

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Microcrystalline Cellulose (10),(16)

As reviewed in the literature, the cellulose which had high crystallinity could be much less accessible to graft copolymerization. Increasing amorphous region resulted in the higher grafting efficiency, which was proved by the determination of the percent conversion of monomer to copolymer and the percent of homopolymer formation which normally occurred as the undesirable side product.

In 1990 Plumpirom, V. studied the graft copolymerization of acrylonitrile on various types of modified cellulose, i.e., microcrystalline cellulose, gelatinized microcrystalline cellulose and decrystallized microcrystalline cellulose. The results illustrated that microcrystalline cellulose was the most suitable form for graft copolymerization.

This literature review led to conclude that cellulose should be modified by acid hydrolysis to yield microcrystalline cellulose before graft copolymerization.

The microcrystalline cellulose is white powder and exhibits the infrared spectrum as shown in Figure 4.1

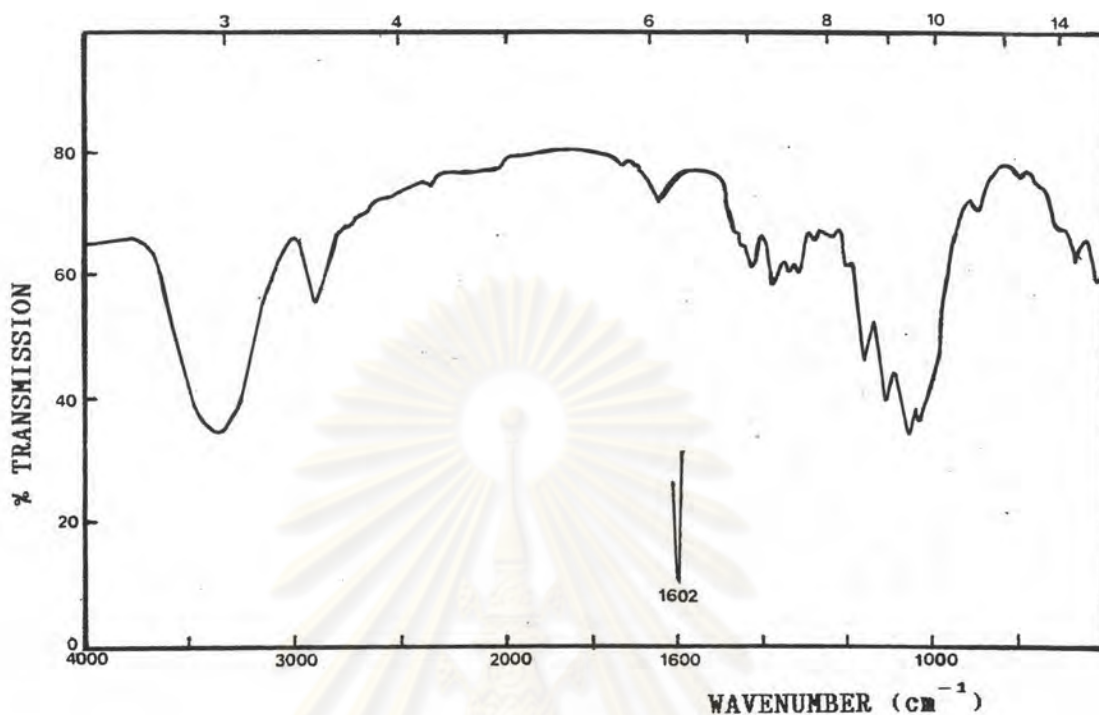


Figure 4.1 Infrared Spectrum (KBr pellet) of Microcrystalline Cellulose

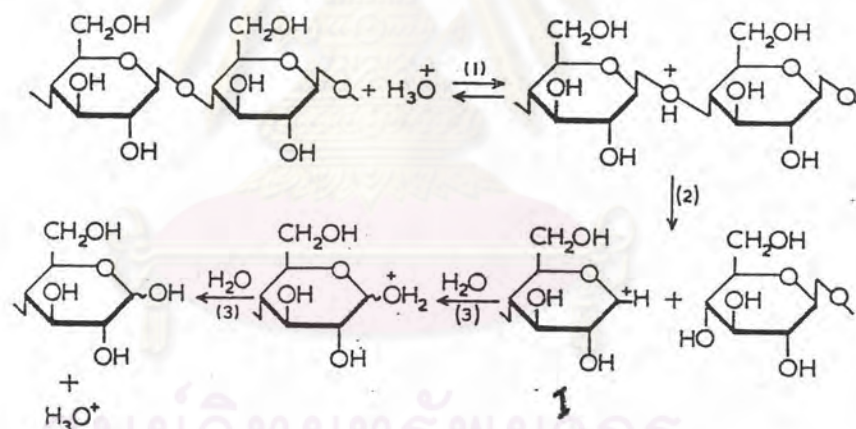
The infrared spectrum of microcrystalline cellulose shows the characteristic absorption band in 1600-800 cm^{-1} region. The weak absorption at 895 cm^{-1} belongs to β -D-glucose and the strong absorption in 1110-1120 cm^{-1} region is due to C-O-C stretching.

In this research cellulose was thus modified to the form which could easily be grafted with acrylic acid and acrylonitrile monomers. The homopolymers were polyacrylic acid and polyacrylonitrile which effected to the decrease in grafting efficiency. The selected method was acid hydrolysis to yield the microcrystalline cellulose.

The only chemical change is the rupture of 1,4-glucosidic

linkages and the shorter cellulose chains will be obtained. The mechanism of the acid hydrolysis reaction is the same as that of simple glycosides.

It comprises three stages: rapid protonation of the glycosidic oxygen atom, slow transfer of the positive charge to C-1 with consequent formation of a carbonium ion and fission of the glycosidic bond, and rapid attack on the carbonium ion by water to give the free sugar residue and to re-form the hydroxonium ion. Finally water attack the hydroxonium ion to give the product and hydronium ion. Mechanism of acid hydrolysis is shown in Scheme 4.1.



Scheme 4.1 Mechanism of Acid Hydrolysis

It is believed that the most stable conformation of the carbonium ion (I) is the half-chair (II) in which C-1, C-2, C-5, and O-5 (the ring oxygen) are all in the same plane as shown in figure 4.2.

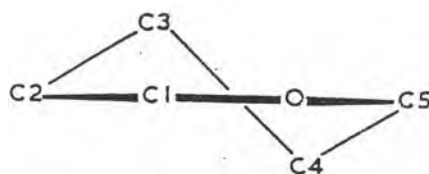


Figure 4.2 Conformation of the Carbonium Ion (II)

Acid hydrolysis is the method that decreases degree of polymerization and molecular weight of cellulose. Cellulose shall be smaller size and the area for reacting with monomer is increased. Therefore the graft copolymerization of acrylic acid and acrylonitrile on microcrystalline cellulose by using ceric ammonium nitrate as initiator should occur better than unmodified cellulose.

4.2 Graft Copolymerization by Acrylonitrile and Acrylic Acid

One method which was usually used to prepare the water-retaining material was the graft copolymerization of suitable monomer on cellulose. The preferred monomer was acrylonitrile which after alkaline hydrolysis of grafted product, it was expected that the high amount of carboxylate groups were obtained. Owing to the alkaline hydrolysis of cellulose-graft-polyacrylonitrile was never completed so the combination of carboxylate and amide groups in hydrolyzed product were obtained. It was the disadvantage of this method.

Thus the monomer which was easier converted to carboxylate group was considered and this monomer was acrylic acid. As reviewed in the literature, it was found that in the graft copolymerization of acrylic

acid on cellulose, the polyacrylic acid grafted branch chain was highly coiled conformation and it tended to occlude further graft copolymerization on cellulose (22).

Therefore the disadvantages of each monomer can be improved by graft copolymerization of these monomers on microcrystalline cellulose. There were many factors effected the graft copolymerization of acrylonitrile and acrylic acid on microcrystalline cellulose. These factors effected the percent conversion of monomer to copolymer and the amount of homopolymer which occurred from homopolymerization. The homopolymerization was the side reaction of graft copolymerization which was the undesirable reaction. Thus the optimum condition for graft copolymerization of acrylonitrile and acrylic acid on microcrystalline cellulose was investigated by varying of the various factors. These factors were amount of water, initiator concentration, quantity of monomers, nitric acid concentration, stirring speed, and temperature.

4.2.1 Effect of the Amount of Water

The important and the first factor to vary was the amount of water or reaction volume which was suitable for the amount of microcrystalline cellulose. Owing to the viscosity was the serious problem in the polymerization and the reaction volume effected to the viscosity of the polymerization system.

Thus the graft copolymerization of acrylonitrile and acrylic acid on microcrystalline cellulose was carried out by varying

the amount of water and fixed other parameters as follow: 0.16 mol fraction of acrylic acid monomer, 1 g weight of micro-crystalline cellulose, 0.01 M concentration of ceric ammonium nitrate, 0.4 M concentration of nitric acid solution, 35°C temperature, and 350 rpm stirring speed. The polymerization was allowed to proceed for 3 hours and the result was shown in Table 4.1.

Table 4.1 Effect of the amount of water on % conversion of monomer to copolymer and % homopolymer

| Reaction volume (mL) | Water (mL) | % Conversion of monomer to copolymer | % Homopolymer |
|-------------------------|---------------|---|---------------|
| 30 | 18.59 | 40.53±0.12 | 10.23±0.17 |
| 40 | 28.59 | 60.20±0.24 | 8.64±0.12 |
| 50 | 38.59 | 76.23±0.76 | 6.46±0.20 |
| 60 | 48.59 | 70.60±0.45 | 7.03±0.12 |
| 70 | 58.59 | 64.06±0.28 | 8.23±0.12 |
| 80 | 68.59 | 56.70±0.32 | 9.06±0.12 |

From Table 4.1 it was observed that the percent conversion of monomer to copolymer increased with an increase of the amount of water until up to 38.59 mL and beyond this amount of water, there was a decrease in percent conversion of monomer to copolymer. So the maximum percent conversion and the low percent homopolymer were

obtained at the amount of water 38.59 mL or the reaction volume 50 mL.

From this result, it was ascribed that the viscosity of the reaction system was increased in the presence of small amount of water or the low level of reaction volume. This was resulted from the absorbing ability of cellulose-graft-poly(acrylonitrile-co-acrylic acid) which could absorb about 3.3 g water /g polymer and in addition to it could also absorb the monomers into itself. Thus the viscous reaction system was obtained and it was expected that in viscous medium, the living free radical polymer resulted in the termination of stabilized and dimerized products as shown in equation 8 and 10 in Scheme 4.2.

Furthermore, at the low level of reaction volume when a large amount of polymer product was produced, the liquid in the system was absorbed by the solid polymer and it hardly agitated. Thus when the initiator solution was added dropwise into the solution, the homopolymerization of the absorbed monomers on the solid polymer was initiated instead of the graft copolymerization. Owing to this phenomenon, the high percent homopolymer and low percent conversion of monomer to copolymer were obtained when the small amount of water or the low level of reaction volume was used.

