

CHAPTER IV

RESULTS and DISCUSSION

4.1 Simultaneous Irradiation Technique

Homopolymer formation always takes place during the graft-copolymerization of vinyl monomers onto a trunk polymer. Therefore, a reduction of homopolymer formation must be determined at the first stage of the experiment.

4.1.1 Reduction of Homopolymer

The first part of this experimental was a reduction of homopolymer (polyacrylonitrile) using several suppression salts and a thin film of metal, i.e. Morh's salts, lead nitrate, aluminium nitrate, and a thin film of aluminium foil, respectively. Graft copolymerization of this part was carried out without any exact temperature control. The results are showed in Table 4.1

Table 4.1 gives the comparative data of percent homopolymer by various salts and a thin sheet of aluminium foil. As mentioned in the previous work, the anions were found to have no effect on homopolymerization or grafting reactions (9). The present results indicate that a thin slice of aluminium foil reduces the homopolymer formation to some significant amount which is vitally important to

this reaction.

TABLE 4.1
Effect of Homopolymer Suppressors on
Percentage of Homopolymer Formation

Salts/Metal ^a	Weight (g)	[Salt]x10 ⁴ (mole/l)	[Cation]x10 ⁴ (g-ion/l)	Homopolymer (%)
CuSO ₄ .5H ₂ O	-	1.7	0.3	44.5
CuSO ₄ .5H ₂ O	-	8.3	1.3	40.7
CuSO ₄ .5H ₂ O	-	16.0	2.5	58.0
CuSO ₄ .5H ₂ O	-	32.0	5.1	58.3
0.1M.CuSO ₄ .5H ₂ O	-	0.5	0.02	61.0
0.1M.CuSO ₄ .5H ₂ O	-	1.0	0.03	57.4
0.1M.CuSO ₄ .5H ₂ O	-	2.0	0.06	47.1
Pb(NO ₃) ₂	-	5.0	2.5	63.2
Al(NO ₃) ₃	-	37.1	2.5	55.1
Al(NO ₃) ₃	-	66.7	4.5	46.0
Al(NO ₃) ₃	-	75.1	5.1	40.1
Aluminium foil	30.40	-	-	35.0
-	-	-	-	58.7

^adose rate 56.2 gray/min, total dose 5.058 kGy

As the reaction medium comprises about 90% (v/v) of water, the radiolysis products of water (in absence of oxygen: H·, OH·, and e⁻_{aq}) may be expected to play a significant role to the reaction. The grafting of AN

in aqueous solution to starch backbone has been studied in the presence of cupric sulfate, lead nitrate, aluminium nitrate, and a thin film of aluminium foil, respectively. The anions were found to impose no effect on grafting or homopolymerization(9).

Based on the above result, at the same cation concentration of 2.5 g-ion/l, Al^{+3} ion imposes a larger effect on suppressing homopolymer than do other cations. Consequently, the concentrations of Al^{+3} ion higher than 2.5 g-ion/l can suppress a large amount of homopolymer.

Disadvantages of mixing the metal other than aluminium in this set of reaction mixture are that the product was coloured and the metal ion was retained in the product. The residue metal ions affect the efficiency of water absorption/retention property.

The entire experiment that followed would make use of the highest suppression by the thin film of aluminium on homopolymer. Therefore, an aluminium foil of size 15 x 20 cm would be inserted into the reactor as the inner wall which in turn reduce the amount of PAN during the grafting copolymerization.

The effect of aluminium atom on the suppression of homopolymerization of acrylonitrile presumed that radical termination occurs by an electron transfer process from a $H\cdot$, $OH\cdot$, and e^-_{aq} to a p-orbital electron of the aluminium atom. However the exact mechanism of such metal has not clearly understood.

4.1.2 Effect of Total Dose on Graft Copolymerization.

The result of the 85°C gelatinized starch under various total dose exposures to the gamma rays is presented in terms of homopolymer, the grafting efficiency, the grafting ratio, the conversion of monomer, and % add-on as shown in Table 4.2

At present, IR spectroscopy was used as a tool to follow up changes in graft copolymerization. The IR spectra of Cassava starch, the graft copolymers after grafting, the graft copolymer after extraction, and after saponification are depicted in Section 4.1.4.1.

4.1.2.1 Relationship between Total Dose and % Homopolymer.

Since gamma irradiation usually involves the generation of β -electron from a cobalt-60 source, and as a consequent, when electrons strike an assembly of organic molecules, many phenomena can be induced. They include:

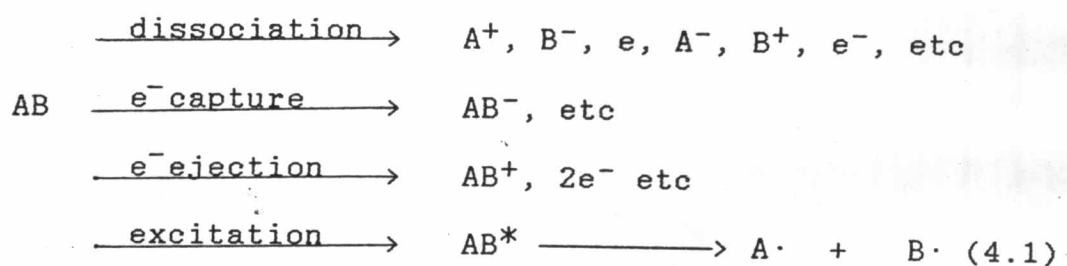


TABLE 4.2
Effect of Total Dose (kgy) on the Grafting of
Acrylonitrile onto Cassava Starch

Total dose ^a (kgy)	Homopolymer formed (%)	Grafting efficiency (%)	Grafting ratio (%)	Conversion of monomer (%)	Percent add-on (%)
1.686	12.3	58.1	24.7	51.7	19.8
2.529	3.4	89.1	40.6	58.0	28.9
3.372	18.4	55.5	37.8	73.0	27.4
4.215	22.9	46.7	39.2	75.1	26.0
5.058	26.1	38.9	29.1	76.2	22.6
5.901	33.8	30.9	24.5	85.8	19.7
6.744	39.3	21.9	22.3	90.6	18.2
8.430	42.0	16.3	16.4	90.9	14.1

^adose rate 56.2 gray/min

The current polymerization reactions are believed to occur predominantly through free radical processes with minimum participation of ions. The presence of water as a reaction medium and the reaction temperature at about 30 ± 1 °C has previously led us to believe that the roles of ions in these processes were suppressed. Therefore, all the explanations below were based on the role of free radical polymerization.

Table 4.2 and Figure 4.1 show the correlation

between the total dose and the homopolymer formed. The amount of homopolymer formed varied from 3.4 to 42.0 % depending on doses. The lowest homopolymer formed occurred at the total irradiation dose of 2.529 kgy; the homopolymer content increased with increasing the amount of total irradiation dose which were higher than 2.529 kgy. To optimize the formation of graft copolymer with the minimum of contaminating homopolymer there are a number of conditions which need to be met. Most importantly, the yield of radicals from radiolysis of polymer (G value) must be, as much as possible, in excess of that from the monomer. Thus the grafting of acrylonitrile onto starch backbone would be favored, since the G(Rad.) from acrylonitrile is about 5-5.6, compared with that of the starch about 10. This suggests that the higher irradiation dose gave a large amount of radiolysis products (in the absence of oxygen): $H\cdot$, $OH\cdot$ and e^-_{aq} of which $G(H\cdot)$, $G(OH\cdot)$ and $G(e^-_{aq})$ are 0.55, 2.8 and 2.7 at pH 4-7, respectively which initiated homopolymerization rather than grafting reaction. The G value or the yield of radicals from radiolysis product, such as solvent of the medium, was closer to the yield of radical from AN than the G value of polymer backbone (56,57). The $H\cdot$ and $OH\cdot$ are frequently chain transfer species to growing chains which consequently terminate the grafting reaction. The total irradiation dose at 2.529 kgy is thus just an optimum dose to generate the least amount of $H\cdot$, $OH\cdot$ and e^-_{aq} for chain transfer of

homopolymer growing chain.

4.1.2.2 Relationship between Total Dose and Grafting Efficiency.

Table 4.2 and Figure 4.2 also show that the grafting efficiency is highest at the total irradiation dose of 2.529 kgy. The grafting efficiency decreased with increasing total irradiation dose of those higher than 2.529 kgy and similarly it decreased with decreasing the total irradiation dose of those lower than 2.529 kgy. It then suggests that the decreasing grafting efficiency is due to the formation of small fragments of $H\cdot$, $OH\cdot$ and e^-_{aq} to form homopolymer at the expense of grafting. A low grafting efficiency, in the other word, a high formation of homopolymer, is not desirable since it would yield a material being composed of a starch backbone grafted with a low amount of synthetic polymer.

4.1.2.3 Relationship between Total Dose and % Conversion.

Table 4.2 and Figure 4.3 show a continuous increase in % conversion of monomer as the amount of total irradiation dose increases. This suggests that an increase in radiolysis products, less likely cationic species due to the existence of water, and most probably free radicals with increasing the total irradiation dose. All the monomers were possibly used up for both

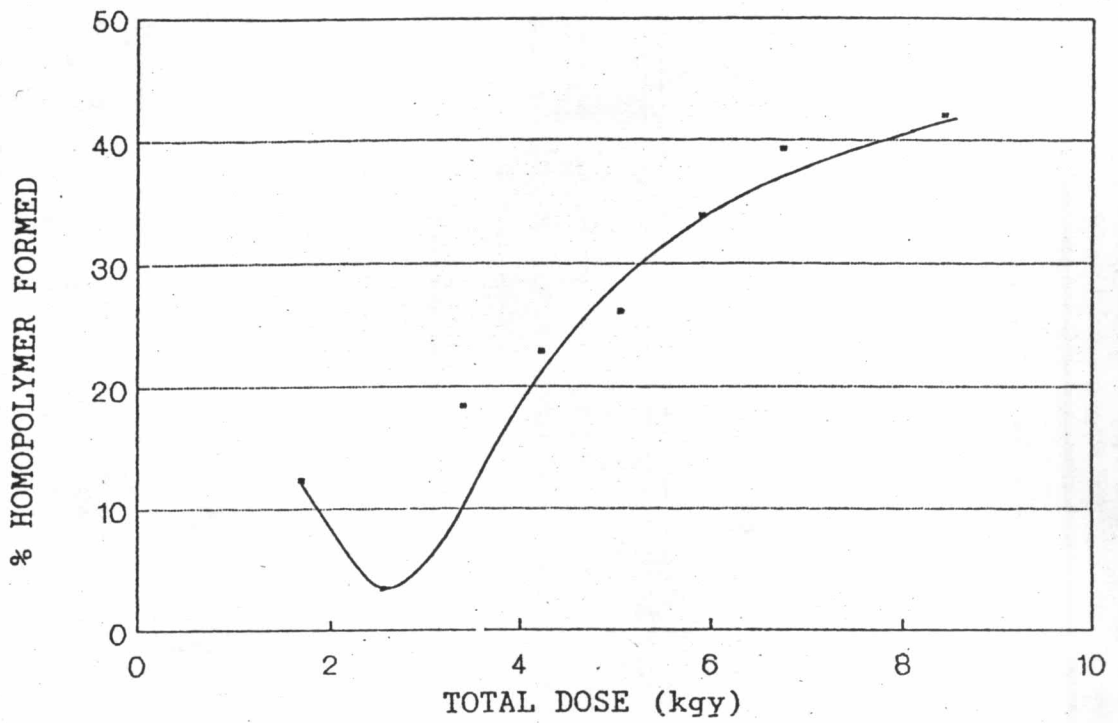


Figure 4.1 Effect of total dose on % homopolymer formed.

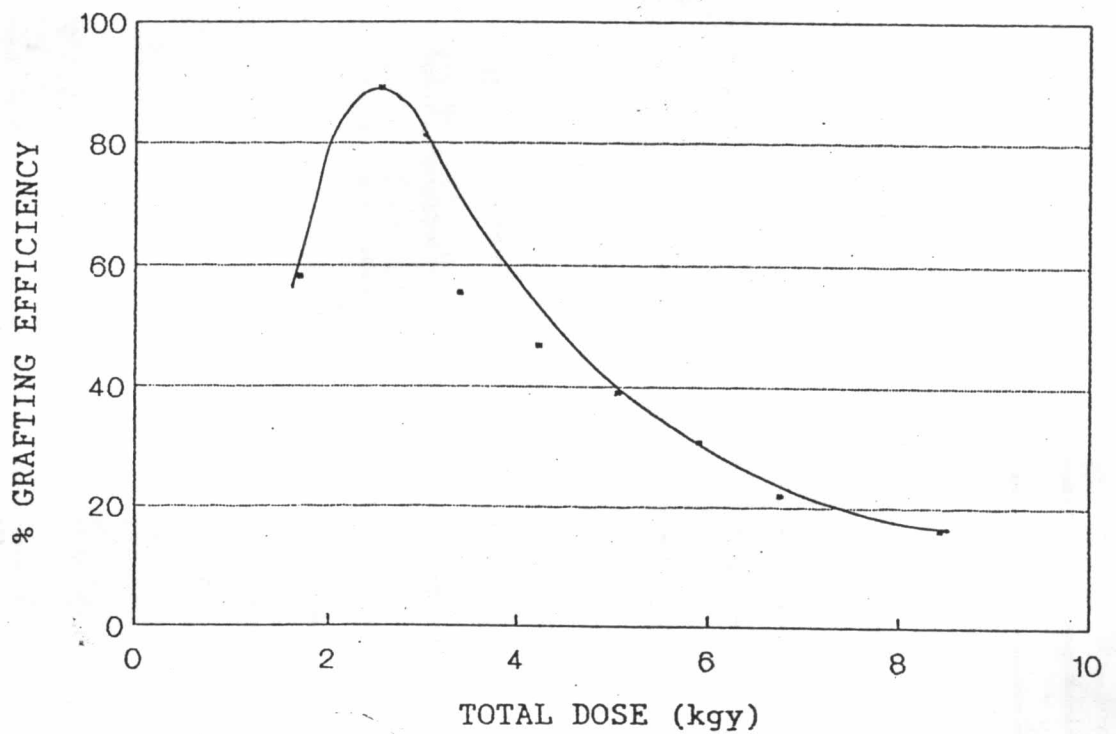


Figure 4.2 Effect of total dose on % grafting efficiency.

the homopolymer formation and grafting reaction under the influence of high dose. AN molecules were activated to induce higher conversion to polymers.

4.1.2.4 Relationship between Total Dose and % Add-on

The experimental data of the effect of total dose on % add-on are given in Table 4.2 and in Figure 4.4. The curve indicates that after reaching a total dose of about 2.529 kgy, the amount of acrylonitrile added to the starch backbone decreases. Such an observation may be speculated as the large polyacrylonitrile formed at the expense of polyacrylonitrile grafted to the starch backbone.

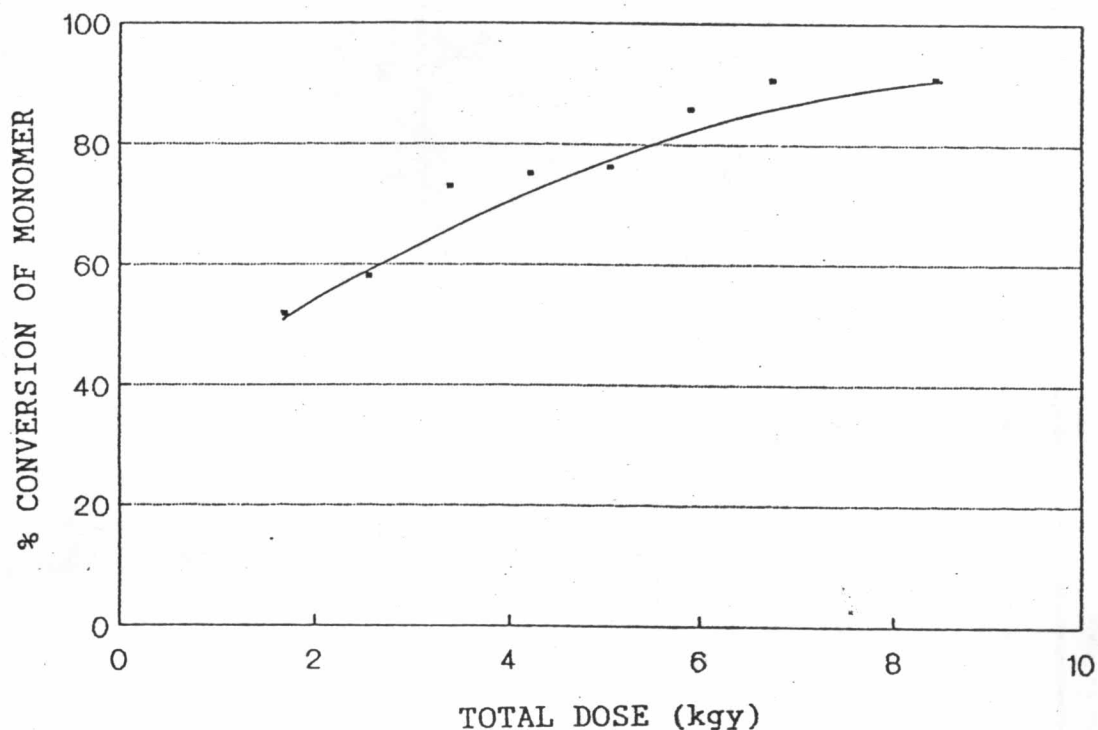


Figure 4.3 Effect of total dose on % conversion of monomer.

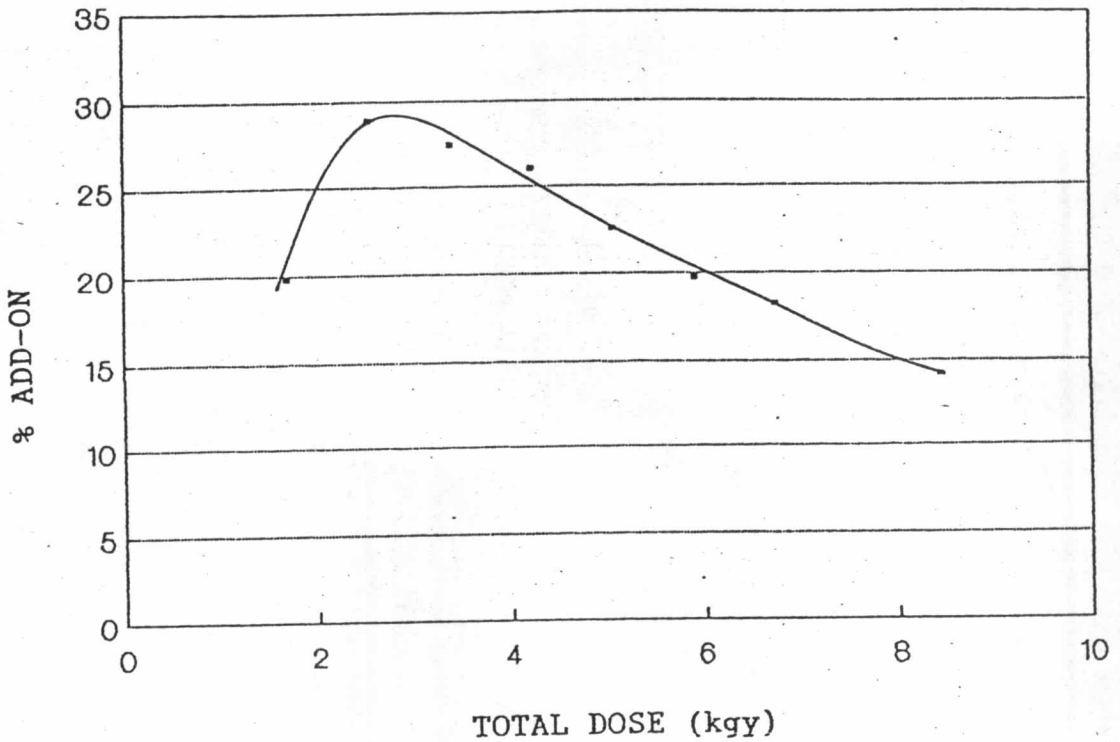


Figure 4.4 Effect of total dose on % add-on.

