

CHAPTER 4

RESULTS and DISCUSSION

4.1 Characterization of the Functional Groups of the Copolymer by FTIR

FT-IR technique was used to follow up changes in graft copolymerization. The FT-IR spectra of cassava starch, and the graft copolymer before extraction, after extraction, and after saponification are given in Tables 4.1-4.3 and Figures 4.1-4.3.

The IR spectrum of cassava starch gives the O-H stretching peak at $3,423\text{ cm}^{-1}$, the C-H stretching peak at $2,927\text{ cm}^{-1}$ and the C-O stretching peak at $1,157$, $1,082$, and $1,013\text{ cm}^{-1}$.

The IR spectra of grafting of acrylamide onto the starch backbone before and after extraction are shown in Figures 4.1. All the characteristic absorption peaks of cassava starch still exist. Additional peaks at $3,200\text{ cm}^{-1}$, $1,654\text{ cm}^{-1}$, and $1,600\text{ cm}^{-1}$ indicate the N-H stretching, C=O stretching, and N-H bending, respectively, which are the characteristics of the $-\text{CONH}_2$ group containing in the acrylamide. When the starch-g-polyacrylamide was saponified carefully for 30 minutes, no additional peaks can be observed. It indicates that under this saponification condition, only a minute amount of acrylamide moiety can be converted into acrylate (shown in Figure 4.1).

For the acrylic acid graft copolymerization, IR spectra in both before and after extraction (Figures 4.2) give all the absorption peaks of cassava starch and give the

additional peaks at $2,700\text{ cm}^{-1}$, $1,718\text{ cm}^{-1}$ and $1,253\text{ cm}^{-1}$ indicating the O-H stretching, C=O stretching and C-O stretching of the -COOH group containing in the acrylic acid, respectively. When starch-*g*-poly(acrylic acid) was saponified, the disappearance of the absorption peaks of -COOH group and the existence of the absorption peaks at $1,570$ and $1,407\text{ cm}^{-1}$ of C=O stretching of carboxylate ion indicate that all acrylic acid moieties has been converted to acrylate (shown in Figure 4.2).

The IR spectra of starch-*g*-poly(acrylamide-*co*-acrylic acid) in both before and after extraction (Figures 4.3) give all the absorption peaks of cassava starch, acrylamide, and acrylic acid. It is therefore confirmed that both acrylamide and acrylic acid have been grafted onto the cassava starch. After starch-*g*-poly(acrylamide-*co*-acrylic acid) was saponified, one can observe the characteristic absorption peaks of acrylamide and acrylate moieties (shown in Figure 4.3).

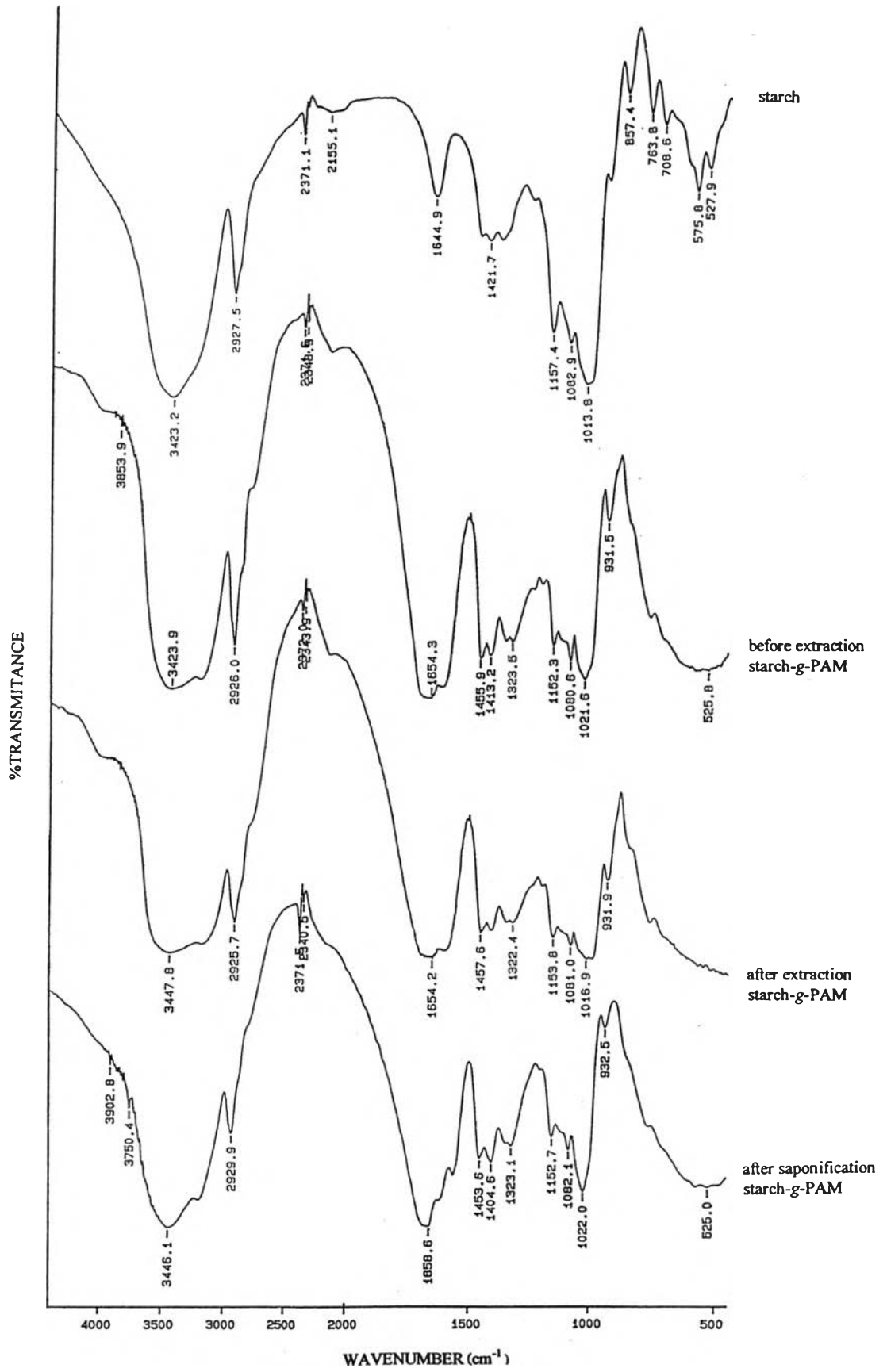


Figure 4.1 Infrared Spectra of Cassava Starch and Starch-g-polyacrylamide Before Extraction, After Extraction, and After Saponification

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

Starch		Starch-g-polyacrylamide before extraction		Starch-g-polyacrylamide after extraction		Starch-g-polyacrylamide after saponification	
wavenumber (cm ⁻¹)	assignment	wavenumber (cm ⁻¹)	assignment	wavenumber (cm ⁻¹)	assignment	wavenumber (cm ⁻¹)	assignment
3,423 (s, broad)	O-H stretching	3,423 (s, broad)	O-H stretching	3,423 (s, broad)	O-H stretching	3,423 (s, broad)	O-H stretching
2,927 (m)	C-H stretching	2,927 (m)	C-H stretching	2,927 (m)	C-H stretching	2,927 (m)	C-H stretching
1,157, 1,082 and 1,013 (s)	C-O stretching	1,157, 1,082 and 1,013 (s)	C-O stretching	1,157, 1,082 and 1,013 (s)	C-O stretching	1,157, 1,082 and 1,013 (s)	C-O stretching
		3,200 (m)	N-H stretching	3,200 (m)	N-H stretching	3,200 (m)	N-H stretching
		1,654 (s)	C=O stretching of carboxamide	1,654 (s)	C=O stretching of carboxamide	1,654 (s)	C=O stretching of carboxamide
		1,600 (m)	N-H bending	1,600 (m)	N-H bending	1,600 (m)	N-H bending

s = strong; m = medium

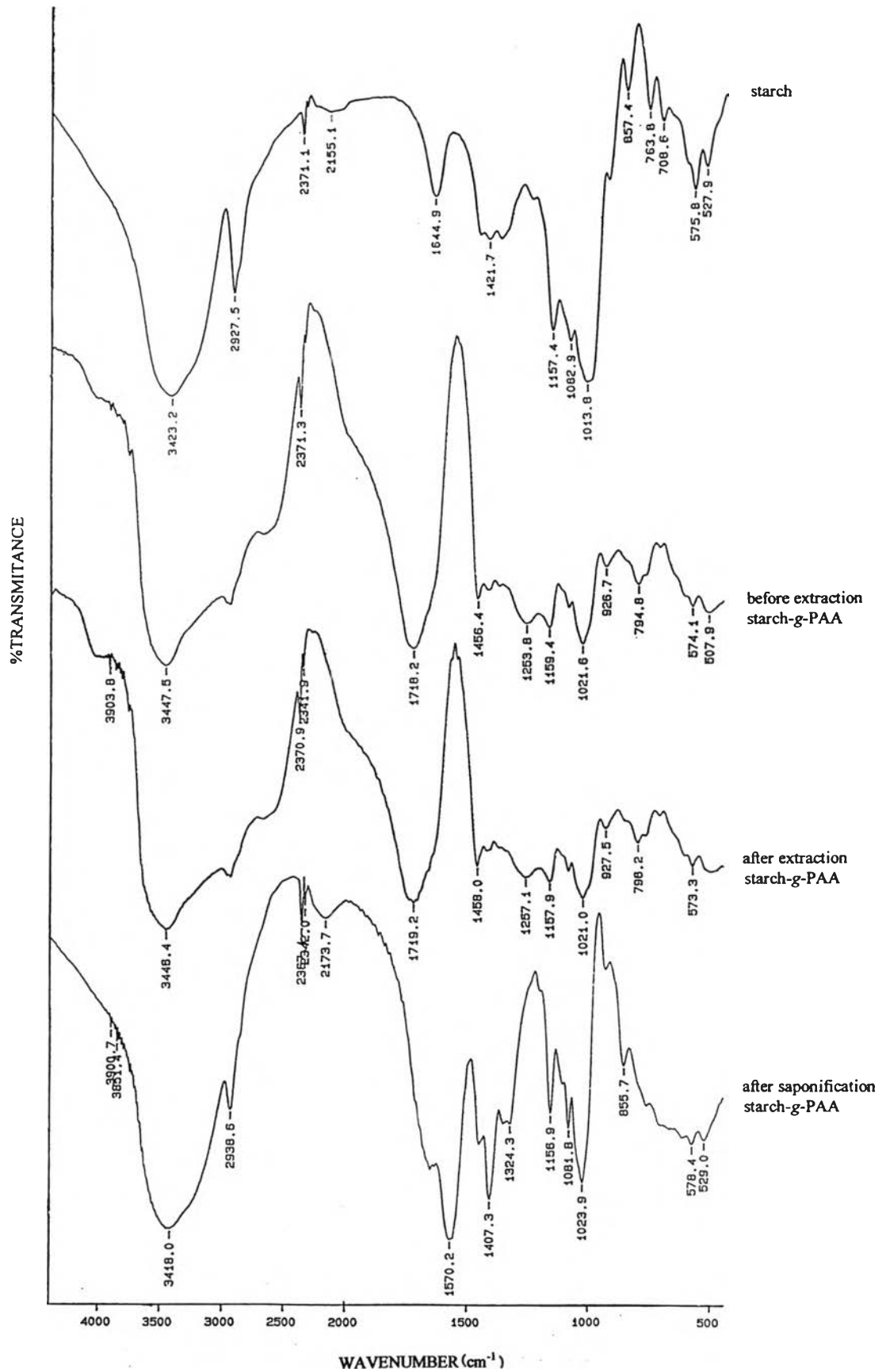


Figure 4.2 Infrared Spectra of Cassava Starch and Starch-g-poly(acrylic acid) Before Extraction, After Extraction, and After Saponification

Table 4.2 The Infrared Absorption of Functional Groups in Cassava Starch and Starch-g-poly(acrylic acid) Before Extraction, After Extraction, and After Saponification

Starch		Starch-g-poly(acrylic acid) before extraction		Starch-g-poly(acrylic acid) after extraction		Starch-g-poly(acrylic acid) after saponification	
wavenumber (cm ⁻¹)	assignment	wavenumber (cm ⁻¹)	assignment	wavenumber (cm ⁻¹)	assignment	wavenumber (cm ⁻¹)	assignment
3,423 (s, broad)	O-H stretching	3,423 (s, broad)	O-H stretching	3,423 (s, broad)	O-H stretching	3,423 (s, broad)	O-H stretching
2,927 (m)	C-H stretching	2,927 (m)	C-H stretching	2,927 (m)	C-H stretching	2,927 (m)	C-H stretching
1,157, 1,082, and 1,013 (s)	C-O stretching	1,157, 1,082, and 1,013 (s)	C-O stretching	1,157, 1,082, and 1,013 (s)	C-O stretching	1,157, 1,082, and 1,013 (s)	C-O stretching
		2,700 (m, broad)	O-H stretching of carboxylic acid	2,700 (m, broad)	O-H stretching of carboxylic acid	1,570 (s) and 1,407 (m)	C=O stretching of carboxylate ion
		1,718 (s)	C=O stretching of carboxylic acid	1,718 (s)	C=O stretching of carboxylic acid		
		1,253 (s)	C-O stretching of carboxylic acid	1,253 (s)	C-O stretching of carboxylic acid		

s = strong; m = medium

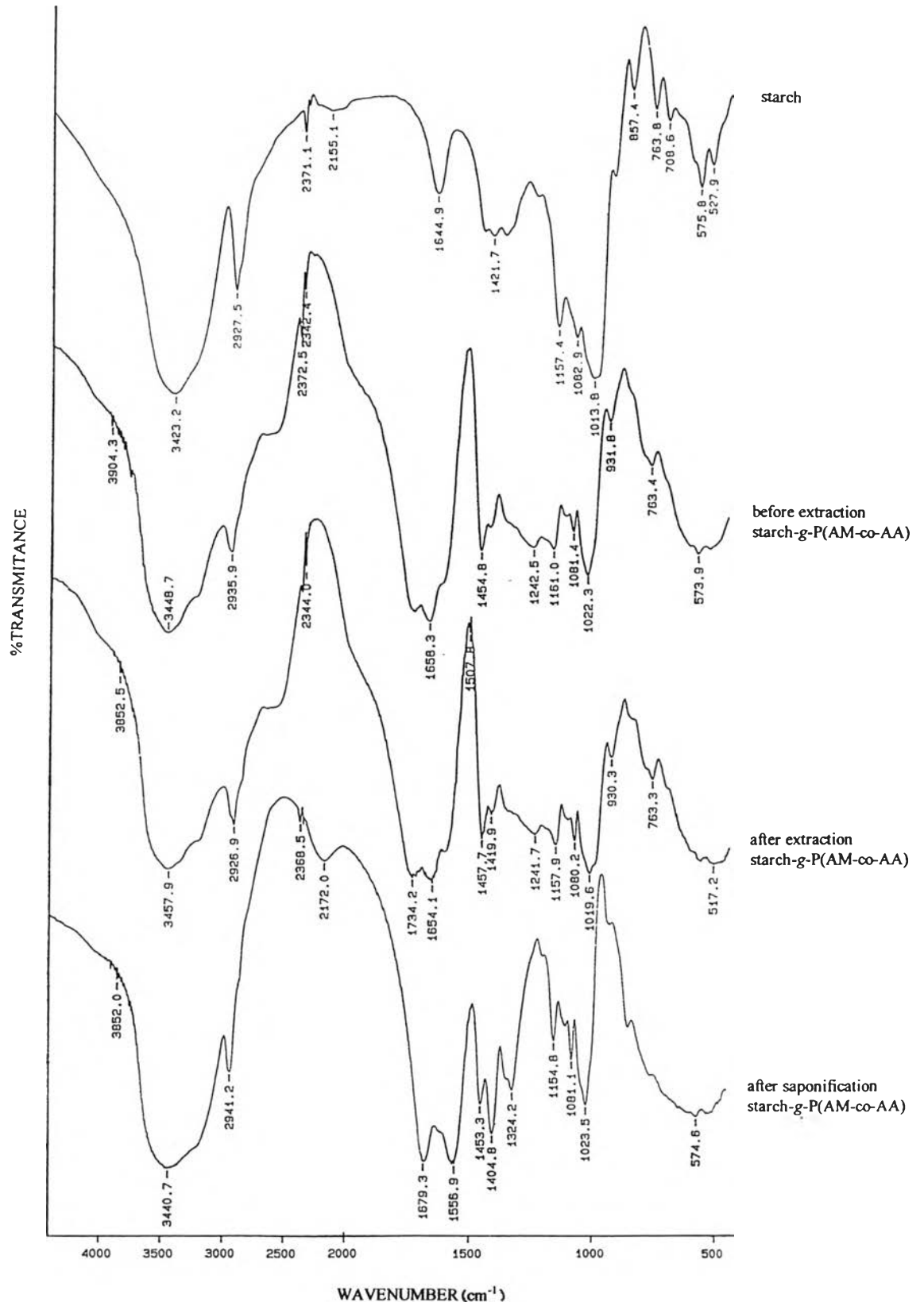


Figure 4.3 Infrared Spectra of Cassava Starch and Starch-g-poly(acrylamide-co-acrylic acid) Before Extraction, After Extraction, and After Saponification