The percent conversion of monomer to copolymer decreased when the amount of water was more than 38.59 mL. It was expected that in the dilute solution, the radical site on microcrystalline cellulose was hardly initiated by Ce^{4+} ion and the monomers could hardly be attacked at the radical site for initiating the grafting

reaction too.

Thus percent conversion of monomer to copolymer decreased because of the high amount of medium. It was indicated that the amount of water was the important factor for grafting reaction and the suitable amount of water was 38.59 mL. So the amount of water was fixed at constant volume in the next experiment.

4.2.2 Effect of the initiator concentration

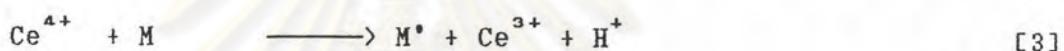
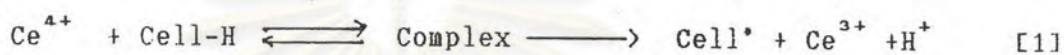
The ceric ion has been widely used to initiate graft copolymerization for various monomers and polymeric substrates because it was the most promising and practical method. The mechanism of ceric ion initiated graft copolymerization were well understood. The mechanism of grafting was shown herein below.

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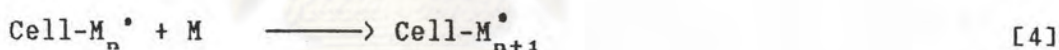


Ogiwara et al (10), suggested the reaction mechanism of graft copolymerization of vinyl monomer onto cellulose by using Ce^{4+} as initiator. The mechanism of graft copolymerization was shown in schemes 4.2

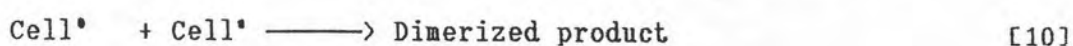
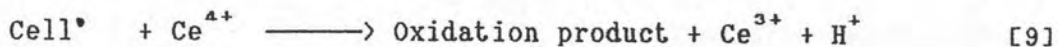
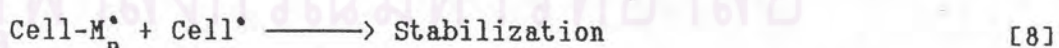
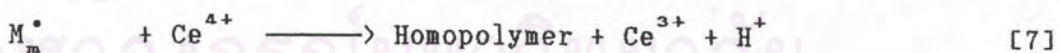
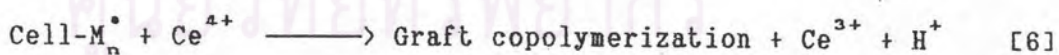
Initiation:



Propagation



Termination



M=monomer

Scheme 4.2 Mechanism of Graft Copolymerization

Detail description of the initiation reaction mechanism in equation [1] was mentioned earlier, which gave a primary alcohol radical. Addition of vinyl monomer, grafting reactions were initiated. The macrocellulosic radical subsequently attacked the monomer resulting in chain initiation as shown in equation [2] this was then followed by propagation as illustrated in equation [4]. Finally the termination of the growing grafted chain was affected by Ce^{4+} according to equation [6] to yield graft copolymerization product and equation [9] to yield oxidative product. In addition, the termination was occurred from mutual combination as shown in equation [8] which gave stabilization product. Dimerized product might occur from combination of two macrocellulosic radicals as illustrated in equation [10]. The homopolymer was concurrently formed according to equation [3],[5] and [7].



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The ceric ion used to initiate graft copolymerization of acrylonitrile and acrylic acid in this experiment was the constituent of ceric ammonium nitrate. The ceric ammonium nitrate was orange crystalline and dissolved well in nitric acid solution and it was available. The amount of ceric ion can be effect on the percent conversion of monomer to copolymer and percent homopolymer of the product. Thus, the investigation of the optimum amount of Ce^{+4} ion was necessary and the result was shown in Table 4.2



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Table 4.2 Effect of the Ce^{4+} concentration on % conversion of monomer to copolymer and % homopolymer

| Ce^{4+} Concentration (M) | % Conversion of monomer to copolymer | % Homopolymer |
|--------------------------------|---|-----------------|
| 0.001 | 60.30 ± 0.37 | 2.53 ± 0.12 |
| 0.002 | 64.76 ± 0.45 | 2.76 ± 0.02 |
| 0.003 | 69.23 ± 0.25 | 2.77 ± 0.13 |
| 0.004 | 75.00 ± 0.32 | 3.06 ± 0.25 |
| 0.005 | 80.76 ± 0.25 | 3.56 ± 0.21 |
| 0.006 | 82.33 ± 0.25 | 3.77 ± 0.20 |
| 0.007 | 81.30 ± 0.37 | 4.36 ± 0.25 |
| 0.008 | 79.80 ± 0.29 | 5.80 ± 0.24 |
| 0.009 | 77.50 ± 0.37 | 6.30 ± 0.24 |
| 0.010 | 76.23 ± 0.76 | 6.47 ± 0.20 |
| 0.011 | 70.16 ± 0.33 | 7.20 ± 0.24 |
| 0.012 | 63.96 ± 0.28 | 8.37 ± 0.12 |

From Table 4.2, it was observed that the increase of concentration of ceric ammonium nitrate up to 0.006 M, the percent conversion of monomer to copolymer increased at all concentration until the maximum value; 82.33 %, and beyond this concentration, there was a decrease in percent conversion of monomer to copolymer. This

result might be attributed to the mutual termination of growing grafted radical chains prevailed over the termination due to metal ion at low ceric ammonium nitrate concentration (below 0.006 M). This resulted in the increase of percent conversion of monomer to copolymer and the high amount of grafted copolymer were obtained.

However, beyond 0.006 M of ceric ammonium nitrate solution, the termination due to metal ion prevailed. This resulted in the decrease of percent conversion of monomer to copolymer. This effect was previously observed from other cellulosic systems by N.C. nayak and et al (23).

The other attribution for this result concerned with the definite amount of microcrystalline cellulose and the initiation of free radical site on microcrystalline cellulose. When the amount of microcrystalline cellulose was constant; 1 g but the amount of Ce^{4+} ion in the solution was further increased. So at the lower Ce^{4+} ion concentration, Ce^{4+} ion could initiate the definite amount of free radical site on microcrystalline cellulose until the concentration of Ce^{4+} ion was 0.006 M. At this concentration the highest amount of free radical was obtained and it resulted in the maximum % conversion of monomer to copolymer. And beyond this concentration, the excess ceric ion remained in the aqueous phase and could initiate homopolymerization of the soluble monomer. This resulted in the decrease of % conversion of monomer to copolymer owing to some part of monomer which was formed as polyacrylonitrile and polyacrylic acid.

Thus the addition of high amount of ceric ion into the reaction system was not necessary. Furthermore, it led to low percent conversion of monomer to copolymer, high percent homopolymer, high cost, and difficult purification. It was also observed that the color of the product gradually changed from white to yellow as the concentration of ceric ion was over 0.008 M.

The investigation of the optimum ceric ion concentration would lead to a reduction of the extent of chain termination reaction by ceric ion and to higher extents of graft copolymer formation. This resulted in the improvement in level of percent conversion of monomer to copolymer. Thus the optimum ceric ion concentration was found to be 0.006 M.

4.2.3 Effect of the monomers quantity

Therefore, the other important factor which effected the grafting reaction of acrylonitrile and acrylic acid on microcrystalline cellulose was the quantity of two monomers. In this experiment the effect of variation of monomer quantity in form of mol fraction of acrylic acid on percent conversion of monomer to copolymer and percent homopolymer has been studied and the result was shown in Table 4.3. The grafted product was monitored by Infrared Spectroscopy and infrared spectrum was shown in Figure 4.3.

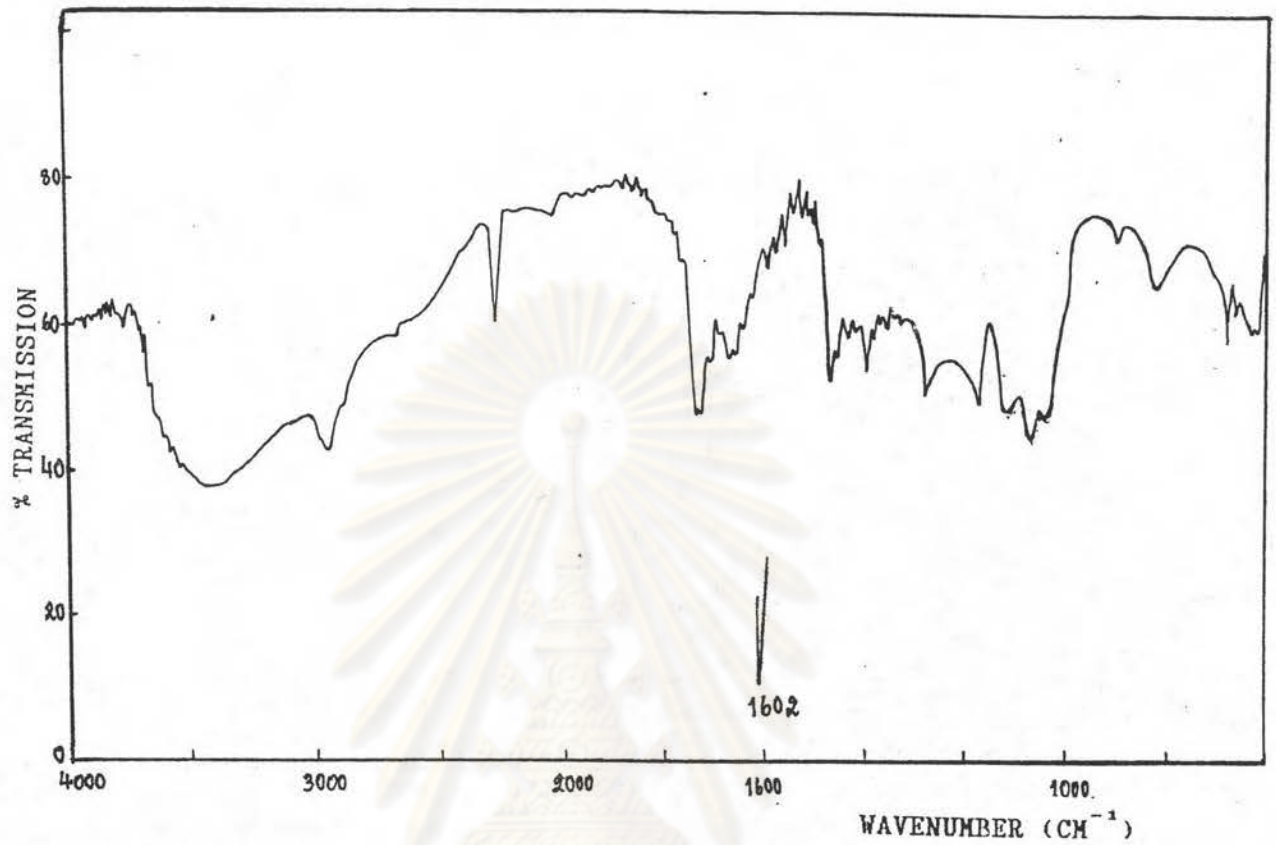


Figure 4.3 Infrared Spectrum (KBr pellet) of Microcrystalline Cellulose - Graft - Poly(Acrylonitrile - co - Acrylic acid) without Homopolymer at 0.48 mol fraction of Acrylic acid .

