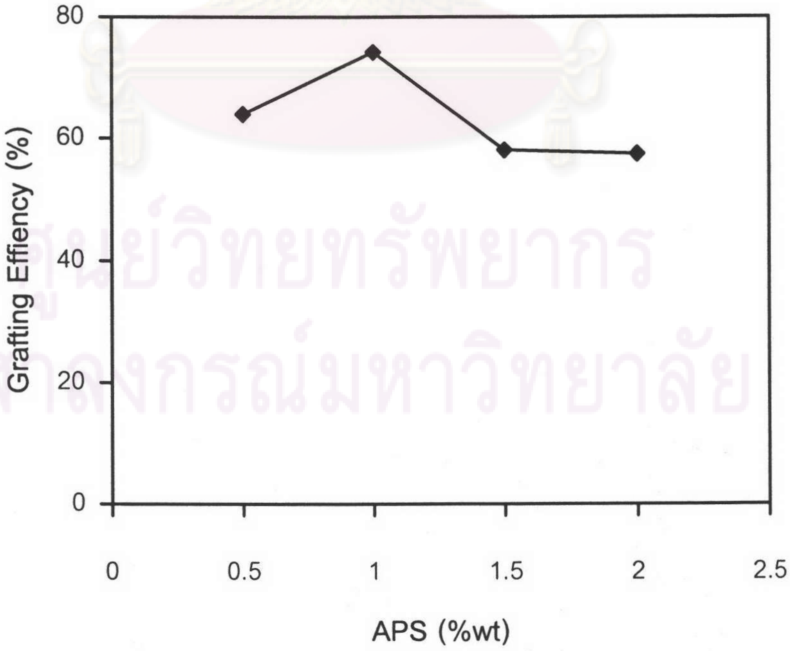


**Figure 4.19** Effect of APS concentration (%) on the percentage of grafting efficiency

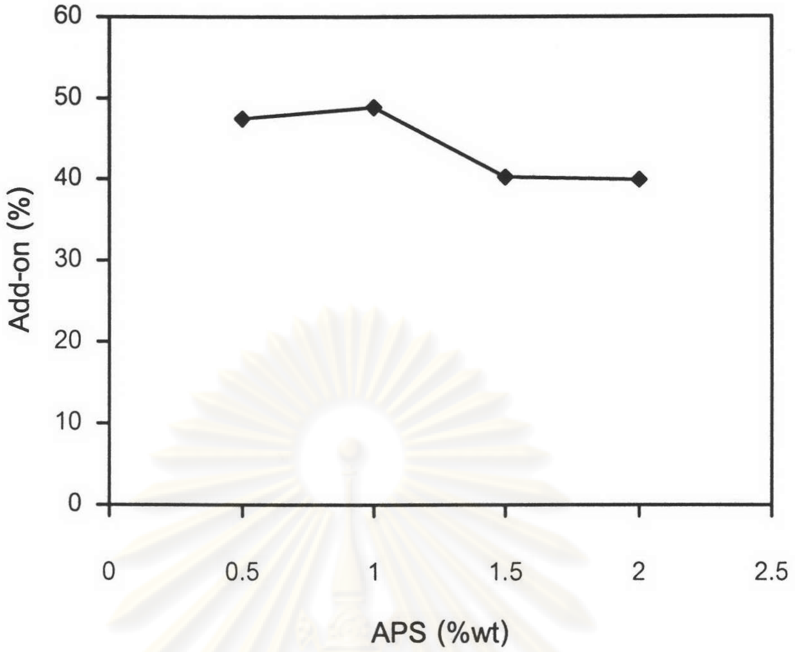


**Figure 4.20** Effect of APS concentration (%) on the percentage of add-on

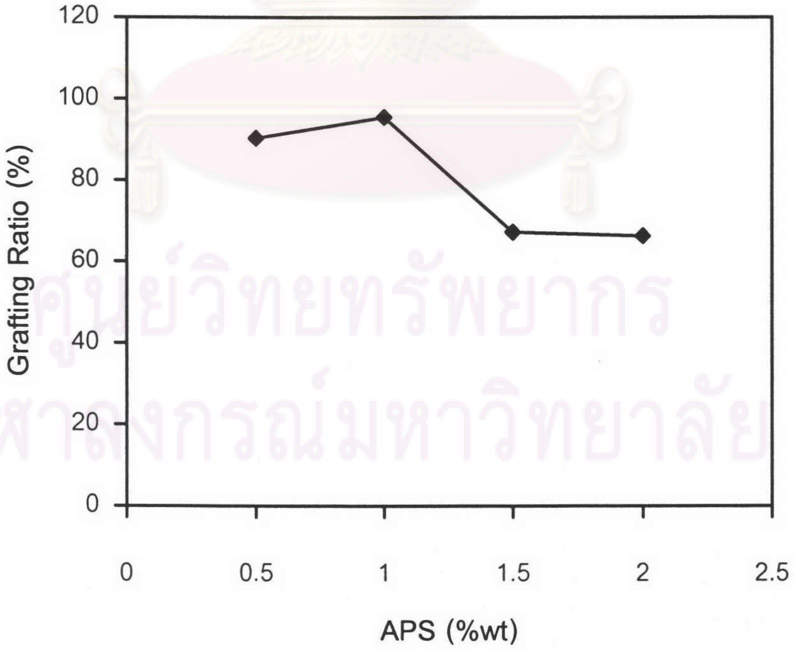


**Figure 4.21** Effect of APS concentration (%) on the percentage of grafting ratio

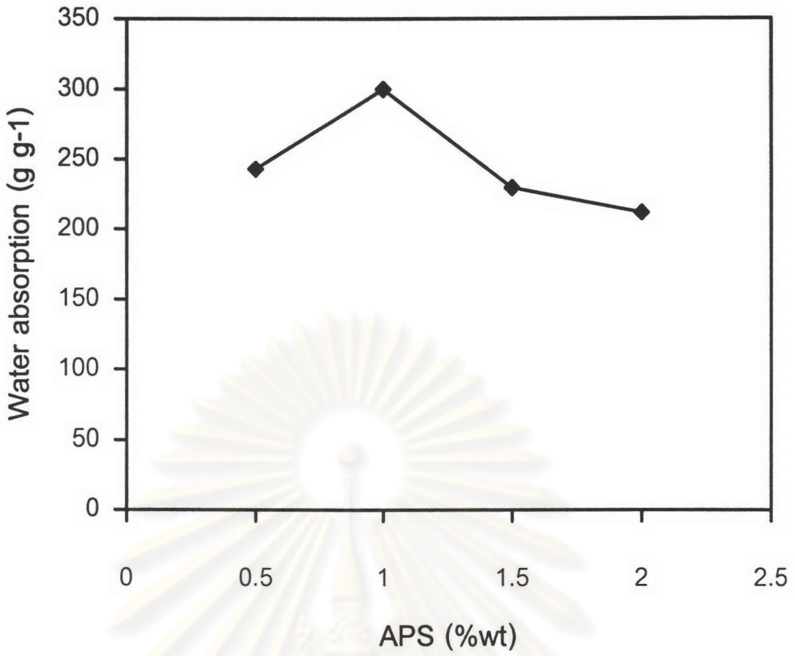


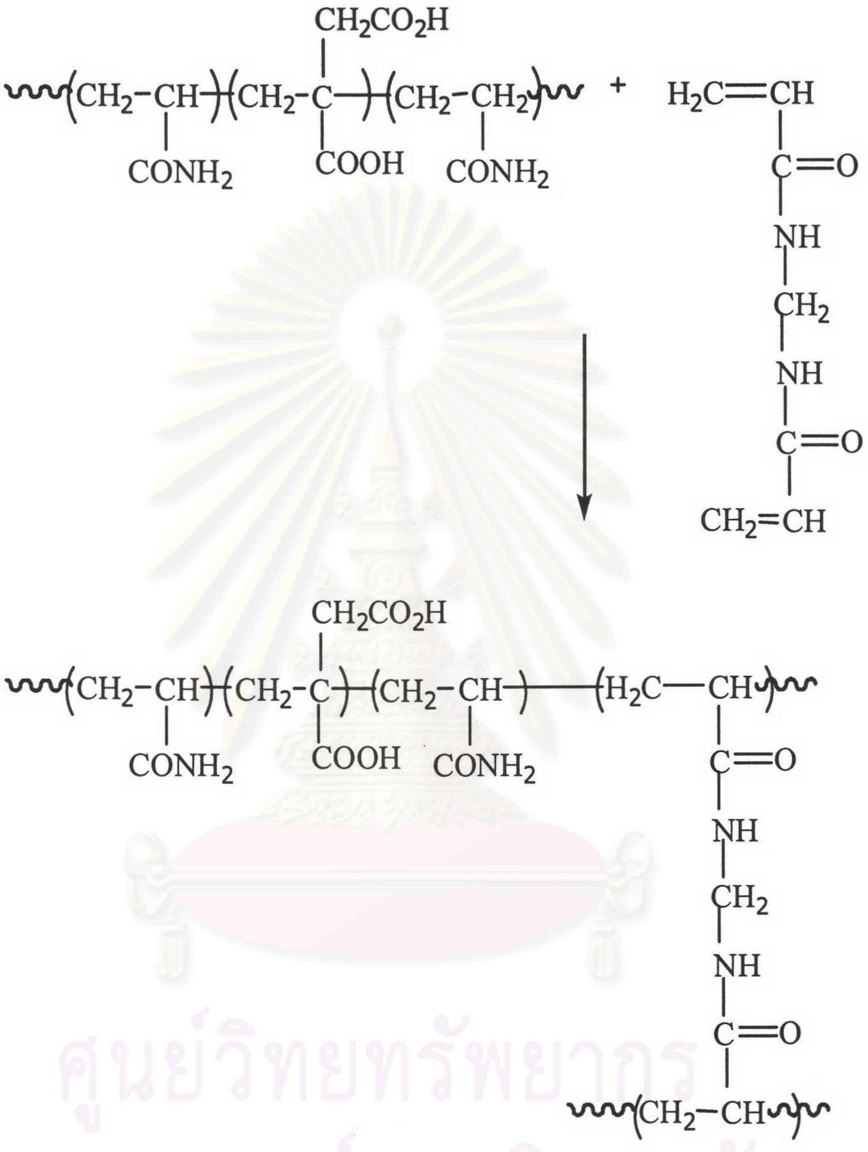
**Figure 4.22** Effect of APS concentration (%) on water absorption

### 4.2.4 Effect of the Crosslinking Agent Concentration on Graft Copolymerization

The effect of the crosslinker, N-MBA, concentration (%weight based on the total monomers) on the grafted copolymer is presented in Table 4.6 and Figures 4.23-4.27.

The free polymer contents decrease with increasing the amount of crosslinker because majority of the monomers was used in a crosslinking copolymerization, which decrease the residue monomer concentration, the extent of which depends on the crosslinker-to-the monomer concentration ratios.

The following represents the synthesis of the graft copolymer by free radical copolymerization using a redox initiator with the N-MBA crosslinking agent as shown in Equation 4.11.



(4.11)

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.

**Table 4.6** Effect of the Crosslinker Concentration on Graft Copolymerization

| N-MBA (%wt) | FP (%) | GE (%) | Add-on (%) | GR (%) | WA (g $g^{-1}$) |
|---|---|---|---|---|---|
| 0.5 | 64.3 | 20.5 | 16.6 | 19.9 | 221±6 |
| 1.0 | 16.9 | 74.2 | 48.9 | 95.5 | 300±2 |
| 1.5 | 18.9 | 72.9 | 50.8 | 103.5 | 298±3 |
| 2.0 | 25.0 | 66.8 | 50.3 | 101.4 | 379±10 |
| 2.5 | 34.4 | 57.9 | 47.2 | 89.5 | 326±6 |

FP = Free Polymers; GE = Grafting Efficiency; GR = Grafting Ratio; WA = Water Absorpion; AM-to-IA ratio = 90:10; Starch-to-monomer ratio = 1:2; Ammonium persulfate 1.0 % wt, at 45°C, 250 rpm, 30 min.