4.1.2.5 Relationship between Total Dose and Grafting Ratio.

The grafting ratios of grafted PAN are also shown in Table 4.2 and in Figure 4.5. The results show that the ratio of the number of PAN in grafts to the weight of starch is maximum in the range of irradiation dose of 2.529 to 4.215 kgy. At lower total dose (1.686 kgy) than 2.529 kgy, there were small number of PAN growing chain to be grafted on the polymer backbone. Likewise, at higher total dose than 2.529 kgy, radiolysis product induced homopolymerization than grafting reaction.

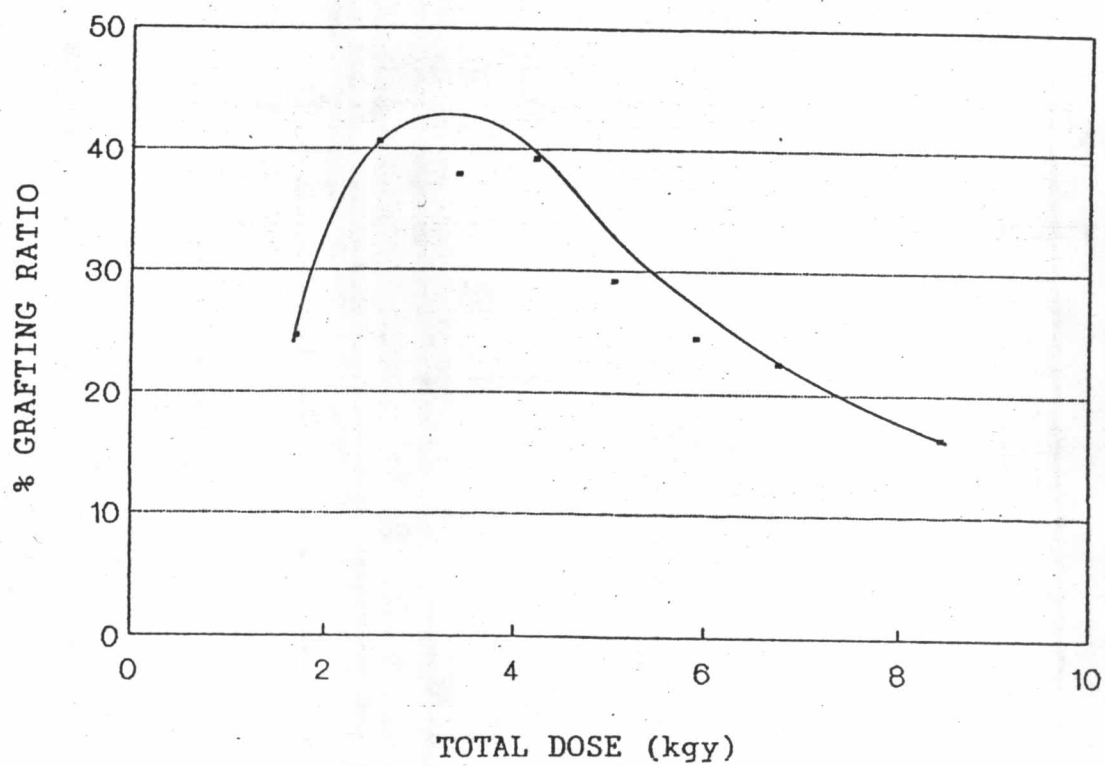


Figure 4.5 Effect of total dose on % grafting ratio.

4.1.2.6 Relationship between Total Dose and Viscosity Average Molecular Weight and Grafting Frequency.

The effect of total irradiation dose on viscosity average molecular weight (\bar{M}_v) and grafting frequency (AGU/chain) is given in Table 4.3

TABLE 4.3

Effect of Total Dose on Viscosity Average Molecular Weight and Grafting Frequency

Total dose (kgy)	Molecular weight (\bar{M}_v)	Grafting frequency (AGU / chain)
1.686	80,000	2,004
2.529	70,700	1,075
3.372	68,300	1,115
4.215	67,400	1,183
5.058	65,600	1,390
5.901	63,700	1,603
6.744	60,300	1,673
8.430	58,300	2,194

a) Relationship between total dose and viscosity average molecular weight.

The molecular weight of grafted polyacrylonitrile is illustrated in Table 4.3 and in Figure 4.6. When increasing the amount of total irradiation dose from 1.686 to 8.430 kgy, the \bar{M}_v of grafted PAN decreased from 80,000 to 58,300. Decrease in the molecular weight of polyacrylonitrile at higher dose was presumed primarily due to that the higher dose produced a substantial amount of short kinetic chain lengths of PAN resulting in a larger number of low molecular weights of PAN. Secondly, the

higher dose could probably induce degradation of the PAN existed in the earlier stage of irradiation.

b) Relationship between total dose and grafting frequency.

Table 4.3 and Figure 4.7 show the effect of total dose on grafting frequency. The grafting frequency is at highest (small number of AGU per chain, more frequently grafted) when the irradiation dose is 2.529 kgy. Before proceeding to further explanation, one should understand that the lower the number of AGU/chain, the higher the grafting frequency, i.e. more PAN being grafted to the polymer backbone. At lower total dose (1.686 kgy) than 2.529 kgy, there were not enough PAN growing chains to be grafted on the polymer backbone. Likewise, at higher total dose than 2.529 kgy, too many PAN radicals induced by radiolysis were produced and such radicals favored homopolymer formation due to diffusion predominance and thus less grafting reaction onto starch backbones.

4.1.2.7 Relationship between Water Absorption and Total Dose.

Water absorption in distilled deionized water by the saponified starch-g-polyacrylonitrile is tabulated in Table 4.4 and shown in Figure 4.8.

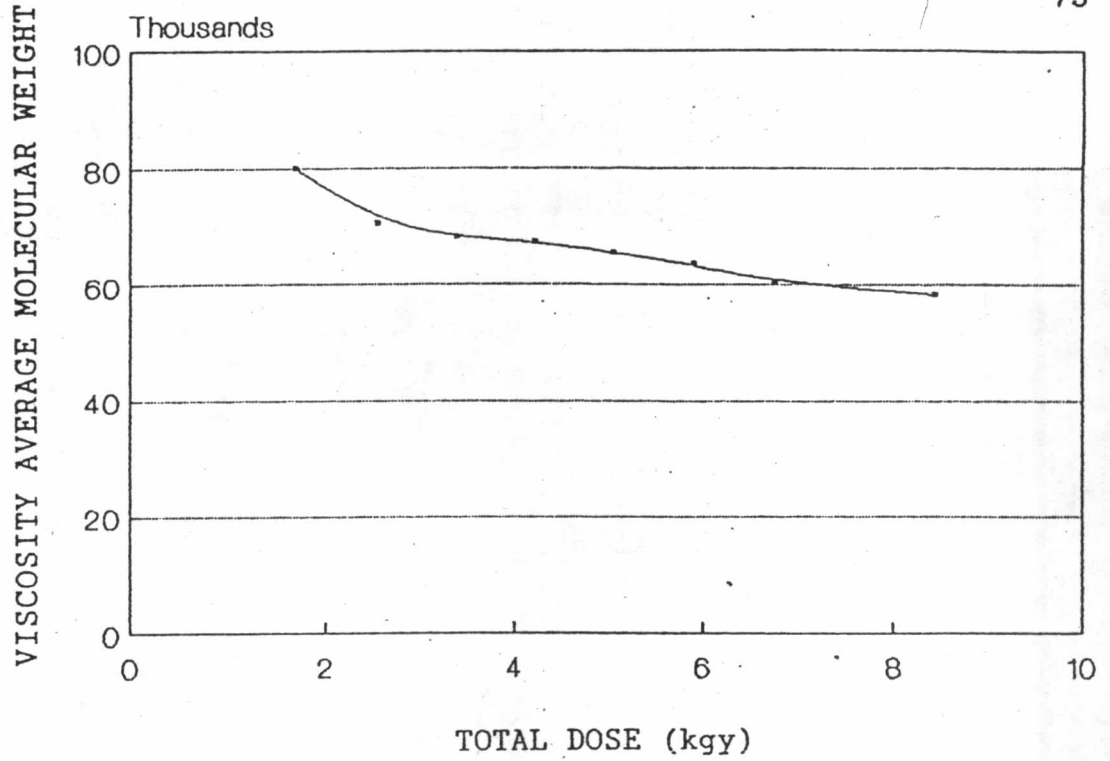


Figure 4.6 Effect of total dose on viscosity average molecular weight (\bar{M}_v) of grafted polyacrylonitrile.

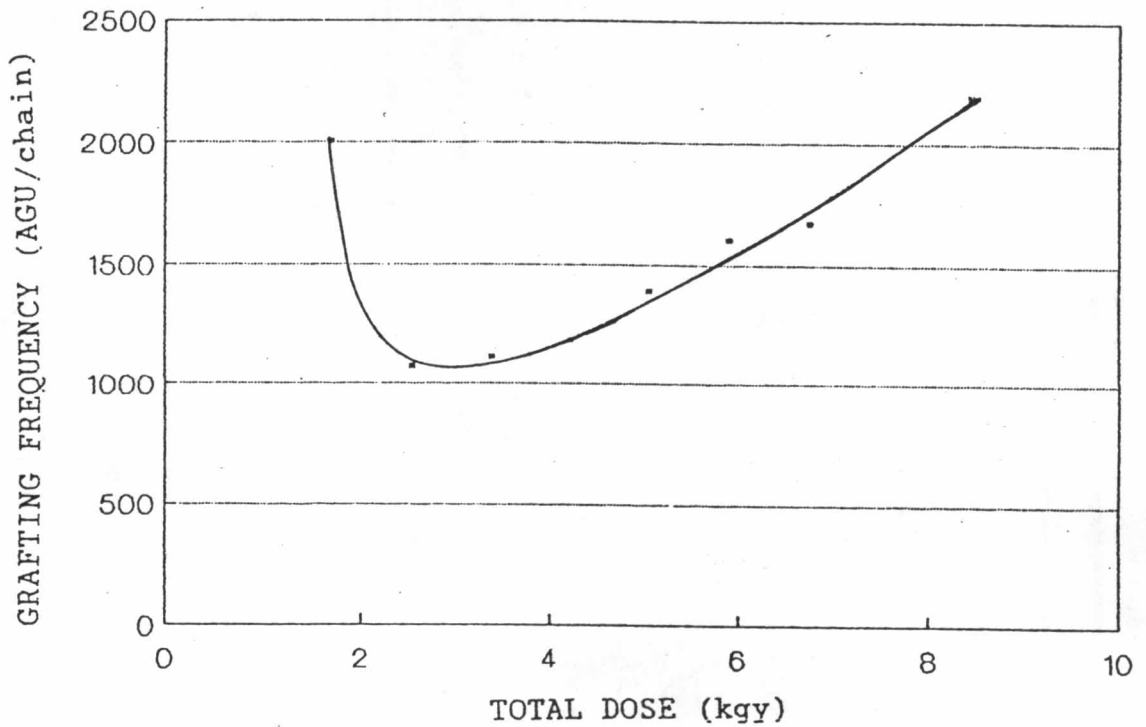


Figure 4.7 Effect of total dose on grafting frequency.

TABLE 4.4
Deionized Diistillated Water Absorption as a Function
of Total Dose

Total dose (kgy)	Water absorption in deionized distilled water(g/g)
1.686	88
2.529	235
3.372	164
4.215	150
5.058	145
5.901	117
6.744	90
8.430	83

The experimental data in Table 4.4 show that at the total dose of 2.529 kgy, the highest water absorption is obtained. Higher water absorption can be thus be correlated with the lowest percent homopolymer, the highest value in grafting frequency, % add-on, efficiency, and grafting ratio.

Figure 4.9 shows the correlation between the % add-on and water absorption. It indicates a linear relationship for this type of copolymerization, i.e. an increase in % add-on results in an increase in water absorption.

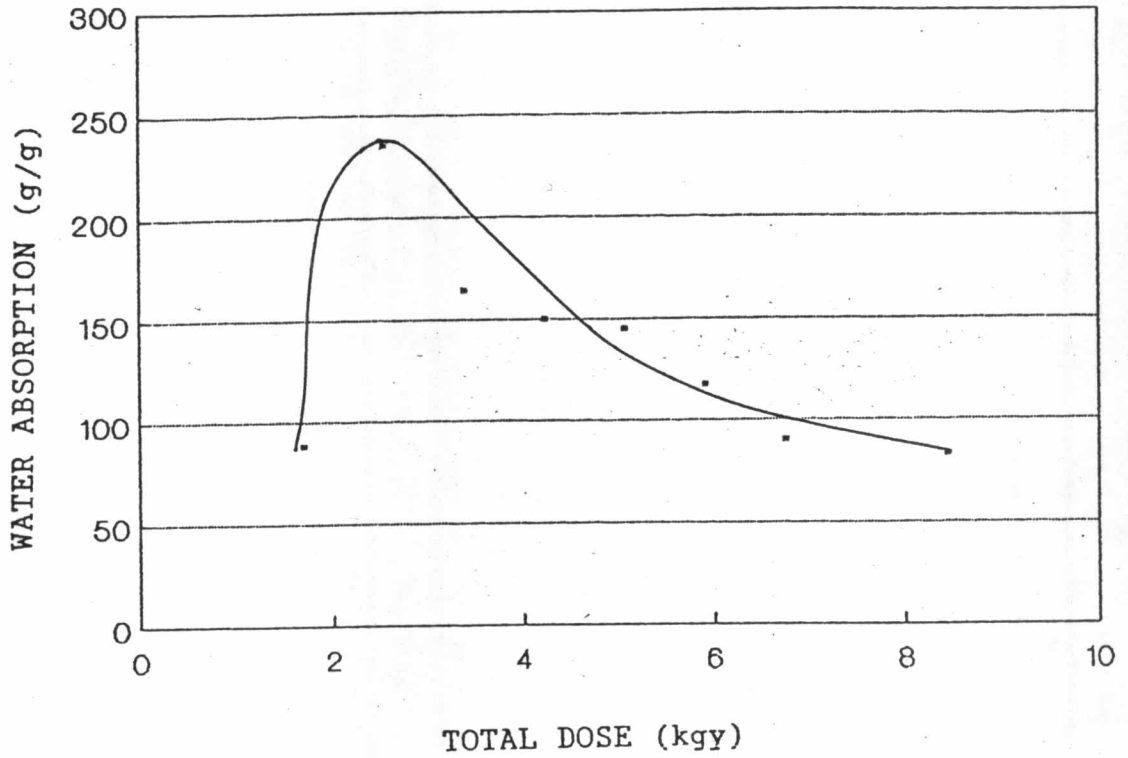


Figure 4.8 Effect of total dose on water absorption of saponified starch-g-polyacrylonitrile.

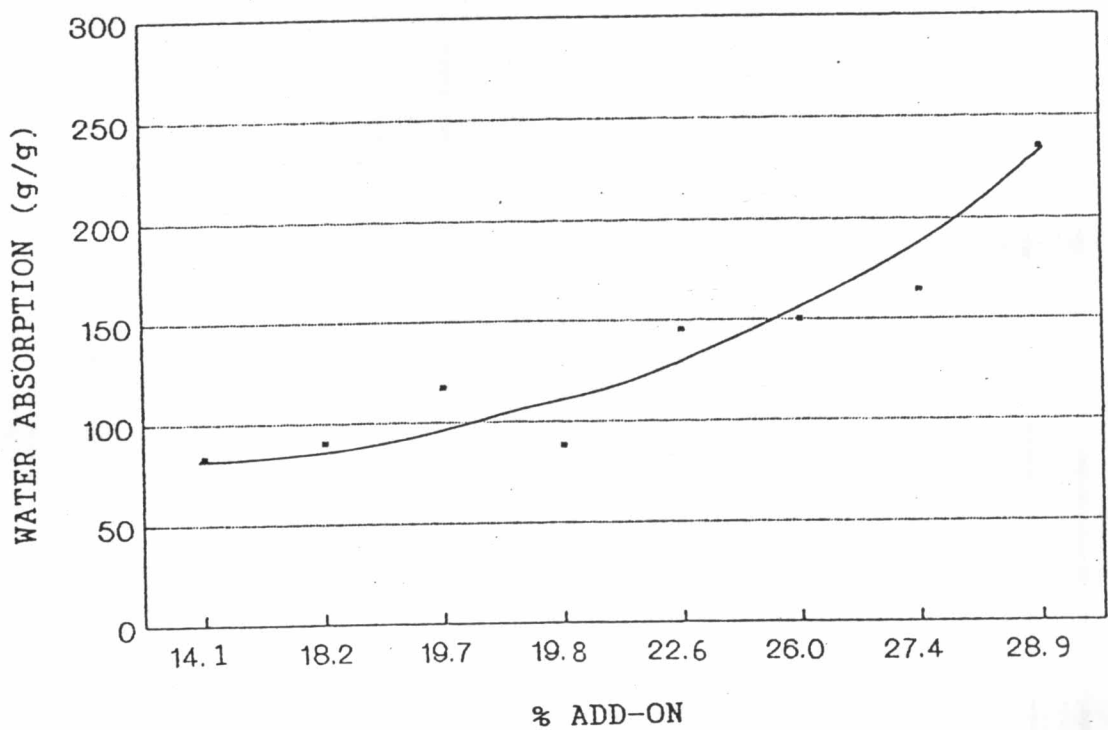


Figure 4.9 Water absorption as a function of % add-on obtained by various total doses.

4.1.3 Effect of Dose Rate (gray/min) on Graft Copolymerization.

The experimental data in the section 4.1.2 give the appropriate total dose for graft copolymerization of this system located at 2.529 kgy. This following section is devoted to the dose rate of gamma irradiation to be investigated by various pitch diameters(cm) of the gamma-ray machine. Figure 4.10 shows the correlation between the pitch diameter(cm) and dose rate (gray/min). It indicates an exponential decrease in dose rate with increasing pitch diameter.