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Table 4.3 Effect of mol fraction of acrylic acid on % conversion of monomer to copolymer and % homopolymer

| Mol fraction of acrylic acid | % Conversion of monomer to copolymer | % Homopolymer |
|------------------------------|--------------------------------------|---------------|
| 0.16 | 82.33± 0.25 | 3.77±0.20 |
| 0.32 | 76.53± 0.28 | 4.93±0.21 |
| 0.48 | 69.23± 0.45 | 6.53± 0.25 |
| 0.65 | 65.80± 0.61 | 7.20± 0.33 |
| 0.82 | 60.16± 0.49 | 8.70± 0.16 |

From the result shown in Table 4.3, it was observed that percent conversion of monomer to copolymer decreased and percent homopolymer increased with the increase of mol fraction of acrylic acid from 0.16 to 0.82. When the mol fraction of acrylic acid was 0.16 the maximum percent conversion of monomer to copolymer and the minimum percent homopolymer were obtained.

This result could be ascribed to the characteristic of acrylic acid polymer. Acrylic acid was water-soluble monomer, but its polymer has highly coiled conformation in the acidic reaction medium and tend to occlude further graft copolymerization on the cellulosic substrate (22).

Therefore, the grafting reaction hardly occurred while the excess acrylic acid in the reaction medium would rather be initiated by Ce^{4+} ion to form polyacrylic acid homopolymer. The percent homopolymer thus increased with increasing the mol fraction of acrylic acid and the decrease of percent conversion of monomer to copolymer was resulted. This indicated the competition between the homopolymerization and grafting reaction, where the former prevailed over the latter at higher mol fraction of acrylic acid monomer.

Consequently, the optimum mol fraction of acrylic acid monomer for the grafting reaction was found to be 0.16.

4.2.4 Effect of nitric acid concentration

The graft copolymerization of acrylonitrile and acrylic acid on microcrystalline cellulose was carried out in aqueous nitric acid medium and the concentration of nitric acid was varied. The result was shown in Table 4.4.

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Table 4.4 Effect of nitric acid concentration on % conversion of monomer to copolymer and % homopolymer

| Nitric acid (M) | % Conversion of monomer to copolymer | % Homopolymer |
|--------------------|---|---------------|
| 0.1 | 85.30 ± 0.37 | 2.70 ± 0.16 |
| 0.2 | 86.00 ± 0.20 | 2.33 ± 0.20 |
| 0.3 | 86.73 ± 0.21 | 2.86 ± 0.21 |
| 0.4 | 82.33 ± 0.25 | 3.77 ± 0.20 |
| 0.5 | 77.43 ± 0.33 | 4.86 ± 0.33 |
| 0.6 | 73.53 ± 0.38 | 4.37 ± 0.25 |

The nitric acid solution was used as the promoter for dissociation of ceric ammonium nitrate in solution and as the medium for grafting reaction. In the first stage of experiment, nitric acid solution functioned as the swelling agent for microcrystalline cellulose.

The variation of nitric acid concentration would influence the reaction. Indeed, the results as shown in Table 4.4 indicated that percent conversion of monomer to copolymer increased gradually with the increasing concentration of nitric acid solution. When the concentration was higher than 0.3 M, however, the percent conversion decreased. The maximum percent conversion of monomer to copolymer was



86.73 % at 0.3 M nitric acid concentration. This result could be attributed to the less effect of nitric acid solution to grafting reaction at low concentration. But beyond 0.3 M the effect of concentration of nitric acid solution prevailed. Considering the reaction mechanism of graft copolymerization, in the initiation step, ceric ion formed chelate with cellulose of which the two protons of cellulose were left in the solution. This step was reversible process as shown in section 2.4.

Therefore, the excess protons from nitric acid should shift the equilibrium of this reaction to the left side. It thus caused the reversible process of this chelation and the cellulose substrate was obtained.

Concomitantly, the ceric ion in the system would rather initiate the homopolymerization as the higher percent of polyacrylonitrile and polyacrylic acid were formed with the increase in nitric acid concentration. Accordingly, the high concentration of nitric acid solution was not only unfavorable to the reaction but also would make the cost of production higher.

Consequently, in the graft copolymerization of acrylonitrile and acrylic acid on microcrystalline cellulose, the high concentration of nitric acid solution should be avoided. From the experiment, 0.3 M of nitric acid solution gave the highest conversion.

4.2.5 Effect of stirring speed

It is reasonable to expect that in a heterogeneous reaction such as grafting, where the growing chains are anchored to insoluble cellulose fibres, the effect of stirring would be important. One might expect further that the rate of polymer formation would depend on monomer solubility in the reaction medium, as this would govern monomer supply to the growing chains (22).

Thus the graft copolymerization of acrylonitrile and acrylic acid on microcrystalline cellulose was carried out by varying the stirring speed. Table 4.5 shows effect of stirring speed on percent conversion of monomer to copolymer and percent homopolymer.

Table 4.5 Effect of stirring speed on % conversion of monomer to copolymer and percent homopolymer

| Stirring speed (rpm) | % Conversion of monomer to copolymer | % Homopolymer |
|-------------------------|---|---------------|
| 150 | 65.23 ± 0.50 | 4.86 ± 0.12 |
| 250 | 74.60 ± 0.33 | 4.70 ± 0.24 |
| 350 | 86.73 ± 0.22 | 2.86 ± 0.21 |
| 450 | 88.43 ± 0.17 | 2.93 ± 0.05 |
| 550 | 60.33 ± 0.49 | 6.60 ± 0.08 |

From Table 4.5, it was observed that the percent conversion of monomer to copolymer increased with an increase of the stirring speed. When the stirring speed was 450 rpm the percent conversion of monomer to copolymer increased at all stirring speed, and beyond this stirring speed, there was a decrease in percent conversion of monomer to copolymer. The maximum percent conversion of monomer to copolymer and the low percent homopolymer were obtained at 450 rpm.

From this result, it was attributed that in the grafting reaction of acrylonitrile and acrylic acid on microcrystalline cellulose, both monomers were soluble in reaction medium and at the low stirring speed the formation of polymer product prevented the formation of a vortex (24). Thus the diffusion of both monomers from monomer droplets into cellulose fibres was difficult to occur and this would govern monomer supply to growing chains. In addition, the complex of Ce^{4+} and microcrystalline cellulose was hardly formed since when the initiator solution was dropped to the reaction medium the transferring of Ce^{4+} to microcrystalline cellulose was also difficult to occur. Thus on the other hand the Ce^{4+} could initiate the homopolymerization to yield the homopolymer product and it was resulted in the low percent conversion of monomer to copolymer and high percent homopolymer.

The maximum percent conversion of monomer to copolymer reached at the sterring speed of 450 rpm and beyond this speed the percent conversion of monomer to copolymer was immediatly dropped. This was attributed to the violently vortex formation of the reaction

medium so liquid in the system which included some part of monomers was thrown out to all inner surface of reactor. Thus some part of monomers was lost from reaction mass and resulted in immediately decreased of percent conversion of monomer to copolymer.

In addition, the high stirring speed also lead to the decrease in the ability to form cellulose-Ce⁴⁺ complex and decrease the stability of this complex, so Ce⁴⁺ could not interact with the cellulose and decreased the percent conversion of monomer to copolymer. This observation trend agreed with the work of Graczyk, T (22).

4.2.6 Effect of temperature

The graft copolymerization of acrylonitrile and acrylic acid on microcrystalline cellulose has been studied by varying temperature and the result was shown in Table 4.6.

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Table 4.6 Effect of temperature on percent conversion of monomer to copolymer and percent homopolymer

| Temperature (°C) | % Conversion of monomer to copolymer | % Homopolymer |
|---------------------|---|---------------|
| 25 | 82.53 ± 0.28 | 2.70 ± 0.80 |
| 30 | 77.33 ± 0.25 | 4.93 ± 0.26 |
| 35 | 88.43 ± 0.17 | 2.93 ± 0.05 |
| 40 | 80.16 ± 0.41 | 3.50 ± 0.21 |
| 50 | 73.93 ± 0.16 | 6.23 ± 0.29 |
| 60 | 66.00 ± 0.24 | 8.53 ± 0.20 |

It was observed that at 30°C percent conversion of monomer to copolymer was lower and percent homopolymer was higher than of 25°C and 35°C. The maximum value of percent conversion of monomer to copolymer was obtained at 35°C. After that percent conversion of monomer to copolymer decreased and percent homopolymer increased when temperature was increased from 40°C to 60°C.

This result could be attributed to the chain transfer reaction which might be accelerated when the temperature increased from 40°C to 60°C and subsequently lead to decrease in percent conversion of monomer to copolymer (23). In addition, it might be simultaneously considered that the chain transfer to monomer

constant(C_m) of acrylonitrile at various temperatures. The chain transfer to monomer constant was the one of the monomer characteristics which shown the opportunity of homopolymerization process. Thus the increase of C_m increased the amount of homopolymer. The C_m of acrylonitrile monomer were 0.105×10^4 at 25°C , 1.5×10^4 at 30°C , and 0.17×10^4 at 40°C (25).

It was found that the C_m of acrylonitrile at 40°C was higher than of 25°C so the high % homopolymer and low percent conversion of monomer to copolymer were obtained at 40°C .

The percent conversion of monomer to copolymer increased to the maximum value when temperature was increased from 30°C to 35°C . This result could be attributed to the enhancement of rate of diffusion of acrylonitrile and acrylic acid monomers to radical site on microcrystalline cellulose backbone where grafting reaction was initiated (23), (26). In addition, the production rate of active free radicals on microcrystalline cellulose backbone was increased which increased the number of grafting sites at a faster rate. Thereby the rate of grafting reaction by these radicals were also increased and this effect was previously observed from other cellulosic system by Samal, R.K. and et.al (27).

Considering percent conversion of monomer to copolymer and percent homopolymer at 30°C , was it was found that percent conversion of monomer to copolymer was lower and percent homopolymer was higher than of 25°C and 40°C . This result could be ascribed by considering the chain transfer to monomer constant of acrylonitril at

25°C, 30°C, and 40°C.

It was found that at 30°C the chain transfer to monomer constant was highest and it resulted in the high percent homopolymer and low percent conversion of monomer to copolymer.

Thus from this result, it could indicate that the optimum temperature for the grafting reaction was 35°C which give the highest percent conversion of monomer to copolymer and low percent homopolymer.

4.2.7 Graft copolymerization of the microcrystalline cellulose at the selected condition

The water-retaining material with high absorbency from cellulose was prepared by graft copolymerization of acrylonitrile and acrylic acid on microcrystalline cellulose in nitric acid solution and Ce^{4+} was used as initiator. The objective of this synthesis was for addition the nitrile and carboxyl group into structure of cellulose as much as possible.

Subsequently, the nitrile and carboxyl group were converted to carboxylate group by alkaline hydrolysis and water-retaining material with high absorbency was obtained. So the effect of various factors influencing the grafting reaction was preliminary studied for determining the optimum condition. These factors were amount of water, concentration of initiator, quantity of two monomers, concentration of nitric acid solution, stirring speed, and temperature.