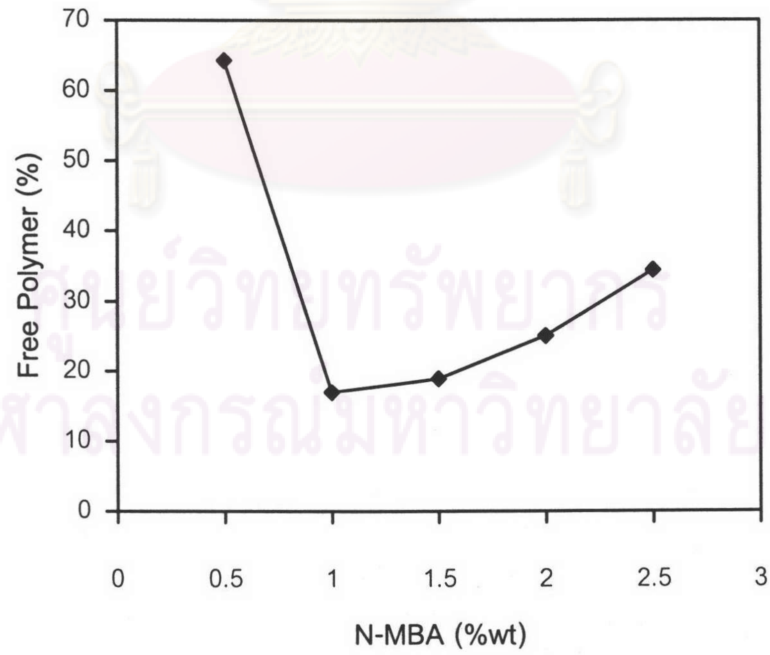


**Figure 4.23** Effect of N-MBA concentration (%) on the percentage of free polymers

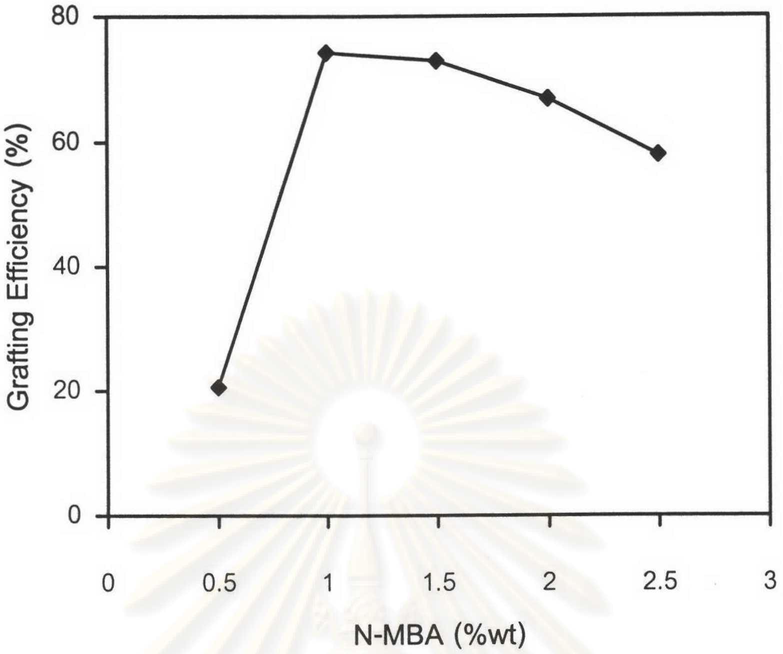


**Figure 4.24** Effect of N-MBA concentration (%) on the percentage of grafting efficiency

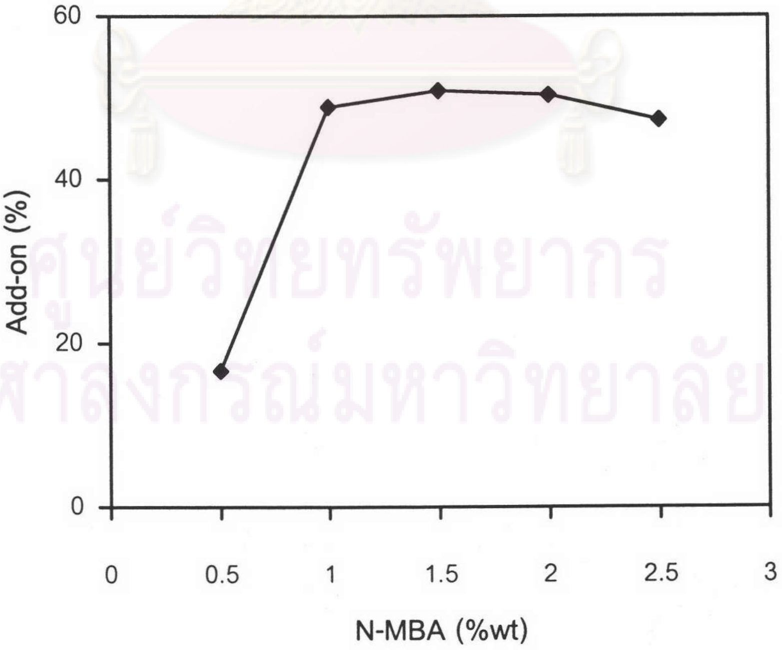


**Figure 4.25** Effect of N-MBA concentration (%) on the percentage of add-on

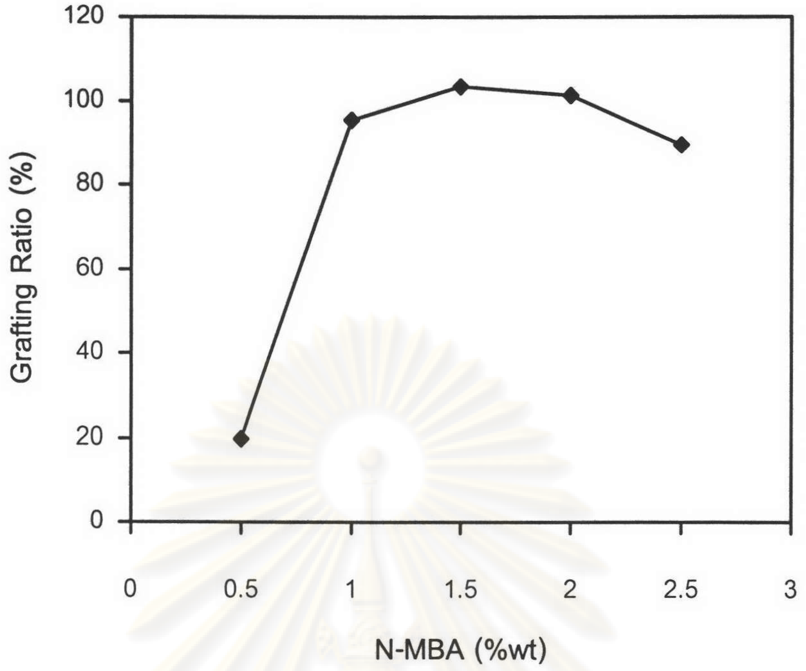


**Figure 4.26** Effect of N-MBA concentration (%) on the percentage of grafting ratio

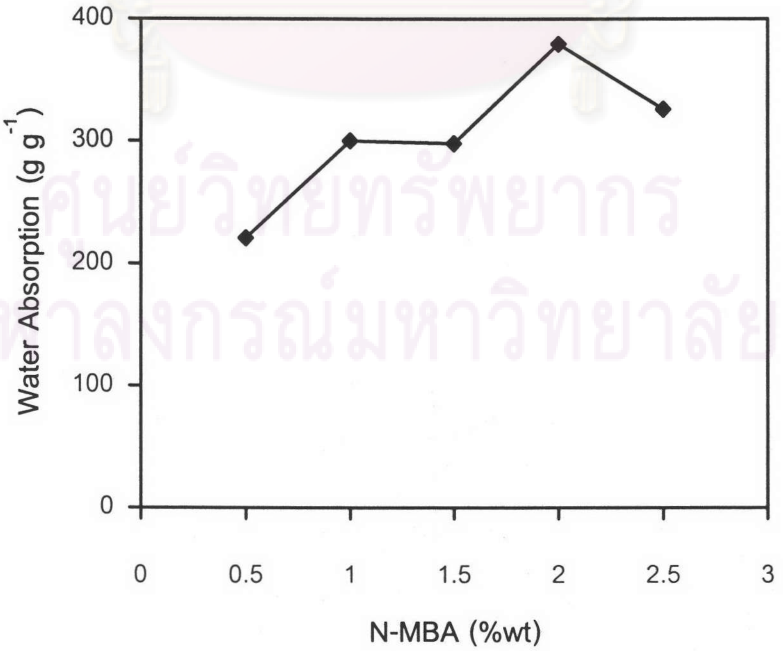


**Figure 4.27** Effect of N-MBA concentration (%) on water absorption

The grafted copolymer which gave the highest water absorption capacity was synthesized with 2.0%wt of N-MBA. At 2.5 % wt N-MBA several point of the crosslinking reaction enhanced the higher gel strength and reduced its water absorption.

### 4.2.5 Effect of Reaction Temperature on Graft Copolymerization

The effect of reaction temperature on the grafted copolymer is presented in Table 4.7 and Figures 4.28-4.32.

**Table 4.7** The Effect of the Reaction Temperature on Graft Copolymerization

| Temperature (°C) | FP (%) | GE (%) | Add-on (%) | GR (%) | WA ($g\ g^{-1}$) |
|---|---|---|---|---|---|
| 35 | 37.8 | 48.8 | 28.8 | 27.5 | 116±2 |
| 45 | 28.6 | 53.5 | 33.0 | 49.2 | 209±7 |
| 55 | 15.7 | 70.4 | 37.5 | 59.9 | 169±3 |
| 65 | 18.3 | 63.3 | 31.6 | 46.2 | 107±1 |

FP = Free Polymers; GE = Grafting Efficiency; GR = Grafting Ratio; WA = Water Absorpion; AM-to-IA ratio = 90:10; Starch-to-monomer ratio = 1:1; Ammonium persulfate = 1.0 % wt, N-MBA = 2.0 %wt. 250 rpm, 30 min.