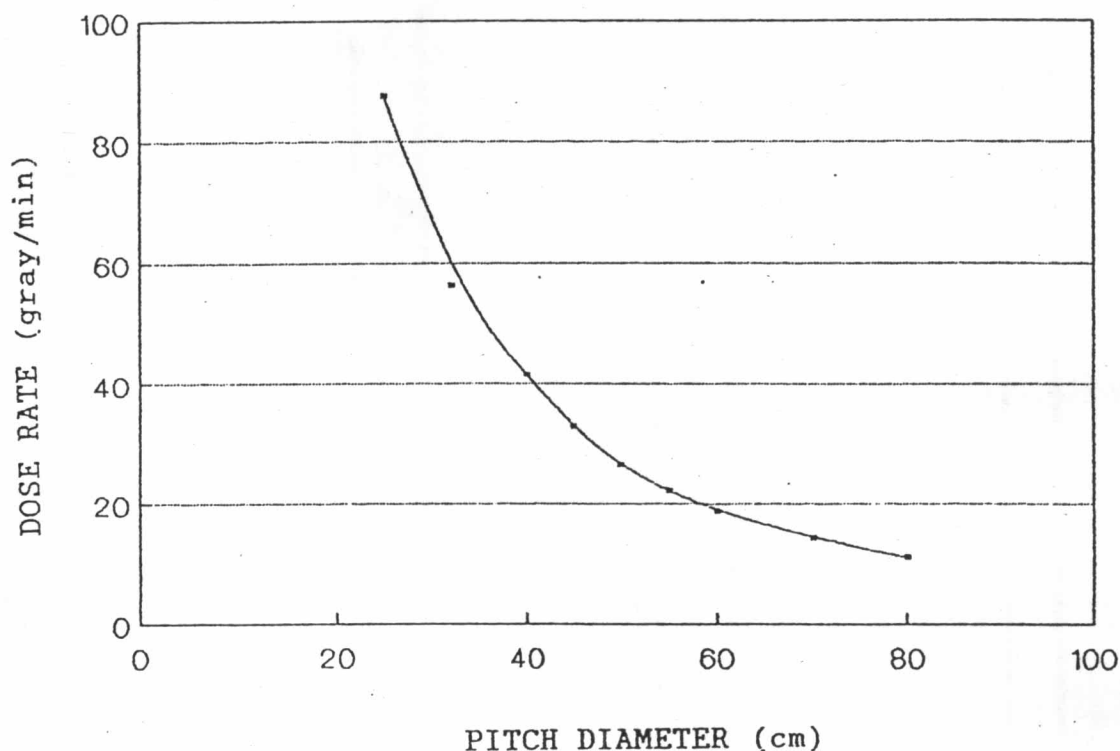


Figure 4.10 Effect of pitch diameter on dose rate of gamma radiation.

The effect of dose rate on the homopolymer formed, % add-on, the conversion of the monomer, the grafting efficiency, and the grafting ratio are tabulated in Table 4.5

TABLE 4.5
Effect of Dose Rate on Grafting of
Acrylonitrile onto Cassava Starch

Dose rate ^a (gray/min)	Homopolymer formed (%)	Grafting efficiency (%)	Grafting ratio (%)	conversion of monomer (%)	Percent add-on (%)
11.09	0.5	98.8	72.6	82.0	40.1
14.33	0.5	98.7	64.7	79.8	39.3
18.80	0.8	97.9	63.9	78.4	39.0
22.10	1.3	97.3	63.0	76.1	38.6
26.50	1.8	95.3	59.0	71.2	37.1
32.80	2.1	94.4	57.5	70.6	36.5
41.40	2.2	92.7	41.8	58.1	34.2
56.20	3.4	89.1	40.6	58.0	28.9
87.60	7.7	74.8	33.7	18.3	28.0

^atotal dose 2.529 kgy

At a higher dose rate, the generation of free radicals is greater accordingly. Basically, recombination of primary radicals in the bulk medium is higher as well at higher dose rate, i.e. with higher electron generation

due to the greater density of tracks.



Therefore, there are fewer radicals to start the chain initiation, the majority of the reaction of radicals occur almost exclusively by the diffusion of the radicals out of the solvent cage in which they were produced. This is also a wastage for graft copolymerization because the half life of the radicals is not very long enough to produce graft copolymer.

4.1.3.1 Relationship of Dose Rate and % Homopolymer.

The experimental data showing the effect of the dose rate on the homopolymer formation are given in Table 4.5 and in Figure 4.11. These data show that the homopolymer formed increases with increasing the quantities of dose rate. It suggests that high dose rates give the more appropriate condition for homopolymerization.

4.1.3.2 Relationship of Dose Rate and % Grafting Efficiency.

Table 4.5 and Figure 4.12 show the effect of dose rate on grafting efficiency. The data show

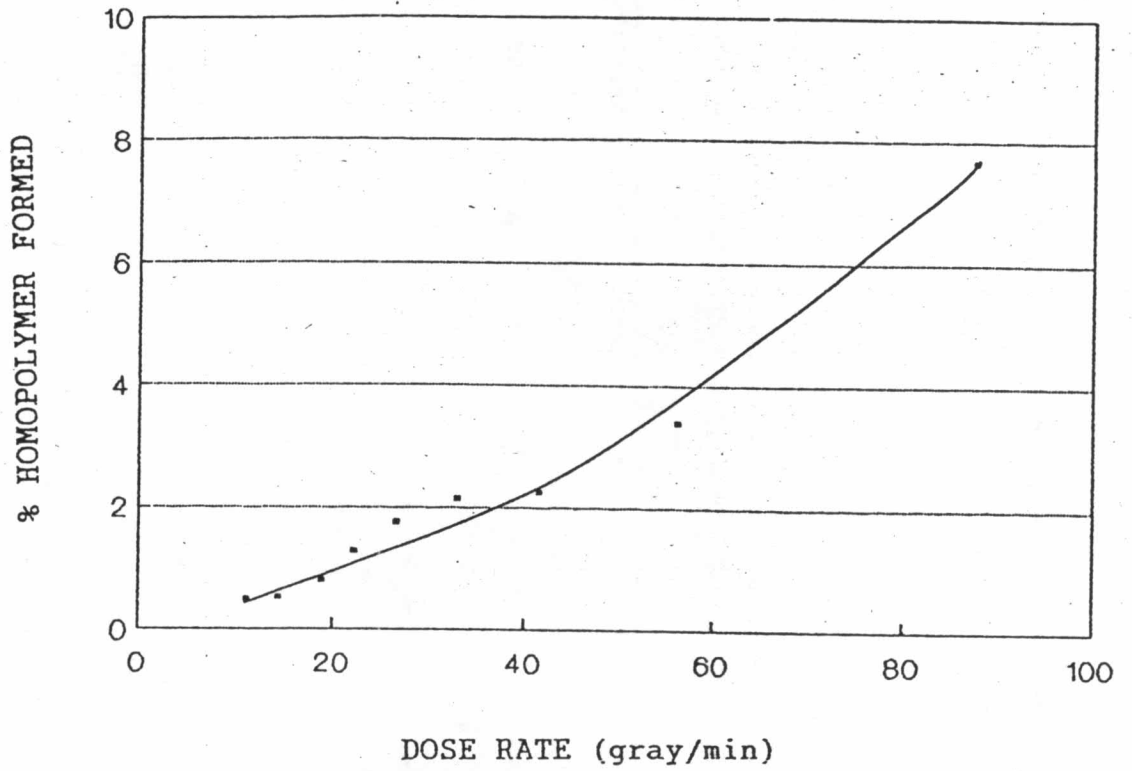


Figure 4.11 Effect of dose rate on % homopolymer formation.

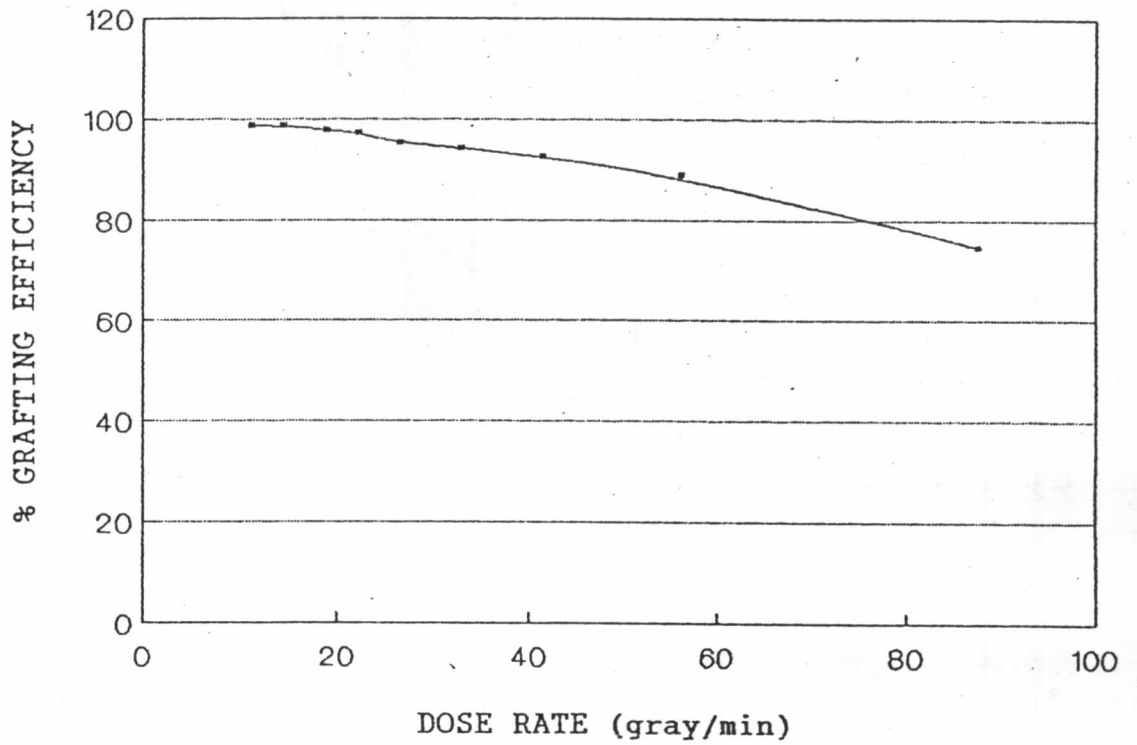


Figure 4.12 Effect of dose rate on % grafting efficiency.

that as the quantities of dose rate increases from 11.09 to 87.60 gray/min, the grafting efficiency decreases gradually from 98.8 to 74.8 %. Figures 4.11 to 4.12 indicate that a decrease in grafting efficiency results from an increase in homopolymer formed when the system was exposed to a shorter irradiation time at the same level of total dose.

4.1.3.3 Relationship of Dose Rate and % Conversion of Monomer.

The effect of the dose rate on the conversion of monomer is given in Table 4.5 and illustrated in Figure 4.13. When increasing the quantities of dose rate from 11.09 to 87.60 gray/min, The conversion of monomer decreased from 81.99 to 18.30 %. The decreasing trend of the conversion of monomer suggests that, in order to keep the total dose at a constant level, a low dose rate requires the longer irradiation time for the reaction to take place than that of a high dose rate to the same level of total dose. The effect of the irradiation time (min) on the quantities of dose rate is illustrated in Figure 4.14.

The lower dose rate implied a few radicals, cationic species in existence for the reactions. It does depend greatly on the magnitude of the half life of radicals. In the normal case, the radical half life could be as long as 3-4 days after exposure to gamma rays which should allow any homopolymer formation and graft copolymer

to occur. But in our particular case, the reaction was stopped immediately after removing it from the source. Therefore, the effect of after irradiation can certainly be ignored. At the higher dose rate of gamma-ray irradiation, several phenomena were observed elsewhere (58). Due to the abundant of free radical produced by gamma rays, although excessive free radicals could initiate a large amount of growing chains of graft copolymer and homopolymer, the existing growing chains were then completely and rapidly scavanged by the monomer, and perhaps those growing chains were also inactive by primary termination which involves propagating radicals reacting with primary radicals. These reactions were the attribute to the low conversion of the system.

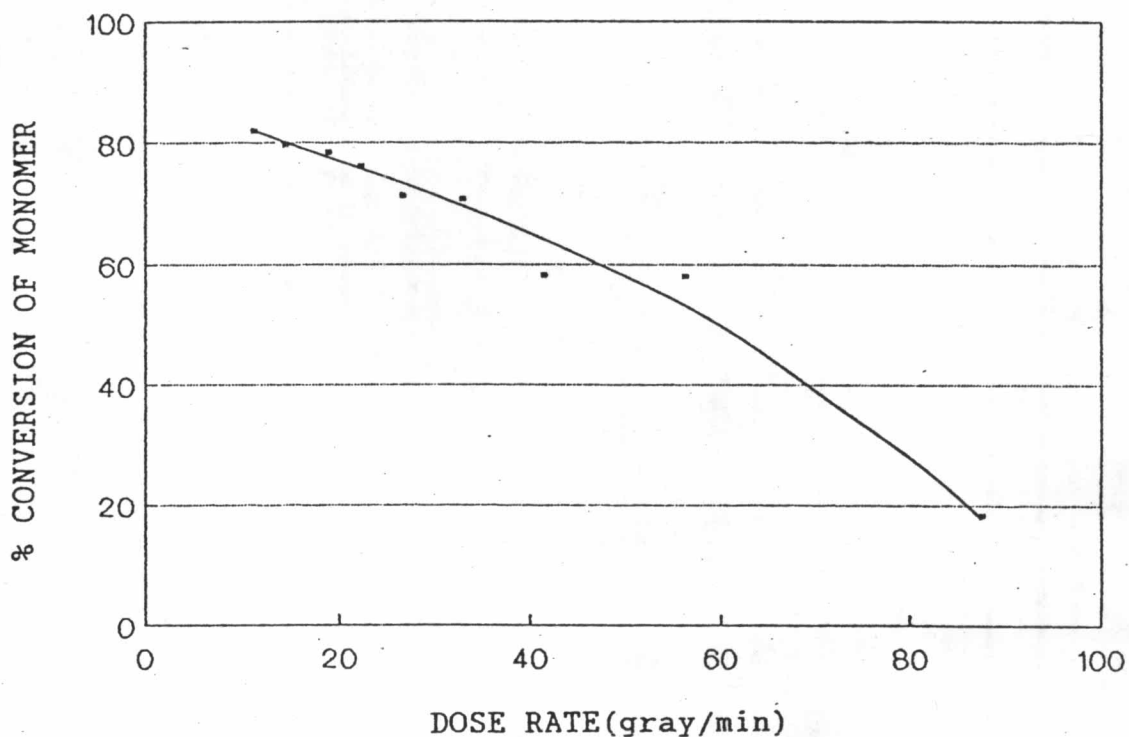


Figure 4.13 Effect of dose rate on % conversion of monomer.

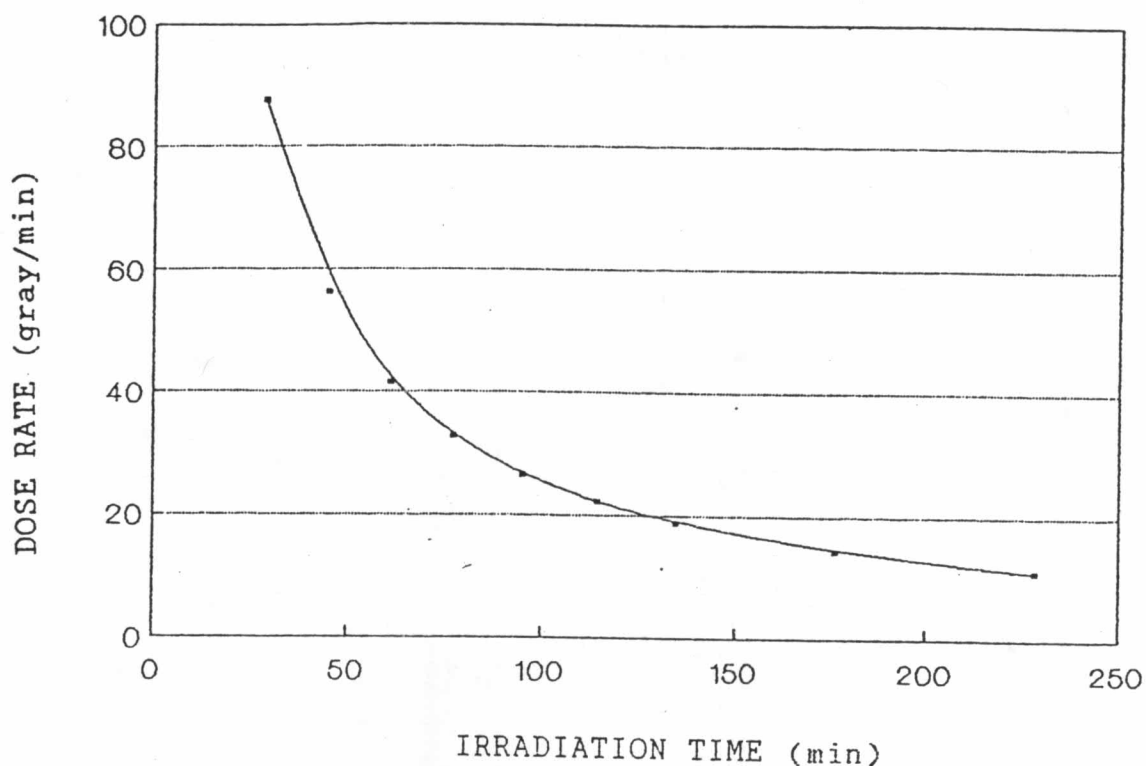


Figure 4.14 Relationship of irradiation time and dose rates.

4.1.3.4 Relationship of Dose Rate and % Add-on

The effect of dose rate on % add-on is given in Table 4.5 and illustrated in Figure 4.15. When increasing the dose rate from 11.09 to 87.6 gray/min, % add-on decreased from 40.1 to 28.0 %. This observation may suggest that the amount of radicals produced at lower dose rate either on the monomer and polymer backbone is more effective for grafting reaction. There were consequently less homopolymers due to less population of free radicals in the aqueous medium to collide between themselves which would thus become homopolymers. Likewise, the chance for these free radicals to diffuse to the polymer growing chain became larger and thus resulting in more grafts at low dose rate.

4.1.3.5 Relationship of Dose Rate and Grafting Ratio.

The effect of dose rate on grafting ratios of the grafted polyacrylonitrile are also shown in Table 4.5 and Figure 4.16. The results show that ratios of PAN in grafts/weight of starch decrease with increasing the dose rate. The higher dose rate, the greater the amount of free radicals produced which caused self-collision to yield less grafting reaction, instead, a greater amount of homopolymer were given.