The study was performed by varying one factor while the others were kept constant. Each factor was selected based on the result of high percent conversion of monomer to copolymer and low percent homopolymer as follow :

| | |
|--|-------|
| Amount of water, mL..... | 38.97 |
| Ce ⁴⁺ concentration, M..... | 0.006 |
| Mol fraction of acrylic acid, M..... | 0.16 |
| Nitric acid concentration, M..... | 0.3 |
| Stirring speed, rpm..... | 450 |
| Temperature, °C..... | 35 |

When the earlier factors was studied and selected, it was fixed in the next experiment whereas each latter factor varied at each experiment. The graft copolymerization was repeated at this condition and the results were shown in Table 4.7.

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Table 4.7 Grafting reaction at the selected condition

| %Conversion of monomer to copolymer | %Homopolymer | %Grafting efficiency | %Add-on | Grafting ratio (g PAN and PAA/g cell) |
|-------------------------------------|--------------|----------------------|--------------|---------------------------------------|
| 86.96 | 2.96 | 96.65 | 88.03 | 7.35 |
| 87.16 | 2.87 | 96.75 | 88.05 | 7.37 |
| 89.25 | 2.51 | 97.16 | 88.30 | 7.55 |
| 87.79 ± 1.04 | 2.78 ± 0.19 | 96.85 ± 0.22 | 88.12 ± 0.12 | 7.42 ± 0.09 |

From the result it was found that at this optimum condition 87.79 % conversion of monomer to copolymer, 96.85 % add-on, 7.42 grafting ratio, 96.85% grafting efficiency, and only 2.78 % homopolymer was obtained.

When compared with the research of Plumpirom, V., the water-retaining material was synthesized by graft copolymerization of acrylonitrile on cellulose, which extracted from water hyacinth, by using Mn^{3+} pyrophosphate complex as initiator.

The graft copolymerization was carried out under the following condition, i.e., amount of water; 1.5 mL/mL monomer-g cellulose, weight ratio of acrylonitrile per cellulose; 6.6, amount

of Mn^{3+} ; 0.90×10^{-3} M/g cellulose, amount of EGDMA; 5 % v/v of monomer, stirring speed; 400 rpm, and reaction temperature; $35^{\circ}C$. The reaction was continuous stirred in the atmosphere of nitrogen for 3 hours.

The conversion of monomer to copolymer 85.47 %, add-on 84.97 %, grafting ratio 5.65, the grafting efficiency 94.93 % and only 4.33 % of homopolymer was obtained.

After that the grafted product was hydrolyzed in potassium hydroxide solution at $95^{\circ}C$ for 2 hours. The water retention value of the hydrolyzed product was about 600 to 700 g water/g polymer.



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4.3 Attempts to Modify cellulose by other potential methods

4.3.1 Graft Copolymerization of Acrylonitrile on Cyanoethylated Microcrystalline Cellulose

As mentioned earlier, the water-retaining material with high water absorbency from cellulose could be prepared by several methods. One of these methods was the substitution of the hydroxyl groups with new chemical groups. In addition, the structure of cellulose was suitable for graft copolymerization. Thus in this research modified cellulose was synthesized by graft copolymerization of acrylonitrile on cyanoethylated microcrystalline cellulose. This synthesis intended to incorporate the nitrile group into the structure of cellulose as much as possible both from the substitution and grafting reaction.

After that the modified cellulose was hydrolyzed in alkaline solution at high temperature for conversion from nitrile group to carboxylate group as much as possible. It was known that the greater amount of carboxylate group in the product the higher water absorbency was obtained. Thus it was expected that the product obtained from graft copolymerization of acrylonitrile on cyanoethylated microcrystalline cellulose should possess high amount of carboxylate group and could absorb high amount of water.

In the first stage, the cyanoethylation of acrylonitrile on microcrystalline cellulose rapidly occurred. The acrylonitrile molecule could easily substitute the proton on microcrystalline

cellulose and the white powder product was obtained. The mechanism of cyanoethylation was shown in section 2.3. The product was characterized by Infrared Spectroscopy and the infrared spectrum was shown in Figure 4.4.

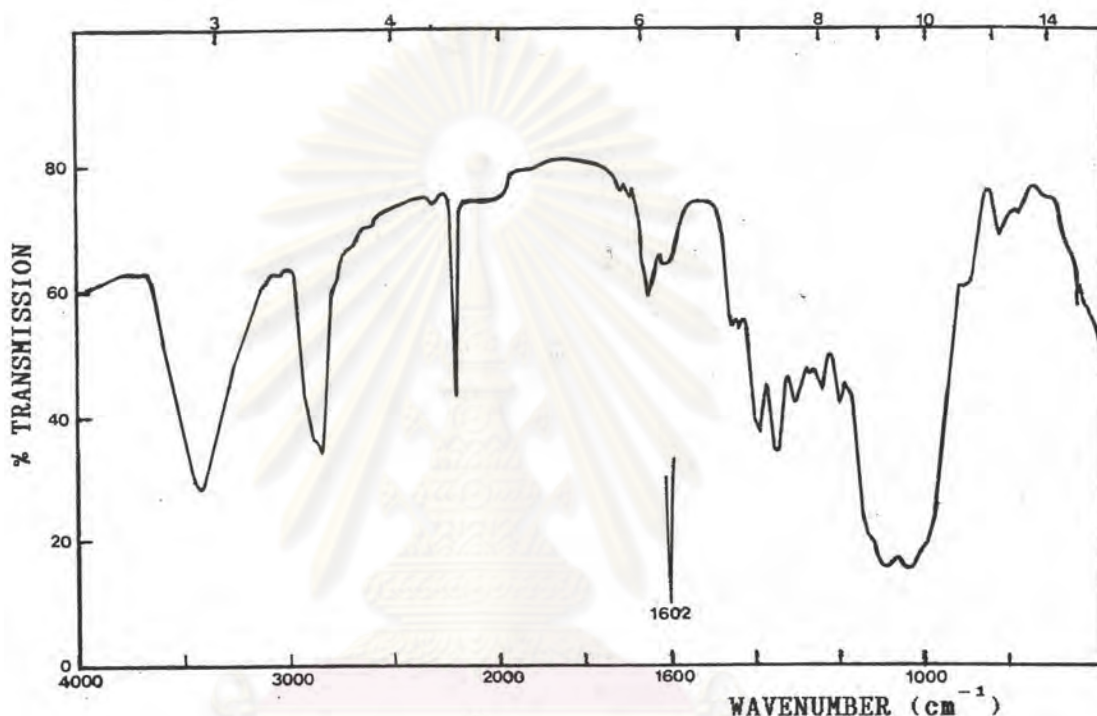


Figure 4.4 Infrared Spectrum (KBr pellet) of Cyanoethylated Microcrystalline Cellulose

From infrared spectrum the sharp and strong absorption peak at 2240 cm^{-1} appeared which indicated that the cyanoethylation could easily occurred. After that the graft copolymerization of acrylonitrile on cyanoethylated microcrystalline cellulose subsequently occurred by using Ce^{4+} ion in nitric acid solution as initiator. The reaction was allowed to proceed until completion, the white powder product was obtained and was characterized by Infrared Spectroscopy. The infrared spectrum was shown in Figure 4.5.

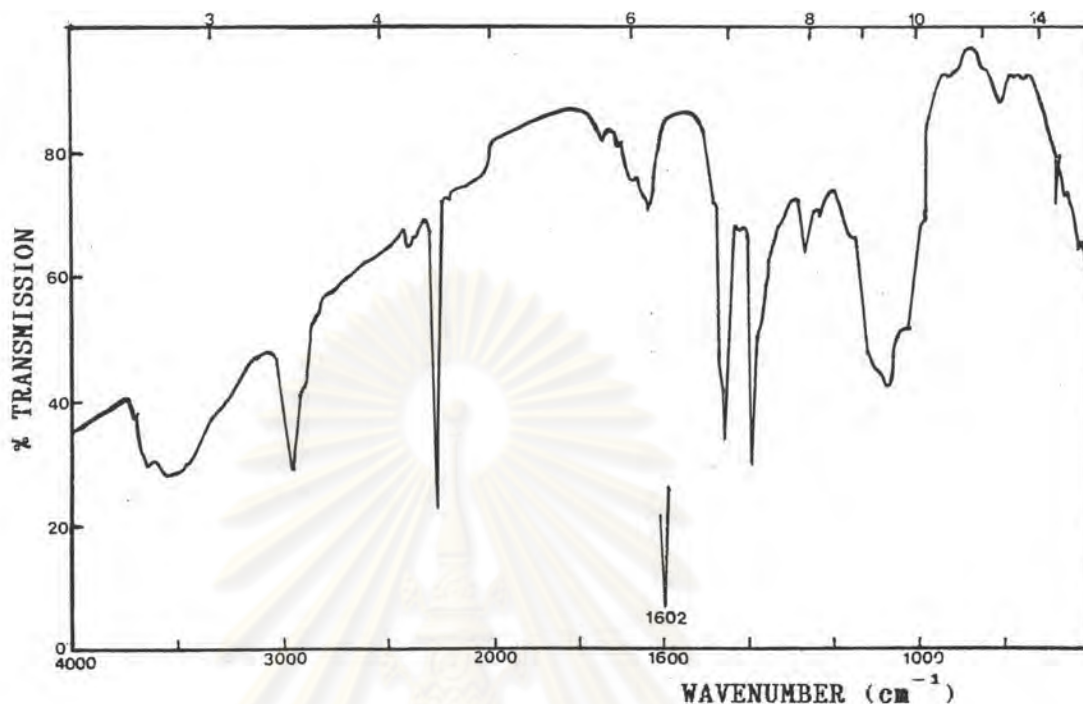
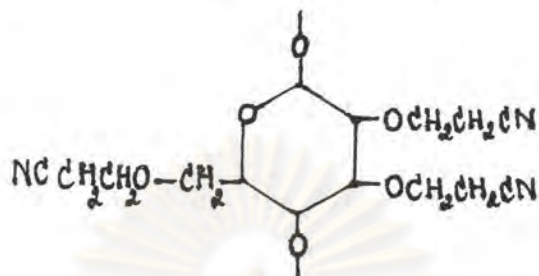


Figure 4.5 Infrared Spectrum (KBr pellet) of Cyanoethylated Microcrystalline Cellulose-Graft-Polyacrylonitrile Copolymer with Homopolymer

Afterward the homopolymer which occurred simultaneously at the same condition of graft copolymerization was separated from the graft copolymer. The homopolymer was polyacrylonitrile and it was extracted with *N,N*-dimethylformamide at room temperature for 24 hours by continuous agitation with magnetic stirrer and the clear and colorless solution was obtained. (Polyacrylonitrile was soluble in *N,N*-dimethylformamide.)

From this result it could be attributed to the solubility of the cyanoethylated microcrystalline cellulose-graft-polyacrylonitrile copolymer. Considering the cyanoethylation, the substitution of

hydroxyl group on microcrystalline cellulose with acrylonitrile molecule could be easily occurred. The structure of cyanoethylated microcrystalline cellulose was shown below.