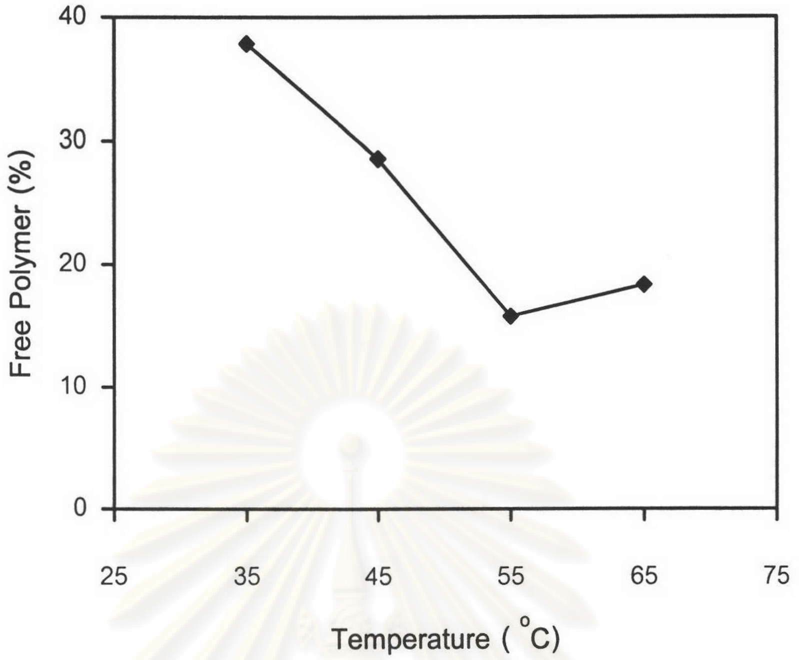


**Figure 4.28** Effect of reaction temperature on the percentage of free polymers

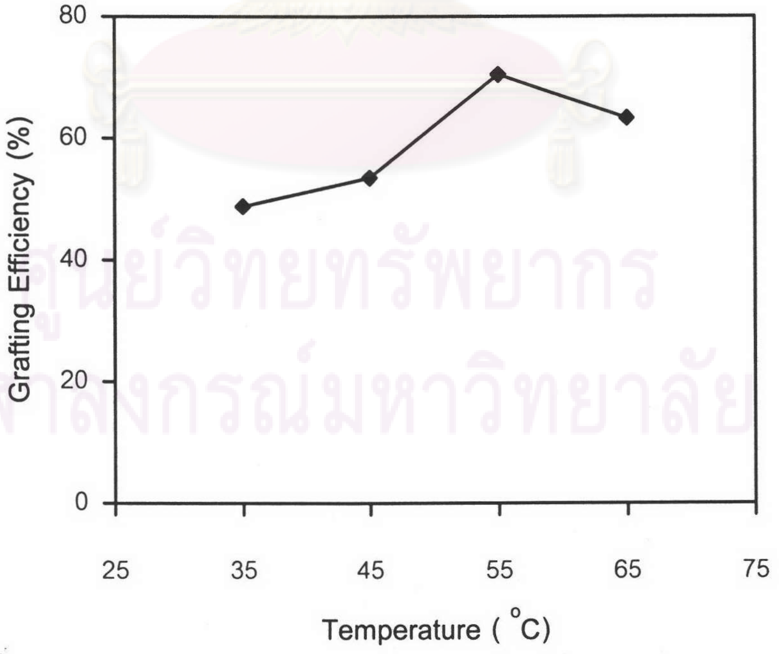


**Figure 4.29** Effect of reaction temperature on the percentage of grafting efficiency

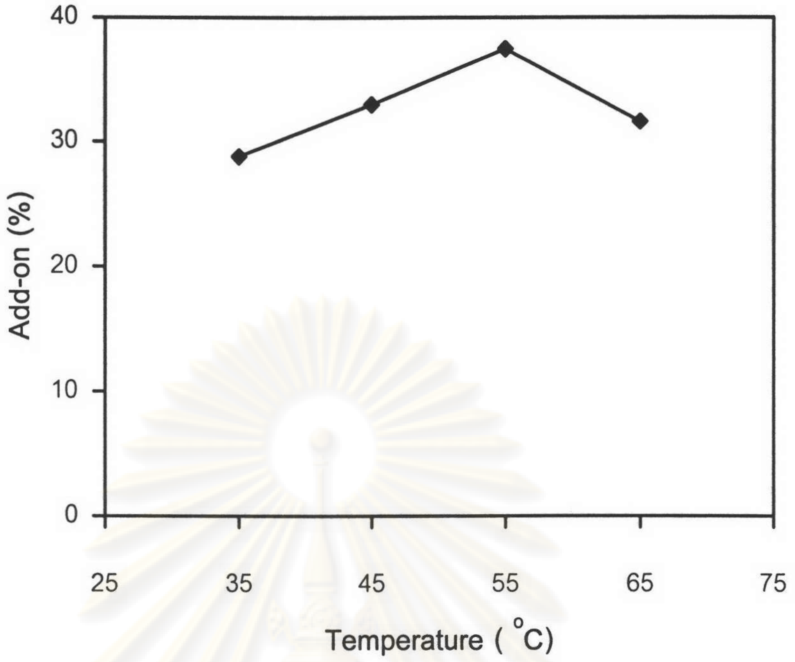


**Figure 4.30** Effect of reaction temperature on the percentage of add-on

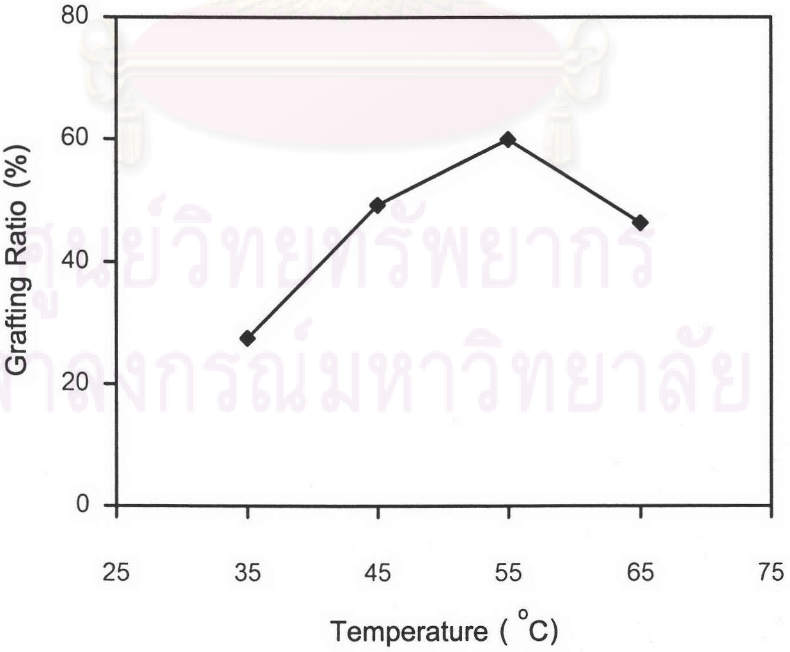


**Figure 4.32** Effect of reaction temperature on the percentage of grafting ratio

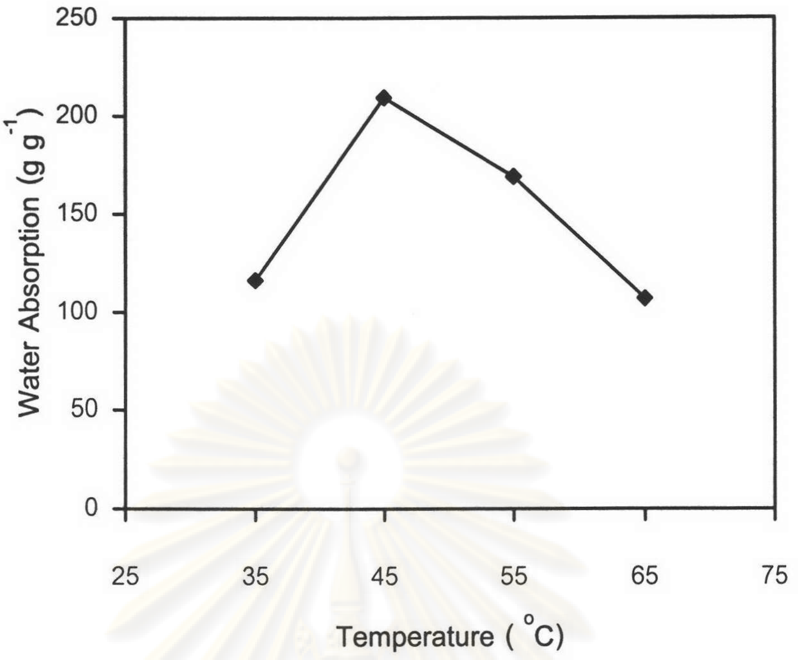


**Figure 4.33.** Effect of reaction temperature on water absorption

This favorable effect of higher temperature on grafting could be associated with the following [35]:

(a) Better decomposition of the redox system, giving rise to more radicals.

(b) Greater swellability of starch.

(c) Increased mobility of the monomer molecules

(d) Higher diffusion from the aqueous phase to starch substrate, and high rate of initiation and propagation of graft chain.

The percentages of grafting efficiency, add-on, and grafting ratio tend to increase with increasing the reaction temperature. The enhancement in grafting by raising the polymerization temperature from 35°C to 55°C could be explained in terms of greater swellability of the starch, diffusion of monomer into starch, mobility of monomer molecules and their collision with starch molecules and propagation of the graft. On the other hand, lowering of the graft yield was found by further increase in temperature (65°C), which may be due to a faster termination rate and a higher amount of homopolymer formation at a higher temperature and the adverse effect of this on grafting [36].

The water absorption of synthesized graft copolymer decreases when polymerization temperature is increased, which can absorb distilled water of the highest amount at the optimum temperature of 45°C and then decreases steadily with further rise in temperature to reach the lowest water absorption at the reaction temperature at 65°C.

### 4.2.6 Effect of Agitation Rate on Graft Copolymerization

The effect of agitation rate on the grafted copolymer is presented in Table 4.8 and Figures 4.33-4.37. The percentages of grafting efficiency, add-on, and grafting ratio tend to increase with increasing agitation rate. The percentages of add-on and grafting ratio at a agitation rate of 250 rpm are the highest values which may contribute to the optimum diffusion of monomer molecules to starch, a higher mobility of the monomer molecules and their collision with starch molecules. At an agitation rate of 300 rpm, enhancements in the termination rate to result in a higher amount of homopolymer formation was realized.

Similarly, at the lower agitation rate, a higher free polymer with lower percentages of grafting efficiency, add-on, and grafting ratio was found. The main reason can be the partitioning of the monomer molecules to the grafting substrate is slow. Therefore, the monomer radicals can terminate by themselves.

**Table 4.8** The Effect of the Agitation Rate on Graft Copolymerization

| Agitation rate (rpm) | FP (%) | GE (%) | Add-on (%) | GR (%) | WA ($g\ g^{-1}$) |
|---|---|---|---|---|---|
| 150 | 29.0 | 58.1 | 40.2 | 67.2 | 193±2 |
| 200 | 24.6 | 66.0 | 47.7 | 91.4 | 264±1 |
| 250 | 25.0 | 66.8. | 50.3 | 101.4 | 379±10 |
| 300 | 26.7 | 64.0 | 47.4 | 90.3 | 253±4 |

FP = Free Polymers; GE = Grafting Efficiency; GR = Grafting Ratio; WA = Water Absorpion; AM-to-IA ratio = 90:10; Starch-to-monomer ratio = 1:2; Ammonium persulfate = 1.0 % wt, N-MBA = 2.0 %wt, at 45°C, 30 min.