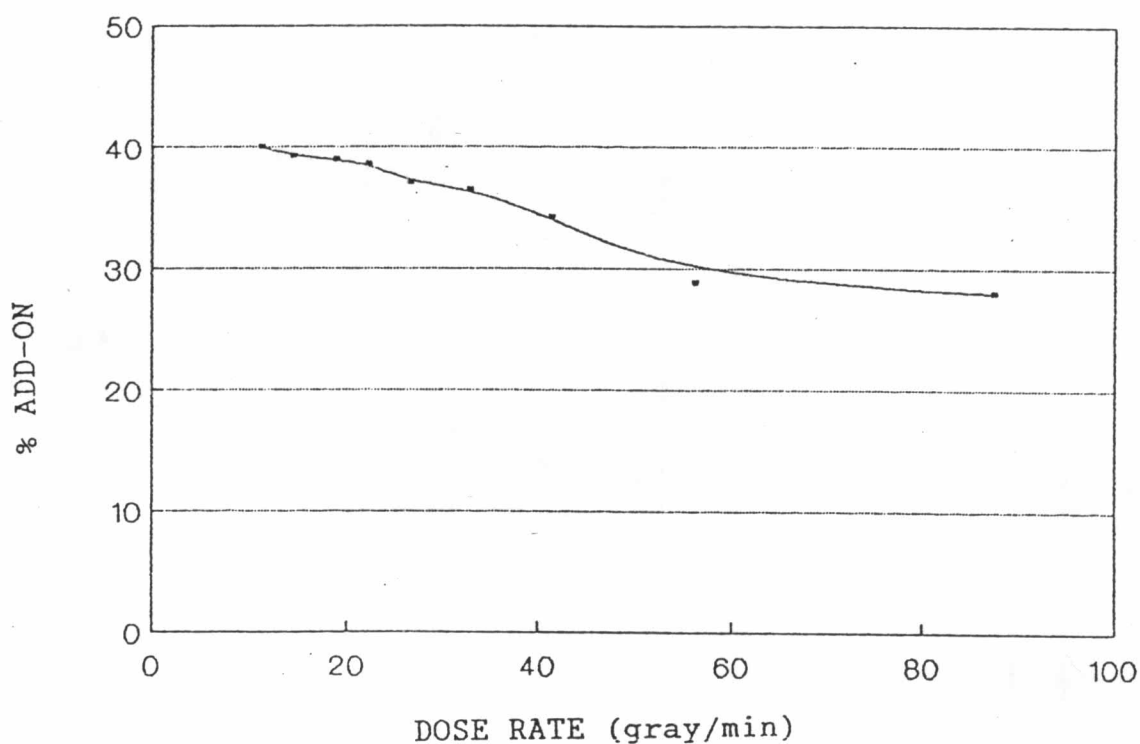


Figure 4.15 Effect of dose rate on % add-on.

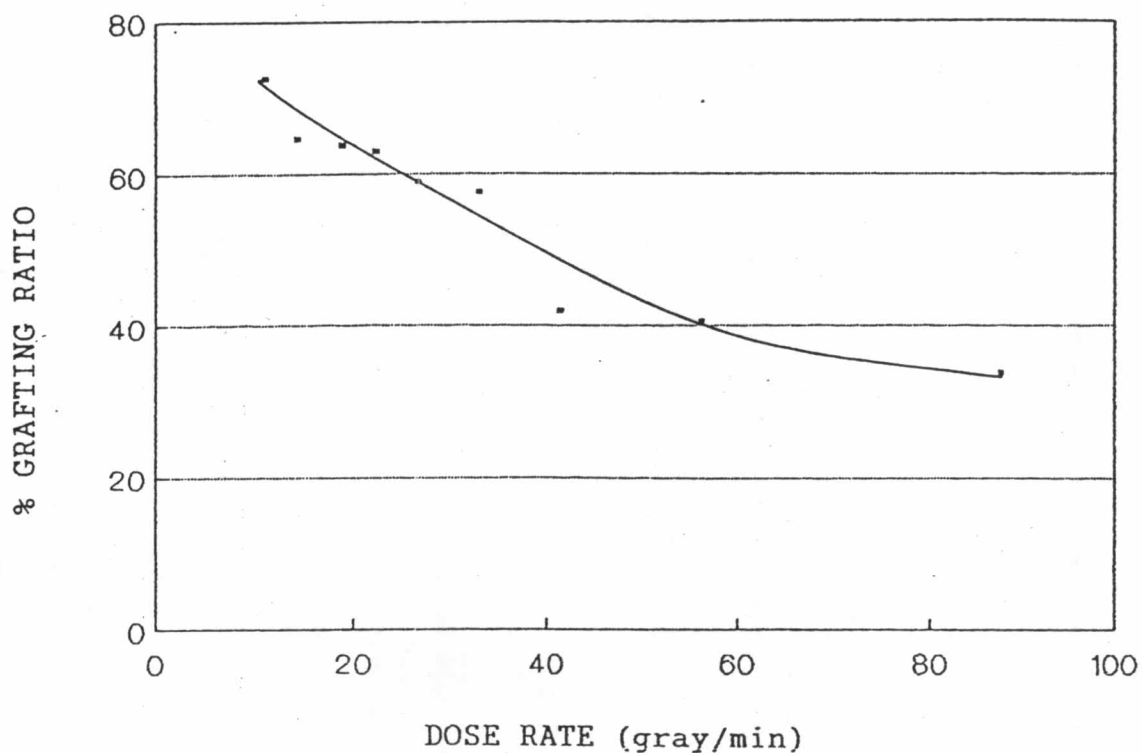


Figure 4.16 Effect of dose rate on % grafting ratio.

4.1.3.6 Relationship of Viscosity Average Molecular Weight and Dose Rate.

The experimental data of the molecular weight (\bar{M}_v) of grafted polyacrylonitrile and grafting frequency by various dose rates to the same level of total dose are given in Table 4.6

TABLE 4.6
Effect of Dose Rate on Viscosity Average
Molecular Weight (\bar{M}_v) and Grafting Frequency

Dose rate (gray/min)	Molecular weight (\bar{M}_v)	Grafting frequency (AGU/chain)
11.09	140,900	1,302
14.33	132,300	1,262
18.80	120,600	1,165
22.10	114,500	1,122
26.50	99,700	1,043
32.80	98,500	1,057
41.40	90,800	1,078
56.20	70,700	1,075
87.60	69,600	1,102

The molecular weight data are summarized in Table 4.6 and presented in Figure 4.17. The data show that as the quantities of dose rate were increased from 11.09 to 87.60 gray/min, the molecular weight decreased from 140,900 to 69,600. This finding can be explained as following: The lower dose rate of radiation produces less free radicals both on the monomer itself and the polymer backbone. There is a greater probability for the radicals to diffuse to the fully swollen polymer growing chains of starch and thus the higher the molecular weight of the grafts.

In addition, the continuous supply of radicals to the monomer is steadily that a longer chain can be realized to obtain the higher molecular weights of the grafts.

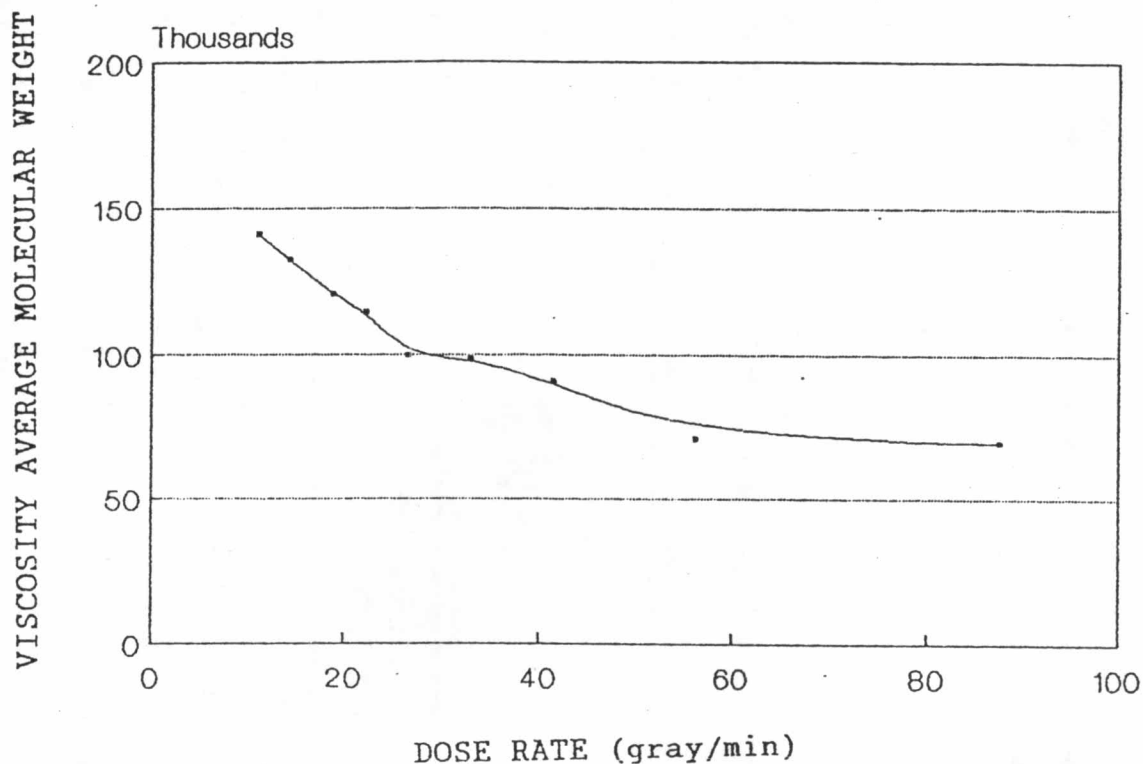


Figure 4.17 Effect of dose rate on viscosity average molecular weight (\bar{M}_v) of grafted polyacrylonitrile.

4.1.3.7 Relationship of Dose Rate and Grafting Frequency.

Figure 4.18 shows the effect of dose rate on grafting frequency. The results show that there is a continuous decrease in grafting frequency as the quantity of dose rate was increased. The onset of plateau of the curve was observed at the dose rate of 26.50 gray/min. Although the supply of monomer free radicals was steadily, there were no more any active sites on the polymer

backbones available for grafting reaction. That meant the minimum number of anhydroglucoside units being grafted per chain or the greater frequency of grafted PAN could exist in the graft copolymer.

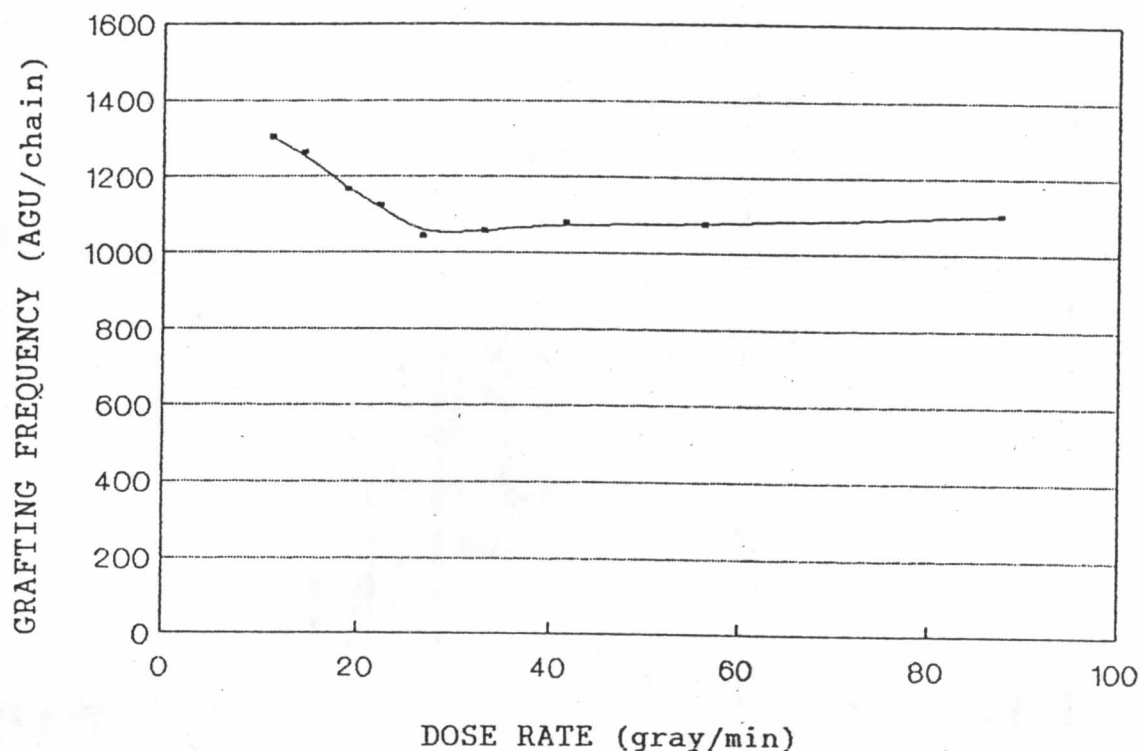


Figure 4.18 Effect of dose rate on grafting frequency.

4.1.3.8 Relationship of Dose Rate and Water Absorption.

The effect of dose rate on water absorption in deionized distilled water by saponified starch-g-PAN is tabulated in Table 4.7 and shown in Figure 4.19. The results show that the highest water absorption occurred at a dose rate of 18.80 gray/min. The higher dose rate gives the lower absorption and, likewise, the dose rates lower than 18.80 gray/min also give the lesser water absorption.

TABLE 4.7
Effect of Dose Rate on Water Absorption in Deionized
Distillated Water

Dose rate (gray/min)	Water absorption in deionized distillated water (g/g)
11.09	368
14.33	398
18.80	445
22.10	369
26.50	339
32.80	318
41.40	312
56.20	235
87.60	175

Water absorption was maximum at the dose rate of 18.80 gray/min where its corresponding % add-on was at 39.0

Figure 4.20 shows the correlation between the % add-on and water absorption. It indicates that increase in % add-on resulting in the increase in water absorption.

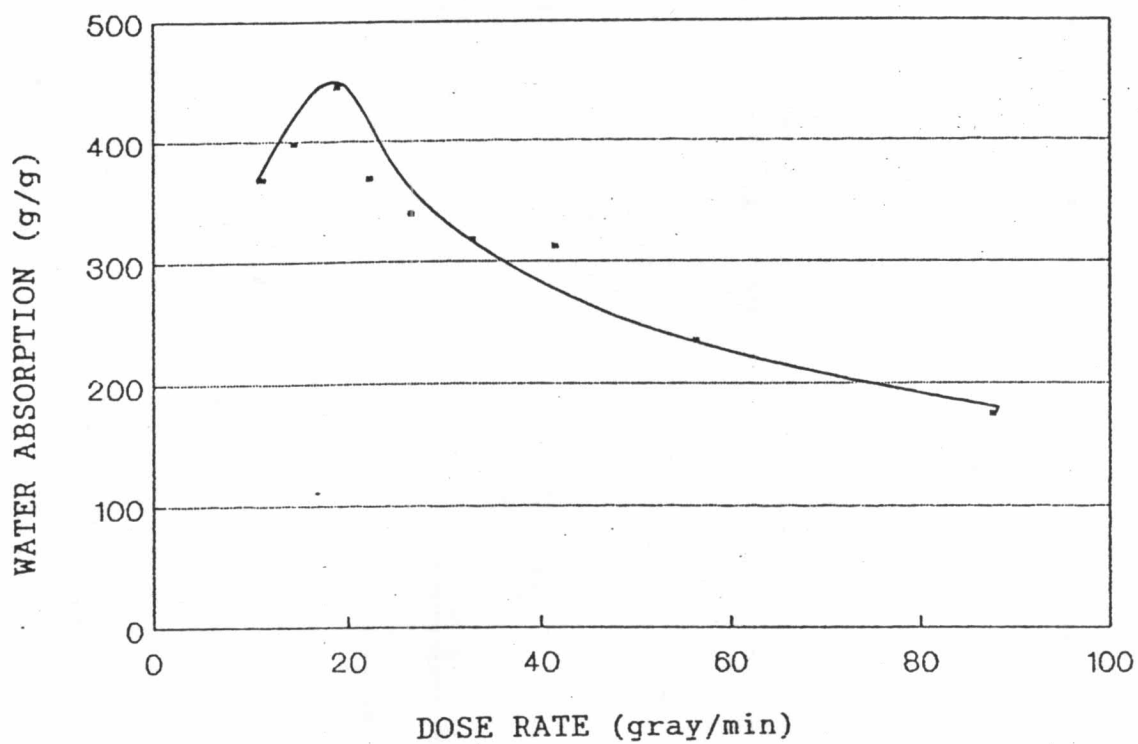


Figure 4.19 Effect of dose rate on water absorption by saponified starch-g-PAN in deionized distilled water

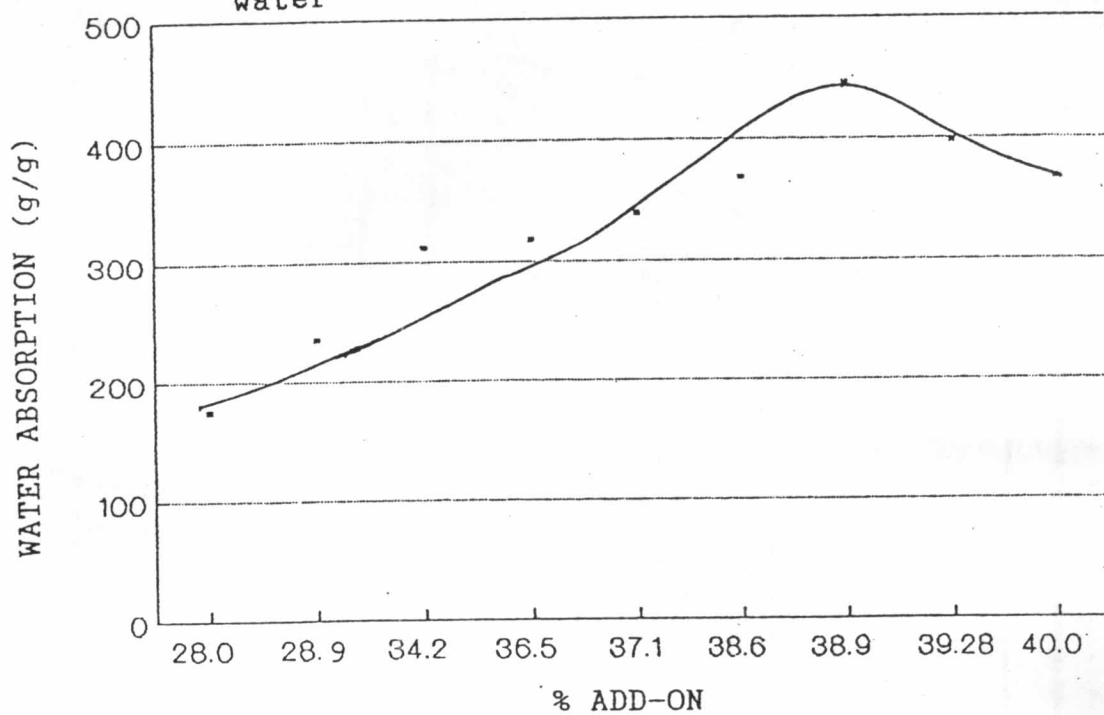


Figure 4.20 Water absorption as a function of % add-on obtained by various dose rates.