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

Starch		Starch- <i>g</i> -poly(acrylamide- <i>co</i> -acrylic acid) before extraction		Starch- <i>g</i> -poly(acrylamide- <i>co</i> -acrylic acid) after extraction		Starch- <i>g</i> -poly(acrylamide- <i>co</i> -acrylic acid) after saponification	
wavenumber (cm ⁻¹)	assignment	wavenumber (cm ⁻¹)	assignment	wavenumber (cm ⁻¹)	assignment	wavenumber (cm ⁻¹)	assignment
3,423 (s, broad)	O-H stretching	3,423 (s, broad)	O-H stretching	3,423 (s, broad)	O-H stretching	3,423 (s, broad)	O-H stretching
2,927 (m)	C-H stretching	2,927 (m)	C-H stretching	2,927 (m)	C-H stretching	2,927 (m)	C-H stretching
1,157, 1,082 and 1,013 (s)	C-O stretching	1,157, 1,082 and 1,013 (s)	C-O stretching	1,157, 1,082 and 1,013 (s)	C-O stretching	1,157, 1,082 and 1,013 (s)	C-O stretching
		3,200 (m)	N-H stretching	3,200 (m)	N-H stretching	3,200 (m)	N-H stretching
		1,654 (s)	C=O stretching of carboxamide	1,654 (s)	C=O stretching of carboxamide	1,654 (s)	C=O stretching of carboxamide
		1,600 (m)	N-H bending	1,600 (m)	N-H bending	1,600 (m)	N-H bending
		2,700 (m, broad)	O-H stretching of carboxylic acid	2,700 (m, broad)	O-H stretching of carboxylic acid	1,570 (s) and 1,407 (m)	C=O stretching of carboxylate ion

s = strong; m = medium

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

Starch		Starch- <i>g</i> -poly(acrylamide- <i>co</i> -acrylic acid) before extraction		Starch- <i>g</i> -poly(acrylamide- <i>co</i> -acrylic acid) after extraction		Starch- <i>g</i> -poly(acrylamide- <i>co</i> -acrylic acid) after saponification	
wavenumber (cm ⁻¹)	assignment	wavenumber (cm ⁻¹)	assignment	wavenumber (cm ⁻¹)	assignment	wavenumber (cm ⁻¹)	assignment
		1,718 (s)	C=O stretching of carboxylic acid	1,718 (s)	C=O stretching of carboxylic acid		
		1,253 (s)	C-O stretching of carboxylic acid	1,253 (s)	C-O stretching of carboxylic acid		

s = strong; m = medium

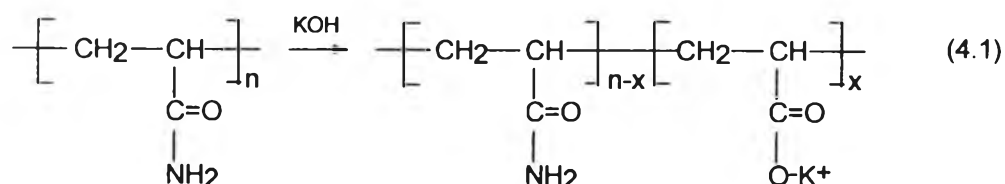
4.2 Effect of Saponification Time on Acrylamide Moiety

The degree of saponification depends on reaction time, temperature, and concentration of alkaline solution [27]. The degree of saponification of starch-g-polyacrylamide prepared at the total dose of 6.0 kGy and the dose rate of 2.24 kGy hr⁻¹ with 5% potassium hydroxide solution at room temperature for various periods of time is presented in term of the amount nitrogen as shown in Table 4.4.

Table 4.4 Compositions Obtained by Elemental Analysis

Period of time for saponification (minute)	Composition of the elements (%)		
	Carbon	Hydrogen	Nitrogen
0 (unsaponified sample)	46.418	6.910	10.968
30	43.587	6.453	10.538
60	42.413	6.679	9.685
90	41.550	6.230	9.304

Table 4.4 shows a continuous increase in the degree of saponification as the saponification time increases. The longer the saponification time, the more the amide groups on the polyacrylamide chains changes to the carboxylate groups through the following chemical reaction:



Thirty minutes of saponification is thus just an optimum saponification time used to convert acrylic acid moieties to acrylate salt without significantly conversion the acrylamide moiety.

4.3 Graft Copolymerization of Acrylamide and Acrylic Acid onto Cassava Starch by Simultaneous Irradiation

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

The effect of monomer-to-starch ratio on the grafting of AM and AA onto cassava starch is presented in terms of the conversion of monomer, homopolymer formed, grafting efficiency, percentage add-on, grafting ratio, and water absorption as shown in Table 4.5.

4.3.1.1 Relationship between Monomer-to-Starch Ratio and Percentage Conversion

Table 4.5 and Figure 4.4 show the correlation between the monomer-to-starch ratio and the conversion of monomer. When increasing the quantity of monomer mixture, percentage conversion does not change for the whole range of monomer quantity and it nearly approached 100%. This result thus indicates that a nearly complete conversion is obtained using this radiation dose.

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

Mono:St (g g⁻¹)	Conv (%)	Homo (%)	GE (%)	Add-on (%)	GR (%)	WA (g g⁻¹)
0.5:1	95.7	30.8	33.6	22.6	29.2	143 ₊₁₂
1:1	96.0	30.8	39.6	29.2	41.2	253 ₊₁₉
1.5:1	95.8	28.7	52.2	43.9	78.3	457 ₊₁₆
2:1	95.8	17.7	73.0	58.5	141.2	755 ₊₂₉
2.5:1	95.9	16.7	74.9	59.6	148.4	730 ₊₂₅
3:1	95.8	15.7	76.6	61.0	157.7	707 ₊₂₉

Mono:St = Monomer-to-Starch Ratio; Conv = Conversion; Homo = Homopolymer; GE = Grafting Efficiency; GR = Grafting Ratio; WA = Water Absorption; The AM:AA = 50:50 with a total dose of 6.0 kGy, and a dose rate of 5.75 kGy hr⁻¹

4.3.1.2 Relationship between Monomer-to-Starch Ratio and Percentage

Homopolymer

Table 4.5 and Figure 4.5 show that the percentage of homopolymer formed decreases with increasing monomer-to-starch ratio. At the lower monomer mixture concentration, a small number of monomers can diffuse to graft on the starch backbone. Most of the monomers are used for homopolymer formation through collision due to the viscous grafting substrate. In addition, the chain transfer to polymer increases with monomer concentration, especially at high extent of conversion, and this results in increasing amounts of branching and self-crosslinking reactions [33]. Thus at high monomer-to-starch ratio, percentage homopolymer may not be determined simply by extraction because cross-linked or intertangled high molecular weight homopolymer remained in the starch.

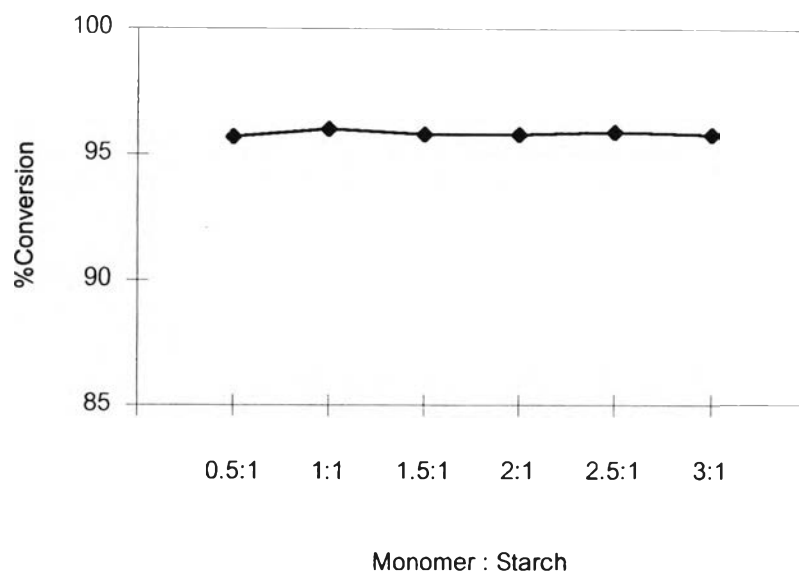


Figure 4.4 Effect of Monomer-to-Starch Ratio on Percentage Conversion

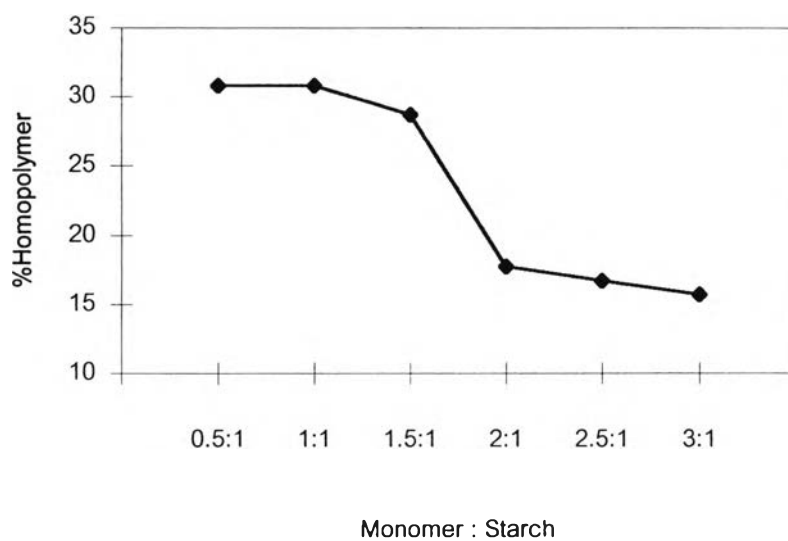


Figure 4.5 Effect of Monomer-to-Starch Ratio on Percentage Homopolymer

4.3.1.3 Relationship between Monomer-to-Starch Ratio and Grafting Efficiency, Percentage Add-on, and Grafting Ratio

Table 4.5 and Figures 4.6-4.8 show that grafting efficiency, percentage add-on, and grafting ratio increase with increasing monomer-to-starch ratio. A higher monomer concentration can enhance grafting yield due to that more monomers can react at grafting sites in the starch trunk polymer.

4.3.1.4 Relationship between Monomer-to-Starch Ratio and Water Absorption

Table 4.5 and Figure 4.9 show the effect of monomer-to-starch ratio on water absorption. The experimental data show that the highest water absorption occurred at the quantity of monomer-to-starch ratio of 2:1.

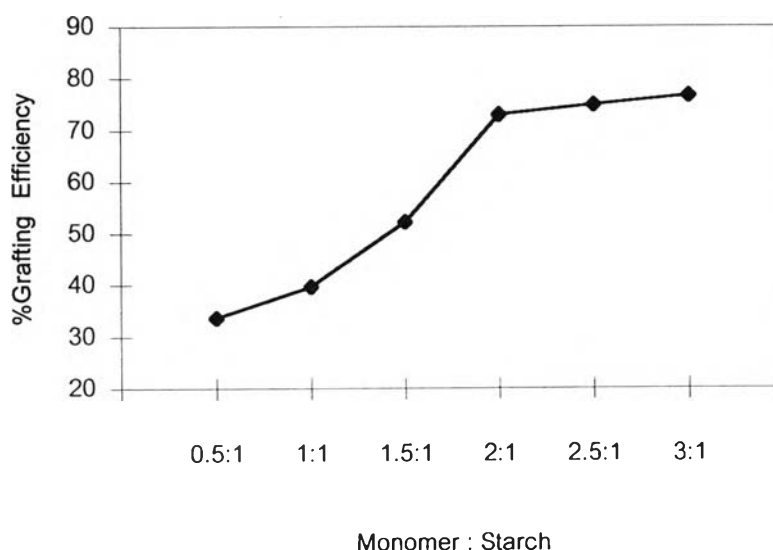


Figure 4.6 Effect of Monomer-to-Starch Ratio on Percentage Grafting Efficiency

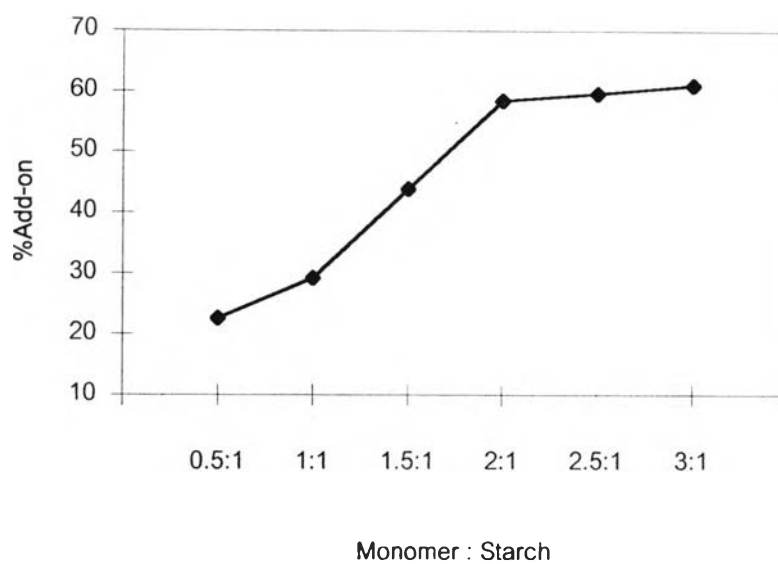


Figure 4.7 Effect of Monomer-to-Starch Ratio on Percentage Add-on

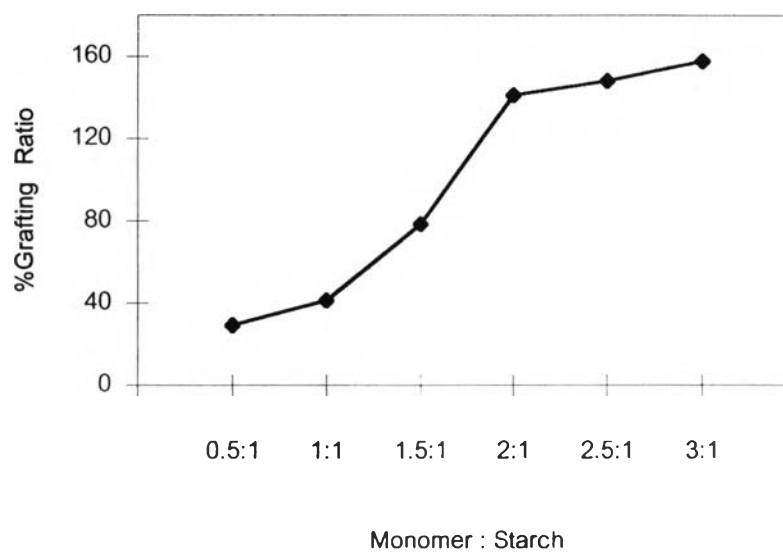


Figure 4.8 Effect of Monomer-to-Starch Ratio on Percentage Grafting Ratio

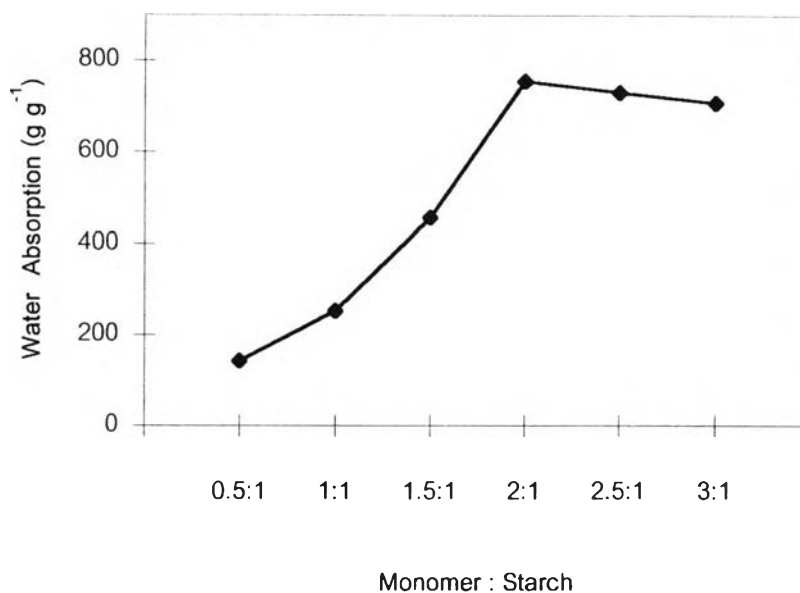


Figure 4.9 Effect of Monomer-to-Starch Ratio on Water Absorption

The saponified starch-*g*-poly(acrylamide-*co*-acrylic acid) is swollen in water on the account of the hydrophilic pendants (amide and carboxylate groups) in its structure. The swelling equilibrium of ionized hydrogels is determined by a balance of three main forces:

1. the free energy of mixing of the network chains with solvent,
2. the osmotic pressure differential resulting from a different in concentration of mobile ions between the interior of the gel and the external solution,
3. the elasticity of the gel resulting from its network structure.