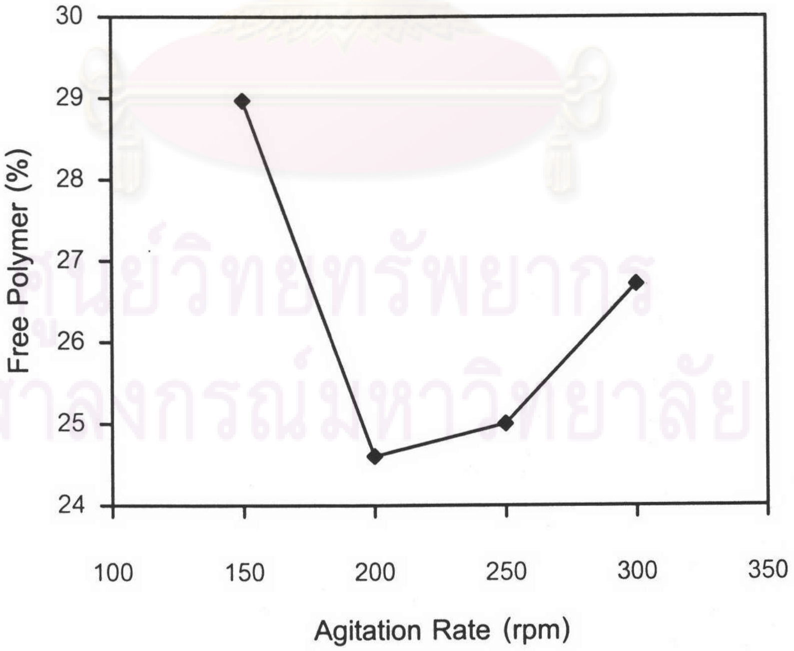


**Figure 4.33** Effect of agitation rate on the percentage of free polymers

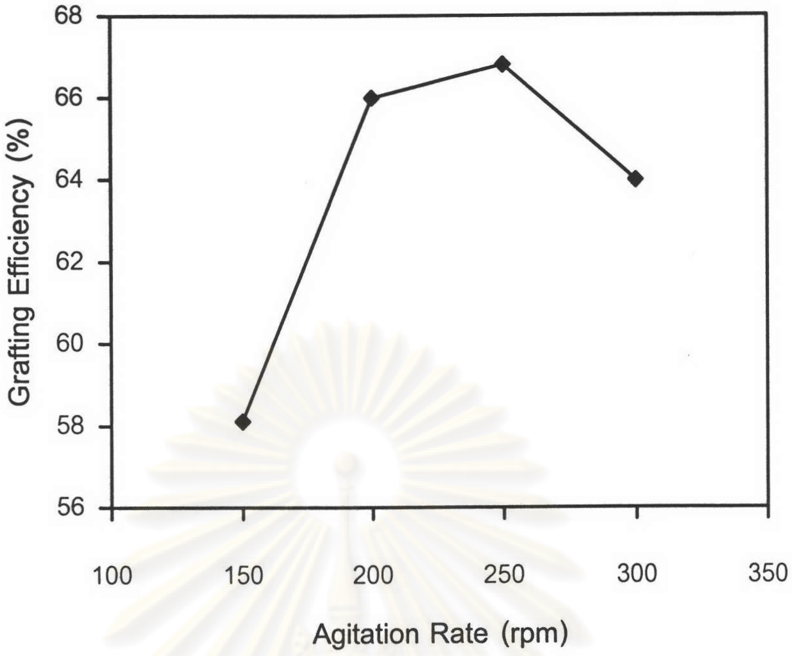


**Figure 4.34** Effect of agitation rate on the percentage of grafting efficiency

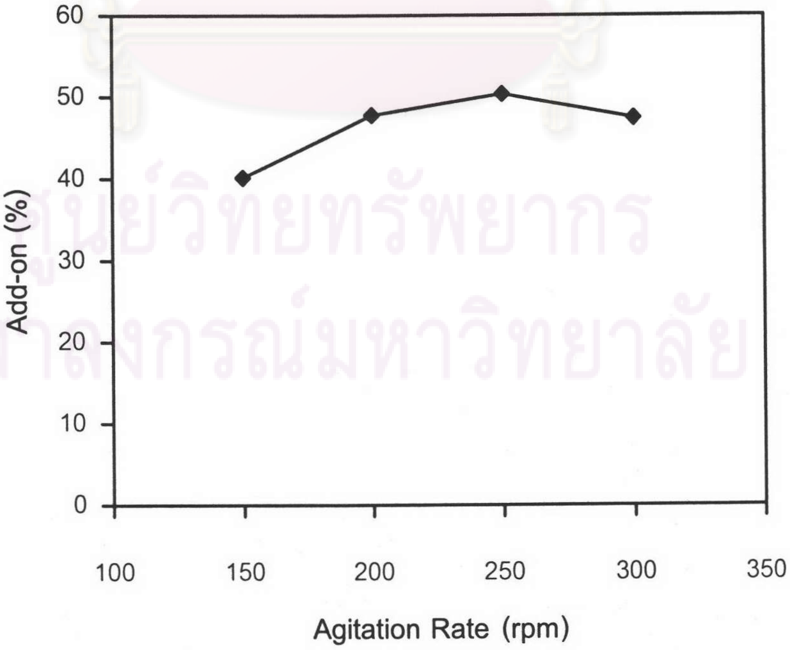


**Figure 4.35** Effect of agitation rate on the percentage of add-on

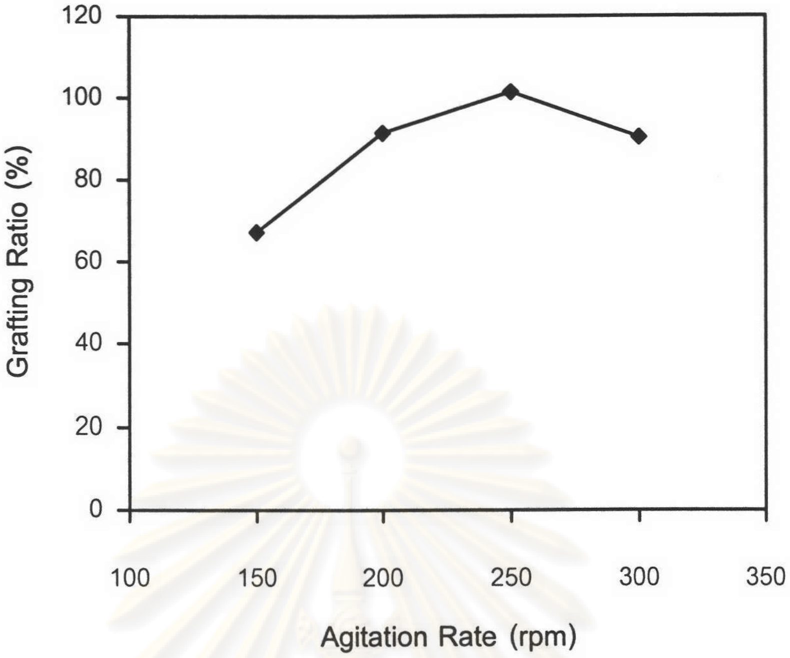


**Figure 4.36** Effect of agitation rate on the percentage of grafting ratio

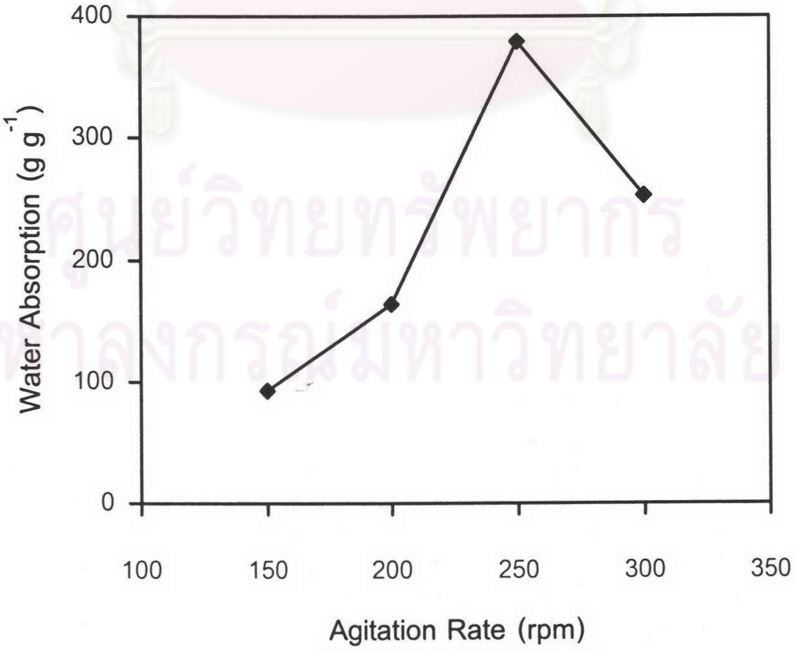


**Figure 4.37** Effect of agitation rate on water absorption

## 4.3 Water Absorption Capacities of the Graft Copolymer in Salt Solutions

### 4.3.1 Effect of Salt Solution on Water Absorption

The graft copolymer with the highest water absorbency was selected to test for the effect of salts in isotonic 0.9% w $v^{-1}$ NaCl, $MgCl_2$ and $CaCl_2$ solutions. Table 4.9 shows the water absorbency of the grafted copolymer in salt solutions.

**Table 4.9** Effect of Salt Solutions on Water Absorption

| Solution | Ionic strength (mol-ion $dm^{-3}$) | Water absorption (g $g^{-1}$) |
|---|---|---|
| Distilled water | - | 379±10 |
| 0.9% w $v^{-1}$ NaCl solution | 0.154 | 36±1 |
| 0.9% w $v^{-1}$ $MgCl_2$ solution | 0.2836 | 11±1 |
| 0.9% w $v^{-1}$ $CaCl_2$ solution | 0.2433 | 4±2 |

$I = ½ \Sigma(C_iZ_i^2)$ where I, $C_i$ and $Z_i$ are the ionic strength, the ionic concentration, and charge on each individual ion, respectively [39].

The water absorption capacity decreases with increasing the ionic strength of the saline solutions. The presence of ions in the solution surrounding the network counteracts the mutual repulsion of the fixed ion on the network itself, and the decrease of the osmotic pressure difference between the gel and the external solution [37]. The salt type and concentration can be expressed in the terms of ionic strength. The effect of the ionic strength on the water absorbency can be expressed by Flory's equation [3].

$$Q^{5/3} = [(i/2\nu_u S^{*1/2})^2 + (1/2 - \chi_1)/\nu_1] / (\nu_e/V_0) \qquad (4.12)$$

Where $Q$ = degree of swelling

$i/\nu_u$ = charge density of polymer

$S^*$ = ionic strength of solution

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

$\nu_e/V_0$ = crosslinking density

According to Equation 4.12, when the ionic strength of saline solution increases, the water absorbency would then decrease. The ionic strength of the solution depends on both the mobile ions and their valency or oxidation state. Small quantities of divalent or trivalent ions can drastically decrease the swelling values. This decreases more significantly by with $Mg^{2+}$, or $Ca^{2+}$ ions, which can be additionally caused by the complex ability of carboxamide or carboxylate groups including intramolecular and intermolecular complex formations, or because one multivalent ion is able to neutralize several charges inside the gel. Consequently, the crosslink density of the network increases while water absorption capacity decreases [38].

### 4.3.2 Effect of the pH Buffer Solution on Water Absorption

The influence of solution pH (3-11) on the water absorption capacity of synthesized graft copolymer, which has the highest water absorption in distilled water is shown in Table 4.10 and Figure 4.38.

**Table 4.10** Effect of pH Buffer Solution on Water Absorbency

| pH of buffer solution | Ionic strength (mol-ion $dm^{-3}$) | Water absorption ($g\ g^{-1}$) |
|---|---|---|
| 3 | 0.0061 | 22±1 |
| 5 | 0.0134 | 35±4 |
| 7 | 0.0190 | 40±1 |
| 9 | 0.0236 | 40±1 |
| 11 | 0.0272 | 39±2 |

$I = \frac{1}{2}\sum(C_iZ_i^2)$ where I, $C_i$ and $Z_i$ are the ionic strength, the ionic concentration, and charge on each individual ion, respectively [39].

The starch-g-poly[acrylamide-co-(itaconic aid)] contains carboxylate and carboxamide groups which are the majority of anionic-type superabsorbent polymer. An anionic-type superabsorbent polymer normally ionizes at a high pH but unionizes at a low pH. At the high pH where the gel is ionized, the equilibrium degree of swelling increases. Consistent with polyelectrolyte behavior, swelling of hydrogels was found to increase with pH. When the pH of the external solution increases beyond 5.0, the ionization of carboxylic groups in the gel matrix causes a sudden increase in swelling due to increased ion osmotic swelling pressure as well as chain relaxation resulting from the electrostatic repulsion among caboxylate groups inside the polymer matrix [40]. In addition, the maximum extent of swelling is reached at pH 7, this being due to the complete dissociation of acidic groups of itaconic acid at this pH value. The first and second dissociation constants of IA are $pK_{a1} = 3.85$ and $pK_{a2} = 5.44$, respectively [41].

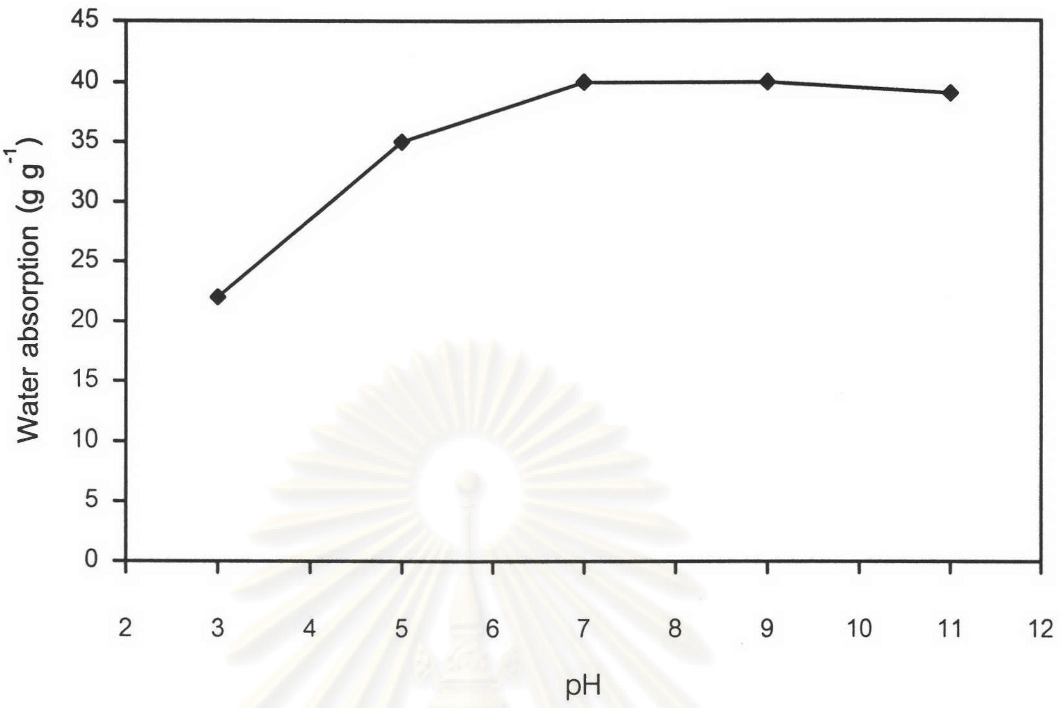


**Figure 4.38** Effect of pH on water absorption of the graft copolymer

The results indicate that under acidic conditions, anionic carboxylate groups are protonated, and the graft copolymer network shrinks significantly. At high pH values, the concentration of anionic groups in the polymer network increases [42]. With further increase in pH, the ion swelling pressure begins to drop again. Because of the increase in ionic strength of the swelling medium, the ion osmotic swelling pressure decreases, which ultimately reduces the equilibrium swelling capacity of the superabsorbent polymer [23].

## 4.4 Surface morphology of the copolymer

The surface appearance and structure of copolymers were observed using scanning electron microscopy. Electron microscopic photographs of the graft copolymers are shown in Figures 4.39-4.41.

The SEM photographs of starch-*g*-poly[acrylamide-*co*-(itaconic acid)], which are polymers of good absorbency, illustrated in Figure 4.39 show that the graft copolymers have a porous structure and a broad network of starch-g-poly[acrylamide-*co*-(itaconic acid)] in (a) and semi-porous structure with thick struts between pores in (b). It is supposed that these pores are regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers. On the other hand, SEM photographs of starch-*g*-poly[acrylamide-*co*-(itaconic acid)] that gives less water absorption, illustrated in Figure 4.40 show that they have smooth surface.

The SEM photographs of the starch-*g*-polyacrylamide in Figure 4.41, have fine network and smooth surface, the water absorbency of the starch-*g*-polyacrylamide was lower than that of the starch-*g*-poly[acrylamide-*co*-(itaconic acid)].

The number of hydrophilic groups of starch-*g*-poly[acrylamide-*co*-(itaconic acid)] is higher than that of the starch-*g*-polyacrylamide, so the swelling of starch-g-polyacrylamide is obviously lower than that additionally contains the itaconic acid moiety.