4.1.4 Effect of Starch(g)/Acrylonitrile(ml) Ratios on Graft Copolymerization.

According to the results of total dose and dose rate appropriate for graft copolymerization of AN onto Cassava starch, the total dose of 2.529 kgy with a dose rate of 18.80 gray/min were found to provide the maximum water absorption in doubly deionized water. The previous studies indicated that there were some cases where the amounts of monomer added were not enough for both reactions. Although the minimum amount of homopolymer formed was desirable, maximum water absorption was still a very important parameter. The effect of starch-to-AN ratios on water absorption is of paramount importance and worthwhile carrying out.

4.1.4.1 Infrared Analyses

Figures 4.21-4.24 show the respective IR spectra of Cassava starch, The reaction product after grafting, the starch-g-PAN with DMF extraction, and the starch-g-PAN after saponification with 8.5% KOH. The IR spectrum of Cassava starch in Figure 4.31 gives absorption bands at 3,400 and 1,000-1,100 cm^{-1} , the characteristics of amylose containing in the starch. After the grafting reaction of acrylonitrile onto Cassava starch, a sharp peak occurred at 2,243 cm^{-1} representing the stretching absorption band of the CN group(59). This peak slightly decreased after DMF extraction of the homopolymer, which occurred as

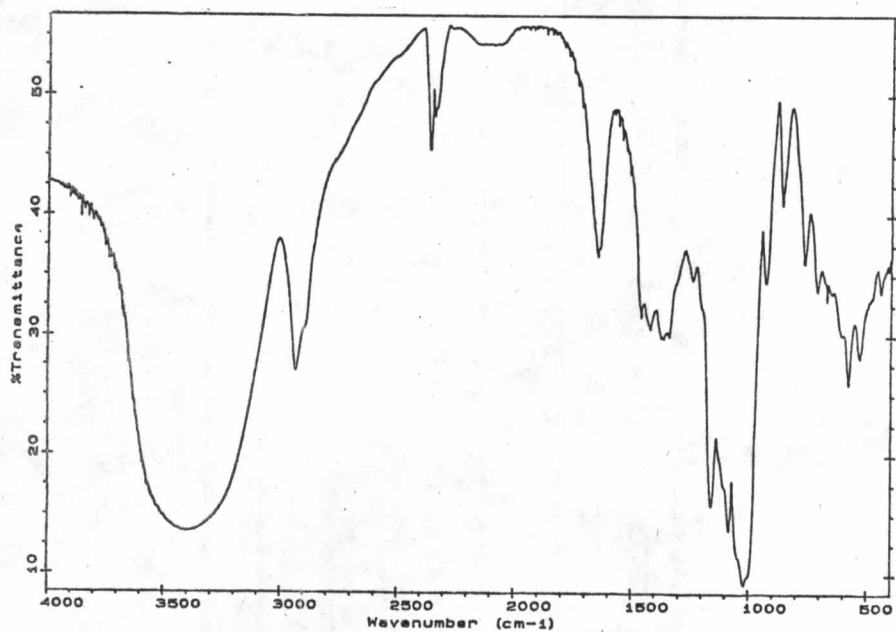


Figure 4.21 Infrared spectrum of dried cassava starch.

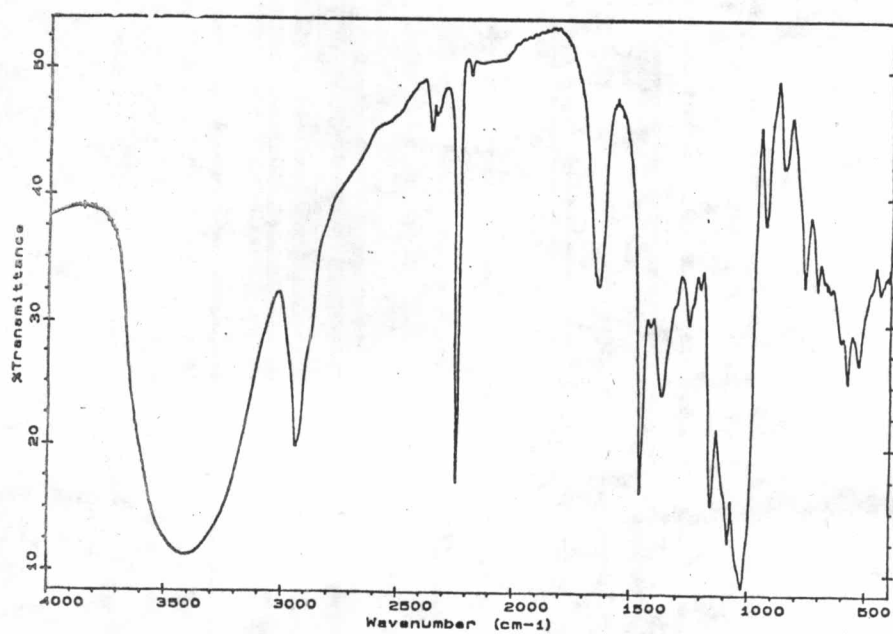


Figure 4.22 Infrared spectrum of the graft copolymer after grafting.

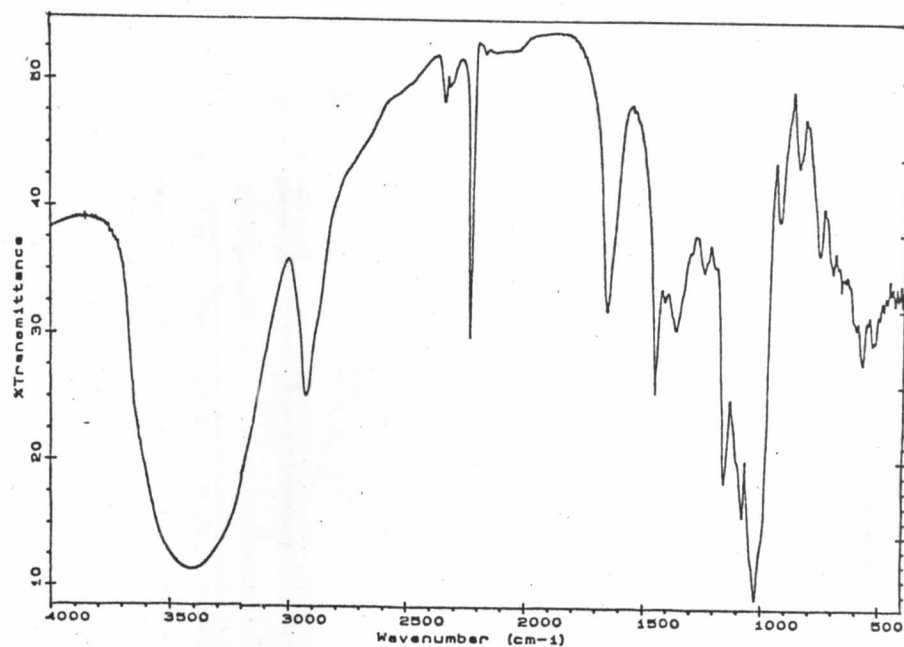


Figure 4.23 Infrared spectrum of the graft copolymer after DMF extract.

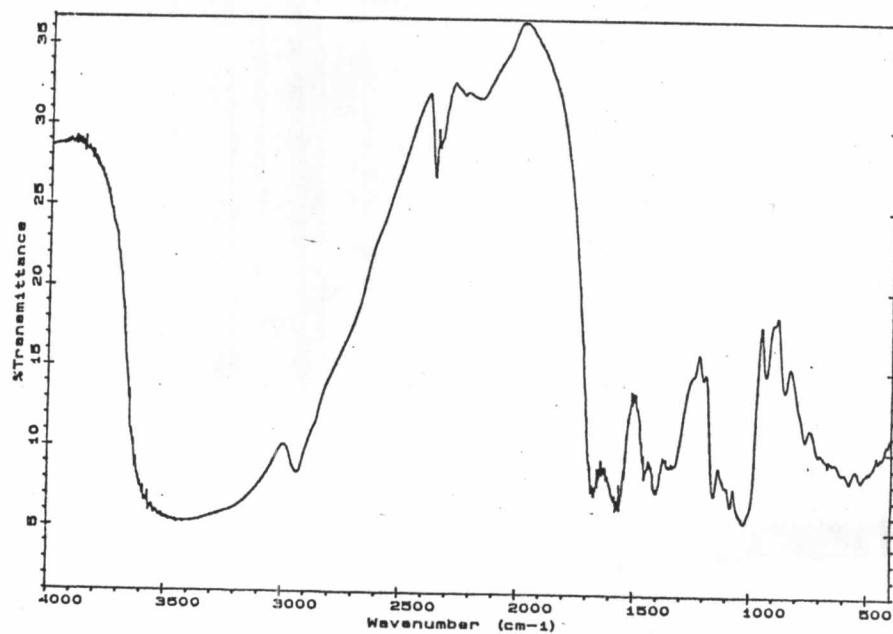


Figure 4.24 Infrared spectrum of the saponified graft copolymer.

a by-product during the grafting reaction. When the graft copolymer was saponified, all CN groups were hydrolyzed into the carboxylate and carboxamide group and resulted in the disappearance with other peaks, we could not detect the C=O stretching bands of carboxylate and carboxamide groups. In addition, the length of C≡N peak at $2,243\text{ cm}^{-1}$ could be used as a measure for the degree of percent conversion of AN to polymers before DMF extraction and of grafting reaction after the similar extraction, when various amounts of starch-to-AN ratios were used in the following experiment.

4.1.4.2 Effect of Starch-to-AN Ratios on Homopolymer

Table 4.8 gives the data of % add-on, the grafting efficiency, the grafting ratio, the homopolymer formed, and the conversion of monomer obtained by various starch (g)/AN (ml) ratios.

The percentage of homopolymer formed varied from 0.7 to 6.5 % as the concentrations of acrylonitrile increased from 5.0 to 40.0 ml. The corresponding percentage of homopolymer was depicted in Figure 4.25. The homopolymer content at the lower ends of monomer concentration increased only slightly and then increased rather significantly with increasing the concentration of AN at the higher concentration.

TABLE 4.8

Effect of Starch(g)/AN(ml) on Graft Copolymerization of Acrylonitrile onto Cassava Starch.

Starch(g)/ AN(ml) ^a	Homopolymer formed (%)	Grafting efficiency (%)	Grafting ratio (%)	Conversion of monomer (%)	Percent add-on (%)
10:5	0.7	97.9	32.8	76.9	24.7
10:10	0.8	97.2	63.9	77.3	39.0
10:15	1.6	96.3	71.4	76.5	41.7
10:20	2.4	95.3	94.4	76.1	48.6
10:25	4.0	93.5	137.7	78.0	57.9
10:30	5.7	91.5	147.6	76.2	59.6
10:35	6.2	91.4	195.8	76.1	66.2
10:40	6.5	91.4	222.7	76.4	69.0

^adose rate 18.80 gray/min, total dose 2.529 kgy.

4.1.4.3 Effect of Starch-to-AN Ratios on Grafting Efficiency.

The effect of starch(g)/AN(ml) ratio on grafting efficiency is given in Table 4.8 and illustrated in Figure 4.26. The result shows that the highest grafting efficiency was obtained with the lowest concentration of acrylonitrile. It decreases from 97.9 to 91.3 % as the concentration of acrylonitrile is increased from 5.0 to 40.0 ml. The effect of high monomer concentra-

tion leading to higher amount of homopolymer at the initiation step, is possibly due to primary termination where an excessive amount of monomer was used to terminate the propagating radicals of homopolymer rather than the graft copolymer. In addition, the initiation rate can be monomer dependent that would directly alter the efficiency of the gamma rays. However, the amount of homopolymer formed at maximum of 6.5% should be significantly unharmed to water absorption. The degree of water absorption at the above mentioned stage should justify the applications. The grafting efficiency is a direct relation to homopolymer. Therefore, up to this point, very high grafting may be desirable for the water absorption of the graft copolymer. However, other physical properties apart from high grafting efficiency, such as gel strength/gel flexibility, are also the main governing parameters for high-water absorption.

4.1.4.4 Effect of Starch-to-AN Ratios on % Conversion

The correlation between percentage of monomer and the amount of acrylonitrile is showed in Table 4.8 and illustrated in Figure 4.27. It indicates a constant relationship for this type of copolymerization. The linear relationship between starch-to-AN ratios and % conversion is that the increasing amount of AN does not increase the conversion of the reaction significantly. The limitation may come from the initiation step where the ionizing

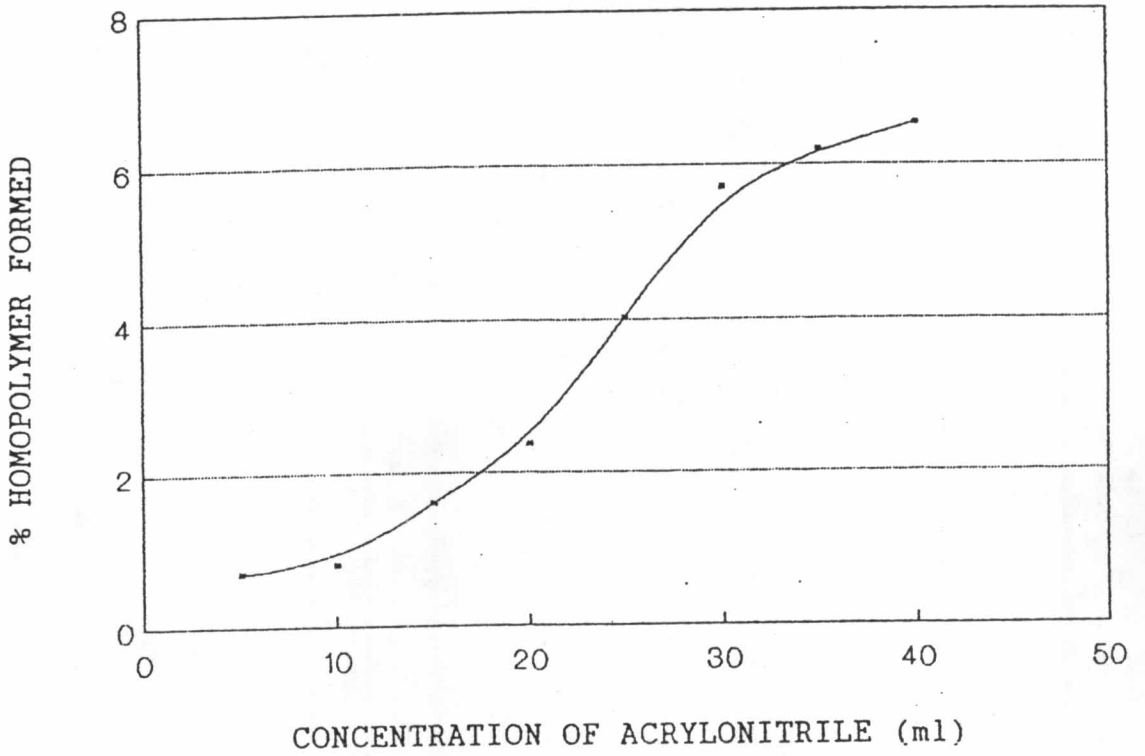


Figure 4.25 Effect of the concentration of acrylonitrile on % homopolymer formation.

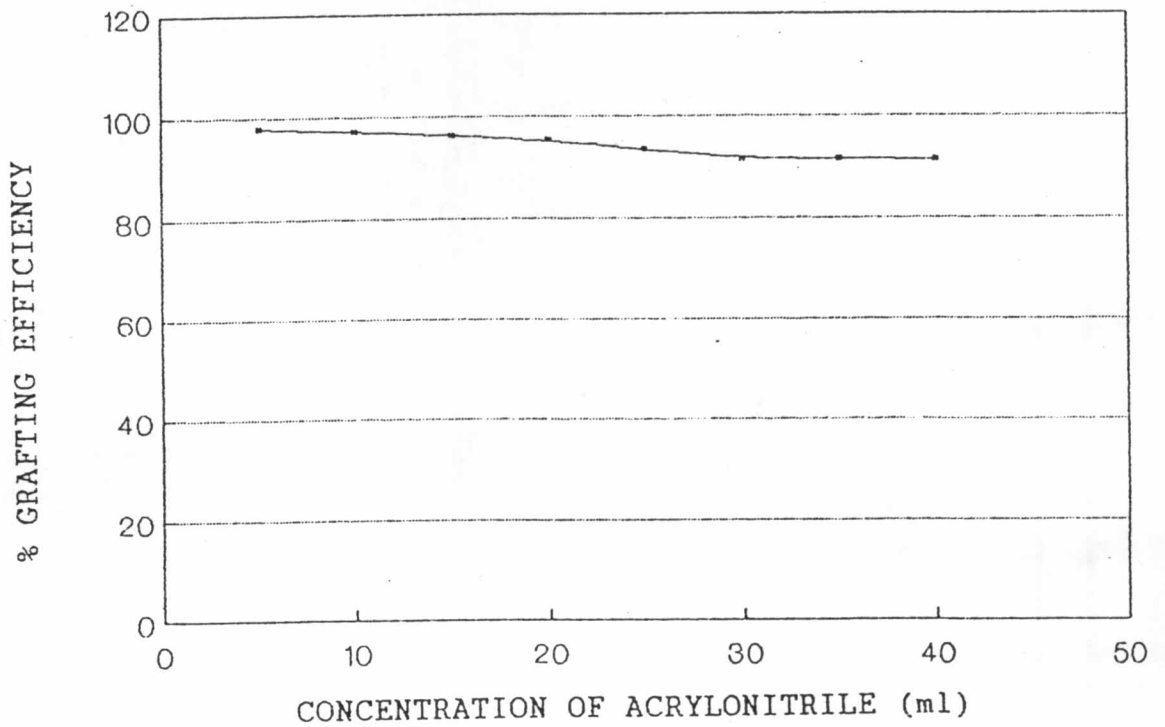


Figure 4.26 Effect of the concentration of acrylonitrile on % grafting efficiency.