The graft copolymerization with higher grafting efficiency gives the saponified graft copolymer containing higher mobile K^+ ions. Thus the swelling increases due to the increase of the different osmotic pressure between inside and outside of the gel. In addition, the swelling also increases due to that the increasing

hydrophilic fraction of the polymer chains (gel) tends to disperse better in the solvent. However, monomer-to-starch ratio higher than 2:1, the water absorption decreases. This may be due to that more crosslinks occurred at high monomer concentration, which restricts the swelling by elastic retraction forces.

4.3.2 Effect of Total Dose and Dose Rate on Graft Copolymerization

Tables 4.6 and 4.7 show the effect of total dose and dose rate on the grafting of AM and AA onto cassava starch in the terms of the conversion of monomer, homopolymer formed, grafting efficiency, percentage add-on, grafting ratio, and water absorption, respectively.

4.3.2.1 Relationship between Total Dose, Dose Rate and Percentage Conversion

Tables 4.6-4.7 and Figures 4.10-4.11 illustrate the conversion of monomer as a function of total dose and dose rate of graft copolymerization of AM and AA onto starch. We found that percentage conversion increases with increasing in the total dose, at all dose rates studied. An increase in the total dose enhances the formation of radicals in the reaction mixture: monomer, starch, and water. All molecules are activated to induce a higher conversion for both homopolymer formation and the grafting reaction.

Increasing the dose rate reduces percentage conversion especially at low total doses. Increasing the dose rate is to increase the radical density. At the high radical density, radical recombination can probably occur. This deteriorates the conversion of monomer. In addition, at high dose rates, the radiation may degrade the naturally occurring sensitive trunk polymer like starch [34] as well as the radiation sensitive monomer, such as AM and AA.

Table 4.6 Effect of Total Dose and Dose Rate on the Graft Copolymerization of Acrylamide onto Cassava Starch

DR (kGy hr ⁻¹)	TD (kGy)	Conv (%)	Homo (%)	GE (%)	Add-on (%)	GR (%)	WA (g g ⁻¹)
2.24	2.9	89.4	21.8	66.3	55.0	122.2	353 ₊₅
	4.3	94.5	19.4	70.2	56.8	131.6	369 ₊₅
	6.0	96.5	13.0	79.5	57.9	137.5	419 ₊₁₂
	7.2	97.5	17.2	74.7	61.4	159.0	391 ₊₅
	8.6	98.4	17.8	74.0	61.7	161.2	384 ₊₆
5.75	2.9	86.4	40.3	43.7	52.4	110.3	309 ₊₇
	4.3	93.9	33.5	51.6	53.8	116.3	324 ₊₇
	6.0	96.0	16.0	74.8	56.5	129.7	404 ₊₆
	7.2	96.8	24.1	64.8	58.4	140.5	375 ₊₇
	8.6	97.6	27.8	61.3	61.1	157.5	361 ₊₇
14.75	2.9	81.1	62.3	18.2	36.6	57.7	217 ₊₈
	4.3	91.1	50.7	29.9	43.8	77.9	302 ₊₄
	6.0	95.0	41.9	40.0	48.1	92.7	360 ₊₇
	7.2	96.2	37.6	46.9	53.1	113.0	362 ₊₅
	8.6	96.7	30.7	55.1	54.3	118.7	355 ₊₆

DR = Dose Rate; TD = Total Dose; Conv = Conversion; Homo = Homopolymer;
 GE = Grafting Efficiency; GR = Grafting Ratio; WA = Water Absorption; AM-to-
 Starch ratio = 2:1

Table 4.7 Effect of Total Dose and Dose Rate on the Graft Copolymerization of Acrylic Acid onto Cassava Starch

DR (kGy hr⁻¹)	TD (kGy)	Conv (%)	Homo (%)	GE (%)	Add-on (%)	GR (%)	WA (g g⁻¹)
2.24	2.9	87.8	12.0	80.5	56.2	128.2	394 ₊₅
	4.3	93.5	9.9	84.0	57.6	135.7	433 ₊₅
	6.0	95.8	8.2	87.2	61.0	156.6	469 ₊₆
	7.2	96.7	6.0	90.8	63.2	171.9	462 ₊₉
	8.6	97.7	4.6	93.0	63.8	176.2	459 ₊₅
5.75	2.9	82.7	15.2	74.3	52.1	108.7	338 ₊₈
	4.3	91.5	14.1	77.1	55.3	123.9	422 ₊₈
	6.0	95.4	13.1	79.7	59.0	144.1	460 ₊₈
	7.2	96.1	11.4	83.0	62.6	167.2	458 ₊₈
	8.6	97.0	8.8	86.7	63.1	171.2	455 ₊₆
14.75	2.9	77.4	15.4	61.9	29.6	42.0	267 ₊₉
	4.3	88.1	15.6	65.7	35.5	55.1	317 ₊₁₂
	6.0	95.1	17.0	71.5	51.4	105.9	453 ₊₇
	7.2	96.0	19.3	69.6	54.7	121.0	438 ₊₁₀
	8.6	96.6	24.6	63.9	57.9	137.5	428 ₊₉

DR = Dose Rate; TD = Total Dose; Conv = Conversion; Homo = Homopolymer;
 GE = Grafting Efficiency; GR = Grafting Ratio; WA = Water Absorption; AA-to-
 Starch ratio = 2:1

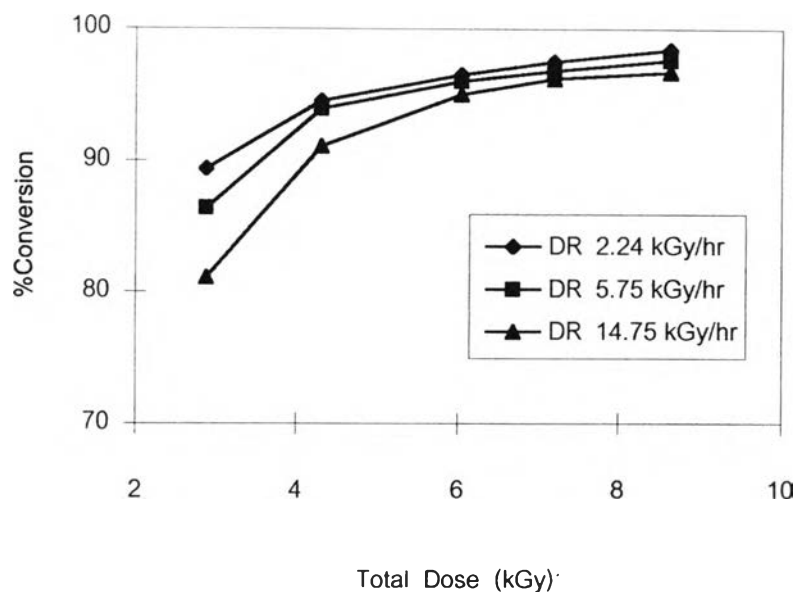


Figure 4.10 Effect of Total Dose and Dose Rate on Percentage Conversion of Graft Copolymerization of AM onto Starch

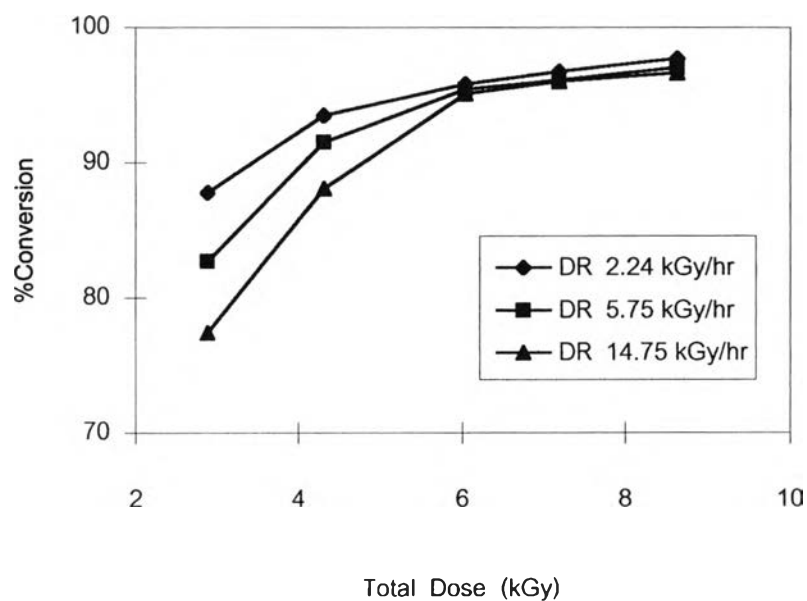


Figure 4.11 Effect of Total Dose and Dose Rate on Percentage Conversion of Graft Copolymerization of AA onto Starch

4.3.2.2 Relationship between Total Dose, Dose Rate, and Percentage Homopolymer

The correlation between total dose, dose rate, and percentage homopolymer of graft copolymerization of AM and AA onto starch is shown in Tables 4.6-4.7 and Figures 4.12-4.13, and the situation is very complex. It appears that increasing the total dose reduces the content of homopolymer because high total dose can induce ample active sites on the starch backbone for monomer to be grafted on. However, in the case of graft copolymerization of AA onto starch at dose rate 14.75 kGy hr⁻¹, the homopolymer content increases with increasing total dose. Similar results are obtained in graft copolymerization of AM onto starch at dose rates 2.24 and 5.75 kGy hr⁻¹ when the total dose are higher than 6.0 kGy. These may be due to that the higher irradiation dose gives the large amount of radiolysis products (in the absence of oxygen): OH[·] and e_{aq}⁻ of which G(OH[·]) and G(e_{aq}⁻) are 2.8, and 2.7 at pH 4-7, respectively, which initiates homopolymerization rather than grafting reaction.

Dose rate can also be an important variable, the homopolymerization formation increases with increasing dose rate, at all total doses studied.

4.3.2.3 Relationship between Total Dose, Dose Rate, and Grafting Efficiency

The experimental data of the effect of the total dose and dose rate on grafting efficiency of graft copolymerization of AM and AA onto starch are given in Tables 4.6-4.7 and Figures 4.14-4.15, respectively. Grafting efficiency increases with increasing total dose. At higher total dose, there are many active sites on the starch backbone and many monomers can diffuse to graft on the starch backbone. When the total dose higher than 6.0 kGy at dose rate 2.24 and 5.75 kGy hr⁻¹ in the case of grafting AM onto starch; and at 14.75 kGy hr⁻¹ in the case of grafting AA onto starch,

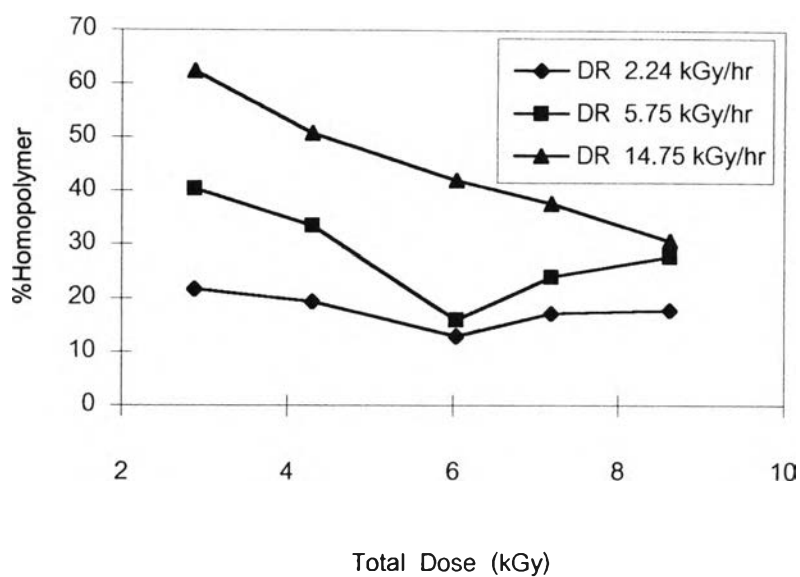


Figure 4.12 Effect of Total Dose and Dose Rate on Percentage Homopolymer of Graft Copolymerization of AM onto Starch

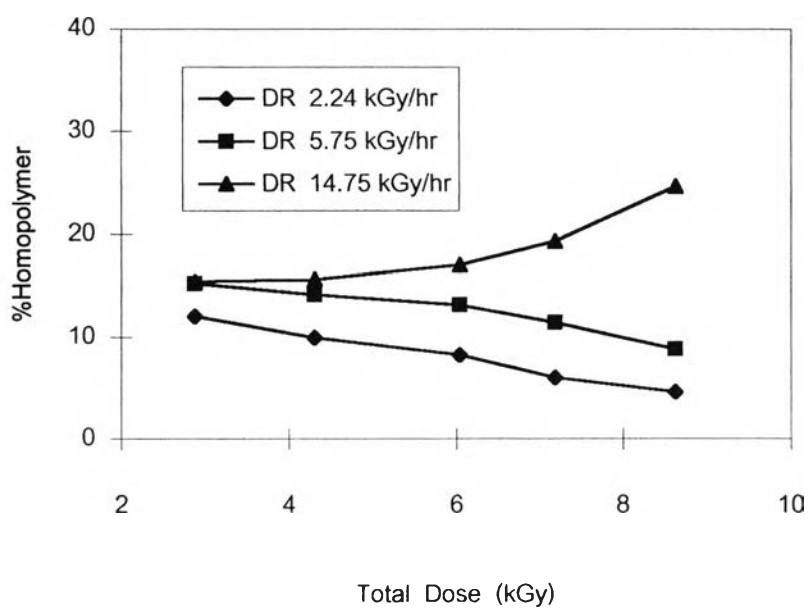


Figure 4.13 Effect of Total Dose and Dose Rate on Percentage Homopolymer of Graft Copolymerization of AA onto Starch