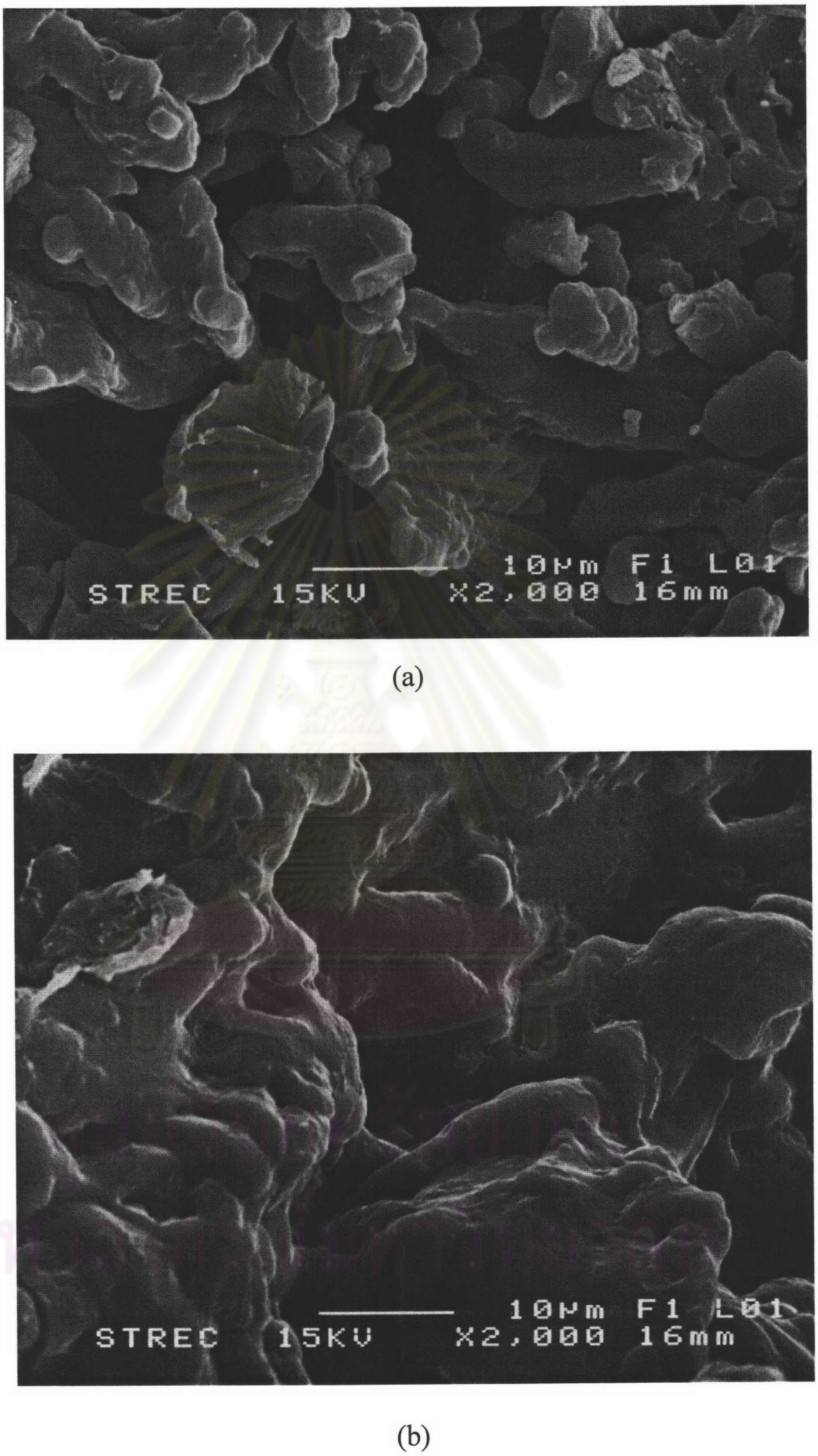
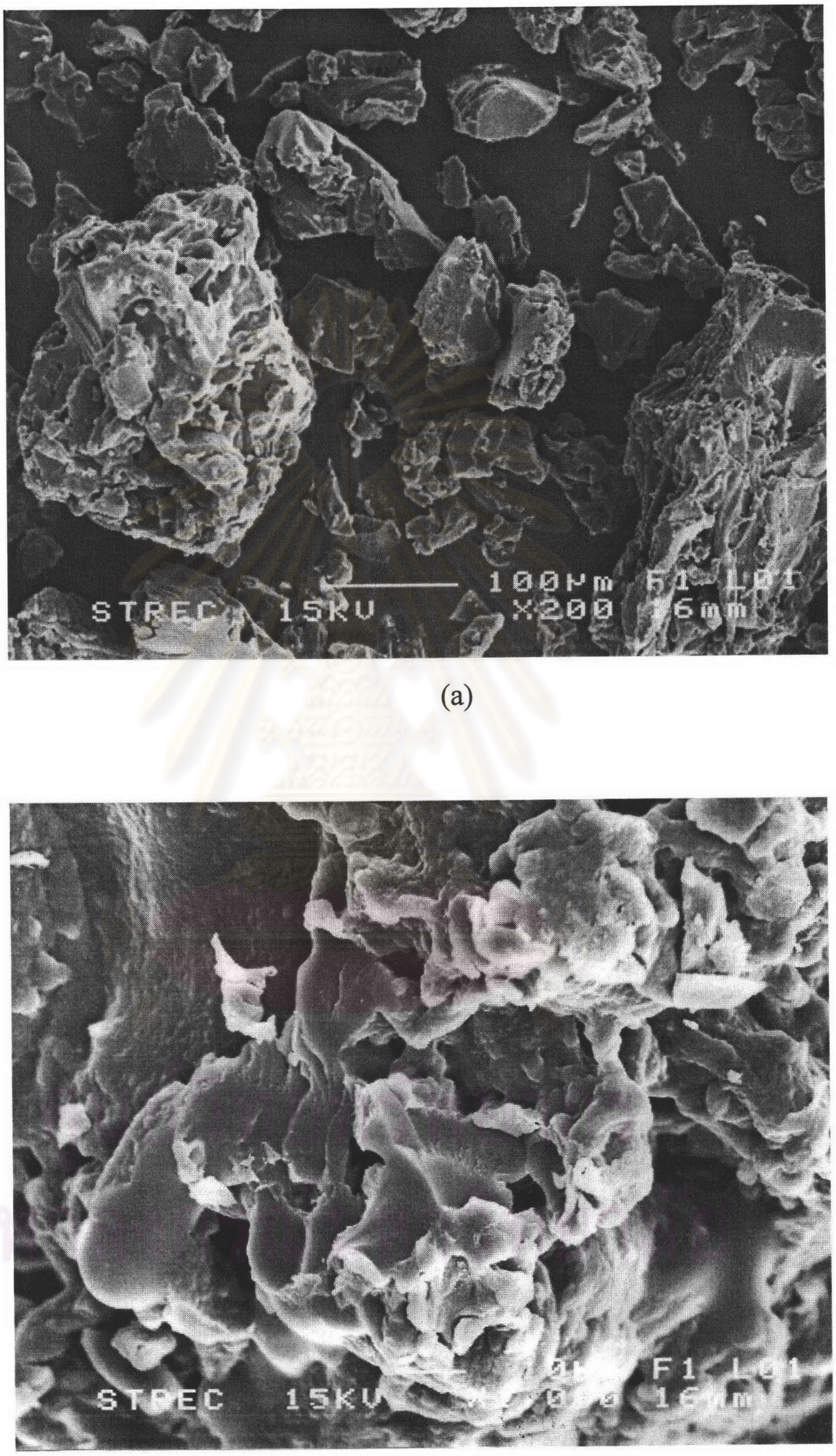


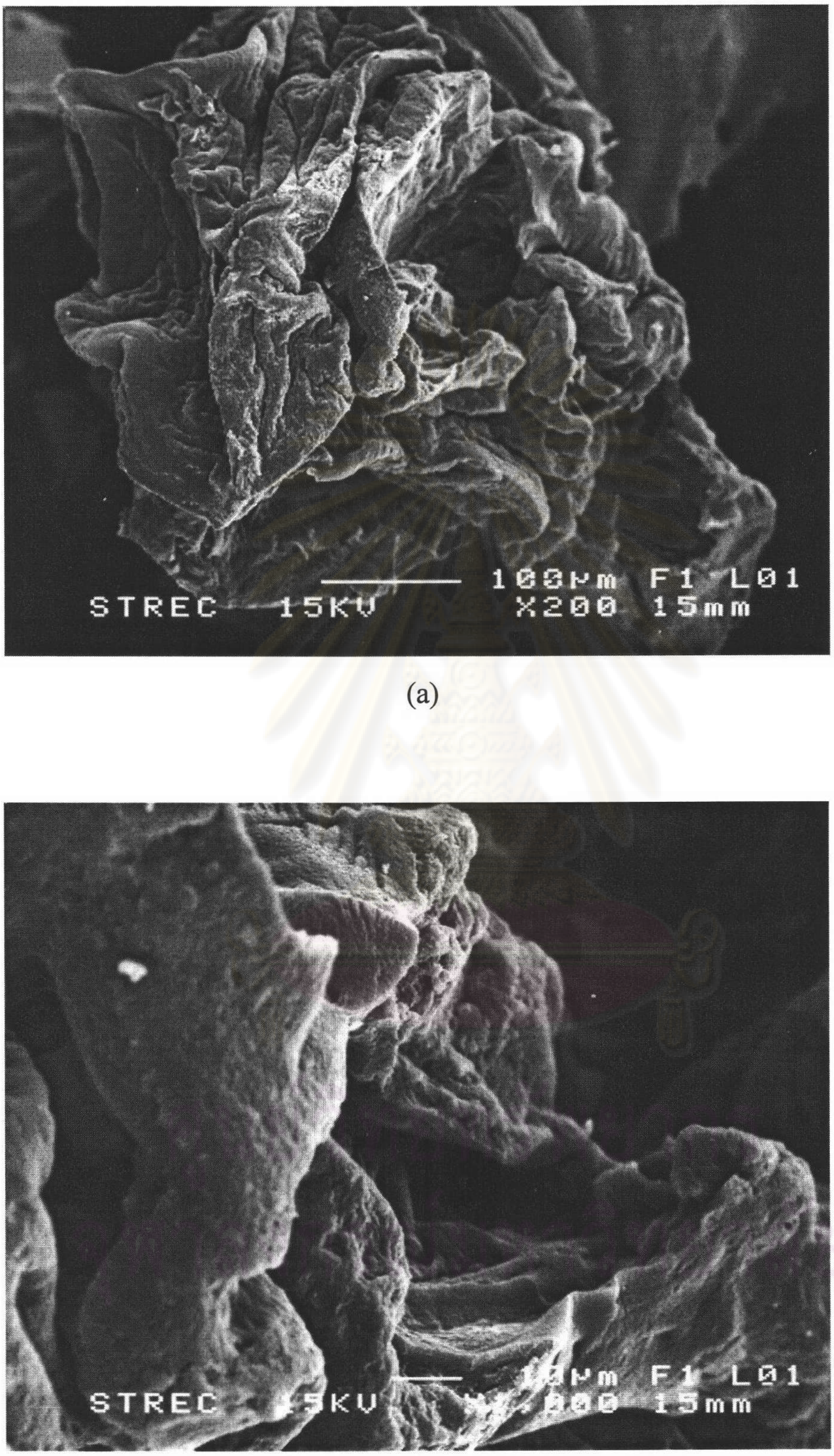
**Figure 4.39** SEM photographs of the starch-g-poly[acrylamide-co-(itaconic acid)] (a) at AM-to-IA ratio of 90:10 (WA = 379±10 g $g^{-1}$) (b) at AM-to-IA ratio of 94:6 (WA = 249±1 g $g^{-1}$)



(a)

(b)

**Figure 4.40** SEM photographs of the starch-g-poly[acrylamide-co-(itaconic acid)] (a) at low magnification (b) at high magnification (WA = 115±0 g $g^{-1}$)



(a)

(b)

**Figure 4.41** SEM photographs of the starch-g-polyacrylamide (a) at low magnification (b) at high magnification (WA = 39±1 g $g^{-1}$)

## 4.5 Determination of Grafting Characteristics of Graft Copolymer by Thermal Gravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) technique was employed to characterize the thermal properties of the obtained graft copolymers. The results revealed that the percentage of the weight loss at the decomposition temperatures of starch proportion, itaconic acid proportion, and acrylamide proportion presented in the starch-*g*-poly[acrylamide-*co*-(itaconic acid)] thermogram can be used to do a calculation of grafting characteristics expressed as the percentages of add-on and grafting ratio.

The thermal behavior of poly[acrylamide-*co*-(itaconic acid)] and starch-*g*-poly[acrylamide-*co*-(itaconic acid)] is very clearly exhibited in the thermograms as shown in Figures 4.42–4.44 and Table 4.11. The percentage of weight loss of each stage of decomposition for these polymers can be calculated subsequently. The percentage of grafting ratio gives information about the extent of a synthetic polymer grafted onto the backbone polymer and hence it is a preferred parameter to study the grafted polymer thermal stability. The thermal stability of graft copolymer can be compared on the basis of the onset temperature of decomposition, and the percentage of weight loss for different stages of the decomposition.