Later on, the graft copolymerization of acrylonitrile on cyanoethylated microcrystalline cellulose took place but it was found that Ce^{4+} ion could not initiate free radical site on cyanoethylated microcrystalline cellulose so the grafting reaction could not occur. Considering the mechanism of graft copolymerization in section 2.4, it indicated that the chelate between Ce^{4+} ion and cyanoethylated microcrystalline cellulose could not form in initiation step. This was resulted from the most of proton on microcrystalline cellulose was substituted by acrylonitrile molecule although a few number of proton was not substituted and could be able to initiate the grafting reaction. Thus the excess Ce^{4+} ion in the system initiated the homopolymerization of acrylonitrile and the high amount of polyacrylonitrile was obtained.

The polyacrylonitrile was separated from the grafted product by extraction with N,N-dimethylformamide but the result showed that all of the product was soluble in N,N-dimethylformamide and the clear and colorless solution was obtained. It was ascribed that polyacrylonitrile and cyanoethylated microcrystalline cellulose-graft-polyacrylonitrile were soluble in N,N-dimethylformamide at room

temperature although the grafting reaction was occurred on the partial cyanoethylated microcrystalline cellulose.

4.3.2 Cyanoethylation of Microcrystalline Cellulose Grafted Copolymer

On the other hand cyanoethylation was tried on grafted microcrystalline cellulose. In the first stage, the graft copolymerization of acrylonitrile on microcrystalline cellulose by using Ce^{4+} ion in nitric acid solution as initiator was carried out and the white powder polymer was obtained. It was characterized by Infrared Spectroscopy and infrared spectrum was shown in Figure 4.6.

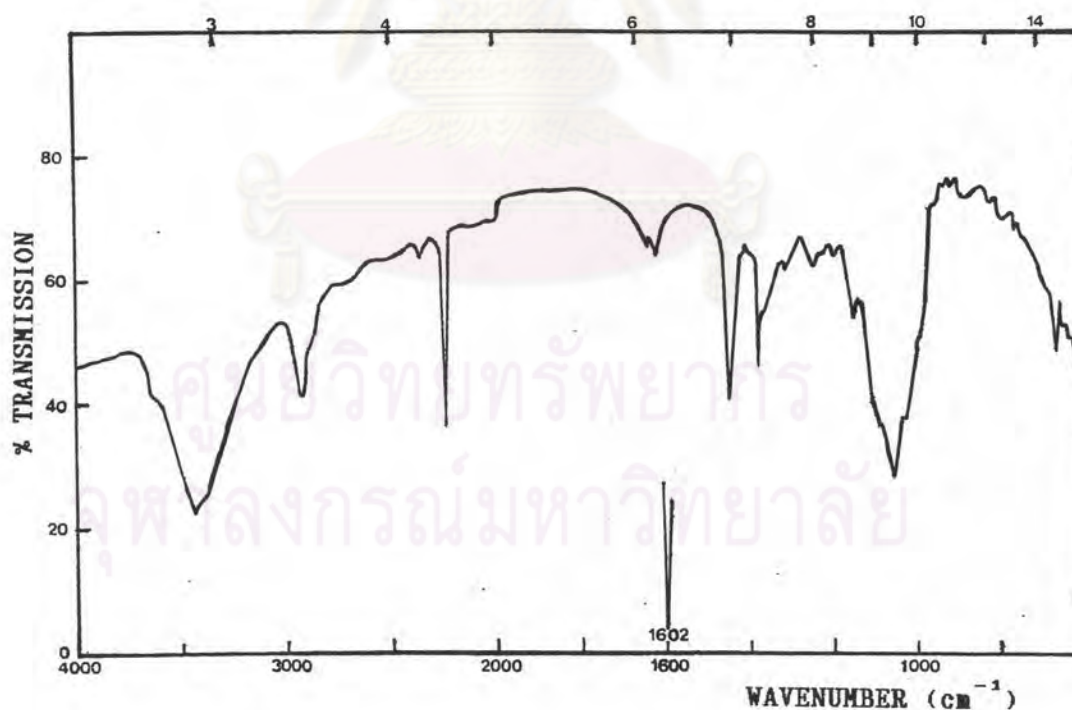


Figure 4.6 Infrared Spectrum (KBr pellet) of Microcrystalline Cellulose - Graft - Polyacrylonitrile Copolymer with Homopolymer

The obtained polymer was purified by extraction with N,N-dimethylformamide by continuous agitation for 24 hours at room temperature for isolation of polyacrylonitrile from the grafted product. The white powder was obtained and characterized by Infrared Spectroscopy and infrared spectrum was shown in Figure 4.7.

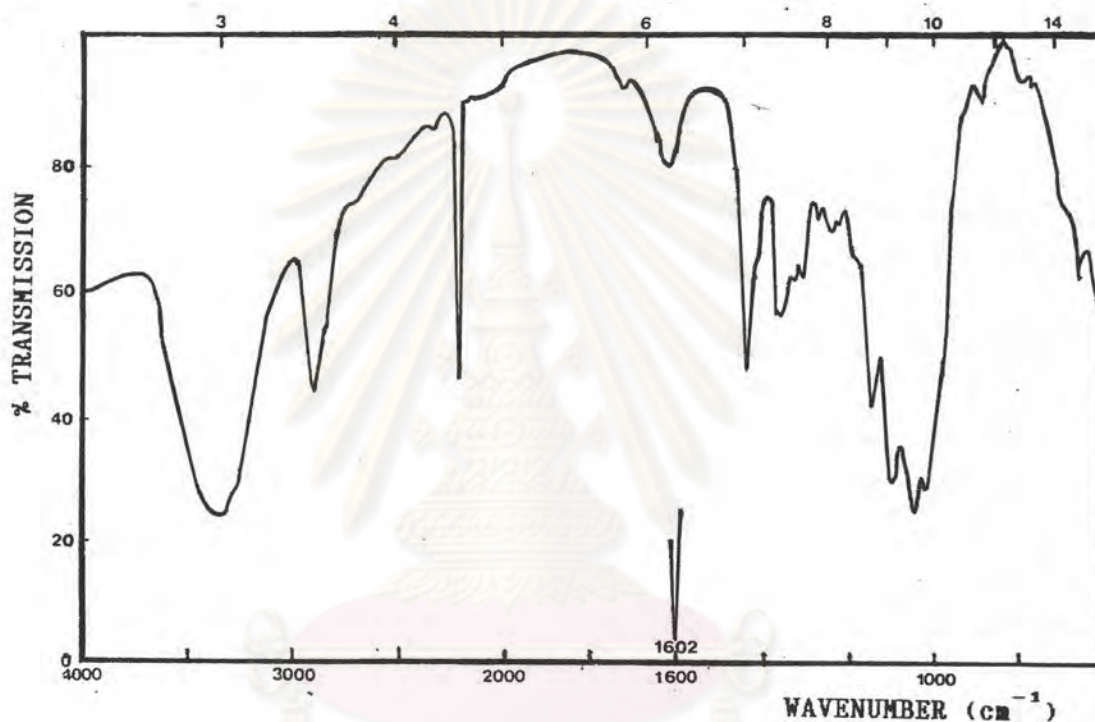


Figure 4.7 Infrared Spectrum (KBr pellet) of Microcrystalline Cellulose - Graft - Polyacrylonitrile Copolymer without Homopolymer

After that the cyanoethylation on pure grafted polymer took place and the white powder product was obtained. It was characterized by Infrared Spectroscopy and infrared spectrum was shown in Figure 4.8.

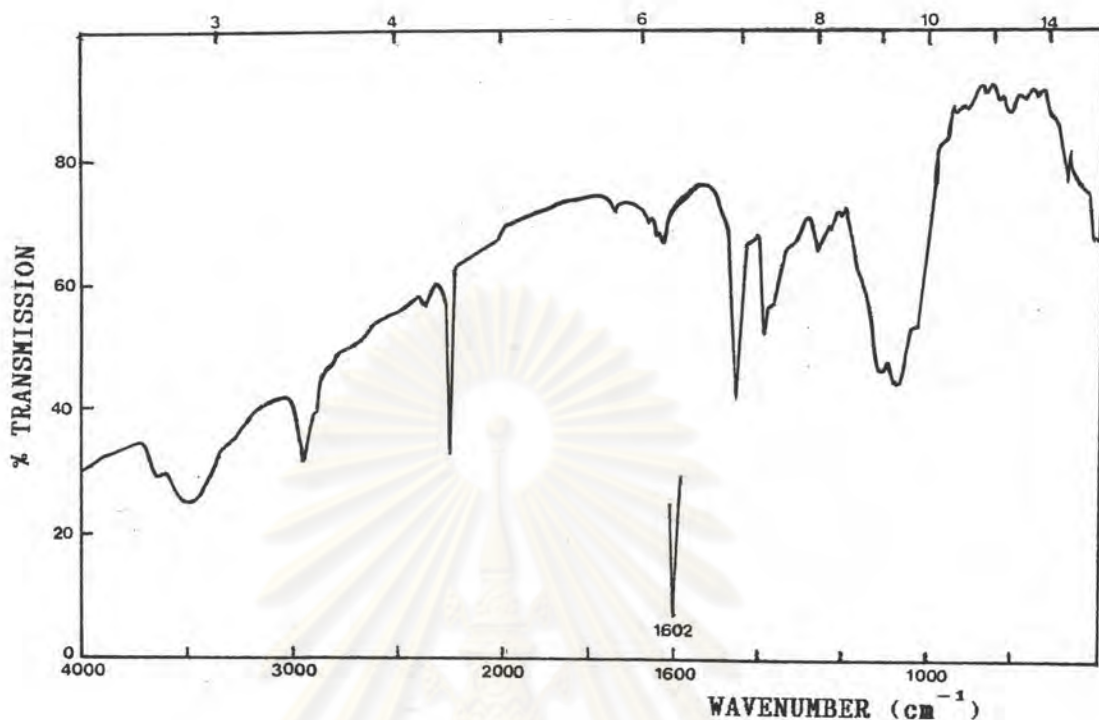


Figure 4.8 Infrared Spectrum (KBr pellet) of Microcrystalline Cellulose-Graft-Polyacrylonitrile After Cyanoethylation

Considering the weight of the obtained product it was found that after cyanoethylation the weight of final product and initial weight of pure grafted polymer were little difference. It indicated that the cyanoethylation on pure grafted polymer could not occur. It was proposed that it resulted from steric effect due to the large amount of grafted branch chains in polymer backbone. Thus the substitution of acrylonitrile on hydroxyl group of cellulose hardly occurred.

It was known that the large amount of nitrile groups in the polymer were converted to the high amount of carboxylate groups after alkaline hydrolysis and it was expected that the high water

absorbency material was obtained. But from the result obtained in this experiment it indicated that the addition of a large amount of nitrile group into microcrystalline cellulose by two methods of graft copolymerization of cyanoethylated microcrystalline cellulose and cyanoethylation on grafted copolymer were unable to use. So it was concluded that the water-retaining material which high water absorption could not be prepared by these two methods.