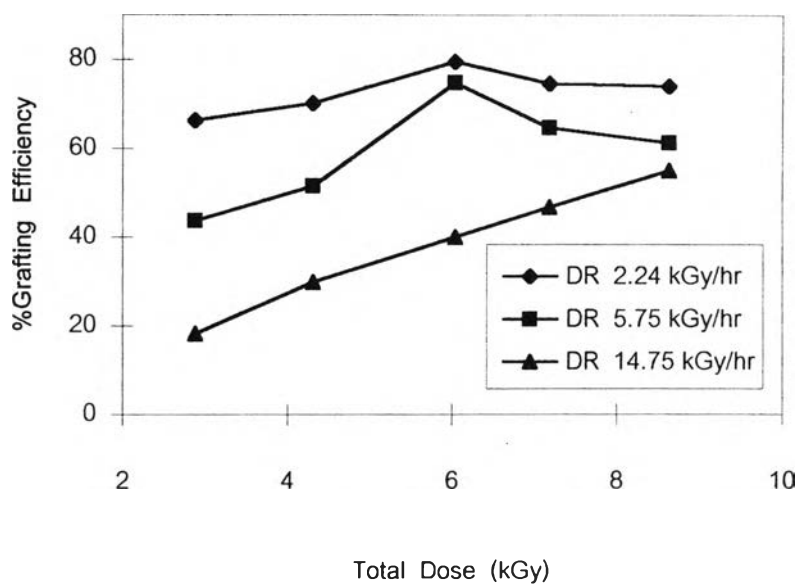


Figure 4.14 Effect of Total Dose and Dose Rate on Percentage Grafting Efficiency of Graft Copolymerization of AM onto Starch

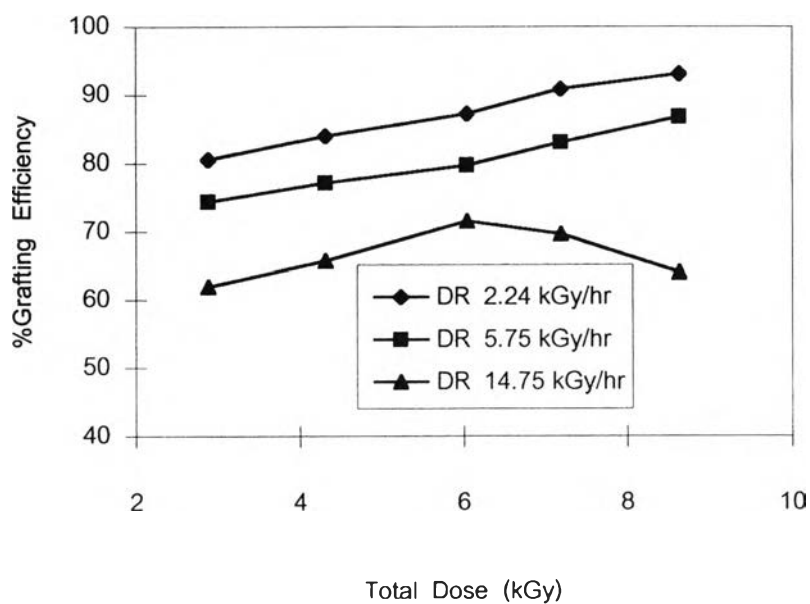


Figure 4.15 Effect of Total Dose and Dose Rate on Percentage Grafting Efficiency of Graft Copolymerization of AA onto Starch

the grafting efficiency decreases. It then suggests that the decreasing grafting efficiency due to the formation of small fragments of OH^\cdot , and e_{aq}^- to form homopolymer at the expense of grafting.

At a fixed total dose studied, the grafting efficiency decreases when increases the dose rate because too high the radicals tend to terminate before leading to the adequate grafting [35].

4.3.2.4 Relationship between Total Dose, Dose Rate, Percentage Add-on, and Grafting Ratio

Tables 4.6-4.7 and Figures 4.16-4.19 show the effect of total dose and dose rate on percentage add-on and grafting ratio of grafting copolymerization of AM and AA onto starch. The experimental data show a continuous increase in percentage add-on and grafting ratio as the total dose increases. At the higher irradiation dose, higher radicals generated produce many growing chains to be grafted on many active sites on the starch backbone.

Likewise, percentage add-on and grafting ratio decrease with increasing the dose rate, at fixed total dose.

4.3.2.5 Relationship between Total Dose, Dose Rate, and Water Absorption

Water absorptions in distilled water by the saponified starch-g-polyacrylamide and saponified starch-g-poly(acrylic acid) are shown in Tables 4.6-4.7 and Figures 4.20-4.21. At the total dose of 6.0 kGy and dose rate of 2.24 kGy hr^{-1} , the highest water absorption of both saponified products is obtained.

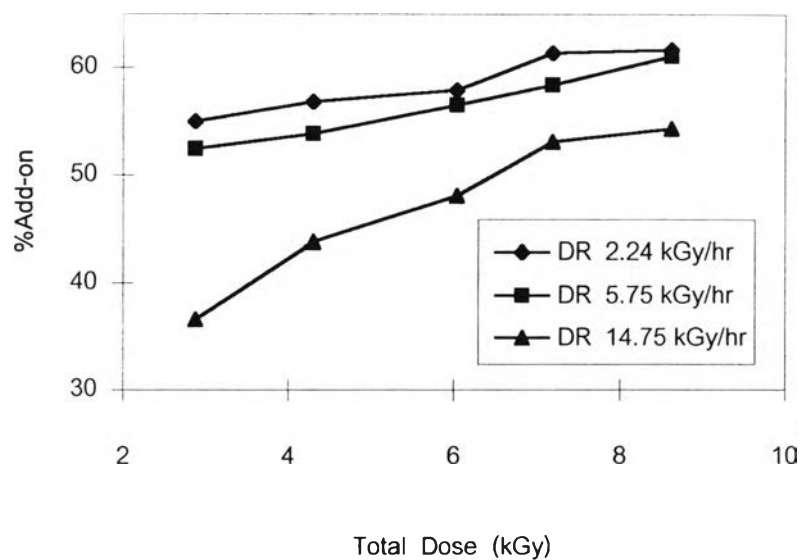


Figure 4.16 Effect of Total Dose and Dose Rate on Percentage Add-on of Graft Copolymerization of AM onto Starch

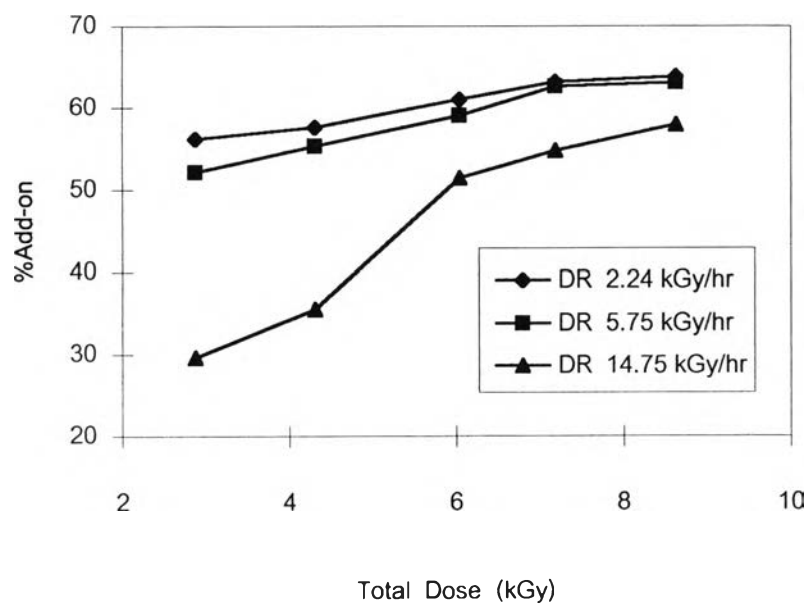


Figure 4.17 Effect of Total Dose and Dose Rate on Percentage Add-on of Graft Copolymerization of AA onto Starch

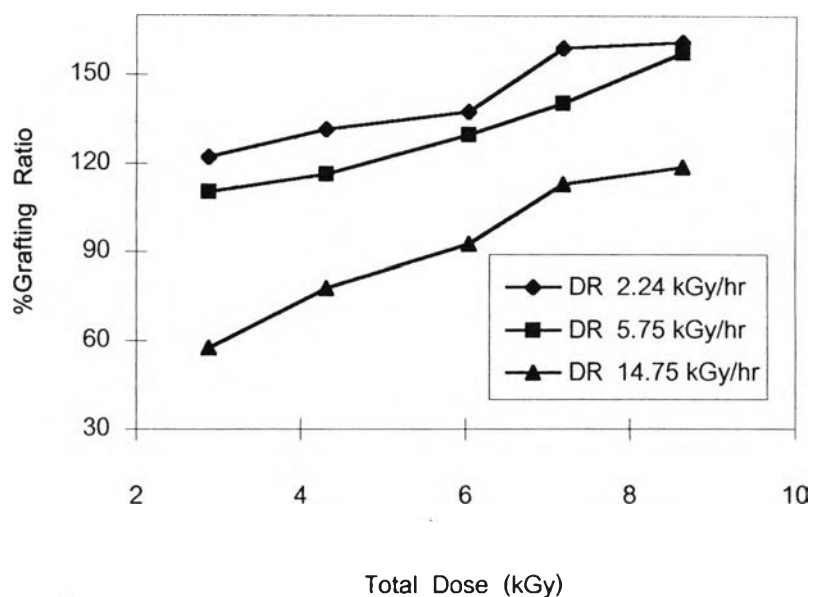


Figure 4.18 Effect of Total Dose and Dose Rate on Percentage Grafting Ratio of Graft Copolymerization of AM onto Starch

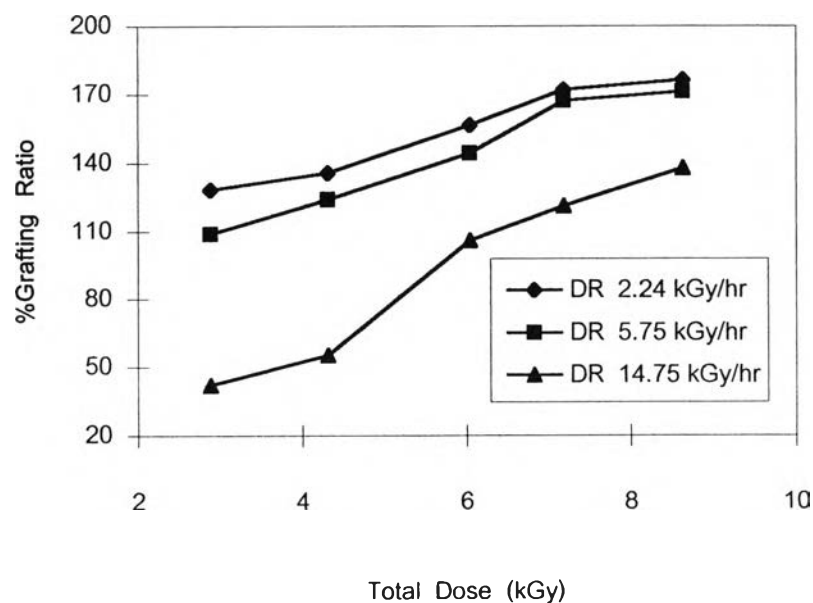


Figure 4.19 Effect of Total Dose and Dose Rate on Percentage Grafting Ratio of Graft Copolymerization of AA onto Starch

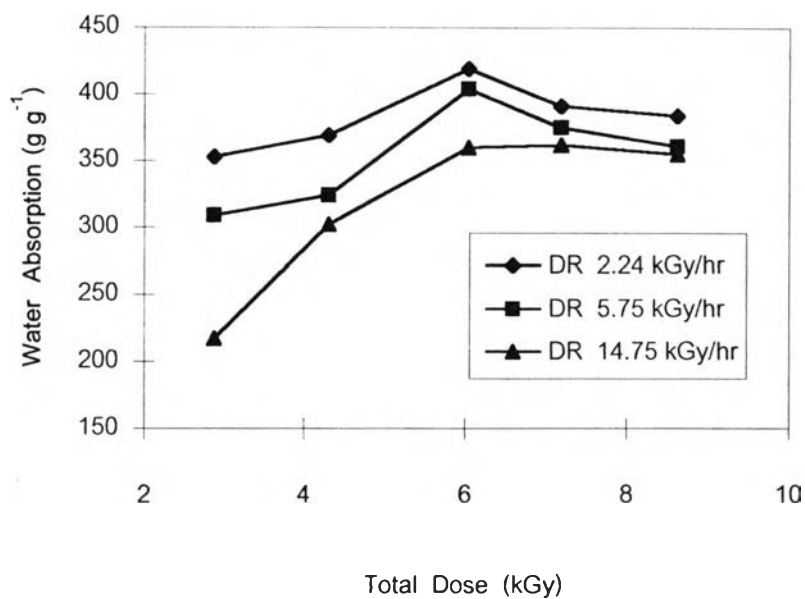


Figure 4.20 Effect of Total Dose and Dose Rate on Water Absorption of Saponified Starch-g-polyacrylamide

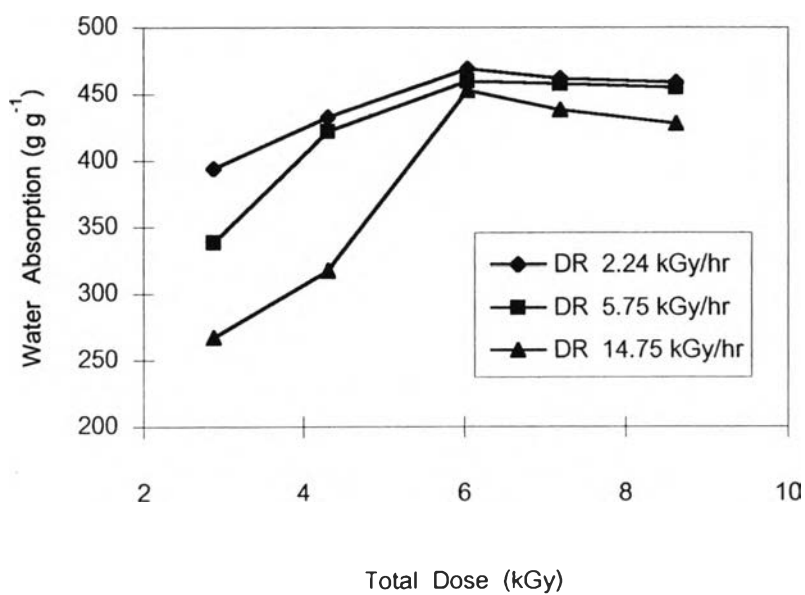


Figure 4.21 Effect of Total Dose and Dose Rate on Water Absorption of Saponified Starch-g-poly(acrylic acid)

4.3.3 Effect of Acid Additives on Graft Copolymerization

In grafting reaction, the presence of additives can influence both the processing conditions and the properties of the finished product. Appropriate additives are included to lower the radiation dose required to achieve a particular percentage graft and also to reduce the levels of detrimental homopolymer formation.

4.3.3.1 *Effect of Acid Additives on Graft Copolymerization of Acrylamide onto Cassava Starch*

Data for the grafting of AM onto cassava starch with nitric or maleic acid are shown in Table 4.8.

Table 4.8 Effect of Acid Additives on Graft Copolymerization of Acrylamide onto Cassava Starch

Additives	Conv (%)	Homo (%)	GE (%)	Add-on (%)	GR (%)	WA (g g⁻¹)
no additive	96.5	13.0	79.5	57.9	137.5	419 ₊₁₂
0.1 M HNO ₃ ^a	96.6	10.3	83.5	58.2	139.7	354 ₊₁₀
2% maleic acid ^b	96.1	16.2	72.8	51.8	107.3	336 ₊₁₄

Conv = Conversion; Homo = Homopolymer; GE = Grafting Efficiency; GR = Grafting Ratio; WA = Water Absorption; The AM-to-starch ratio = 2:1 with a total dose of 6.0 kGy, and a dose rate of 2.24 kGy hr⁻¹

^a 10 ml of 0.1 M HNO₃

^b 2% maleic acid (by wt. of the monomer)

4.3.3.1a) *The Effect of Nitric Acid on Graft Copolymerization of Acrylamide onto Cassava Starch*

As shown in Table 4.8, the conversion of monomer does not change when the acid was used. At the total dose given, the ionizing radiation can initiate a certain number of free radicals that are used both for homopolymerization and graft copolymerization in a proper ratio.