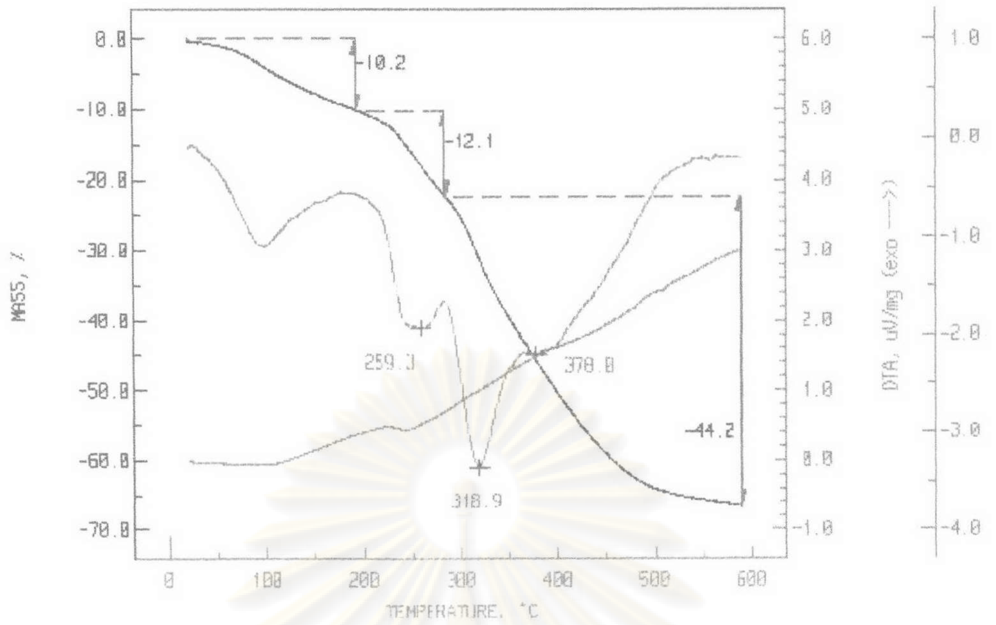


**Figure 4.42** Thermogram of poly[acrylamide-co-(itaconic acid)]

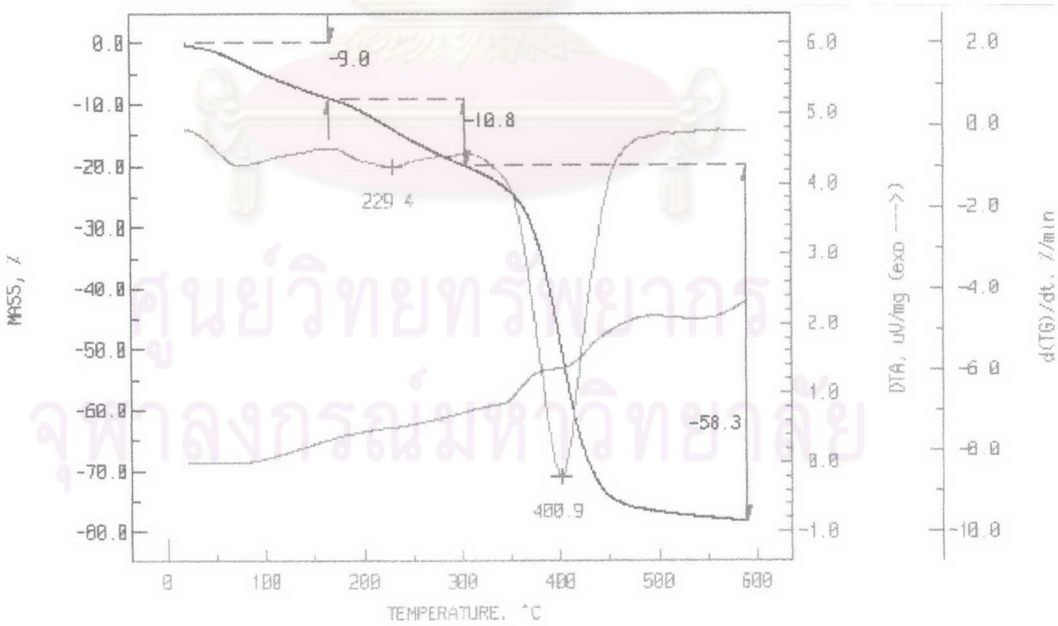
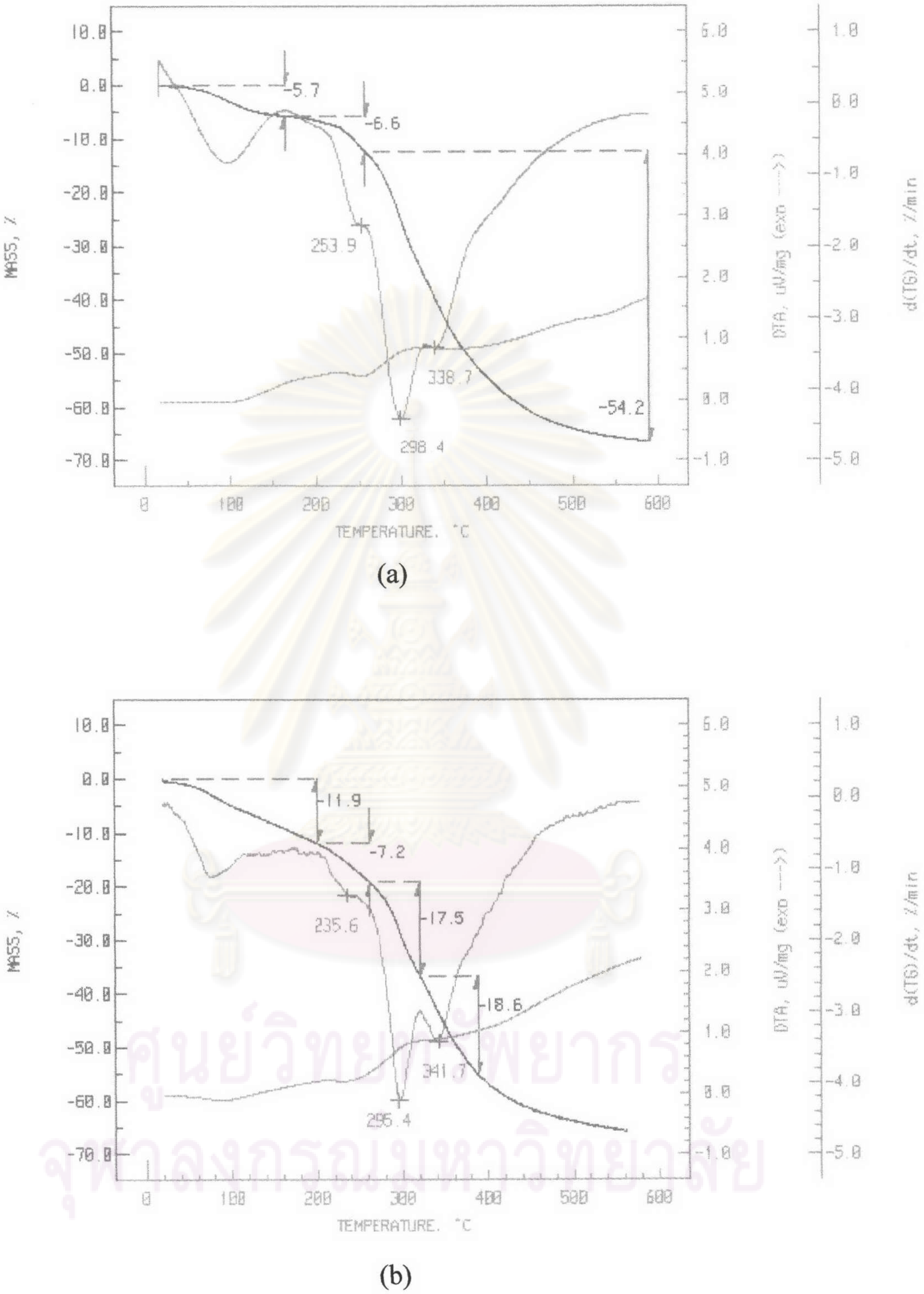


**Figure 4.43** Thermogram of starch-*g*-poly[acrylamide-co-(itaconic acid)] after acid hydrolysis



(a)

(b)

**Figure 4.44** Thermogram of starch-*g*-poly[acrylamide-co-(itaconic acid)] at different AM-to-IA ratio (a) AM:IA 90:10, and (b) AM:IA 98:2

**Table 4.11** Thermogravimetric Data of Graft Copolymer

| Polymer | Number of decomposition stage | Temperature range (°C) | $T_{max}$ (°C) | %weight loss |
|---|---|---|---|---|
| Starch | 1 | 37-100 | 42 | 11.8 |
| | 2 | 233-417 | 308 | 75.5 |
| P(AM-*co*-IA) | 1 | 25-200 | 100 | 10.2 |
| | 2 | 200-289 | 259.3 | 12.1 |
| | 3 | 289-372 | 318.9 | 44.2 |
| St-g-P(AM-*co*-IA)[a] | 1 | 25-167 | 100 | 5.7 |
| | 2 | 167-261 | 253.9 | 6.6 |
| | 3 | 261-328 | 298.4 | 23.1 |
| | 4 | 328-400 | 338.7 | 31.1 |
| St-g-P(AM-*co*-IA)[b] | 1 | 25-200 | 100 | 11.9 |
| | 2 | 200-256 | 235.6 | 7.2 |
| | 3 | 256-322 | 295.4 | 17.5 |
| | 4 | 322-400 | 341.7 | 18.6 |
| St-g-P(AM-*co*-IA)[c] | 1 | 25-167 | 100 | 9.0 |
| | 2 | 167-300 | 229.4 | 10.8 |
| | 3 | 300-472 | 400.9 | 58.3 |

[a] AM-to-IA ratio = 90:10

[b] AM-to-IA ratio = 98:2

[c] after acid hydrolysis

Figure 4.42 shows the thermogravimetric diagram of poly[acrylamide-*co*-(itaconic acid)] where one points out three main degradation steps similar to all formulations, in which at about 100°C, there is a 10.2% weight loss assigned to the water evaporation, at about 259°C, a 12.1% weight loss to the decarboxylation of IA coupled with the chain scission [44] and 44.2% weight loss in the third or main stage of decomposition was about 319°C corresponding to the degradation of acrylamide proportion and finally at a temperature higher than 400°C results in a rapid decomposition to carbon dioxide and volatile hydrocarbons.

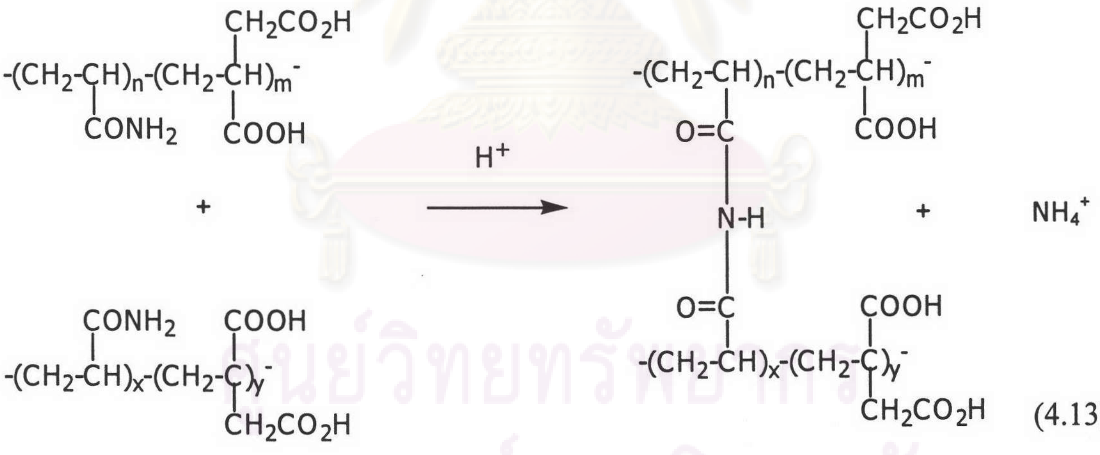
Pure starch showed a characteristic two-step thermogram, wherein the major weight loss (75.5%) occurred in the second step within the temperature range of 233-368°C, the temperature for maximum decomposition was 308°C [20].

In case of starch grafted with poly[acrylamide-*co*-(itaconic acid)], four stages of decomposition were observed. (Figure 4.44a). It is suggested that in initial stage of thermal diagram, in the range from ambient temperature to about 150°C, the weight loss is a result of the dehydration process of the water contained in such a hydrophilic hydrogel. At the second stage, from 167 to 261°C, there is a decomposition in the side groups and branches of the graft copolymer (carboxyl group in itaconic aicd proportion). At the third stage, from 261 to 328°C, there is a degradation of starch in graft copolymer. However, at the forth stage, about 336°C, the weight loss was found in the polymer chain and matrices (degradation of acrylamide proportion).

A careful comparison of the degradation data for starch and starch-g-copolymer was done (Table 4.11), the degradation temperature of starch proportion in graft copolymer was found to decrease. When compared between starch-g-copolymers and the free copolymer (Figure 4.42), the graft copolymers have significantly higher thermal stability than that of ungrafted copolymer, which was caused by the strong bonding between the grafting polymer chain and matrices in the graft copolymer.

In comparison between different compositions of AM-to-IA ratio (Figures 4.44a and 4.44b), the degradation temperature shifted towards the decrease of IA contents in the graft copolymer. The reason for this is a formation of the imide group by cyclization of amide groups [43].

Figure 4.41 shows the thermogram of grafted poly[acrylamide-*co*-(itaconic acid)], which was separated from the starch backbone by heating the graft copolymer under refluxing in acid solution. Strong acidic conditions were used in the hydrolysis reaction of starch that can lead to a progressive insolubilization of the reaction product in a form of an imidization of amide pendants in the copolymer as shown in Equation 4.13, resulting to very highly thermal stability (400°C).



$$\text{-}(CH_2\text{-}\underset{CONH_2}{CH})_n\text{-}(CH_2\text{-}\overset{CH_2CO_2H}{\underset{COOH}{C}}H)_m\text{-} \; + \; \text{-}(CH_2\text{-}\overset{CONH_2}{CH})_x\text{-}(CH_2\text{-}\overset{COOH}{\underset{CH_2CO_2H}{C}})_y\text{-} \xrightarrow{H^+} \text{imide-bridged copolymer } (O{=}C\text{-}N\text{-}H\text{-}C{=}O) \; + \; NH_4^+$$

(4.13)

The thermogram of starch-*g*-poly[acrylamide-*co*-(itaconic acid)] was used to in the calculation of grafting characteristics expressed as the percentage of add-on and grafting ratio as shown in Equations 4.14 and 4.15:

$$\%\text{add-on} = \frac{\sum(\text{Weight loss at decomposition stages 2 and 4}) \times 100}{\sum(\text{Weight loss at decomposition stages 2, 3, and 4})} \qquad (4.14)$$

$$\%\ \text{Grafting ratio} = \frac{\sum (\text{Weight loss at decomposition stages 2 and 4}) \times 100}{\sum (\text{Weight loss at decomposition stage 3})} \qquad (4.15)$$

**Table 4.12 Determination of %Add-on and %Grafting Ratio by Differential Method in TGA**

| Grafting Characteristics | Method | |
|---|---|---|
| | Gravimetric measurement | TGA |
| %add-on | 55.6 | 59.2 |
| %Grafting ratio | 125.2 | 145.0 |

The calculated values were compared with the gravimetric method to verify the possibility of using TGA method as an option for determination of grafting characteristics of a graft copolymer. From the two techniques, TGA gave the higher values (%add-on and % grafting ratio) than the gravimetric method by 3.6 and 19.8, respectively.

## 4.6 Biodegradation Study of the Graft Copolymer

The standard curve was prepared for the DNS analysis by applying the assay procedure given below to each of the standard glucose solutions as shown in Figure 4.45. The linear relation presented in this figure was used as a calibration curve for the determination of the amount of reducing sugar.