4.3.3 Graft Copolymerization of Acrylonitrile and Sodium Allyl Sulfonate on Microcrystalline Cellulose

In 1990, Yao Kejun successfully prepared base-hydrolyzed starch-graft-poly(acrylonitrile-co-sodium allyl sulfonate) by alkaline hydrolysis of the graft copolymer. The hydrolyzed product was an excellent water absorbent, which absorbed 1900 times of weight of deionized water. Grafting of mixed vinyl monomers, acrylonitrile and sodium allyl sulfonate, on starch was carried out in aqueous, gelatinized corn starch by using ceric ammonium nitrate as an initiator at 30°C under nitrogen atmosphere. After that the graft copolymer was hydrolyzed in aqueous sodium hydroxide at 80-100°C to obtain base-hydrolyzed starch-graft-poly(acrylonitrile-co-sodium allyl sulfonate) (28).

Thus in this research, preparation of material with high water absorbency was attempted by graft copolymerization of acrylonitrile and sodium allyl sulfonate on microcrystalline cellulose by using ceric ammonium nitrate as initiator at 35°C under nitrogen atmosphere and followed by alkaline hydrolysis. Firstly, sodium allyl

sulfonate monomer was synthesized and monitored with Infrared Spectroscopy and ^1H NMR Spectroscopy. Infrared spectrum and ^1H NMR spectrum were shown in Figure 4.9 and 4.10.

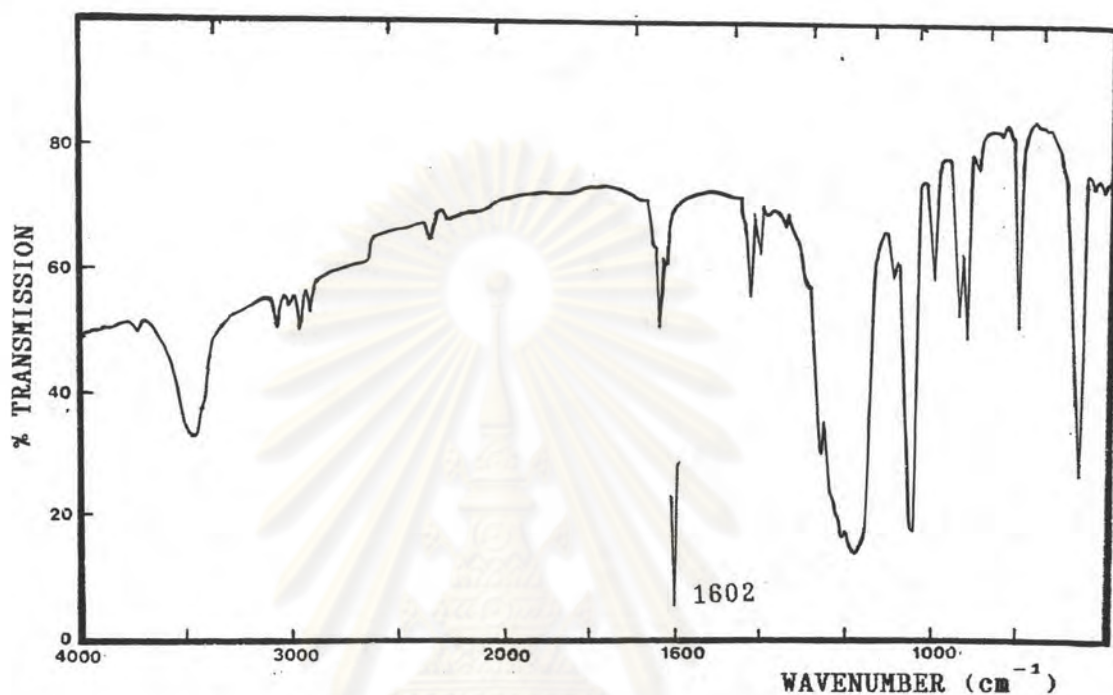


Figure 4.9 Infrared Spectrum (KBr pellet) of Sodium Allyl Sulfonate Monomer

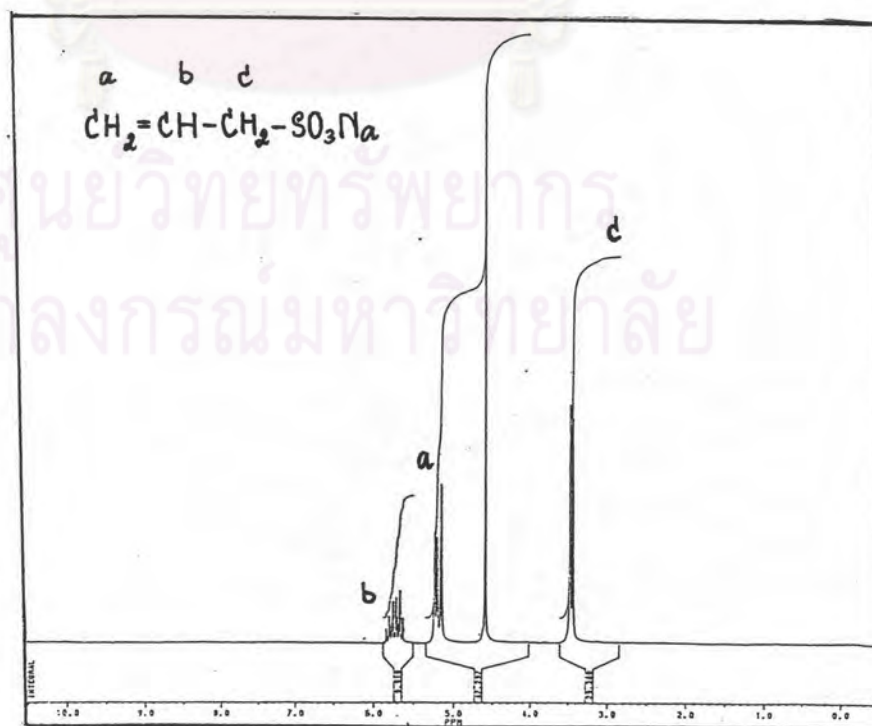


Figure 4.10 ^1H NMR Spectrum of Sodium Allyl Sulfonate Monomer

The infrared spectrum showed the characteristic absorption band of C=C stretching at $1660-1600\text{ cm}^{-1}$, sharp and high absorption peak at 1048 cm^{-1} was due to sulfonate group. The sharp and medium peak at 985 cm^{-1} and 910 cm^{-1} belong to C-H bending which was used to characterized a terminal vinyl group.

The ^1H NMR spectrum showed the chemical shift at 5.70 was due to =CH-, chemical shift at 5.20 was belong to $\text{CH}_2=$, and chemical shift at 3.45 was due to $-\text{CH}_2-$ (29).

In addition, double bond in sodium allyl sulfonate was tested by using KMnO_4 solution and Br_2 in CCl_4 and it was found that the color of KMnO_4 solution and Br_2 in CCl_4 disappeared. From these results it was confirmed that sodium allyl sulfonate monomer was synthesized.

After that the graft copolymerization of acrylonitrile and sodium allyl sulfonate on microcrystalline cellulose was carried out and the grafted product was monitored by Infrared Spectroscopy and infrared spectrum was shown in Figure 4.11.

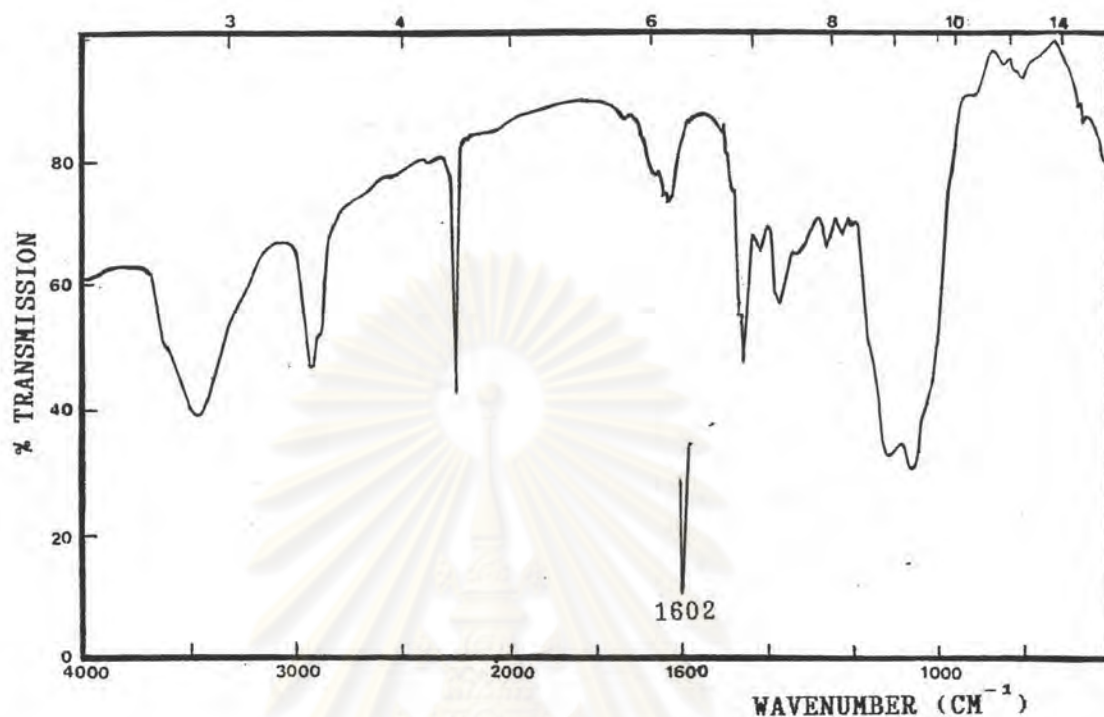


Figure 4.11 Infrared Spectrum of Microcrystalline Cellulose-Graft-Poly(Acrylonitrile - co - Sodium Allyl Sulfonate) without Homopolymer

From the result it was found that sodium allyl sulfonate monomer could not graft on microcrystalline cellulose and it could be attributed to the difference between polymerization system when compared with the experiment of Yao Kejun. The polymerization system of corn starch was homogeneous while the system of microcrystalline cellulose was heterogeneous. The corn starch was gelled in water at 85°C under nitrogen atmosphere for 30 minutes to obtain the starch solution before grafting but microcrystalline cellulose was in solid phase and dispersed in reaction medium. In homogeneous system the starch free radical could easily attack monomers which included acrylonitrile and sodium allyl sulfonate. On the other hand, the

microcrystalline cellulose in heterogeneous system was in solid phase and the reaction occurred on only surface area so the grafting reaction could be more difficult to occur and in addition the acrylonitrile monomer was more reactive than sodium allyl sulfonate monomer.

Thus from these causes it resulted in the ungrafted of sodium allyl sulfonate on microcrystalline cellulose. Accordingly, the water-retaining material could not be prepared from base-hydrolyzed microcrystalline cellulose-graft-poly(acrylonitrile-co-sodium allyl sulfonate).