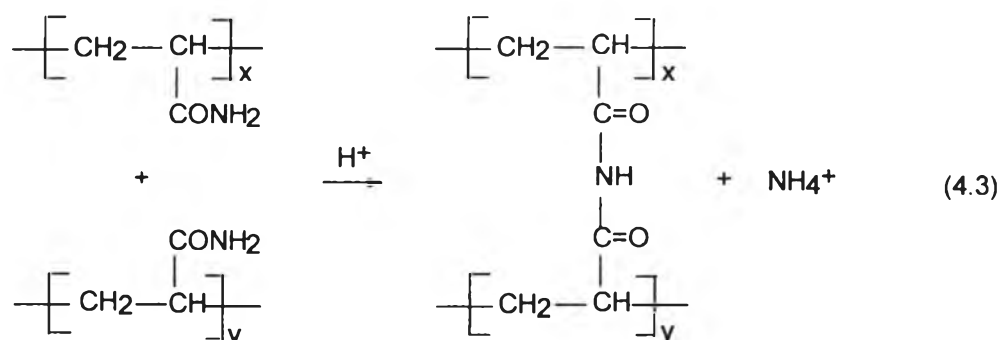
The mechanism of an acid effect is complicated, however, evidence suggests that a contributing process involves an increase in hydrogen atom yield $[G(H)]$ from secondary electron capture by H^+ as in Equation 4.2. The presence of these additional radicals in the system can lead to further activation of the backbone polymer by abstraction reaction [36].



Besides enhancing grafting sites on the starch backbone, the acid has a role in partitioning phenomena. In terms of this concept, increased partitioning of monomer occurs in the graft region of the backbone polymer when acid is dissolved in the bulk grafting solution, thus permitting higher concentrations of monomer to be available for grafting at a particular site. These mechanisms of an acid effect in grafting initiated by ionizing radiation cause an increase in grafting efficiency, percentage add-on, and grafting ratio and decreasing the homopolymer formation.

The water absorption of saponified starch-g-polyacrylamide when the acid was used is lower than that in the absence of the acid. This may be due to the occurrence of imidization that usually takes place in the polymerization of acrylamide in concentrated solution and at high temperature or very long reaction times.

Imidization is accelerated by strong acids [37]. The imidization of the amide pendants in the copolymer is shown in Equation 4.3.



4.3.3.1b) The Effect of Maleic Acid on Graft Copolymerization of Acrylamide onto Cassava Starch

The experimental data of the effect of maleic acid (MA) which is diprotic acid on the grafting of AM onto starch are given in Table 4.8. As the MA was used, the conversion of monomer is rather constant at the given total dose because the ionizing radiation can initiate a certain number of free radicals.

When the monomers of AM and MA have been irradiated with ionization rays, free radicals are generated. Random reactions of these radicals with the monomers lead to the formation of copolymers of AM and MA [38]. The results show that both monomers preferred to copolymerize as an ungrafted, free copolymer rather than grafted copolymers onto the starch backbone. The water absorption decreases due to an increase in the ungrafted material, at a sacrifice of the grafting monomer of AM [39].

4.3.3.2 Effect of Acid Additive on Graft Copolymerization of Acrylic Acid onto Cassava Starch

Table 4.9 shows the effect of nitric acid on the grafting of AA onto cassava starch in the terms of the conversion of monomer, homopolymer formed, grafting efficiency, percentage add-on, grafting ratio, and water absorption.

Table 4.9 Effect of Acid Additive on Graft Copolymerization of Acrylic Acid onto Cassava Starch

Additive	Conv (%)	Homo (%)	GE (%)	Add-on (%)	GR (%)	WA (g g ⁻¹)
no additive	95.8	8.2	87.2	61.0	156.6	469 ₊₆
0.1 M HNO ₃ ^a	94.8	12.0	81.3	59.5	146.9	520 ₊₁₃

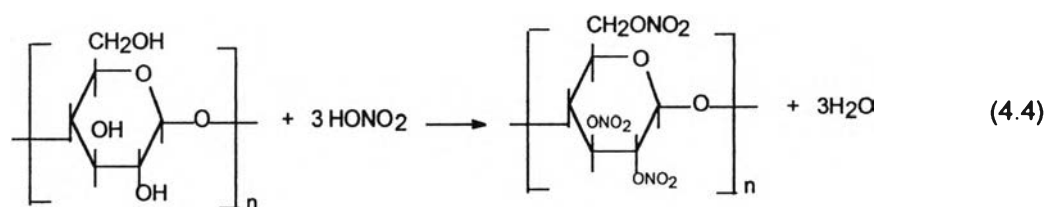
Conv = Conversion; Homo = Homopolymer; GE = Grafting Efficiency; GR = Grafting Ratio; WA = Water Absorption; The AA-to-starch ratio = 2:1 with a total dose of 6.0 kGy, and a dose rate of 2.24 kGy hr⁻¹

^a 10 ml of 0.1 M HNO₃

As shown in Table 4.9, conversion, grafting efficiency, percentage add-on, and grafting ratio decrease but homopolymer formed increases when the nitric acid was used. This is due to that the amount of acid used might be too high and starch might be hydrolyzed before it can be grafted with AA.

The product obtained after irradiation when the nitric acid was used is light yellow. It is presumed that the nitrite and/or nitrate compounds may occur. Irradiation of nitric acid solution gives radiolysis products (in the absence of oxygen): H₂O₂ and NO₂⁻ as G(H₂O₂) and G(NO₂⁻) are 0.74 and 0.3, respectively [40]. These

NO_2^- fragments may react with starch molecules and give nitrite compounds. On the other hand, nitrate compound may form in a similar manner as that formation of cellulose nitrate, or nitrocellulose. Nitration of cellulose may be compared to a typical equilibrium esterification, where the reaction of an alcohol and an acid (HNO_3) produces an ester and water (shown in eq. 4.4) [41].



$n = \text{degree of polymerization (DP)} = 500\text{-}2,500$

In these reactions, the other function of acrylic acid (besides that of the monomer) may be to remove the water formed during the condensation reactions and drive the equilibrium of reactions toward the desired product.

IR spectra of starch-g-poly(acrylic acid) in the presence of nitric acid as an additive of both before and after extraction are shown in Figures 4.22. However, two $\text{N}=\text{O}$ stretching bands and $\text{N}-\text{O}$ stretching band of the nitrite group at $1,681\text{-}1,648 \text{ cm}^{-1}$, $1,625\text{-}1,605 \text{ cm}^{-1}$, and $814\text{-}751 \text{ cm}^{-1}$, respectively, cannot be clearly seen. Similarly, the NO_2 asymmetric stretching band, NO_2 symmetric stretching band, $\text{N}-\text{O}$ stretching band, and NO_2 bending band of the nitrate group at $1,660\text{-}1,625 \text{ cm}^{-1}$, $1,300\text{-}1,255 \text{ cm}^{-1}$, $870\text{-}833 \text{ cm}^{-1}$, and $763\text{-}690 \text{ cm}^{-1}$, respectively, cannot be clearly seen. Unlikely, these bands of the nitrate group in the IR spectra of cellulose nitrate, or nitrocellulose (Figure 4.23) are clearly observed. This may be due to their low intensity of these bands and overlapping with the existing bands of starch-g-poly(acrylic acid) at around these wavenumbers.

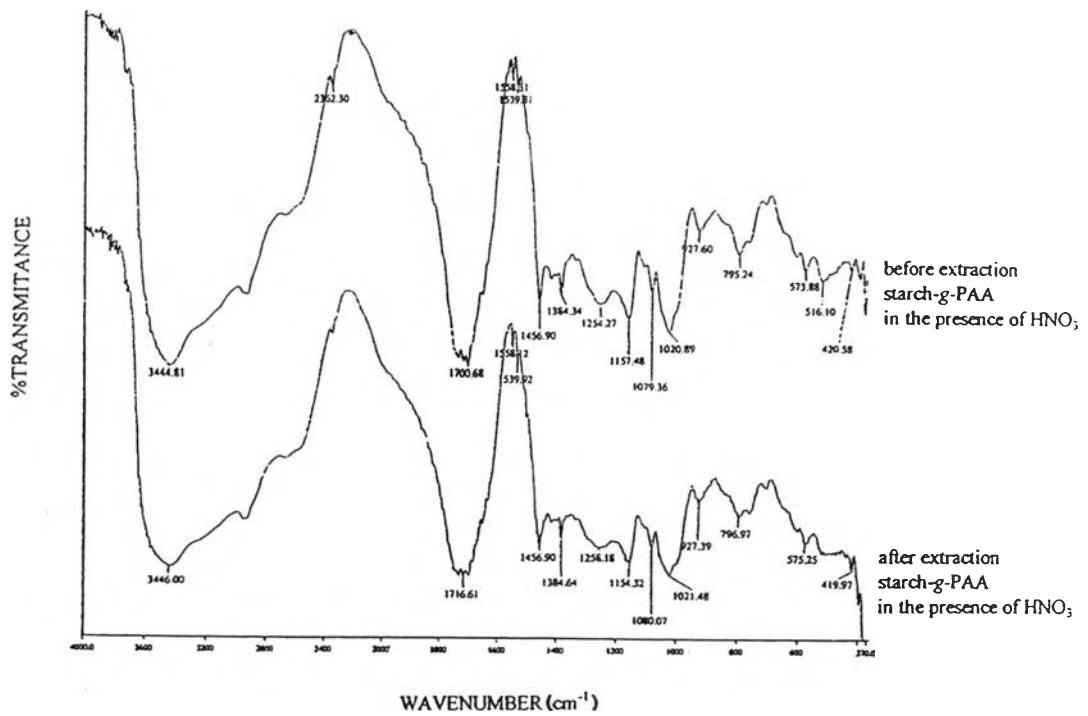


Figure 4.22 Infrared Spectra of the Starch-g-poly(acrylic acid) in the Presence of Nitric Acid as an Additive Before and After Extraction

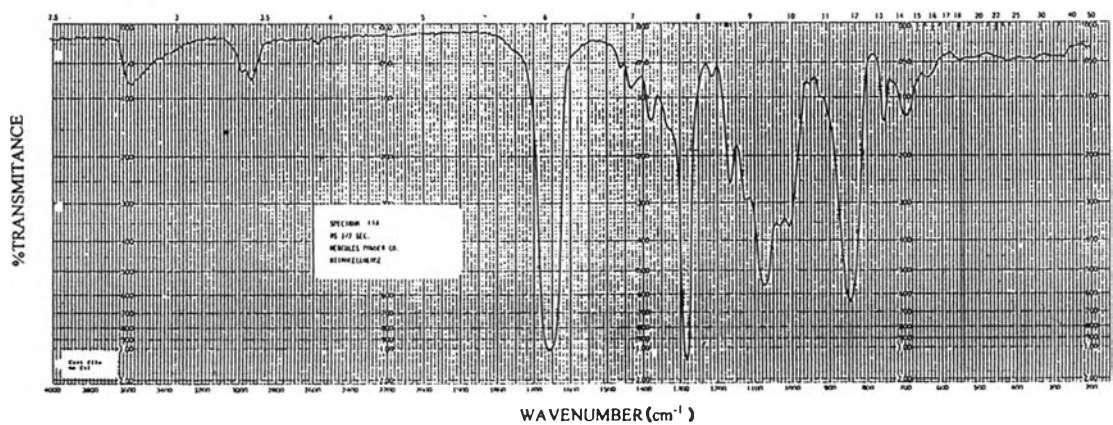


Figure 4.23 Infrared Spectrum of the Nitrocellulose (Cellulose Nitrate)

The water absorption of saponified starch-g-poly(acrylic acid) when the nitric acid was used as an additive is higher than that in the absence of the acid. It then suggests that the increasing water absorption is due to that the grafted nitrite and/or nitrate function groups which are hydrophilic functional groups can assist in water absorption.

4.3.3.3 Effect of Acid Additives on Graft Copolymerization of Acrylamide and Acrylic Acid onto Cassava Starch

Data for the grafting of AM and AA onto cassava starch with various concentrations of nitric acid are shown in Table 4.10 and Figures 4.24-4.29.

Table 4.10 Effect of Acid Additives on Graft Copolymerization of Acrylamide and Acrylic Acid onto Cassava Starch

Additive	Conv (%)	Homo (%)	GE (%)	Add-on (%)	GR (%)	WA (g g ⁻¹)
no additive	96.3	16.1	74.9	57.3	134.5	1138 ₊₂₆
0.01 M HNO ₃ ^a	95.1	17.6	72.2	55.4	124.4	1054 ₊₃₂
0.1 M HNO ₃ ^b	93.0	18.6	70.4	54.3	119.0	1013 ₊₁₉
1 M HNO ₃ ^c	92.1	22.8	64.6	53.9	116.9	938 ₊₃₄

Conv = Conversion; Homo = Homopolymer; GE = Grafting Efficiency; GR = Grafting Ratio; WA = Water Absorption; The AM:AA = 50:50 with a total dose of 6.0 kGy, and a dose rate of 2.24 kGy hr⁻¹

^a 10 ml of 0.01 M HNO₃

^b 10 ml of 0.1 M HNO₃

^c 10 ml of 1 M HNO₃

As shown in Table 4.10 and Figures 4.24-4.29, the conversion of monomers decreases as nitric acid concentration proceeds from 0.01 to 1 M. The initiator radicals formed tend to initiate homopolymerization rather than grafting reaction. Similar results were obtained by Garnett [42] in grafting of styrene in methanol to cellulose. At higher concentration of nitric acid (higher acidity) appears to attack and hydrolyze the starch before sufficient protective grafting can occur. Too high an acid concentration causes random cleavage of the $\alpha 1 \rightarrow 4$ and $\alpha 1 \rightarrow 6$ linkages in the starch molecules [4]. The graft copolymer with lower grafting efficiency gives the saponified product with a lower water absorption.