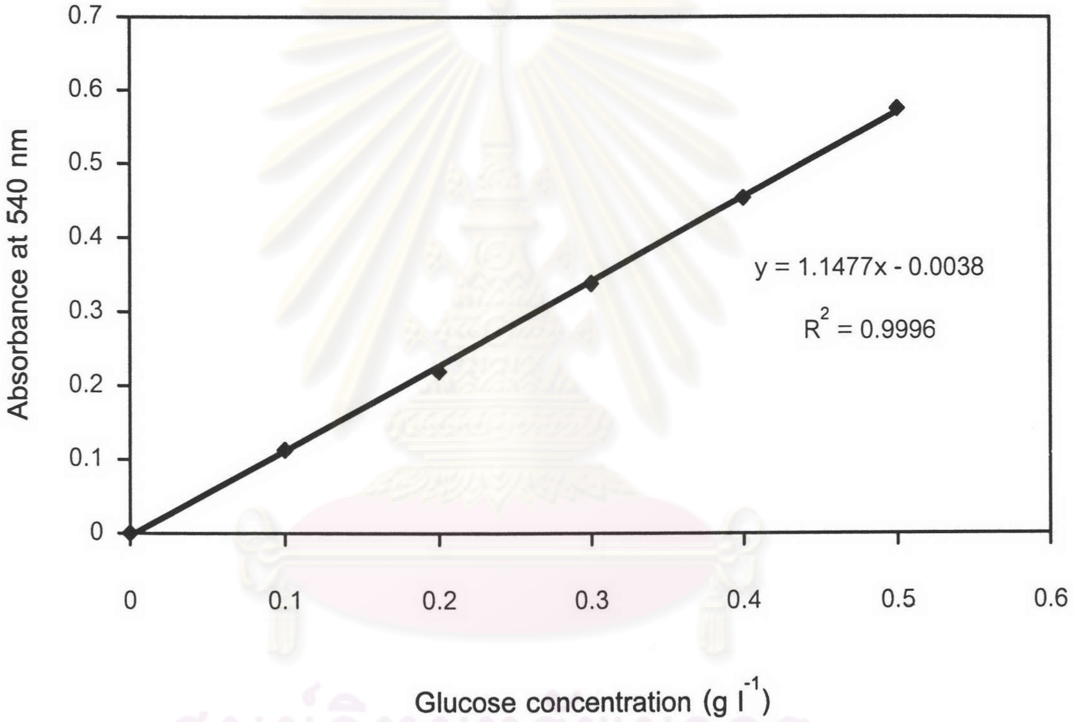
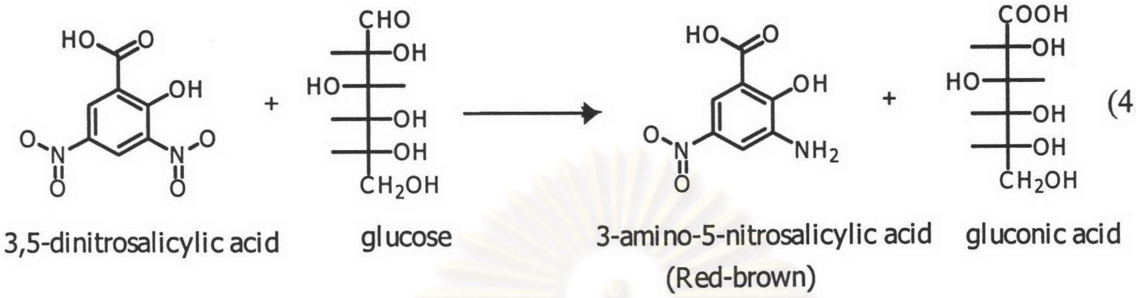


**Figure 4.45** Standard curve of pure α-amylase activity on glucose solution at pH 7

A reducing sugar is any mono-, oligo-, or polysaccharide that has a free or potentially free aldehyde or ketone group, for example the C1 (aldehyde) or C2 (ketone) carbon is not involved in the covalent linkage other than that of cyclization. The DNS assay is based on the reduction of 3,5-dinitrosalicylic acid by the sugar to 3-

amino-5-nitrosalicylic acid which has a strong absorbance at 540 nm as shown in Equation 4.13 [2].



(4.16)

### *4.6.1 Enzymatic Hydrolysis of the Graft Copolymers*

One of the pathways of biodegradation is hydrolysis. Enzyme hydrolysis of starch-*g*-polymer is accompanied by the liberation of glucose. Determination of the amount of reducing sugar (g $l^{-1}$) during exposure will therefore give an indication of the extent of biodegradation.

Another important factor, which also affects the kinetics of starch hydrolysis is the mode of interaction between the enzyme and the polymeric chains. Hydrolysis of insoluble starch substrates differ distinctly from that of soluble substrates. Indeed, the hydrolysis of starch composed of mainly insoluble fraction involves four steps [22] :

(i) Diffusion of enzyme molecules from the bulk aqueous phase to the gel surface.

(ii) Adsorption of the enzyme onto the gel substrate, resulting in the formation of the enzyme-substrate complex.

(iii) Hydrolysis of the $\alpha$-(1$\rightarrow$4)-glucose bond, and finally

(iv) Diffusion of the soluble degradation products from the gel substrate into the bulk aqueous phase.

### *4.6.1.1 Effect of enzyme concentration*

The swollen gel of graft copolymer was incubated at 37°C for 24 h in a phosphate buffer pH 7.0 containing α-amylase at different concentrations ranging from 2040 to 30600 U $cm^{-3}$. The effect of α-amylase concentration is shown in Figure 4.46, the increasing in α-amylase concentration led to increase in the amount of reducing sugar. However, this relation leveled off after 20400 U $cm^{-3}$ had been added. Thus, a maximum amount of reducing sugar of 2.4352 g $l^{-1}$ was observed

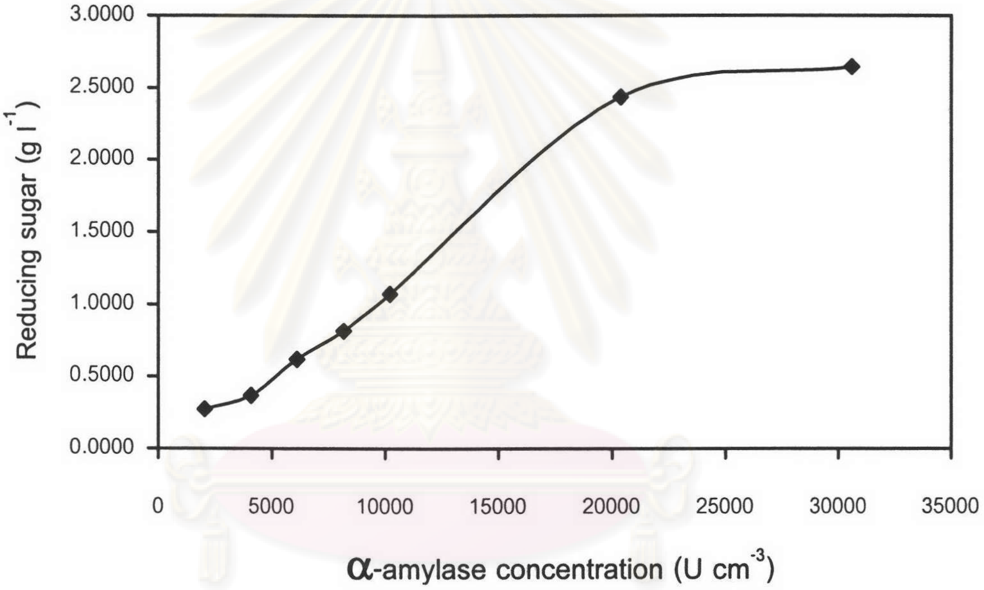


**Figure 4.46** Effect of α-amylase concentration on the amount of reducing sugar

The result of the enzymatic hydrolysis of the starch-*g*-polymer is presented in Table 4.13. The swollen gel of graft copolymer was incubated at 37°C in a phosphate buffer pH 7.0 containing α-amylase concentration of 20400 U $cm^{-3}$. When the swollen graft copolymers were hydrolyzed by α-amylase, the amount of the reducing sugar increased.

**Table 4.13** Enzymatic Hydrolysis of the Graft Copolymer

| Ingredient | | Enzyme concentration (U cm$^{-3}$) | Time (day) | Amount of reducing sugar (g l$^{-1}$) | Iodine test | Benedict's test |
|---|---|---|---|---|---|---|
| St:Mn | AM:IA | | | | | |
| 8:8 | 90:10 | - | 1 | 0.0000 | +ve | -ve |
| | | 2040 | | 0.2745 | -ve | +ve |
| | | 4080 | | 0.3703 | | |
| | | 6120 | | 0.6186 | | |
| | | 8160 | | 0.8147 | | |
| | | 10200 | | 1.0717 | | |
| | | 20400 | | 2.4352 | | |
| | | 30600 | | 2.6460 | | |
| 8:8 | 90:10 | 20400 | 1 | 2.4352 | -ve | +ve |
| | | | 2 | 4.4150 | | |
| | | | 3 | 4.9347 | | |
| | | | 4 | 5.2763 | | |
| | | | 5 | 5.4545 | | |
| 8:8 | 100:0 | 10200 | 1 | 2.3525 | -ve | +ve |
| | 95:5 | 10200 | | 1.7600 | | |
| | 90:10 | 10200 | | 1.0717 | | |
| 4:8 | 90:10 | 10200 | 1 | 1.1664 | -ve | +ve |
| 10:8 | 90:10 | 10200 | | 1.2478 | | |

Iodine test: +ve give a blue color. St:Mn = Starch:Monomer ratio

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

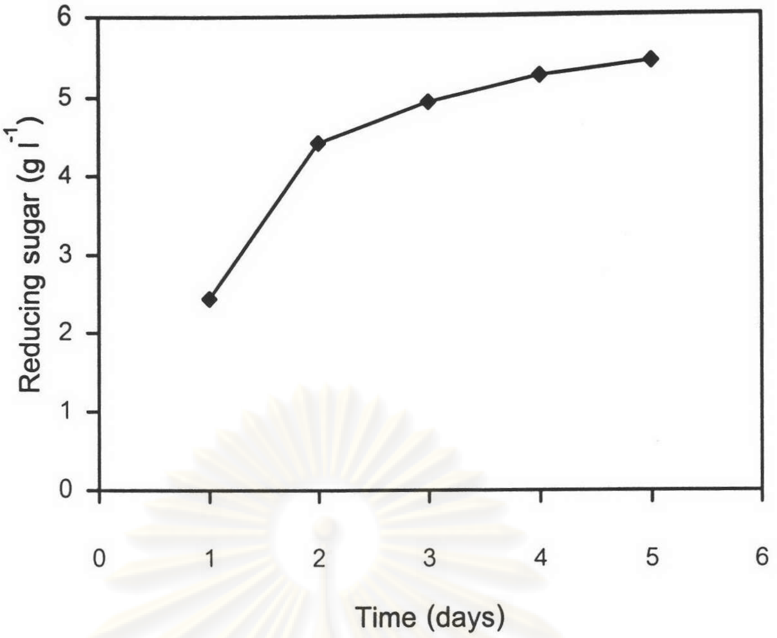
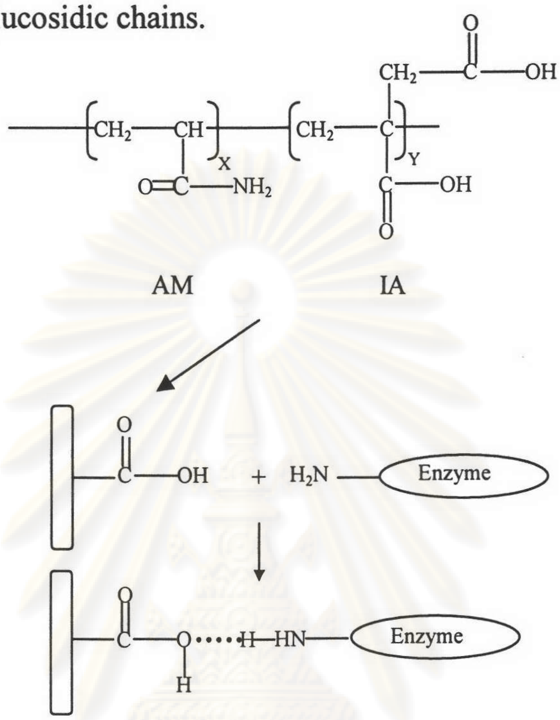


**Figure 4.47** Effect of time on the degradation of starch-*g*-poly[acrylamide-*co*-(itaconic acid)] at the starch-to-monomer ratio = 1:1 and AM:IA = 90:10

The effect of time on the degradation of the starch-g-copolymer was incubated in a phosphate buffer pH 7.0 containing 20400 U $cm^{-3}$ of $\alpha$-amylase was varied at 1, 2, 3, 4, and 5 days. As can be seen in Figure 4.47, when the time is increased, the amount of reducing sugar is also increased. After 5 days of degradation, the amount of reducing sugar is 5.4545 g $l^{-1}$.