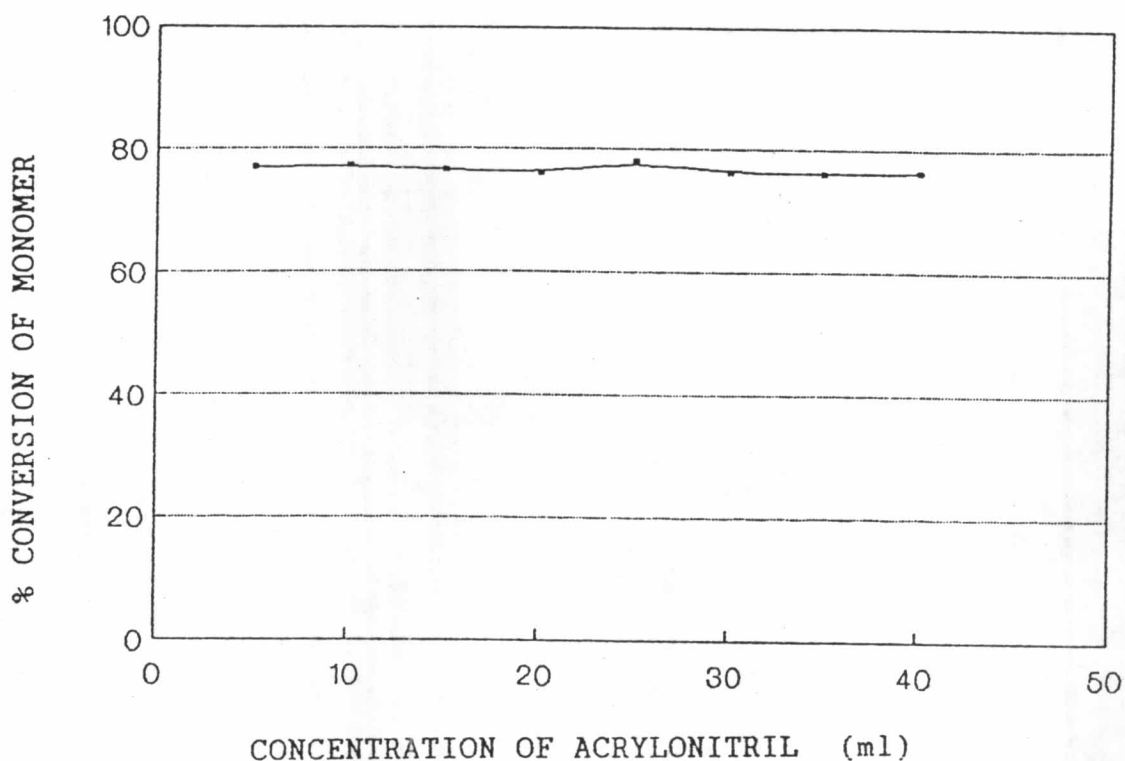


Figure 4.27 Effect of the concentration of acrylonitrile on % conversion of monomer.

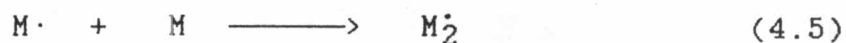
radiation cannot initiate any more free radicals than a certain number of radicals. In case that more doses were given to this system, The % conversion would increase accordingly.

4.1.4.5 Effect of Starch-to-AN Ratios on % Add-on.

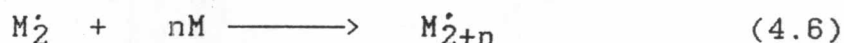
Figure 4.28 shows that the effect of starch/AN ratios on % add-on could still increase if more AN was used for the grafting reaction. This result indicates the necessity of adding more AN molecules so that high probability for each AN molecule to be excited and propagated could achieve for better gel structure. The

possibly simple explanation could be as follows:

Initiation:



Propagation:



Where M = AN molecules

When n is larger number, more monomer molecules would participate more in % add-on.

4.1.4.6 Effect of Starch-to-AN Ratios on Grafting Ratio.

The effect of the amount of AN on grafting ratio is also shown in table 4.8 and Figure 4.29. It indicates that the grafted PAN/weight of starch still increase if more of acrylonitrile was added. According to the definition of percent grafting ratio, the higher the number, the more grafted PANs were joint to the cellulose matrix. The amount of percent grafting would indicated the extent of flexibility in the chain which affects water absorptivity and retention.

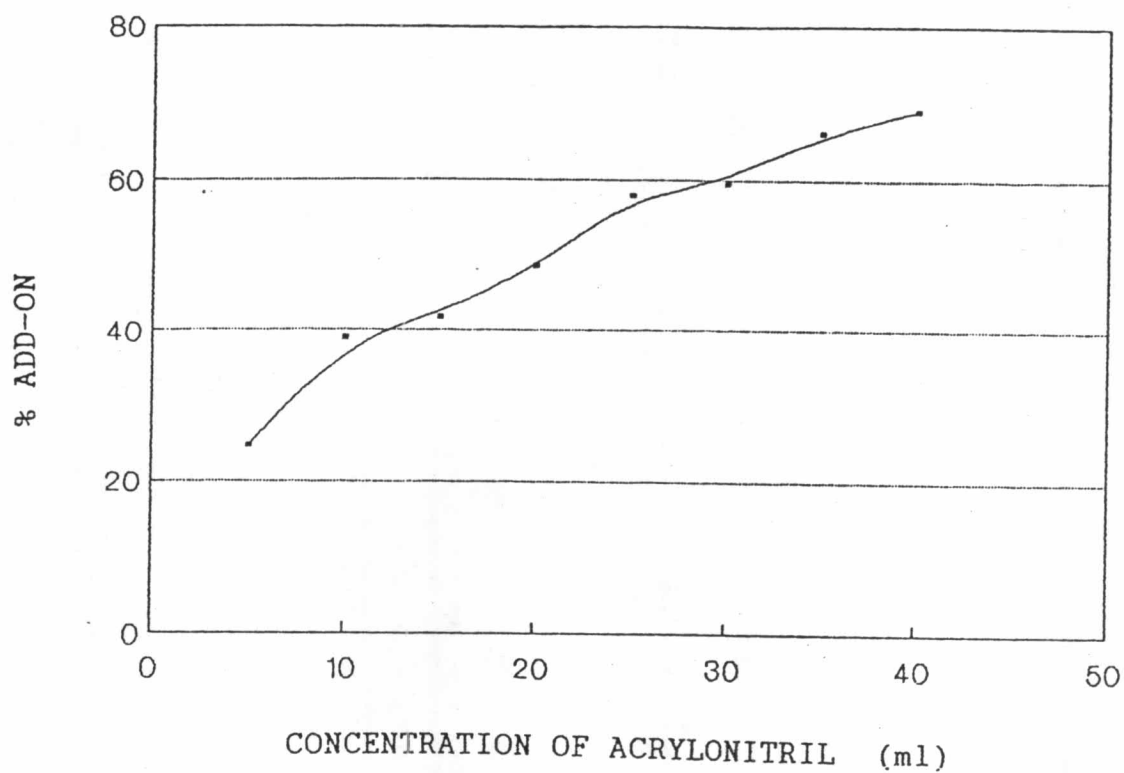


Figure 4.28 Effect of the concentration of acrylonitrile on % add-on.

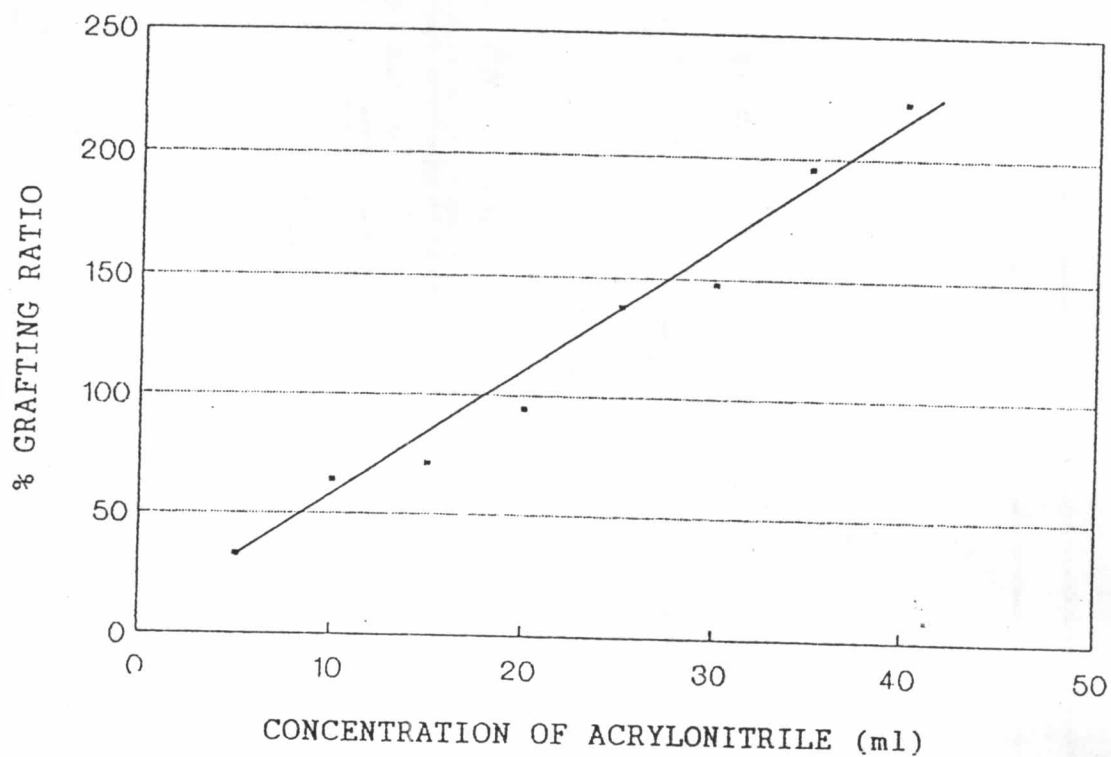


Figure 4.29 Effect of the concentration of acrylonitrile on % grafting ratio.

4.1.4.7 Effect of Starch-to-AN Ratios on Viscosity Average Molecular Weight.

The data of effect of the concentration of acrylonitrile on the viscosity average molecular weight (\bar{M}_v) and the grafting frequency are given in Table 4.9

TABLE 4.9
Effect of Starch(g)/ AN(ml) Ratios on
the Molecular Weight and the Grafting Frequency

Starch(g)/AN(ml)	Molecular weight (\bar{M}_v)	Grafting frequency (AGU/chain)
10:5	38,600	727
10:10	120,600	1,165
10:15	150,800	1,303
10:20	173,600	1,135
10:25	220,000	985
10:30	230,200	962
10:35	269,000	848
10:40	289,000	826

Figure 4.30 and Table 4.9 illustrate the effect of concentration of AN on the molecular weight (\bar{M}_v) of grafted PAN. When increasing the amount of acrylonitrile from 5.0 to 40.0 ml, the \bar{M}_v of grafted PAN increased from 38,600 to 298,000 respectively. As more AN were present in the reaction mixtures, there were more probability that AN

could be both grafted on the starch backbone and/or converted to homopolymer. Molecular weight increased drastically from 5 ml to 10 ml of AN, at a factor 40 times. It simply implied that at low AN concentrations, the grafted polymer could be soluble to yield a slurry or a suspension of grafted polymer. Therefore, the molecular weight of the grafted polymer must be, at least, high enough to be insoluble in water or organic solution.

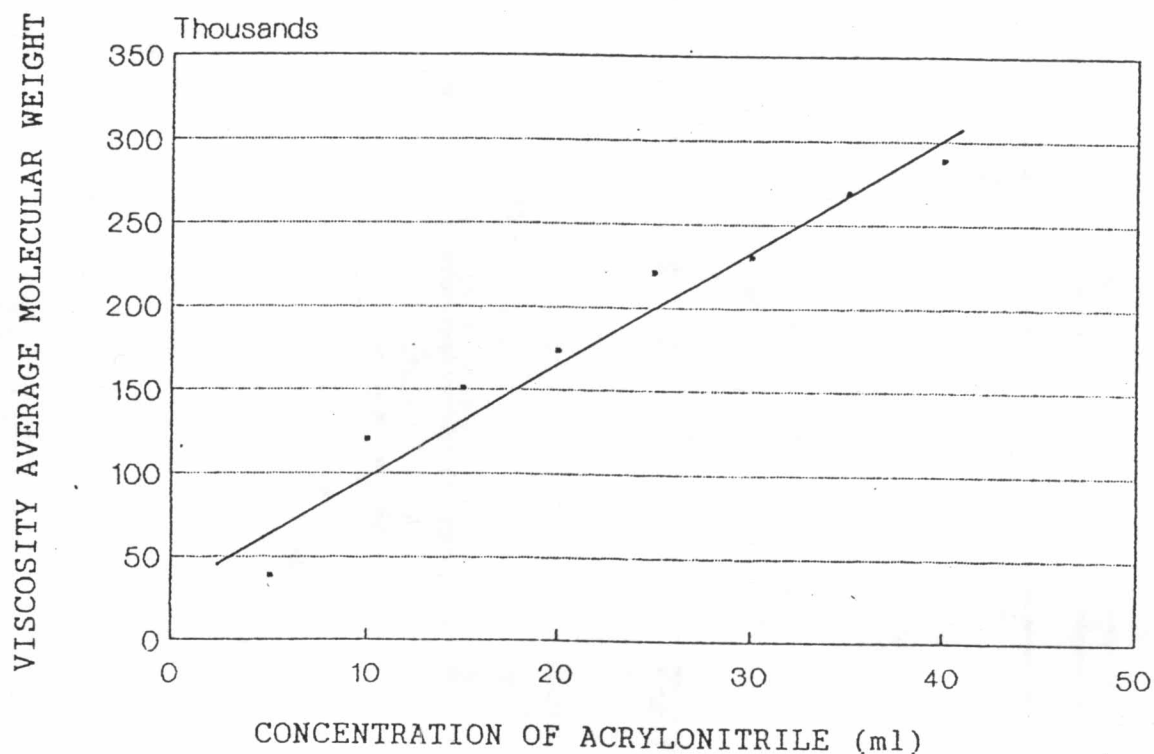


Figure 4.30 Effect of the concentration of acrylonitrile on the viscosity average molecular weight (\bar{M}_v) of grafted PAN.

4.1.4.8 Effect of Starch-to-AN Ratios on Grafting Frequency.

The effect of the concentration of AN on grafting frequency is tabulated in Table 4.8 and

illustrated in Figure 4.31. The grafting frequency is the minimum at the concentration of acrylonitrile is 15 ml. This means that it was the maximum number of anhydroglucoside units separated by the two grafted PAN, provided by the amount of 15 ml of AN involving with the grafting reaction.

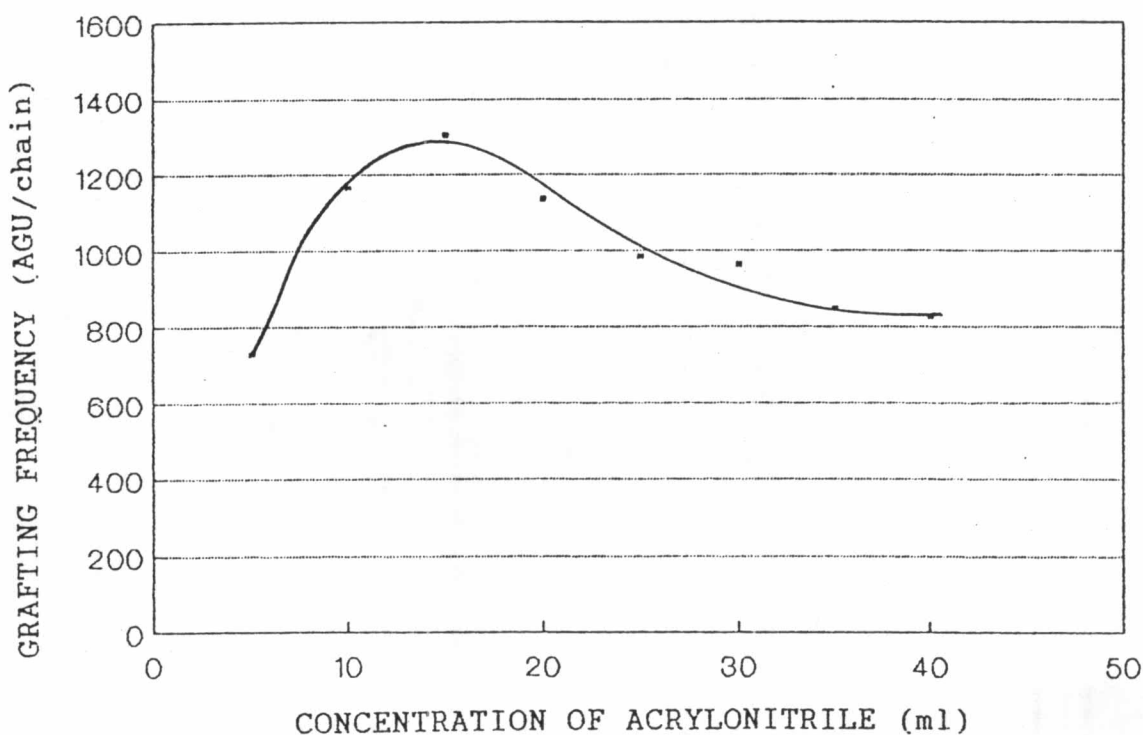


Figure 4.31 Effect of the concentration of acrylonitrile on grafting frequency.

4.1.4.9 Effect of Starch-to-AN Ratios on Water Absorption.

The effect of starch/AN ratio on the water absorption of the saponified starch-g-PAN in deionized water is tabulated in Table 4.10 and shown in Figure 4.32.

TABLE 4.10

Effect of the Concentration of AN on Water Absorption in Deionized Distillated Water

Starch(g) / AN(ml)	Water absorption in deionized distillated water (g/g)
10:5	31
10:10	445
10:15	665
10:20	620
10:25	536
10:30	483
10:35	607
10:40	551

The experimental data shows that the highest water absorption occurred at the concentration of AN about 15 ml. The results correlate quite well with the mechanistic model of the enhanced water absorbency-grafted polysaccharides (60) that is identical to the same as that described by Grignon and Scallman for the swelling of cellulose gels (61). The swelling is considered to be caused by osmotic pressure differential resulting from a difference in concentration of mobile ions between the interior of the gel and the external solution. The concentration of mobile

K^+ ions in the polymer gel, resulting from the saponification step, is higher than those in deionized water which comprises only hydrogen and oxygen atoms. As the ionic groups cannot move out of the gel, the solution within the gel is regarded as separated from the external solution by a semipermeable membrane which confines to the potassium carboxylate and carboxamide groups, but gives passages of water. The gel swells as a result of the difference in ion concentrations. Swelling continues until the osmotic pressure differential is equal to the resistance to further expansion, i.e., when the ion concentration between inside and outside the gel has reached equilibrium. Okiemen and Ebhoaye(62) suggested that the water absorption properties of cellulosic materials are thought to result from interaction through hydrogen bonding of the hydroxyl groups on the cellulose with water molecules.

In conclusion, the effect of water absorption depends on the frequency of interposition of the grafted polymer chains on the cellulosic starch backbone, and the nature of the grafted polymer which means the amount of grafting chain or acrylonitrile and its molecular weight are some of the determining factors for water absorption.