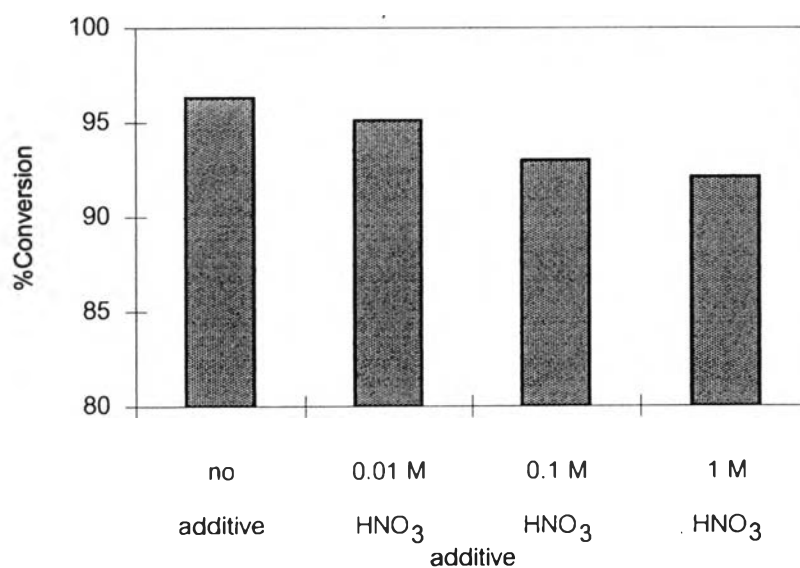


Figure 4.24 Effect of Nitric Acid on Percentage Conversion

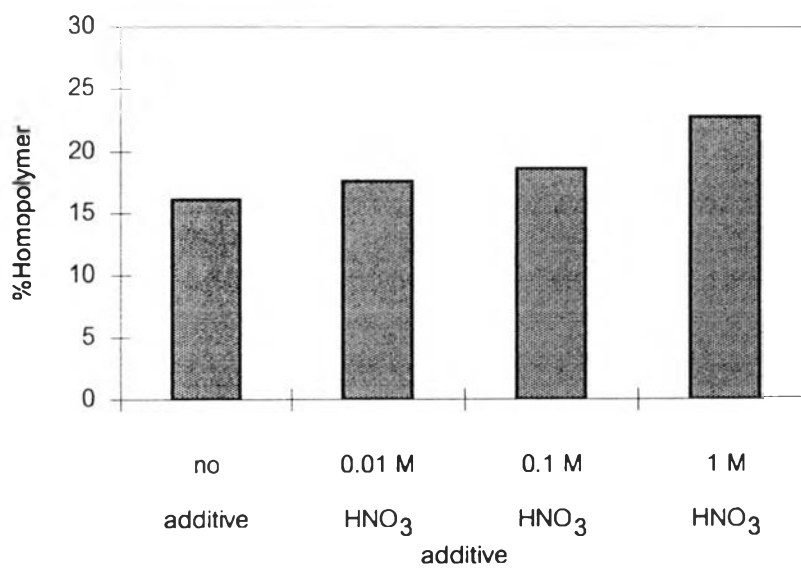


Figure 4.25 Effect of Nitric Acid on Percentage Homopolymer

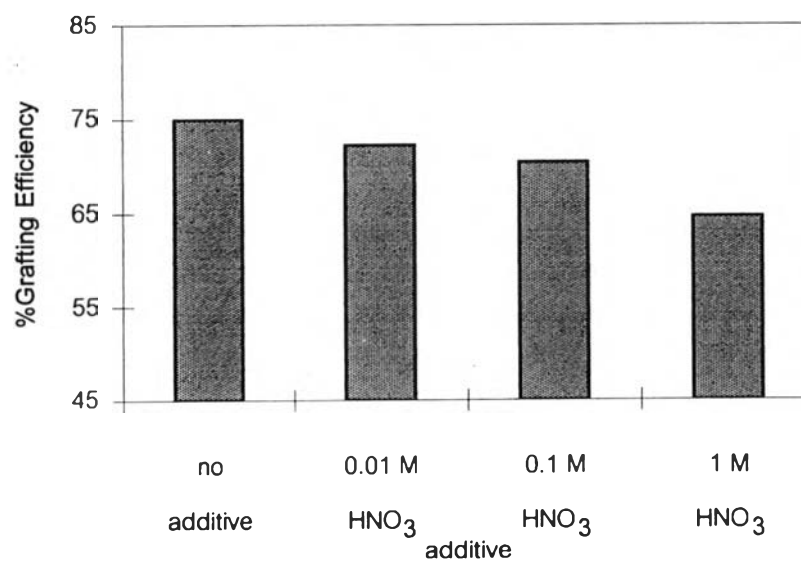


Figure 4.26 Effect of Nitric Acid on Percentage Grafting Efficiency

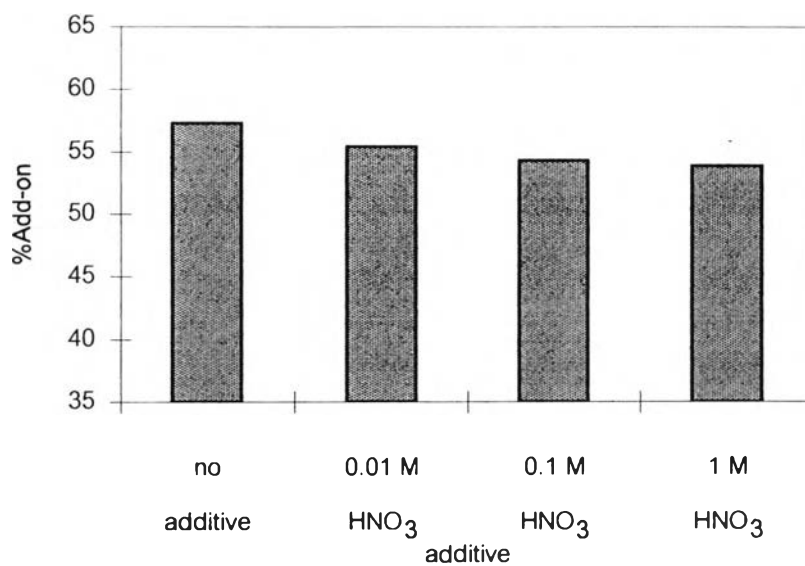


Figure 4.27 Effect of Nitric Acid on Percentage Add-on

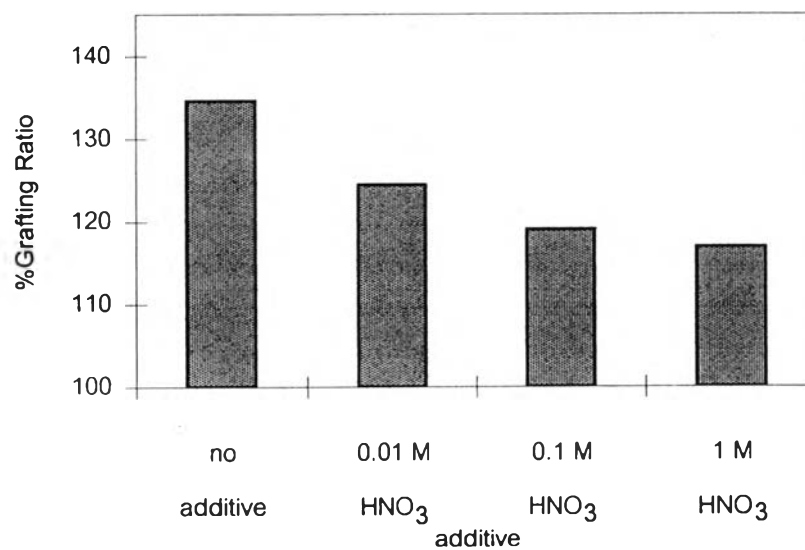


Figure 4.28 Effect of Nitric Acid on Percentage Grafting Ratio

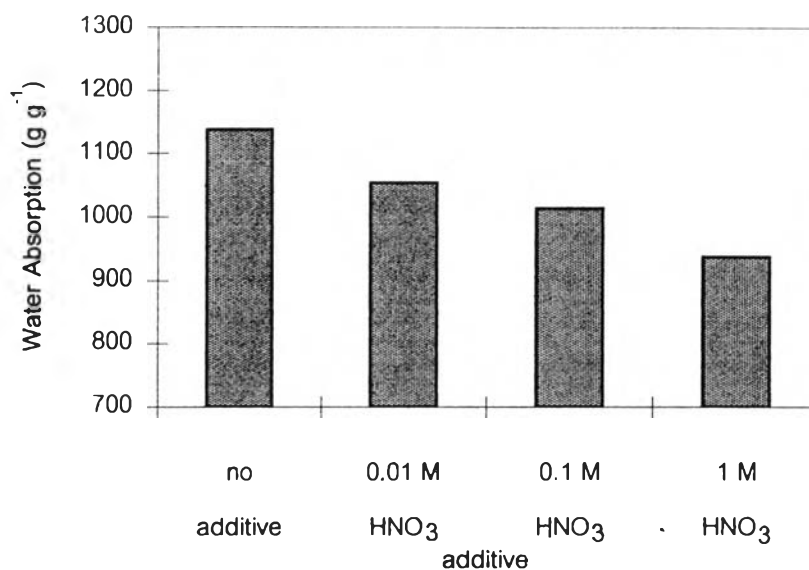


Figure 4.29 Effect of Nitric Acid on Water Absorption

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

Table 4.11 and Figures 4.30-4.35 illustrate the effect of AM-to-AA ratio on graft copolymerization of AM and AA onto cassava starch in terms of the conversion of monomer, homopolymer formed, grafting efficiency, percentage add-on, grafting ratio, and water absorption.

When the AM-to-AA ratio is changed, percentage conversion is constant for the whole range of AM-to-AA ratios (Figure 4.30). This is due to that the ionizing radiation can initiate a certain number of free radicals which are used both for homopolymerization and graft copolymerization of the monomers in a proper ratio, at the given total dose.

For the radical copolymerization of AM (M_1)-AA (M_2) with $r_1 = 0.60$ and $r_2 = 1.43$ [43], the greater reactivity of the AA results in its being incorporated preferentially into the first-formed copolymer. As the reaction proceeds the feed and the copolymer become therefore progressively enriched in AM. The structure of the

Table 4.11 Effect of Acrylamide-to-Acrylic Acid Ratio on Graft Copolymerization

AM-to-AA Ratio	Conv (%)	Homo (%)	GE (%)	Add-on (%)	GR (%)	WA (g g ⁻¹)
100:0	96.5	13.0	79.5	57.9	137.5	419 ₊₁₂
70:30	96.4	15.6	75.5	57.0	132.7	1142 ₊₁₅
50:50	96.3	16.1	74.9	57.3	134.5	1138 ₊₂₆
30:70	96.1	20.8	67.7	54.8	121.1	852 ₊₁₁
0:100	95.8	8.2	87.2	61.0	156.6	469 ₊₆

Conv = Conversion; Homo = Homopolymer; GE = Grafting Efficiency; GR = Grafting Ratio; WA = Water Absorption; The monomer-to-starch ratio = 2:1 with a total dose of 6.0 kGy, and a dose rate of 2.24 kGy hr⁻¹

copolymer consisted of more acrylic acid units gives the saponified graft copolymer with higher ionic functional group. The water absorbency increases with increasing number of hydrophilic and ionic functional groups. In contrast, if the flexibility of polymer chain was more important factor, the water absorbency should increase with increasing number of acrylamide units in the polymer chain since the glass transition temperature (T_g) of potassium acrylate is higher than that of acrylamide, i.e., 194°C and 165°C, respectively [43, 44]. Thus the graft copolymer must have an optimum ratio of AM-to-AA, in order to have a balance of hydrophilic/ionic functional groups and chain flexibility to produce the saponified graft copolymer with highest water absorption capacity.

Graft copolymers obtained by the copolymerization of both AM and AA onto the starch give the saponified product with a higher water absorption than that obtained by the copolymerization of either AM or AA. The optimum ratio of AM:AA

used in graft copolymerization is in the range between 70:30 and 50:50. These conditions produce the graft copolymer with a suitably high grafting efficiency and give the saponified graft copolymer having the higher water absorption. When the amount of AA in the monomer mixture is higher than this range (AM:AA = 30:70), a greater amount of homopolymer and ungrafted copolymer are formed at the expense of the grafting reaction so that saponified graft copolymer so obtained has a lower water absorption.