#### *4.6.1.2 Effects of Mole Percent of AM-to-IA ratio and Starch-to-Monomer Ratio*

The amount of reducing sugar depends on the mole percent of IA in graft copolymer as shown in Figure 4.48. Increasing the IA content causes also an decrease in the amount of reducing sugar. The reason of this decrease can be caused by an increase in a specific interaction (intermolecular hydrogen bonding) between enzyme molecule and itaconic acid in the graft copolymer (Equation 4.17) [45,46], which decreases the enzymatic activity in the degradation. The activity of enzyme ∝-amylase on the starch-g-polyacrylamide is more effective than superabsorbent polymers containing only the itaconic acid moiety, which need more enzymatic activity to break the glucosidic chains.



(4.17)

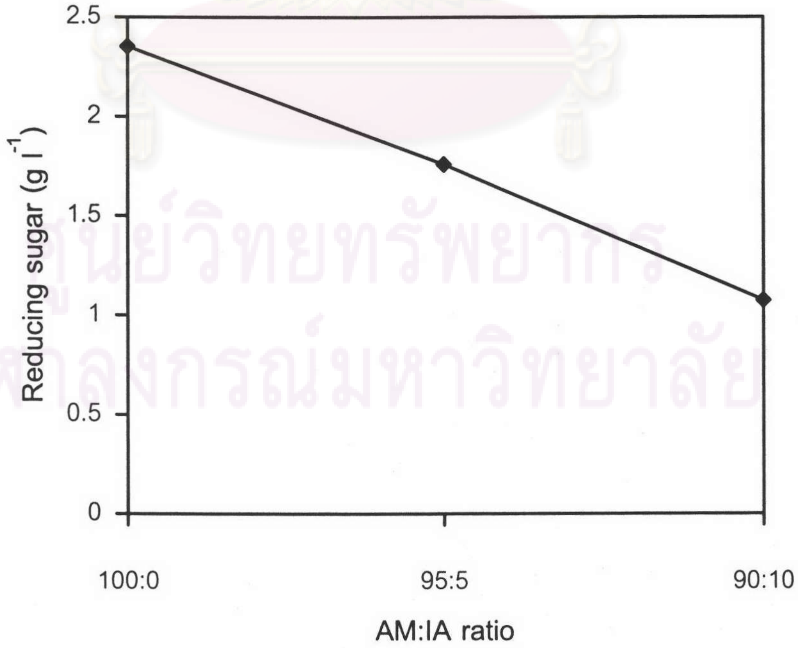


**Figure 4.48** Effect of mole percent of acrylamide-to-itaconic acid ratio on degradation

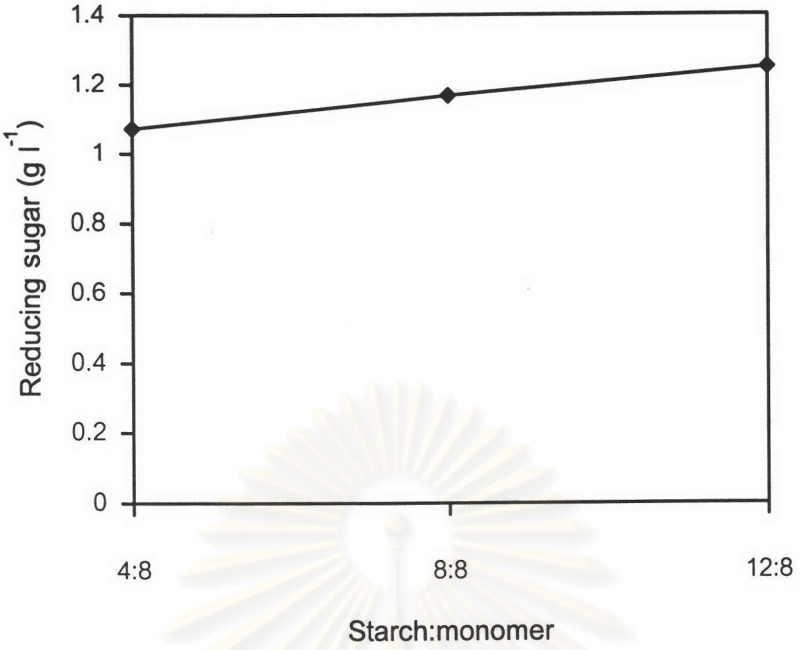


**Figure 4.49** Effect of starch-to-monomer ratio on degradation

The effect of starch-to-monomer ratio on degradation is shown in Figure 4.49. The amount of reducing sugar increases with increasing the starch-to-monomer ratio, which the enzyme selectively hydrolyzes the starch, so the enzymatic activity increases with an increase in the starch content.

Another approach, which confirms the existence of a short chain of starch, is iodine test and Benedict's test. 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. Benedict's solution is used for checking a reducing sugar, if the sample has a reducing sugar, the solution will gave a red precipitate of cuprous oxide, which is then called a positive test. For the present research, both test solutions gave a positive result 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.

### 4.6.2 Surface Morphology of the Degraded Copolymer

The surface appearance of cassava starch, the graft copolymer, and the degraded graft copolymer was viewed by scanning electron microscopy as shown in Figures 4.50-4.52. As a comparison, the surface of degraded graft copolymer however, is rougher with many flexibly cellular structures than that of the undegraded graft copolymer. As presented in Figures 4.52(b)- 4.52(d), the surface of the degraded graft copolymer exhibited very rough, distinct surface, and many flexibly cellular structures indicating that the graft copolymer (Figure 4.52(a)) was degraded by ∝-amylase.

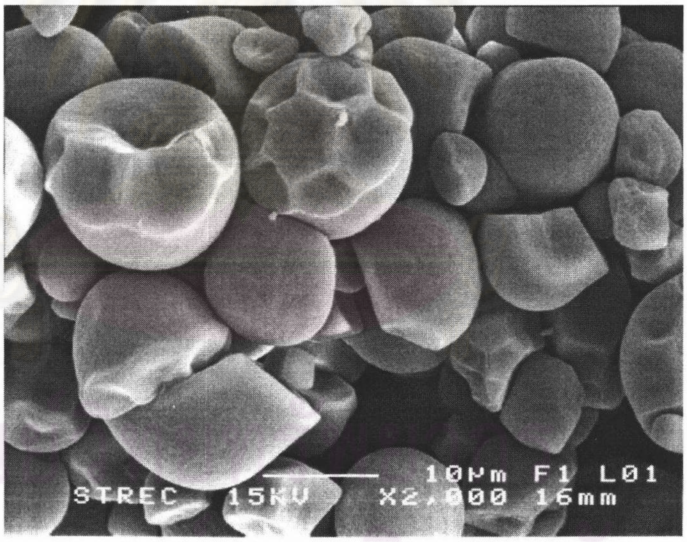
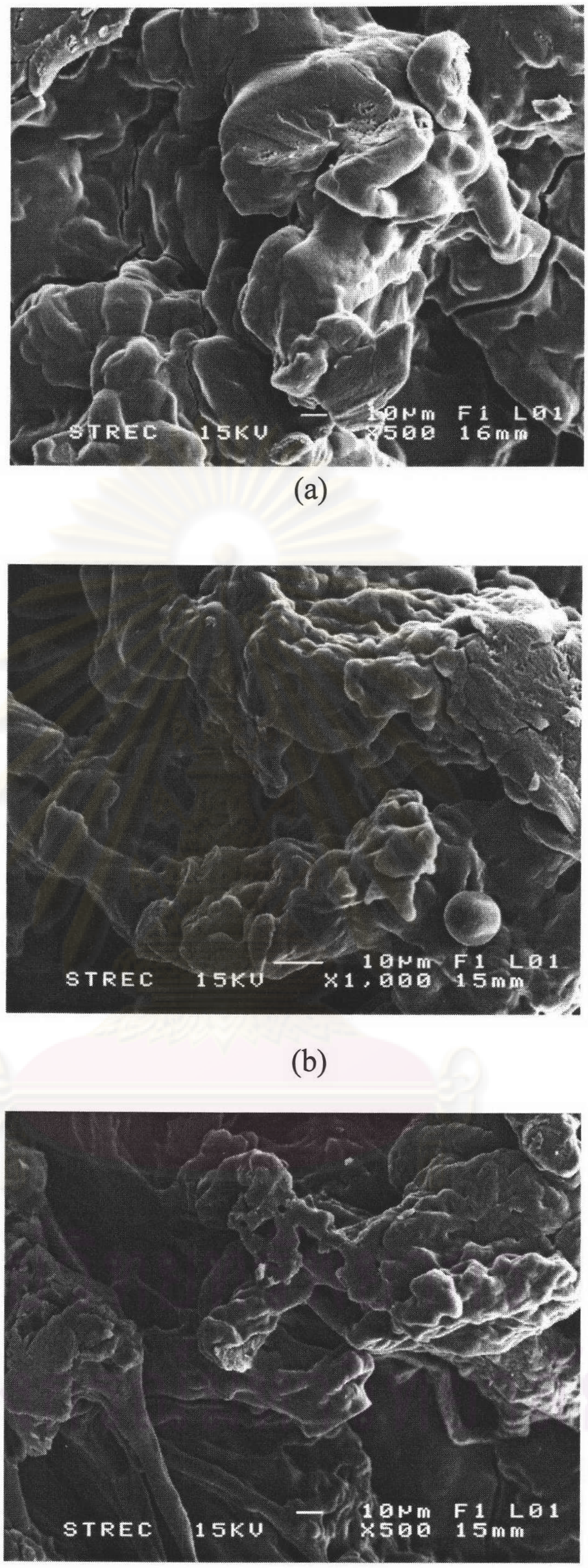


**Figure 4.50** SEM photograph of the cassava starch

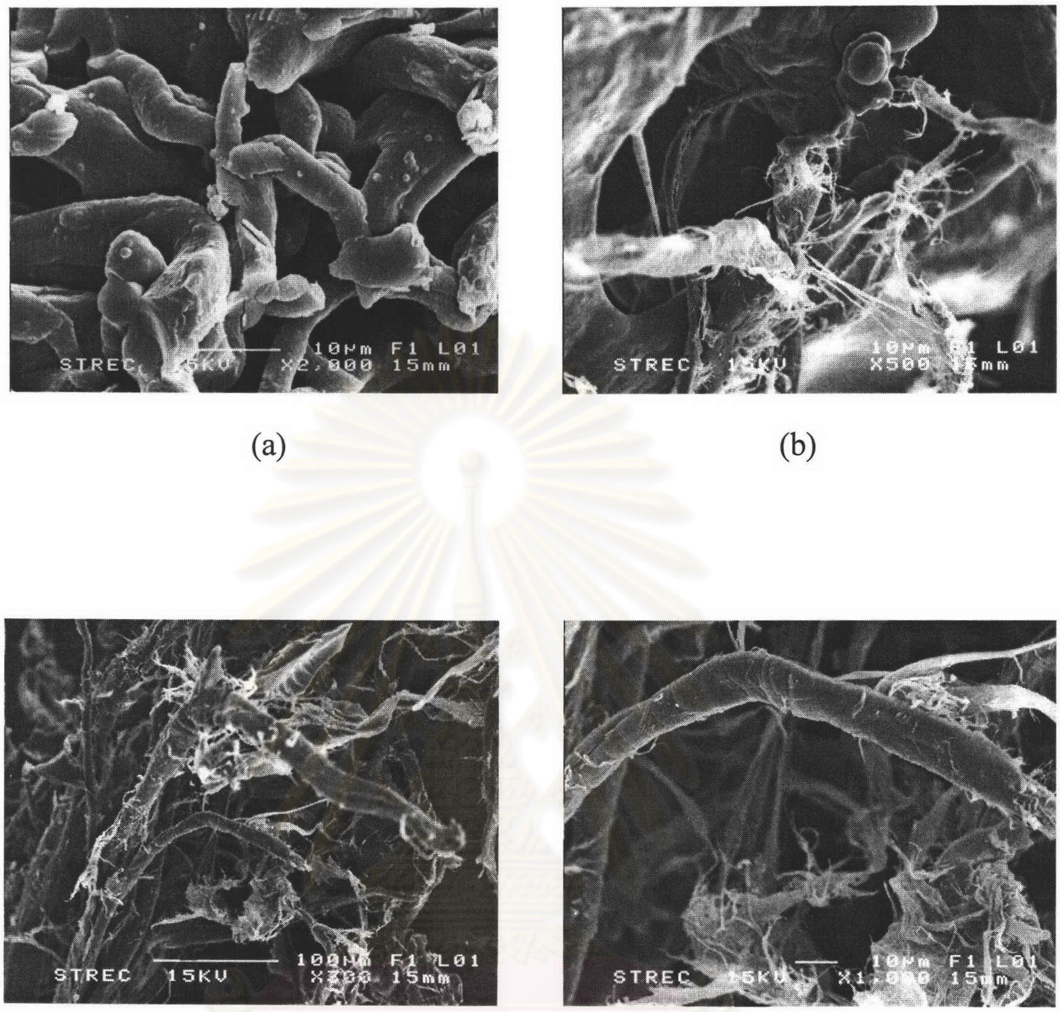


(a)

(b)

(c)

**Figure 4.51** SEM photographs of starch-g-poly[acrylamide-co-(itaconic acid)] incubated for 1 day in phosphate buffer (pH 7.0), containing ∝-amylase at different concentrations : (a) control, (b) 2040 U $cm^{-3}$, and (c) 10200 U $cm^{-3}$



(a) (b)

(c) (d)

**Figure 4.52** SEM photographs of starch-g-poly[acrylamide-co-(itaconic acid)] was incubated in phosphate buffer (pH 7.0) containing ∝-amylase at 20400 U $cm^{-3}$ for: (a) undegraded, (b) 2 days, (c) 5 days (low magnification), and (d) 5 days (high magnification)