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4.4 Acid Hydrolysis

One of the important properties of polymer was molecular weight which can be determined by Gel Permeation Chromatography. In this research, the molecular weight of grafted side chain of cellulose-graft-poly(acrylonitrile-co-acrylic acid) was investigated. In addition, the optimum condition for acid digestion of all cellulose substrate in grafted polymer was also searched.

In the first stage, all of cellulose substrate in cellulose-graft-poly(acrylonitrile-co-acrylic acid) was digested in acid. The acid hydrolysis was done by refluxing the cellulose-graft-poly(acrylonitrile-co-acrylic acid) in hydrochloric acid and sulphuric acid at various conditions.

It was found that the optimum condition for acid digestion was to reflux in 5 M sulphuric acid for 24 hours. After acid hydrolysis the product was investigated the residual cellulose by Infrared Spectroscopy and the infrared spectrum was shown in Figure 4.12.

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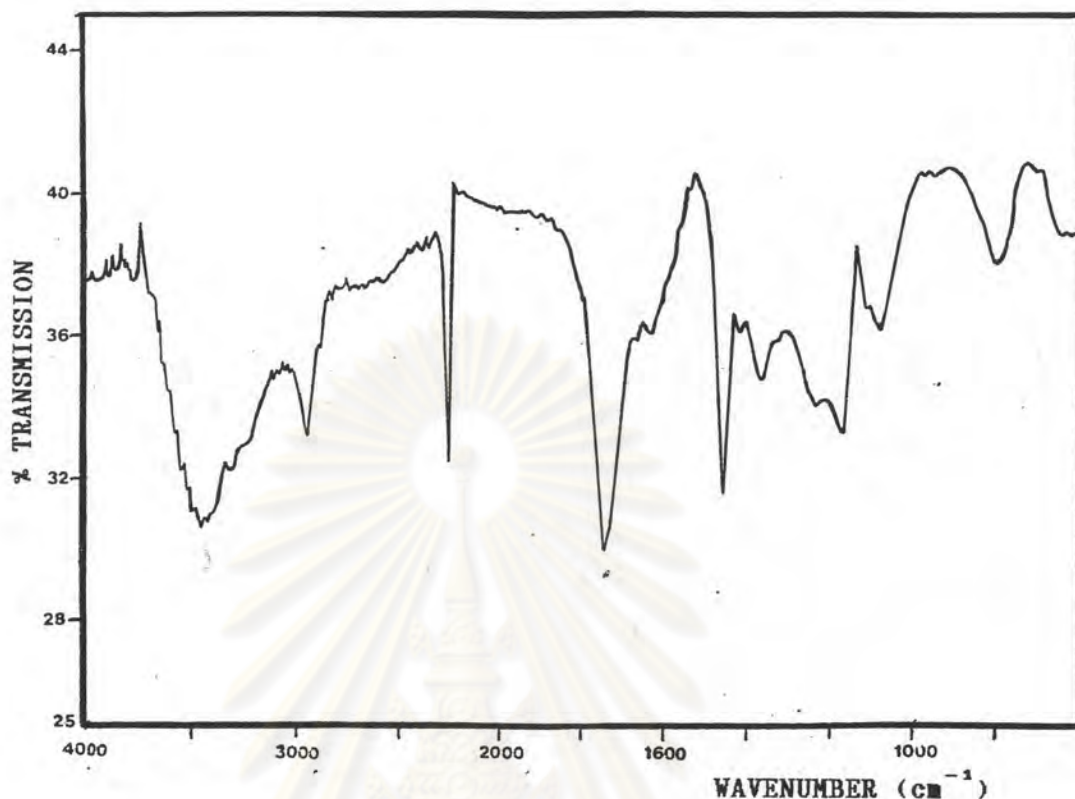


Figure 4.12 Infrared Spectrum (KBr pellet) of Microcrystalline Cellulose-Graft-Poly(Acrylonitrile-co-Acrylic Acid) After Acid Hydrolysis at Optimum Condition

From infrared spectrum, it should not be the characteristic absorption of cellulose at 1110-1120 and 890-900 cm^{-1} . It indicated that all cellulose substrate was digested. The residual polyacrylonitrile grafted side chain were hydrolyzed by acid to acrylamide and acrylic acid which able to detect by Infrared Spectroscopy. As shown in figure 4.11, it found that the C=O absorption band at 1740 cm^{-1} and N-H absorption band at 1620 cm^{-1} was increased. After that the grafted side chain was investigated the molecular weight by Gel Permeation Chromatography and the detail of this step was herein below.

The grafted side chain was dissolved in N,N-dimethylformamide by continuous stirring at room temperature for 24 hours but it could not dissolve. So it was refluxed in N,N-dimethylformamide with continuous stirring for 24 hours and the partial polymer was dissolved and the insoluble part of polymer was swelled in N,N-dimethylformamide. This result was expected due to the partial crosslink of polyacrylamide and polyacrylic acid. The similar observation has also been reported by Plumpirom, V. in 1990.

Finally the solution of grafted side chain in N,N-dimethylformamide was used to investigate the molecular weight. The solution of standard polystyrene at various molecular weight were prepared and the molecular weight of polystyrene were varied between 2994905 and 7059. The result was shown in Table 3.10.

From Table 3.10, it indicated that the molecular weight of grafted side chain of the cellulose-graft-poly(acrylonitrile-co-acrylic acid) was 20489

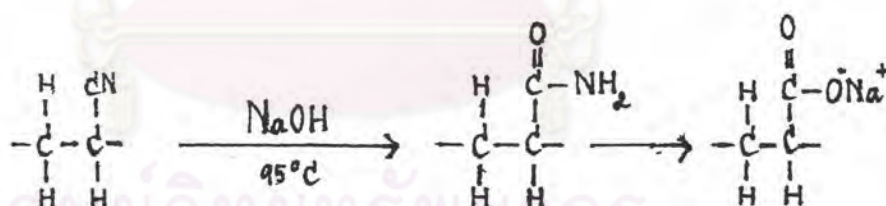
4.5 The Alkaline Hydrolysis

Polymer-modified microcrystalline cellulose was well suited to be used as an absorptive medium in diapers and other disposable pads. Of particular value were insoluble and high water absorptive property. This polymer product was prepared by graft copolymerization of acrylonitrile and acrylic acid on microcrystalline cellulose as mentioned earlier and subsequently enhanced the absorbing ability by alkaline hydrolysis under controlled condition to obtain alkali metal

polymer-modified microcrystalline cellulose product.

During alkaline hydrolysis the nitrile groups on polyacrylonitrile grafted branch chain should be hydrolyzed to carboxylate group as much as possible. It was well known that the carboxyl group on polyacrylic acid grafted branch chain should be hydrolyzed to carboxylate group at the weaker alkaline condition when relative with nitrile group. (The carboxyl group could be easier converted to carboxylate than nitrile group.) Thus at the same alkaline hydrolysis condition in this experiment the nitrile and carboxyl groups on grafted branch chain were hydrolyzed to carboxylate groups.

The alkaline hydrolysis of nitrile group on polyacrylonitrile to sodium carboxylate proceeded through an amide intermediate as followed.



Because of neighboring group effects, hydrolysis was never complete and combination of carboxylate and amide groups in hydrolyzed product was obtained. The amount of carboxylate and amide groups in hydrolyzed product therefore depended on alkaline hydrolysis condition (30). The completeness in alkaline hydrolysis was done by this following calculation method.

The percent nitrogen residual at the various concentrations of alkaline from section 3.3.8.2 was used to calculate percent carboxyl group and percent amide group which based upon the amount of total nitrile groups 18.49%. The calculation was done by using the following equations :

$$\% \text{ Carboxyl groups} = \{ [18.49 - \% \text{ nitrogen residue}] / 18.49 \} \times 100$$

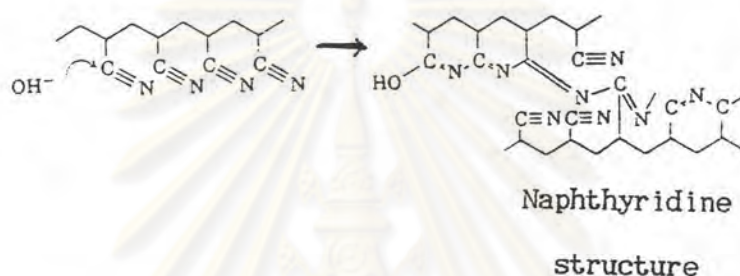
$$\% \text{ Amide groups} = \{ \% \text{ nitrogen residue} / 18.49 \} \times 100$$

The result were illustrated the completeness of alkaline hydrolysis.

Table 4.3 Percentage of carboxyl and amide groups in the alkaline-hydrolyzed product

| Concentration of Sodium hydroxide (M) | % Nitrogen residue | % Carboxyl groups | % Amide groups |
|---|--------------------|-------------------|----------------|
| 0 | 18.49 | 0 | 0 |
| 1 | 5.46 | 70.44 | 29.55 |
| 2 | 5.38 | 70.90 | 29.09 |
| 3 | 4.78 | 74.12 | 25.87 |
| 4 | 4.20 | 77.28 | 22.71 |
| 5 | 4.04 | 78.17 | 21.82 |
| 6 | 3.46 | 81.26 | 18.73 |

During alkaline hydrolysis, first the grafted polymer was dispersed in sodium hydroxide solution and the reaction was allowed to proceed for 2 hours at 95°C. The color of grafted copolymer was developed from white to deep-red color. The deep-red color was shown the formation of a partly hydrogenated naphthyridine type structure (31). The mechanism of this formation is shown herein below.



The hydroxide ion from alkaline acted as nucleophile and attacked on carbon atom of nitrile groups. After that the propagation crosslinks between nitrile groups of neighboring chains occurred and caused the polymer insoluble (32). Finally the intermediate form were subsequently hydrolyzed and the color developed again from deep-red to light yellow solution. The result obtained in this step shown that the conjugated system of $(=C-N)_n$ disappeared and the amide and carboxylate groups were formed. At this step the water-retaining material was obtained and characterized by Infrared Spectroscopy. Infrared spectrum was shown in Figure 4.13.