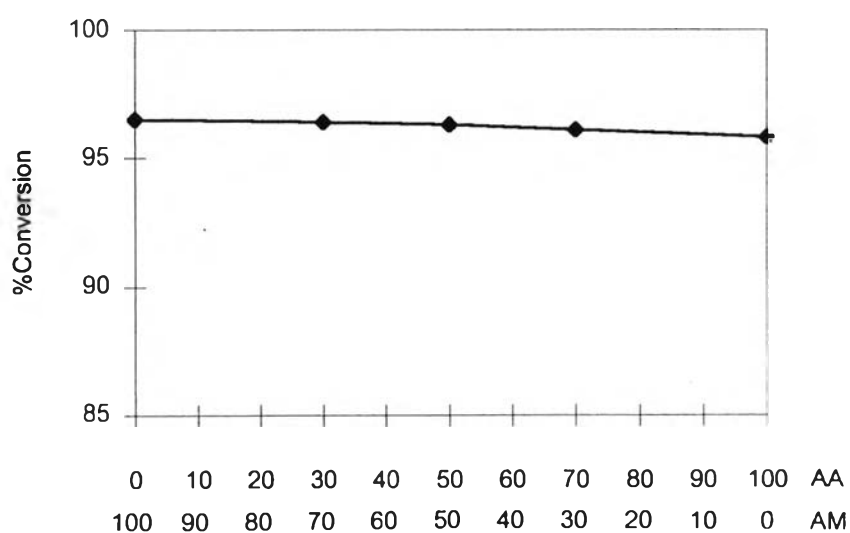


Figure 4.30 Effect of AM-to-AA Ratio on Percentage Conversion

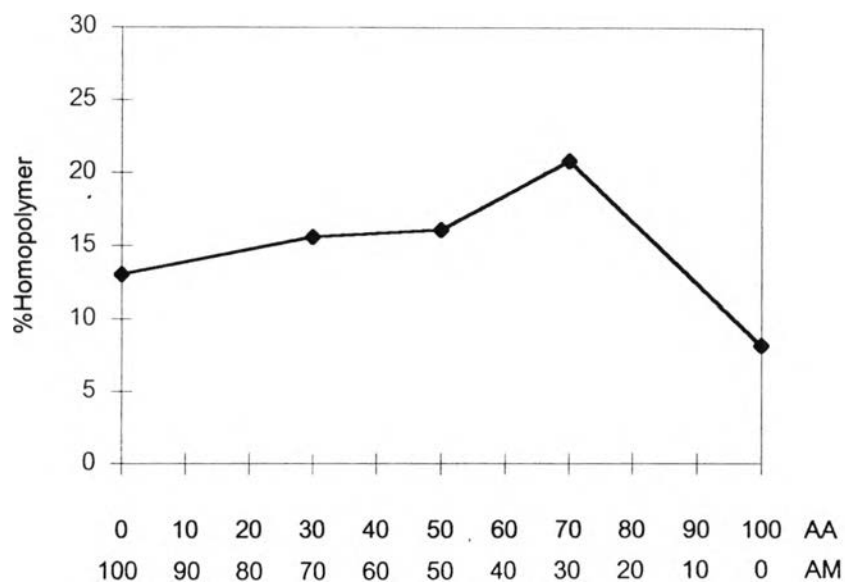


Figure 4.31 Effect of AM-to-AA Ratio on Percentage Homopolymer

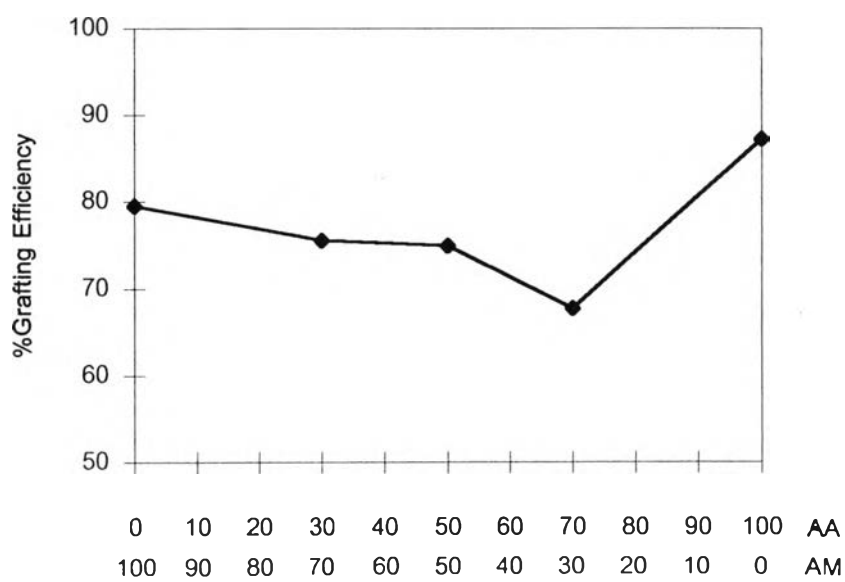


Figure 4.32 Effect of AM-to-AA Ratio on Percentage Grafting Efficiency

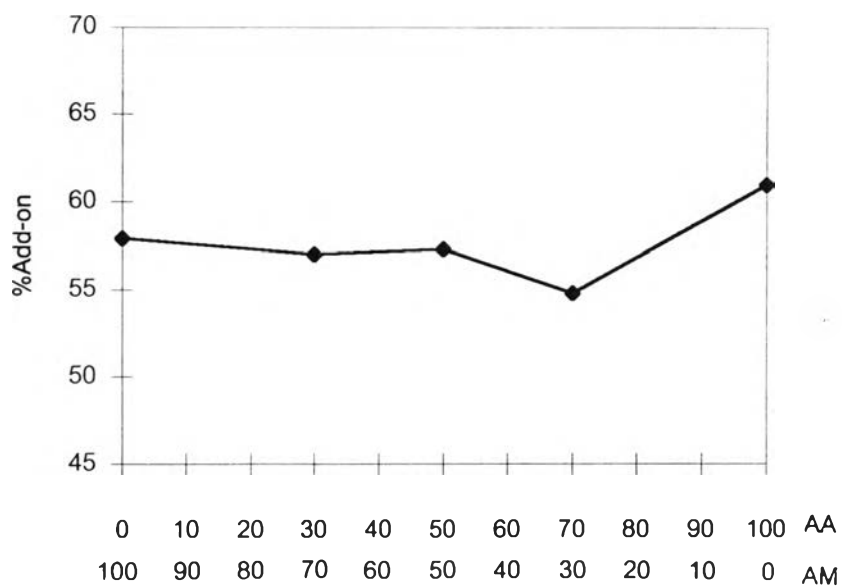


Figure 4.33 Effect of AM-to-AA Ratio on Percentage Add-on

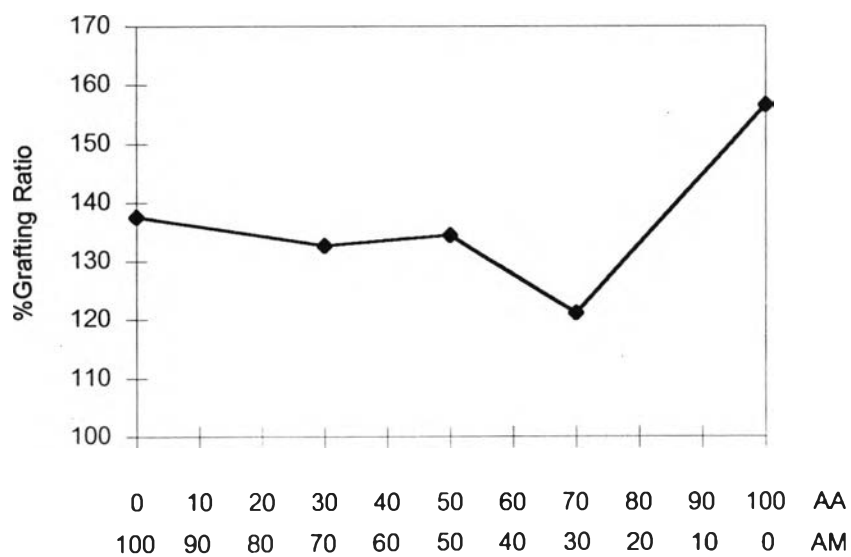


Figure 4.34 Effect of AM-to-AA Ratio on Percentage Grafting Ratio

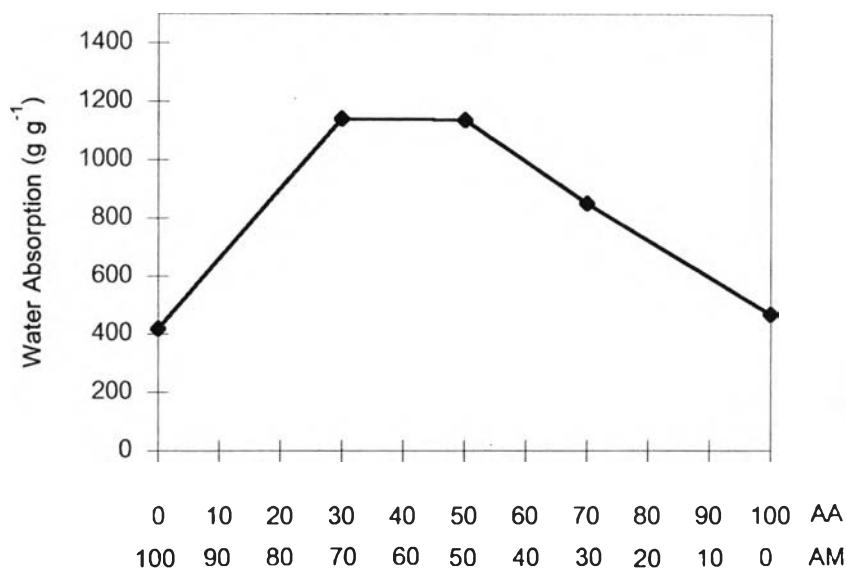


Figure 4.35 Effect of AM-to-AA Ratio on Water Absorption

4.3.5 Effect of Salt Solution on Water Absorption

Since the starch-*g*-poly(acrylamide-*co*-acrylic acid) absorbent is a kind of anionic gel, the surrounding environment, such as temperature, pH, ionic strength, etc. affects its absorbency. Table 4.12 shows the swelling of starch-*g*-poly(acrylamide-*co*-acrylic acid) absorbent in salt solutions. The highest water-absorbing copolymer, obtained earlier, having a water absorbency of 1142 g g⁻¹ was selected to test the salt effect in an isotonic fluid of 0.9% w v⁻¹ of NaCl, MgCl₂, and CaCl₂ solutions.

Table 4.12 Effect of Salt Solution on Water Absorption

Solution	Ionic Strength (mole-ion dm ⁻³)	Water Absorption (g g ⁻¹)
Distilled Water		1142 ₊₁₅
0.9% w v ⁻¹ NaCl Solution	1.54 x 10 ⁻¹	79 ₊₆
0.9% w v ⁻¹ MgCl ₂ Solution	1.33 x 10 ⁻¹	56 ₊₄
0.9% w v ⁻¹ CaCl ₂ Solution	2.43 x 10 ⁻¹	49 ₊₅

The decreases in water absorption depend on the oxidation state of the cation as shown in Table 4.12. The decrease of the expansion of the network is due to screening of the ionic charges bound to the network (the presence of ions in the solution surrounding the network counteracts the mutual repulsion of the fixed ions on the network itself) and to the decrease of the osmotic pressure difference between the gel and the external solution. The effect of the ionic strength on the swelling has been determined using Flory's equation [2].

$$Q^{5/3} = [(i/2v_u S^{*1/2})^2 + (1/2 - \chi_1)/v_1] / (v_e/V_0) \quad (2.1)$$

Where

- Q = degree of swelling
- i/v_u = charge density of polymer
- S^* = ionic strength of solution
- $(1/2 - \chi_1)/v_1$ = polymer-solvent affinity
- v_e/V_0 = crosslinking density

According to Equation 2.1, the ionic strength of solution increases the water absorbency would then decrease. The ionic strength of the solution depends on both the mobile ion concentration and their valency. Small quantities of divalent or trivalent ions can decrease drastically the swelling values. This decrease, more significant with Mg^{2+} or, Ca^{2+} ions, can be due to the complexing ability of carboxylate groups including intramolecular and intermolecular complexes formation. Consequently, the crosslink density of the network increases [16].

4.3.6 Effect of pH on Water Absorption

The influence of solution pH (3-11) on the water absorption capacity of the synthesized graft copolymer which has the highest water absorption in distilled water (1142 g g^{-1}) is shown in Table 4.13 and Figure 4.36.

Table 4.13 Effect of pH on Water Absorption

pH of Buffer Solution	Water Absorption (g g^{-1})
pH3	39 \pm 2
pH5	83 \pm 3
pH8	91 \pm 2
pH11	86 \pm 7

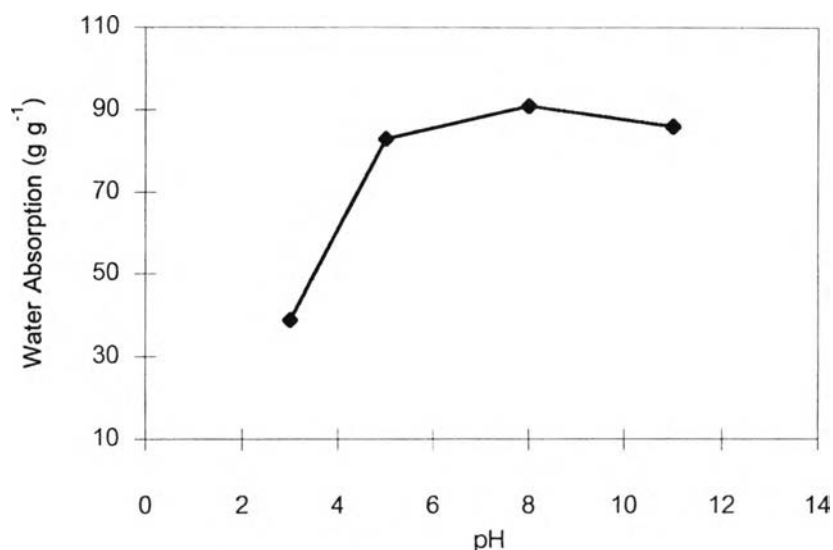


Figure 4.36 Effect of pH on Water Absorption of Copolymer

The water absorbency of the anionically starch-grafted AA/AM absorbent is markedly affected by pH of buffer solution. The swelling of saponified graft copolymer increases significantly from pH 3 to pH 5, and remains relatively constant afterwards. As the pH is lowered to strongly acidic region, the carboxylate side chains of the potassium acrylate become hydrolyzed to be the carboxylic groups, thus decreasing the charge density of anions on the network. The concomitant decreases in mobile counterion content of the network sharply decrease the internal osmotic pressure, which retards the observed swelling transitions.

4.4 Surface Morphology of the Copolymers

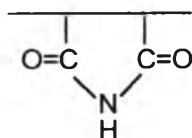
The surface appearance and structure of copolymers were observed using the scanning electron microscopy. The photographs taken by the electron microscope of the saponified graft copolymers and the grafted polymers are shown in Figures 4.37-4.41, and Figures 4.42-4.43, respectively.

The SEM photographs of saponified starch-*g*-poly(acrylamide-*co*-acrylic acids), which are the polymers of good absorbency, shown in Figures 4.37-4.38 show that the saponified graft copolymers have porous structure. It is supposed that these pores are the regions of water permeation and interaction with the hydrophilic groups of the saponified graft copolymers.

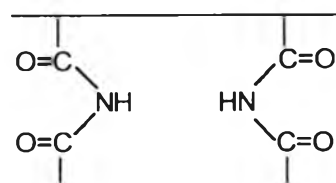
For the SEM photographs of saponified starch-*g*-poly(acrylic acid) shown in Figures 4.39-4.40, the mixture of porous and non-porous structures can be observed.

In the case of the saponified starch-*g*-polyacrylamide, the SEM photographs show that the saponified graft copolymer has a non-porous structure (Figure 4.41).

Figures 4.42-4.43 show the SEM photographs of grafted poly(acrylamide-*co*-acrylic acid) and grafted polyacrylamide, which were separated from the starch backbone by heating the graft copolymer under refluxing in acid solution. It is apparent from the photographs that grafted polymers are composed of irregular crosslinked polymers. Strong acidic conditions were used in the hydrolysis reaction of starch that can lead to a progressive insolubilization of the reaction product because of the formation of cyclic imide structures (structures IV or V) [45].



(IV)



(V)

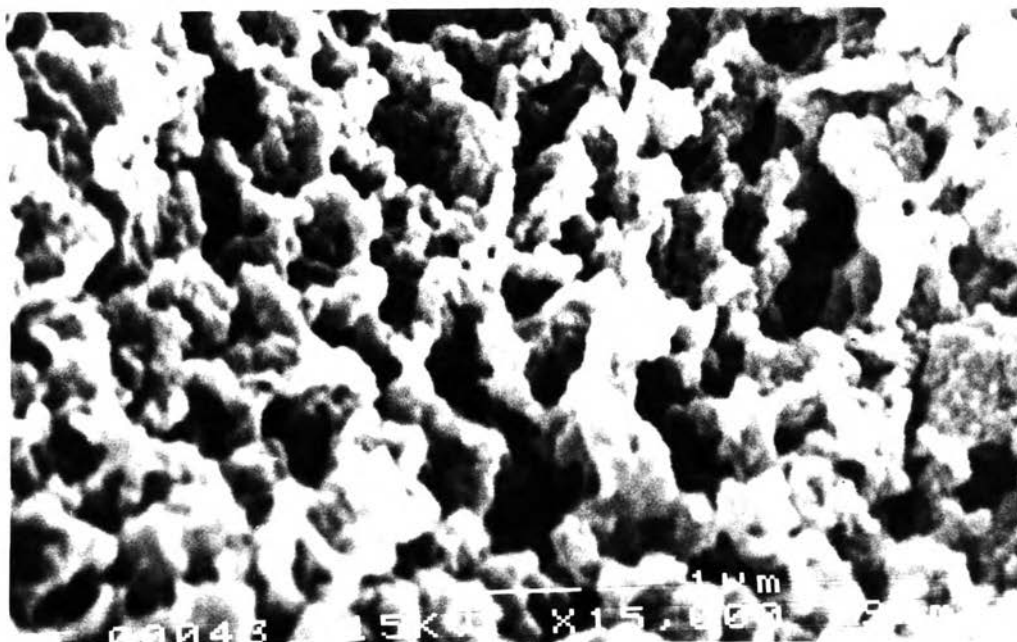
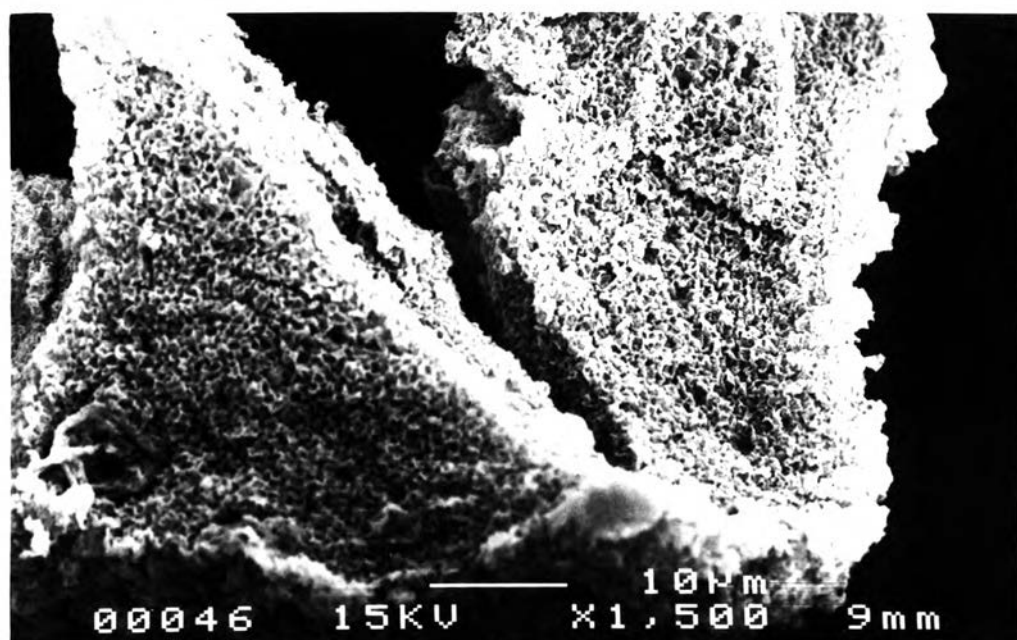


Figure 4.37 SEM Photographs of the Saponified Starch-g-poly(acrylamide-co-acrylic acid)