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

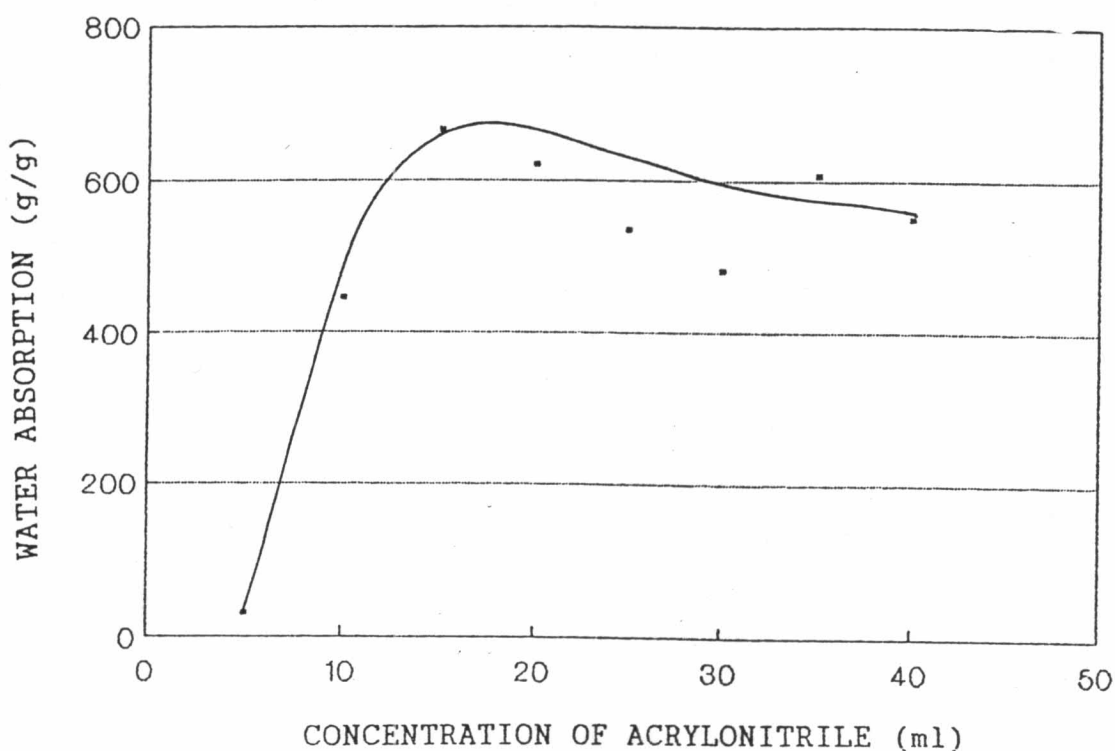


Figure 4.32 Effect of the concentration of acrylonitrile on water absorption of saponified starch-g-PAN in deionized distilled water

or carboxyl substituents at the drying temperature (63).

4.1.4.10 Effect of NaCl Solutions on Water Absorption.

The effect of the presence of NaCl solutions at the concentrations of 0.1, 0.5, 1.0, and 2.0 % w/v on the water absorption is clearly illustrated in Table 4.11 and Figure 4.33. The water absorption efficiency of the saponified starch-g-polyacrylonitrile is very dependent on the ion concentration. Indeed, the effect of NaCl at different concentrations shows a dramatic decrease in water absorption in the presence of ions.

TABLE 4.11

Effect of NaCl Concentrations on Water Absorption

Starch(g)/AN(g)	Water Absorption in g/g			
	0.1 % ^a	0.5 % ^b	1.0 % ^c	2.0 % ^d
10:5	30.6	29.0	28.5	24.7
10:10	119.8	90.0	67.1	52.0
10:15	158.3	91.2	72.4	53.4
10:20	142.2	95.4	67.8	56.8
10:25	148.0	100.0	65.5	53.9
10:30	147.2	100.2	65.4	54.1
10:35	148.0	101.1	67.0	56.0
10:40	148.6	103.0	68.3	57.1

^a $[Na^+] = [Cl^-] = 0.017$, $[Na^+] + [Cl^-] = 0.034$ mole-ion/l

^b $[Na^+] = [Cl^-] = 0.085$, $[Na^+] + [Cl^-] = 0.170$ mole-ion/l

^c $[Na^+] = [Cl^-] = 0.171$, $[Na^+] + [Cl^-] = 0.342$ mole-ion/l

^d $[Na^+] = [Cl^-] = 0.342$, $[Na^+] + [Cl^-] = 0.684$ mole-ion/l

The effect of salt concentration on the water retention values is best explained in terms of the swelling of modified starch gels containing anionic groups. This treatment was first proposed by Proctor which was then extended and further clarified by Scallan and Grignon (61) in terms of swelling of such gels as described above. Briefly this approach may be summarized in the following way:

The ions attached to the macromolecular network in the gel are immobile and are considered to be separated from the external solution by a semipermeable membrane, which confines the immobile ions, but give passage to water and all simple ions. The excess concentration of mobile ions in the gel phase is calculated using Donnan's equilibrium model. This excess concentration is directly proportional to osmotic pressure differential, and this, in turn, is assumed to be directly proportional to degree of swelling, i.e., to the water sorption itself (67).

In this case the graft copolymer is present as the anion of potassium salt(polycarboxylate) and polycarboxamide, which is assumed to be strong electrolyte. Saponified starch graft copolymer was placed in NaCl solutions. At the surface of this material the behavior as semipermeable membrane exists. To maintain electrical neutrality on the both sides of the membrane, Na^+ and Cl^- ions have diffused through the membrane from external solution to the interior of gels. The amount of NaCl diffused from external solution to the interior of gel is inversely proportional to the concentration of non-diffusibile ion, polycarboxylate. This unequal distribution of the diffusible ions(Na^+ and Cl^-) in the two compartments is the result of the Donnan effect (68), assume that saponified starch graft copolymer has the same behavior as the sodium salt of protein.

The osmotic pressure of this system is now determined by the difference between the number of particles in the external solution and that in the interior of the gels. Assume that K^+ ions in the interior of the gel have the same concentration (mole-ion/l) as that of polycarboxylate.

Then,

$$\pi = \left(\frac{2a^2 + 2ab}{a + 2b} \right) RT \quad (4.8)$$

Where,

π : osmotic pressure, atm

a : concentration of polycarboxylate and K^+ ions in the interior of the gel, mole-ion- l^{-1}

b : concentration of Na^+ and Cl^- ions in the external solution, mole-ion- l^{-1}

R : gas constant, $8.314 \text{ J K}^{-1}\text{mol}^{-1}$

T : temperature, K

According to eq. 4.8 the concentration of salt solution increases, the osmotic pressure of this system would then decrease. The more ions are present, the less water is absorbed. In soil environment, a similar effect is expected as soils contain various types of ions and plant nutrients. The use of fertilizer in agriculture, horticulture, and arboriculture also has such an effect, a reduction in water absorption. In order to compensate for the decrease in water intake, the use of more superabsorbent polymer is therefore necessary.

4.1.4.11 Effect of $MgCl_2$ Solutions on Water Absorption.

The water absorption with magnesium chloride concentration is given in Table 4.12 and Figure 4.34.

TABLE 4.12
Effect of Different $MgCl_2$ Concentrations
on Water Absorption

Starch(g)/AN(ml)	Water Absorption in g/g			
	0.1 % ^a	0.5 % ^b	1.0 % ^c	2.0 % ^d
10:5	27.0	21.2	16.8	5.1
10:10	90.2	24.3	21.8	20.0
10:15	108.0	30.1	24.0	22.2
10:20	123.7	32.1	26.0	23.5
10:25	120.4	30.0	25.9	26.0
10:30	122.1	31.1	28.6	24.3
10:35	123.2	30.2	28.0	21.8
10:40	122.5	31.4	29.4	25.9

^a $[Mg^{+2}] = 0.010$, $[Cl^{-}] = 0.020$, $[Mg^{+2}] + [Cl^{-}] = 0.030$ mole-ion/l

^b $[Mg^{+2}] = 0.052$, $[Cl^{-}] = 0.105$, $[Mg^{+2}] + [Cl^{-}] = 0.157$ mole-ion/l

^c $[Mg^{+2}] = 0.105$, $[Cl^{-}] = 0.210$, $[Mg^{+2}] + [Cl^{-}] = 0.315$ mole-ion/l

^d $[Mg^{+2}] = 0.210$, $[Cl^{-}] = 0.420$, $[Mg^{+2}] + [Cl^{-}] = 0.630$ mole-ion/l

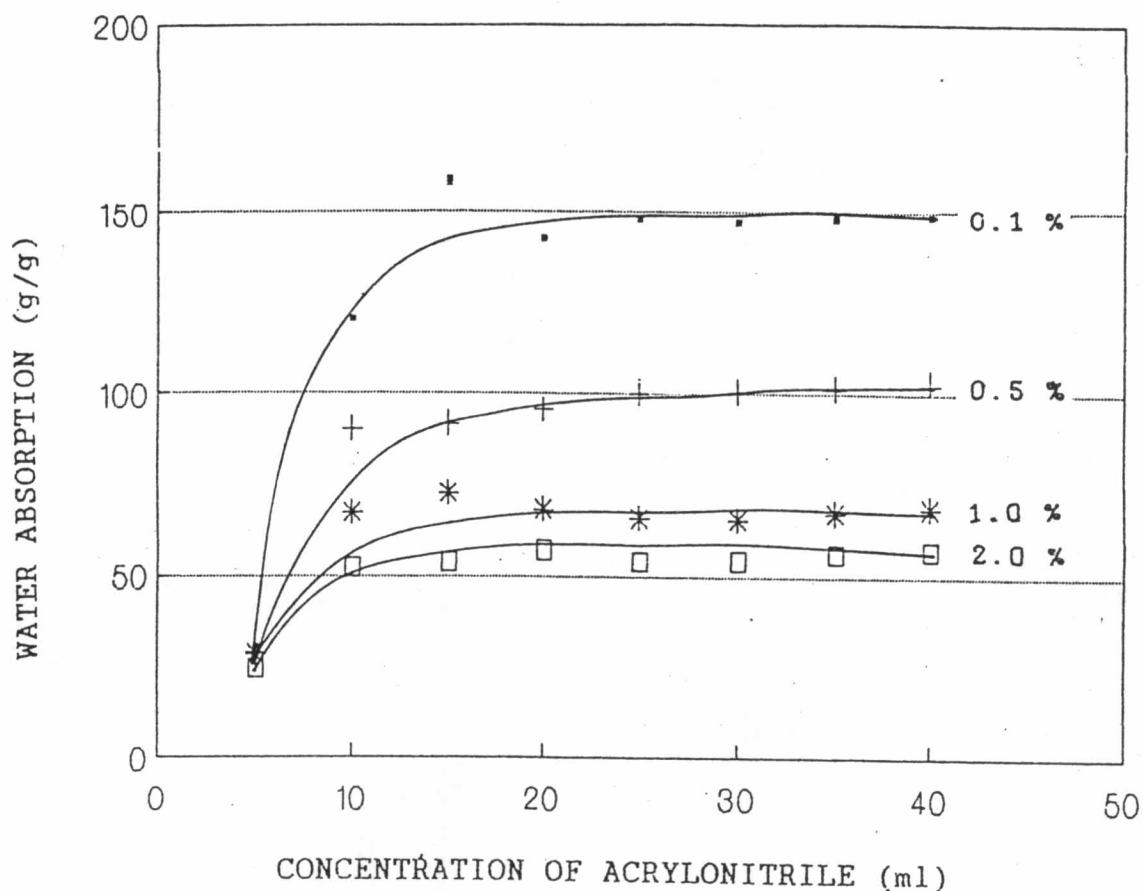


Figure 4.33 Water absorption of saponified starch-g-PAN in NaCl solutions of 0.1, 0.5, 1.0, and 2.0% w/v.

On observing the case of $MgCl_2$, the water absorption decreased even more with increasing magnesium chloride concentrations. However, the curves of 0.5, 1.0, 2.0% $MgCl_2$ concentrations are almost identical, with the 0.5% addition having a slightly higher absorption only. This suggests that the osmotic pressure is reached earlier in the presence of the divalent ion. As a consequence, the absorption with $MgCl_2$ solution is much less than does NaCl. Here the highest water intake of $MgCl_2$ solution is less than 130 g/g, while that of NaCl the value obtained is 160 g/g.

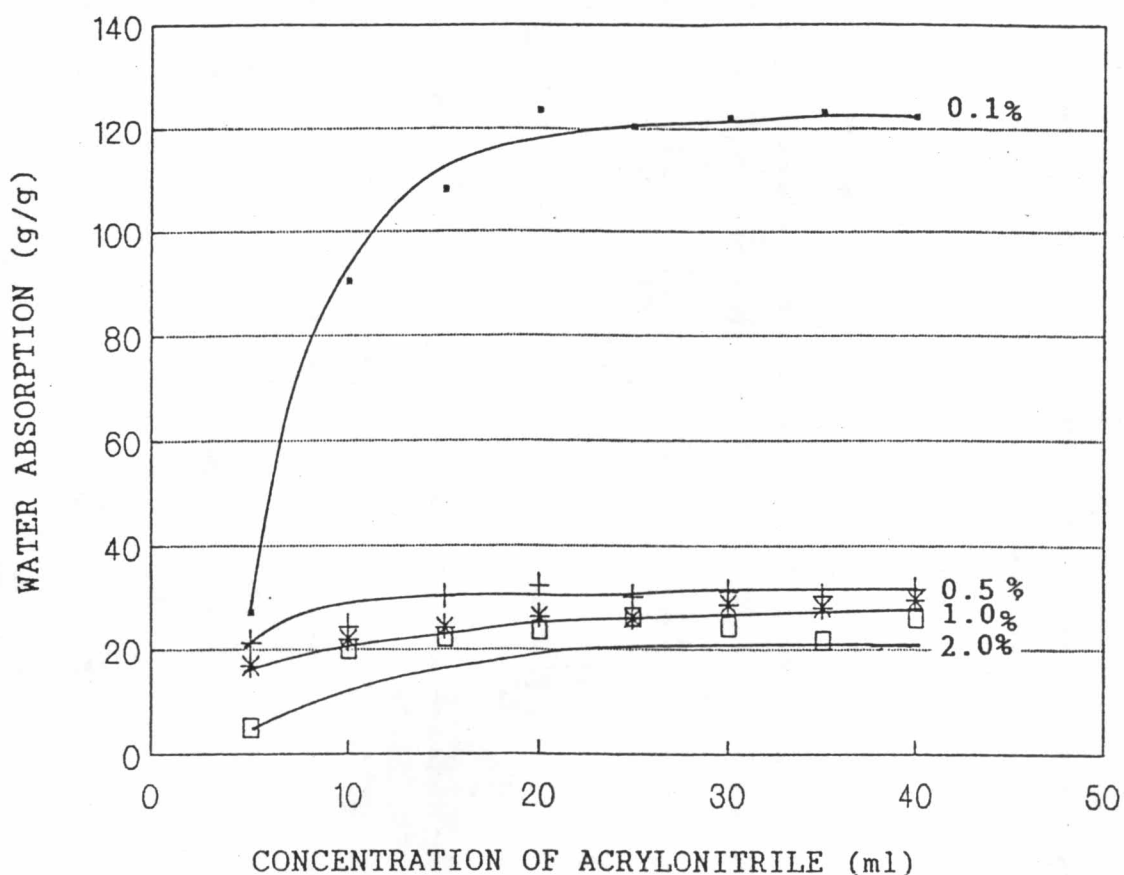


Figure 4.34 Water absorption of saponified starch-g-PAN in $MgCl_2$ solutions of 0.1, 0.5, 1.0 and 2.0 % w/v.

The water absorption of the starch based superabsorbent in distilled deionized water as compared to the water absorptions of 0.1 % w/v of NaCl and $MgCl_2$ is shown in Figure 4.35. At the concentration of 0.1 % w/v of NaCl and $MgCl_2$ have ions concentration of 0.34 and 0.30 mole-ion/l respectively. As a function of the amount of acrylonitrile, the absorption in distilled deionized water and salt solution exhibits the same absorption pattern. The figure indicates an increase at lower concentration and then levels off at around 15.0 ml of AN. The salt effect is clearly evidenced as a result of the osmotic pressure differential

between the internal solution in the gel and external solution, due to the different ion concentration(60). The water intake by the gel reduced the osmotic pressure until an ion concentration equilibrium was reached.

4.1.4.12 Effect of $K_3PO_4 \cdot 3H_2O$, KCl , NH_4Cl , and $(NH_4)_2HPO_4$ Solutions on Water Absorption.

The water absorption of the graft copolymer in the presence of $K_3PO_4 \cdot 3H_2O$, KCl , NH_4Cl , and $(NH_4)_2HPO_4$ is given in Table 4.13 and Figure 4.36. All of these salts have the concentration of 0.9 % w/v.

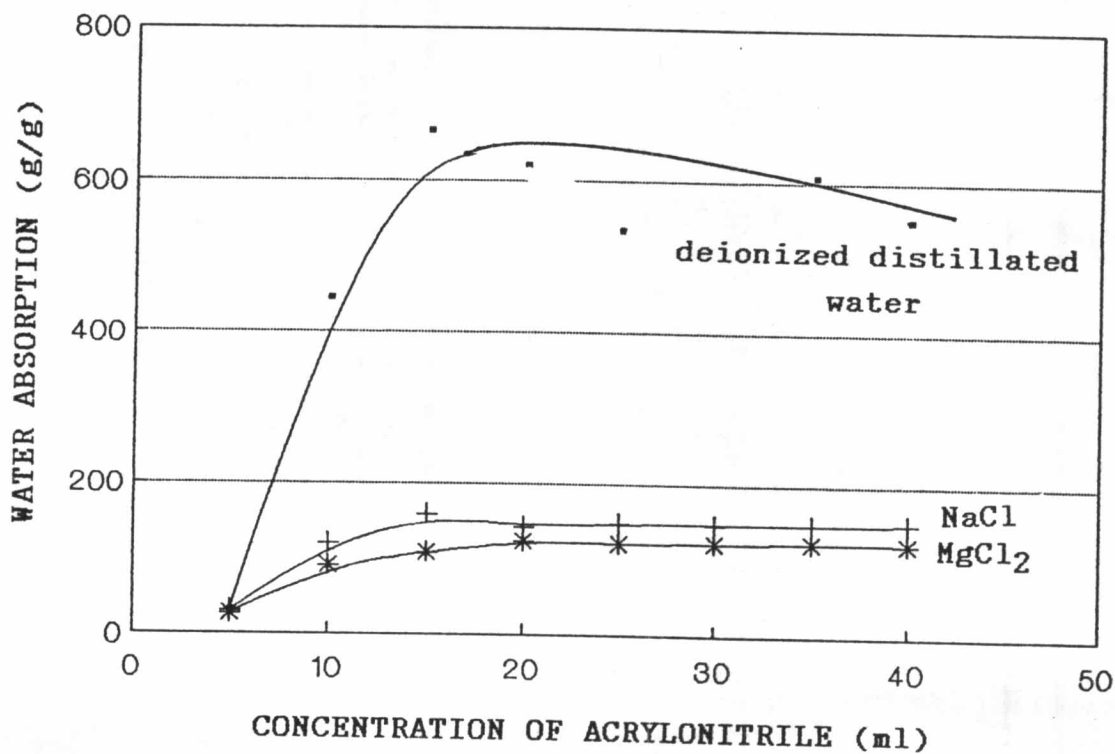


Figure 4.35 Comparative water absorption study between deionized distilled water and 0.1% w/v of $NaCl$ and $MgCl_2$.

TABLE 4.13

Effect of $K_3PO_4 \cdot 3H_2O$, KCl , NH_4Cl , and $(NH_4)_2HPO_4$ with Identical Concentration of 0.9 % w/w on the Water Absorption of the Saponified Starch-g-Polyacrylonitrile.

Starch(g) /AN(ml)	Water absorption in $K_3PO_4 \cdot 3H_2O^a$ (g/g)	Water absorption in KCl^b (g/g)	Water absorption in NH_4Cl^c (g/g)	Water absorption in $(NH_4)_2HPO_4^d$ (g/g)
10:5	18.3	16.4	22.7	30.5
10:10	84.0	64.9	58.1	80.2
10:15	91.4	92.7	77.0	88.3
10:20	90.8	92.5	76.1	89.6
10:25	91.4	93.7	77.1	88.2
10:30	90.1	91.7	76.1	88.3
10:35	90.1	92.2	77.2	88.2
10:40	91.8	91.3	77.0	91.4

^a $[K^+] = 0.101$, $[PO_4^{-3}] = 0.034$, $[K^+] + [PO_4^{-3}] = 0.135$ mole-ion/l

^b $[K^+] = [Cl^-] = 0.121$, $[K^+] + [Cl^-] = 0.242$ mole-ion/l

^c $[NH_4^+] = [Cl^-] = 0.168$, $[NH_4^+] + [Cl^-] = 0.336$ mole-ion/l

^d $[NH_4^+] = 0.136$, $[HPO_4^{-2}] = 0.068$, $[NH_4^+] + [HPO_4^{-2}] = 0.204$ mole-ion/l

The result in the above Table shows that the water absorption decreases in relation to that of deionized water. The absorbency of the saponified starch-g-PAN is presumably dependent upon the following three factors:

- a) the osmotic pressure;
- b) the molecular chain expansion resulting from repulsion between the electrolyte anions in the polymer chains;
- c) the extent of crosslink affecting the degree of swelling of the polymer;

The absorbency (Q) can be expressed by the Flory's equation shown as following:

$$Q^{5/3} = \left(\frac{i}{2 \cdot v_u S^{*1/2}} \right)^2 + (1/2 - x_1)/v_1 (\sqrt{v_e/V_0}) \quad (4.9)$$

where,

i : degree of ionization of polymer electrolyte

S^* : ionic strength of salt solution added

$(1/2 - x_1)/v_1$: affinity between ionic network and
the absorbed water

v_u : molar volume of polymer repeating unit

$\sqrt{v_e/V_0}$: crosslinking density

Figure 4.37 shows the relationships between the absorbency (Q) and the factors mentioned above (63).

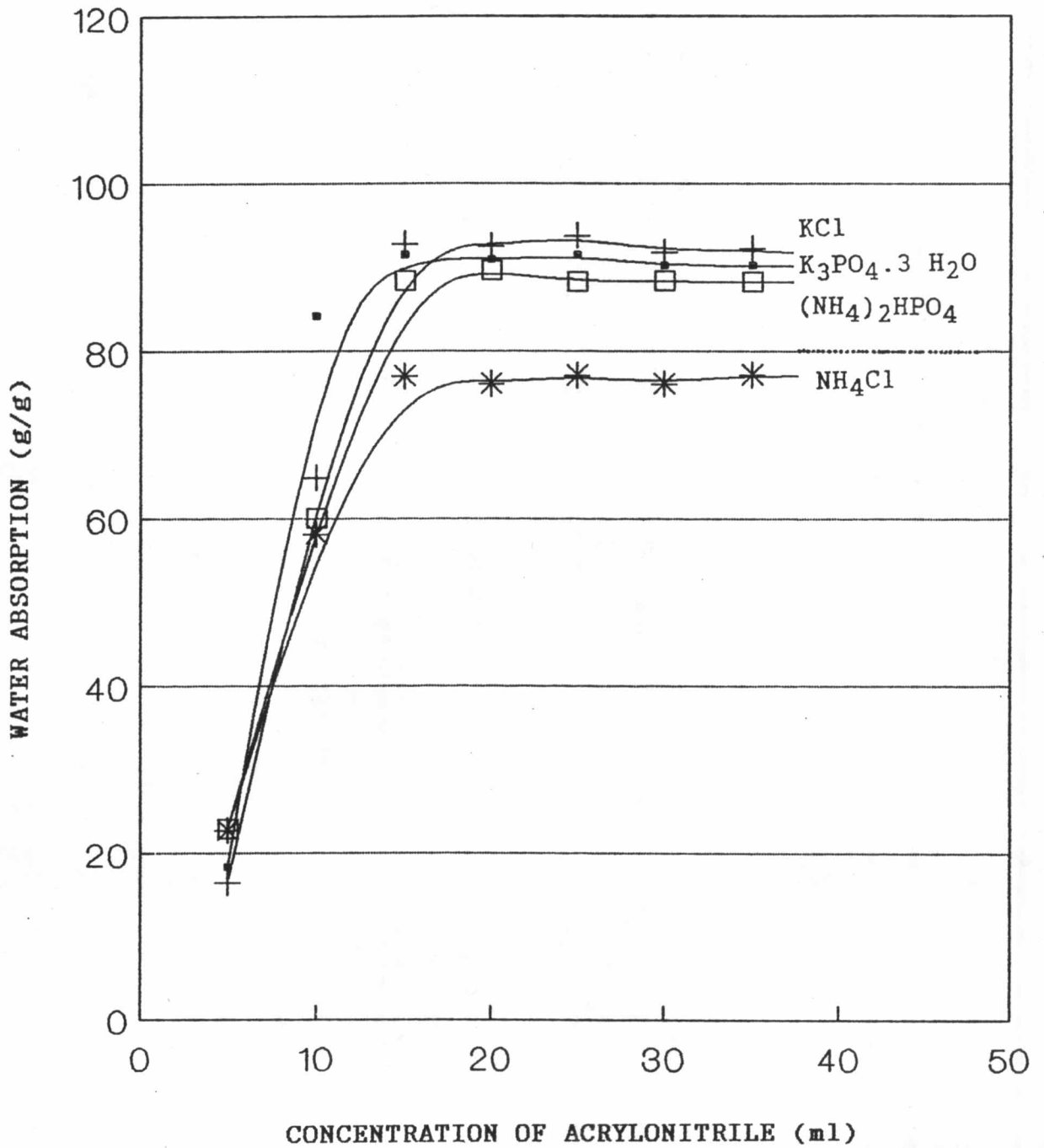


Figure 4.36 Water absorption of saponified starch-g-PAN in KCl, $K_3PO_4 \cdot 3 H_2O$, NH_4Cl , and $(NH_4)_2HPO_4$ solutions of 0.9% w/w.

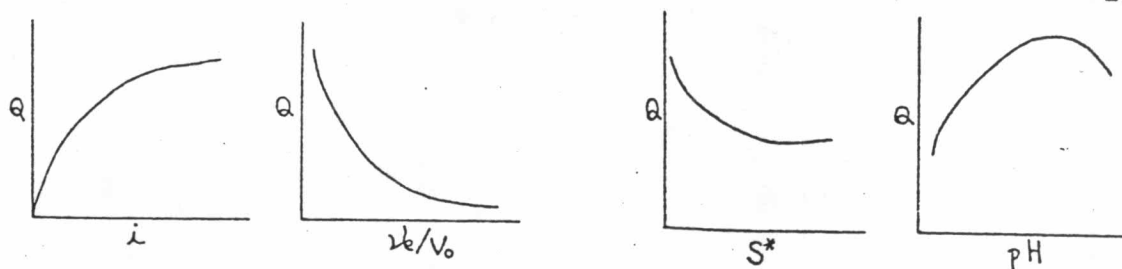


Figure 4.37 Relationships between swelling degree and ionization degree of polymer electrolyte, crosslinking density of polymer network, ionic strength of salt solution, and pH of polymer solution.

The different water absorption in the solution of salts depends on the effect of osmotic pressure as described in eq. 4.8, ionic strength of salt solution, and other factors described in eq. 4.9: crosslinking density, molar volume of polymer repeating unit and the affinity of between the polymer network and the absorbed water.

4.1.4.13 Water Absorption in Sand Alone and Sand with Saponified Starch-g-Polyacrylonitrile.

In order to determine the water retention capacity in soil environment, the newly synthesized copolymer was tested by mixing it with sand with the particle size average larger than 200 mesh at the concentrations of 0.5, 1.0, 2.0, and 3.0 %. The absorption data are given in Table 4.14 and illustrated in Figure 4.38 and the absorption of sand alone is 0.3 g/g. They

clearly show that the water absorption in sand depends to a large extent, on the amount of polymer used. There is a linear relationship between water retention and polymer concentration, i.e. the concentration of the grafted copolymer increased, so did the water retention.

TABLE 4.14

Water Retention on Sand Mixed with Different Concentrations of Saponified Starch-g-Polyacrylonitrile

Starch(g) / AN(ml) ratio	Water retention (g/g)			
	0.5% polymer in sand	1.0% polymer in sand	2.0% polymer in sand	3.0% polymer in sand
10:5	24.1	25.2	27.3	28.1
10:10	212.3	218.8	224.2	250.7
10:15	230.2	235.5	240.1	268.2
10:20	238.1	246.7	252.7	278.5
10:25	247.4	251.8	257.8	281.7
10:30	254.3	260.2	263.3	290.8
10:35	262.2	267.1	271.6	299.4
10:40	271.9	284.3	292.2	306.3

The absorption efficiency of the copolymer also plays an important role in water retention of sand. Indeed, as the starch/AN ratio goes from 10:15, the water retention

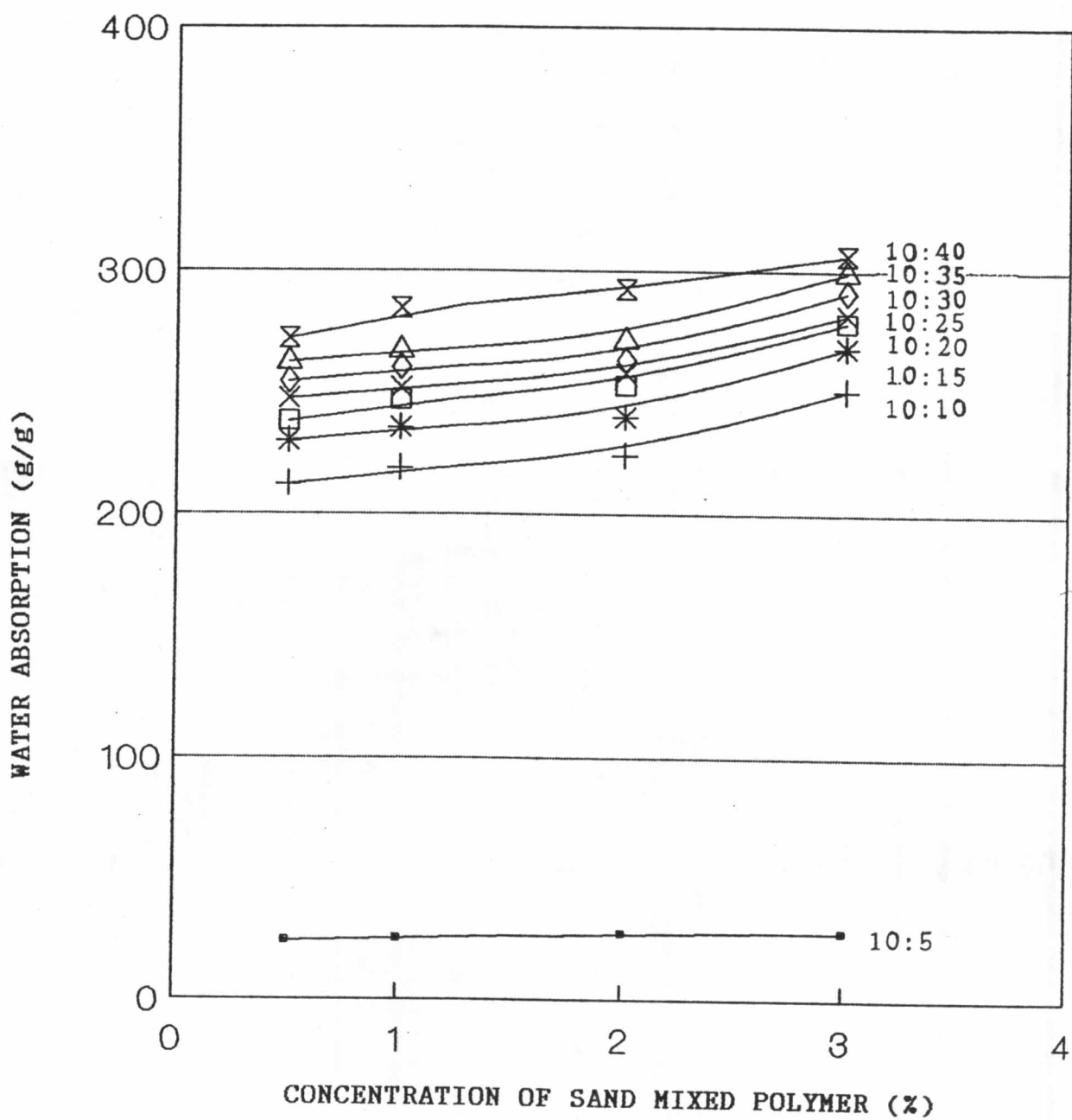


Figure 4.38 Water retention of sand mixed with the saponified starch-g-PAN with different concentrations.

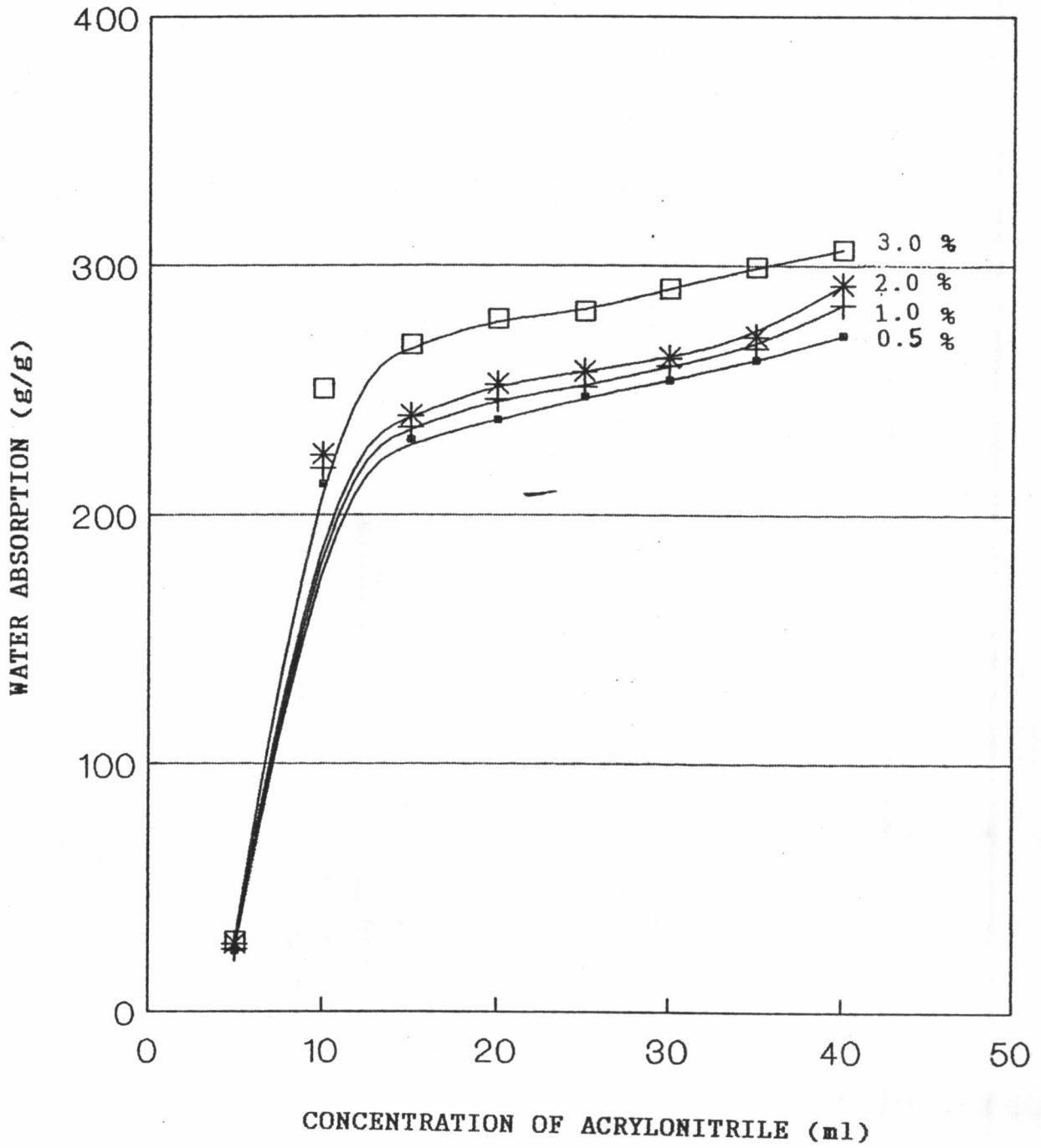


Figure 4.39 Water retention of sand mixed with saponified starch-g-PAN synthesized with different AN concentration.

increases as well as those for 10:20, 10:25, 10:30, 10:35 and 10:40 ratios, however, the water retention pattern is almost identical as showed in Figure 4.39.

4.2 Preirradiation Technique

The experimental procedure as described in Section 3.2.2.2 gave the yellowish product. The materials after grafting, after extraction and drying were inspected on an infrared spectrometer, There were no $C\equiv N$ stretching bands at $2,243\text{ cm}^{-1}$ in the IR spectrum. Upon saponification the solution mixture changed from yellowish to black color. It can be concluded that, this technique of preirradiation could not induce the graft copolymerization of acrylonitrile onto cassava starch. It is speculated that, free radicals on the backbone polymer have quite a short half life/life time. The radicals can probably decay before the addition of acrylonitrile to start the polymerization. Furthermore, the presence of nitrogen gas flowed during the preirradiation period may prevent the formation of hydroperoxide radicals which, in turn, would initiate the reaction.