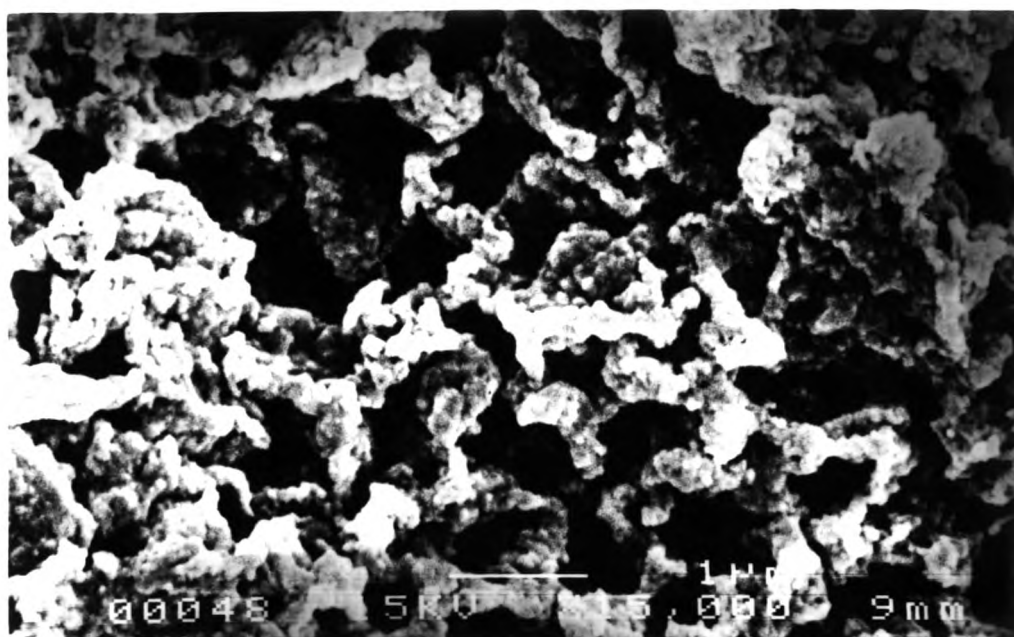
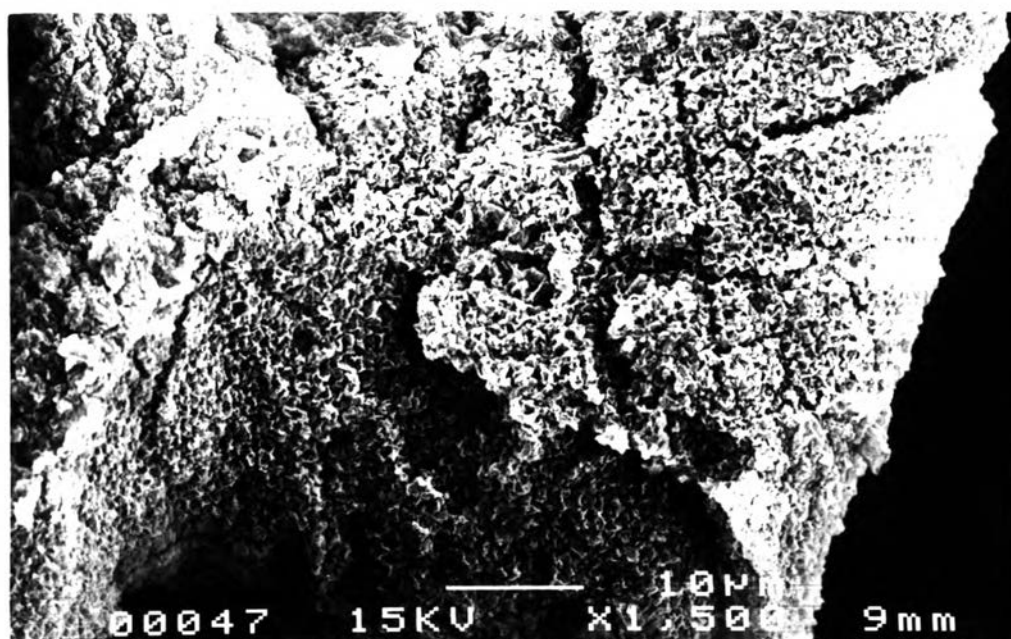


Figure 4.38 SEM Photographs of the Saponified Starch-g-poly(acrylamide-co-acrylic acid), with 0.01 M HNO₃ as an Additive

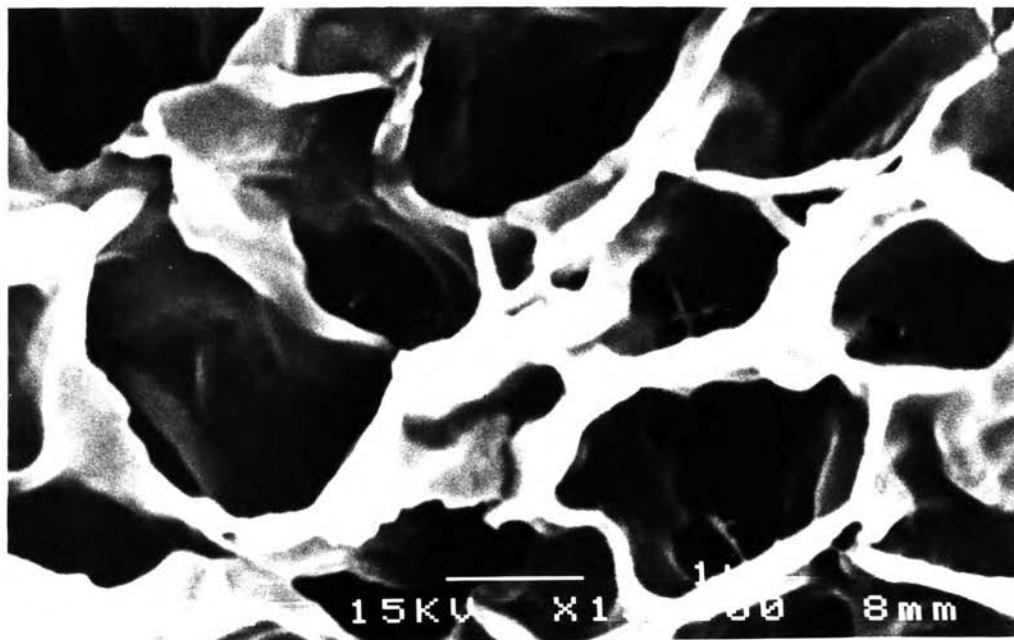
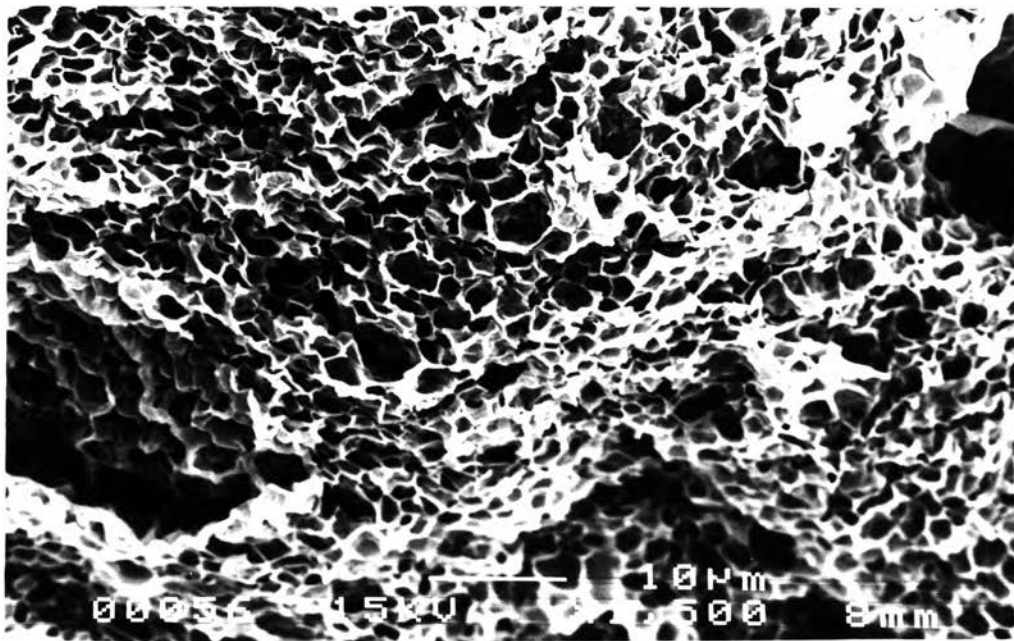


Figure 4.39 SEM Photographs Showing the Porous Structure of the Saponified Starch-g-poly(acrylic acid)

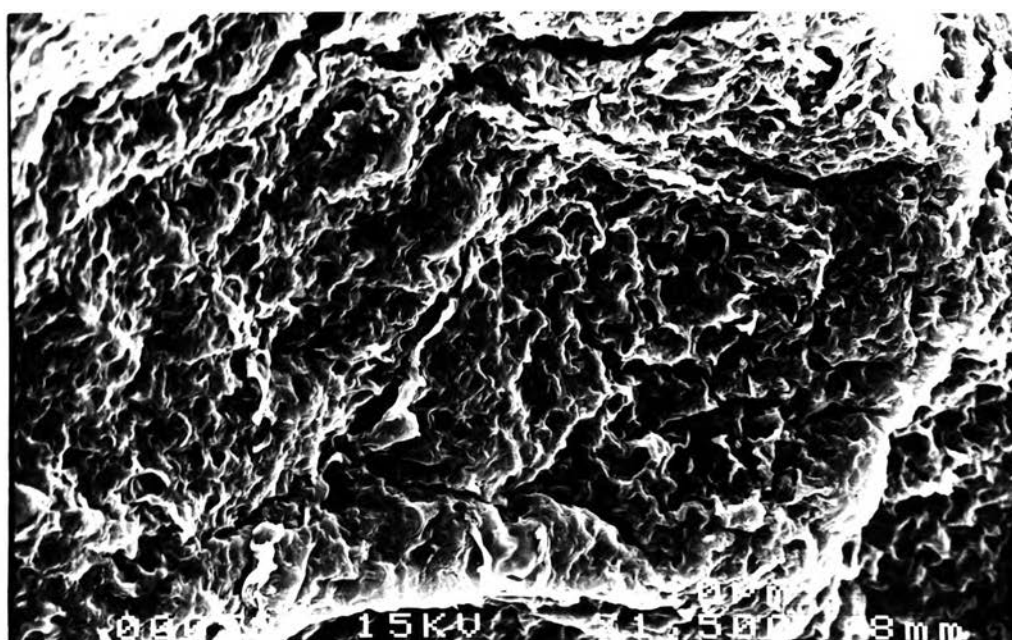


Figure 4.40 SEM Photographs Showing the Non-porous Structure of the Saponified Starch-g-poly(acrylic acid)

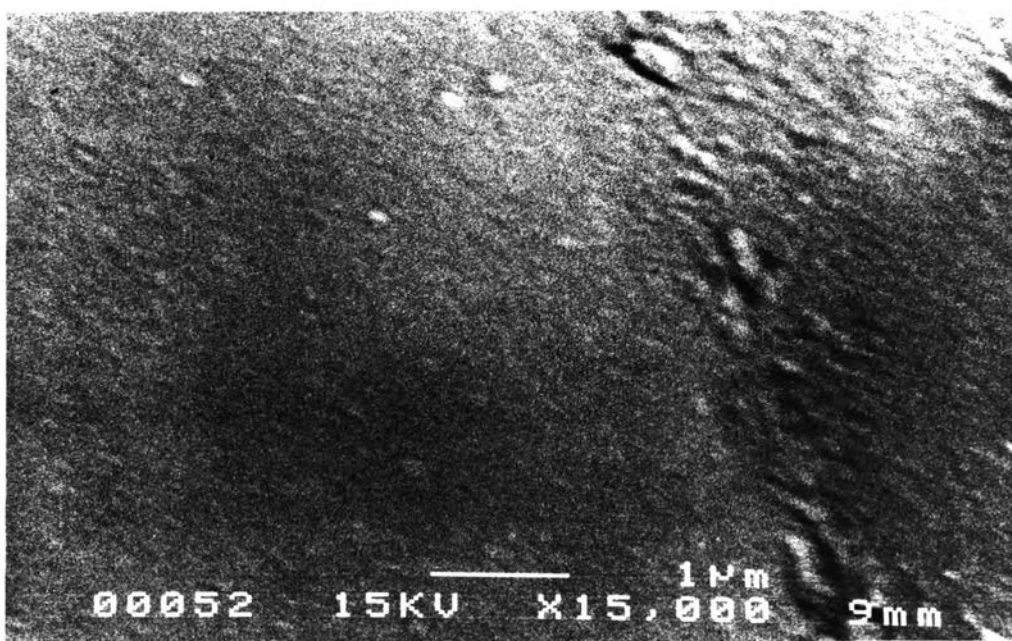


Figure 4.41 SEM Photographs of the Saponified Starch-g-polyacrylamide

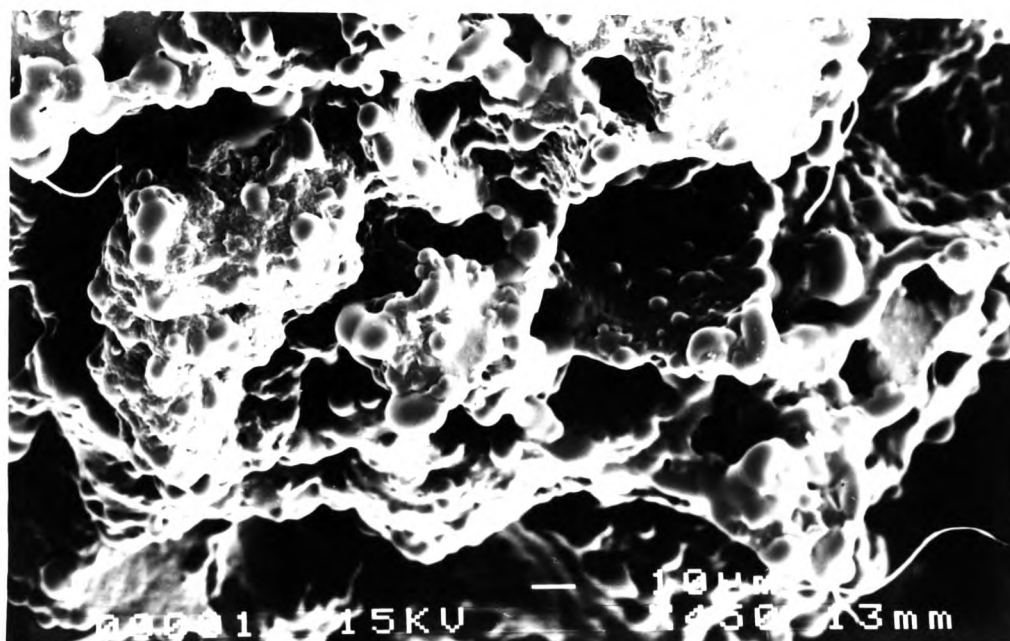


Figure 4.42 SEM Photograph of the Grafted Poly(acrylamide-*co*-acrylic acid)

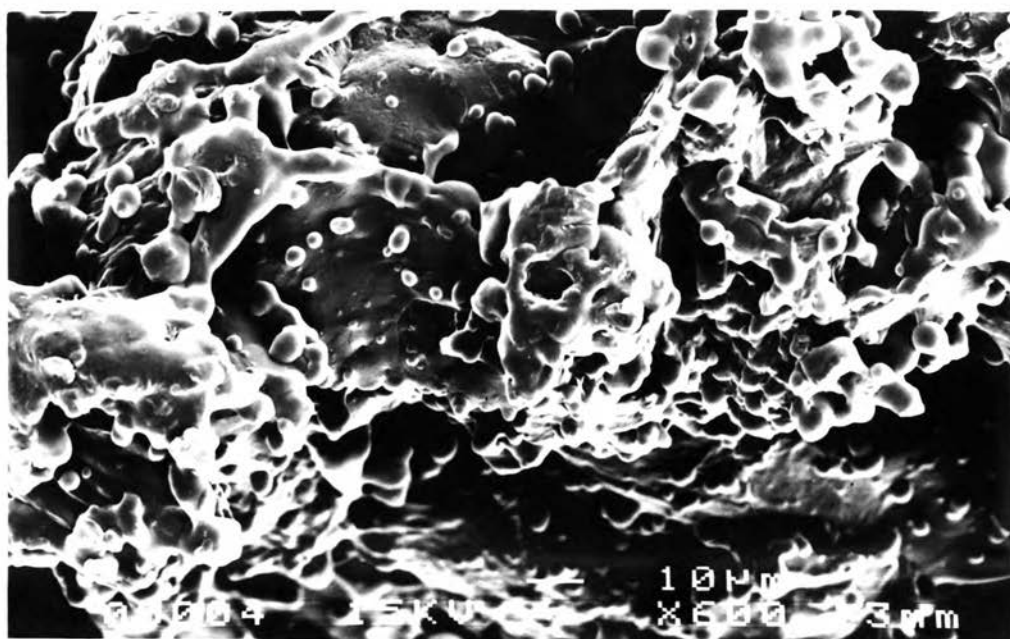


Figure 4.43 SEM Photograph of the Grafted Polyacrylamide