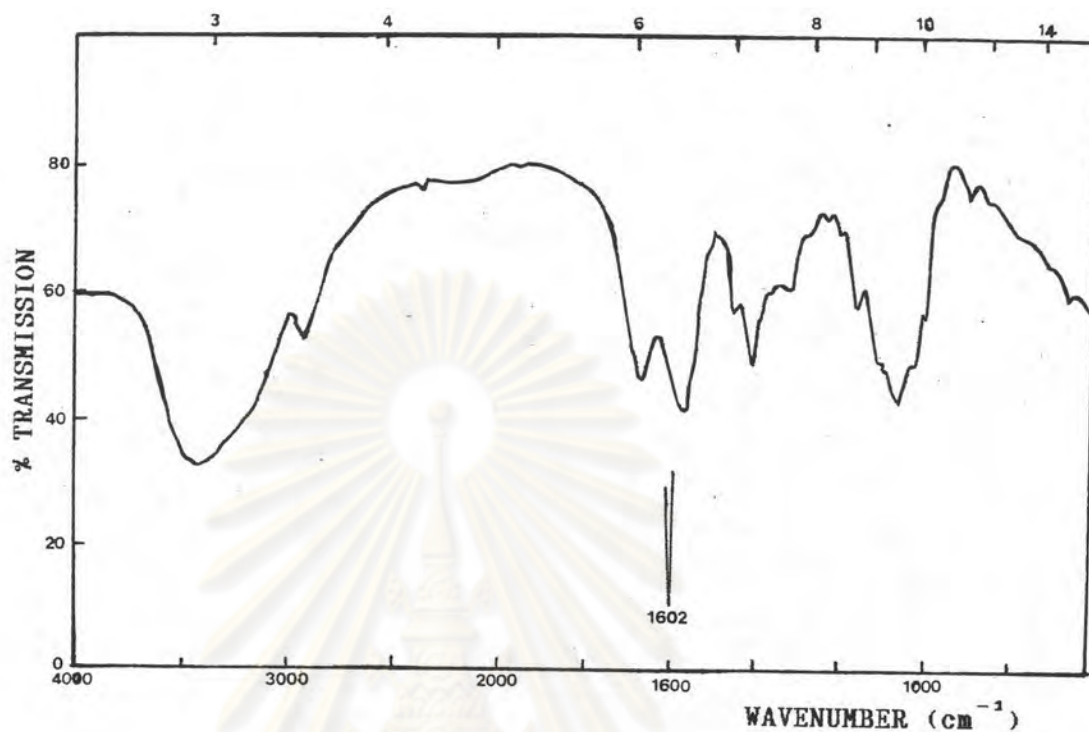


Figure 4.13 Infrared Spectrum (KBr pellet) of Sodium Polyacrylate-Polyacrylamide Cellulose-Graft-Copolymer (Water-Retaining Material)

From infrared spectrum it was found that after alkaline hydrolysis, the sharp and high absorption peak of nitrile group at 2240 cm^{-1} and the medium absorption peak of carbonyl group at $1710\text{--}1760\text{ cm}^{-1}$ disappeared. (The medium absorption peak at $1710\text{--}1760\text{ cm}^{-1}$ was belong to carbonyl group of carboxylic in polyacrylic acid.) The absorption band of carboxylate group at 1670 , 1570 , and 1400 cm^{-1} appeared concomitant with the absorption band of amide group at $3200\text{--}3500\text{ cm}^{-1}$, $1550\text{--}1650\text{ cm}^{-1}$, 1425 cm^{-1} , and $800\text{--}600\text{ cm}^{-1}$.

The alkaline hydrolysis at various alkaline concentrations has been studied for determining the absorptive ability of the product, the completeness of alkaline hydrolysis which considering from the nitrogen residue in product, and the amount of carboxylate and amide groups which converting from nitrile group. In addition to the degradation of polymer during alkaline hydrolysis was also investigated by measuring the viscosity of suspended alkaline-hydrolyzed polymer at various alkaline concentrations.

From Table 3.12 it was found that water retention value increased with increasing concentration of alkaline. Thus it indicated that the higher water absorption was obtained at the higher alkaline concentration. But at 4 M sodium hydroxide solution the maximum of water retention value was obtained. Beyond 4 M the water retention value did not increase and the absorbing polymer was like glue.

This result could be attributed to the water absorptive property of polymer which was well known that the absorption of polymer occurred due to the hydrogen bonding between H_2O molecule and the group in polymer. This group was carboxylate which was converted from nitrile and carboxyl groups in polymer and this conversion depended on alkaline concentration. Thus the less carboxylate group in the product resulted in the less water absorption.

At lower alkaline concentration the less amount of carboxylate group in product was obtained as seen in table 4.8. Accordingly, the increase of alkaline concentration resulted in the increase of carboxylate group and water retention value until the alkaline



concentration was 4 M the maximum water retention value was obtained.

At this point the polymer product was at least 77.28 % carboxyl groups and 22.71 % amide groups which converted from polyacrylonitrile. Beyond 4 M sodium hydroxide the water retention value did not increase and the absorbing polymer could easily disperse in water like gule which was undesirable. This result was ascribed to the degradation of polyacrylonitrile and polyacrylic acid grafted side chain at high alkaline concentration.

From Table 3.13 and 3.14, it indicated that the increase of alkaline concentration beyond 4 M shown little difference of nitrogen residue in the polymer but the very excess of alkaline caused the polymer degradation. In addition, the hydrolyzed product was difficult to wash and adjust to neutral which resulted in the lost of time and high cost. The degradation of polymer was determined by measuring of the viscosity of absorbing polymer in water at 0.15 % aqueous at room temperature by Brookfield Viscometer. Lepoutre, R. (1973) had reported that the alkaline hydrolysis was defective process due to the scission of some grafted polymer chain on cellulose (33). Thus the high alkaline concentration should be avoided to use in alkaline hydrolysis and the optimum alkaline concentration was 4 M. However, the method used to confirm the degradation of grafted side chain in alkaline hydrolysis is measuring the viscosity of poly (acrylate-co-acrylamide) solution and Ubbelohde Viscometer will be used instead of Brookfield Viscometer. This solution was obtained from filtration of absorbed water-retaining material in excess of water.

4.6 The Residual Sodium and Cerium in the Water-Retaining Material

As mentioned in section 4.5, the enhancement of absorbing ability of cellulose-graft-poly(acrylonitrile-co-acrylic acid) was hydrolysis in alkaline solution. The nitrile and carboxyl groups were converted to carboxylate salt in alkaline hydrolysis. The alkaline solution was sodium hydroxide solution so the water-retaining material was in a form of sodium carboxylate salt. Thus the quantity of residual sodium was determined by Flame Emission Photometer and the result shown that the residual sodium in water-retaining material was 5.24 % by weight. This quantity was not quite high and there were some compounds of sodium in the soil so it could not pollute the environment. In addition, this product was suitable for plant growing because of it was not toxic for human body.

The quantity of residual cerium in water-retaining material was also determined. Owing to the graft copolymerization of acrylonitrile and acrylic acid on microcrystalline cellulose used ceric ammonium nitrate as initiator for initiating radical site on polymer backbone. When the polymerization was completed the cerium ion which remaining in the grafted product was separated as much as possible by washing several times with double-distilled water. Thus the determination of residual cerium was necessary and it could be done by Inductively Coupled Plasma Emission Spectrometer.

From the result, it indicated that the residual cerium in water-retaining material was 0.0006 % by weight which was a very small quantity. Accordingly, it could not pollute the environment and was

not toxic to human body. Thus it was expected that the water-retaining material was useful for many application especially for agriculture.



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4.7 Product Characterization

4.7.1 The Physical Appearance



Figure 4.14 Microcrystalline Cellulose Substrate



Figure 4.15 Microcrystalline Cellulose-Graft-Poly (Acrylonitrile-co-Acrylic Acid)

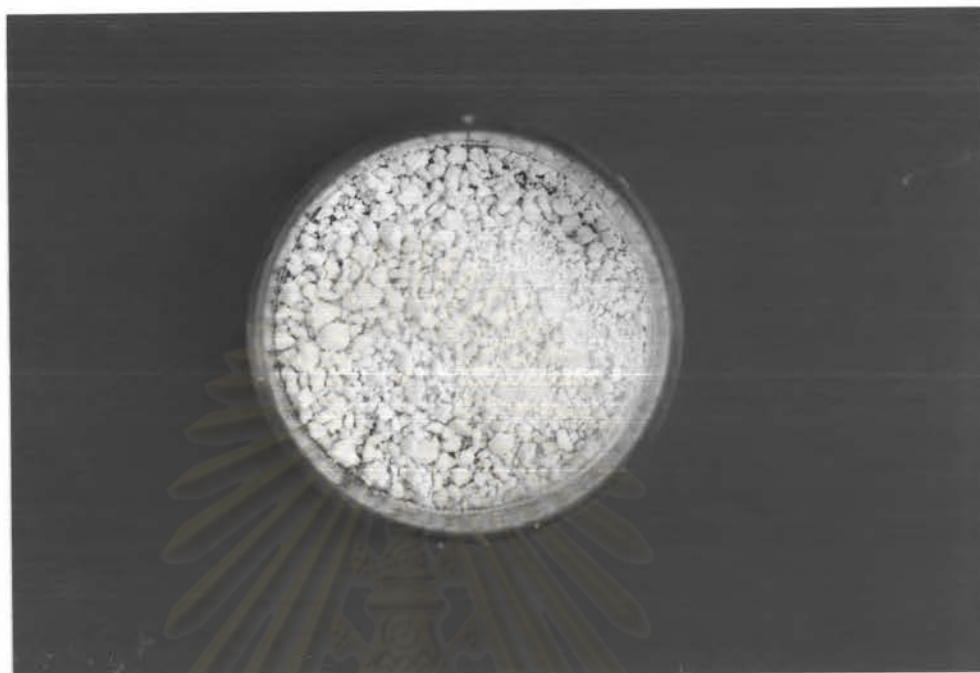


Figure 4.16 Water-Retaining Material End Product

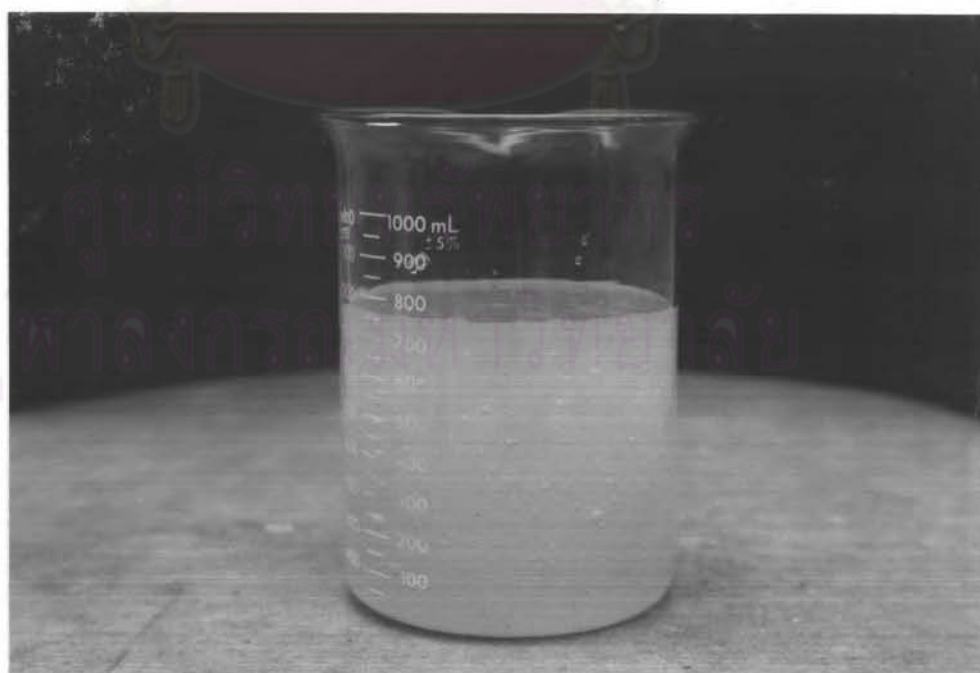


Figure 4.17 Water-Retaining Material After Absorbed Water

4.7.2 Infrared Spectrum of the Polymer Product

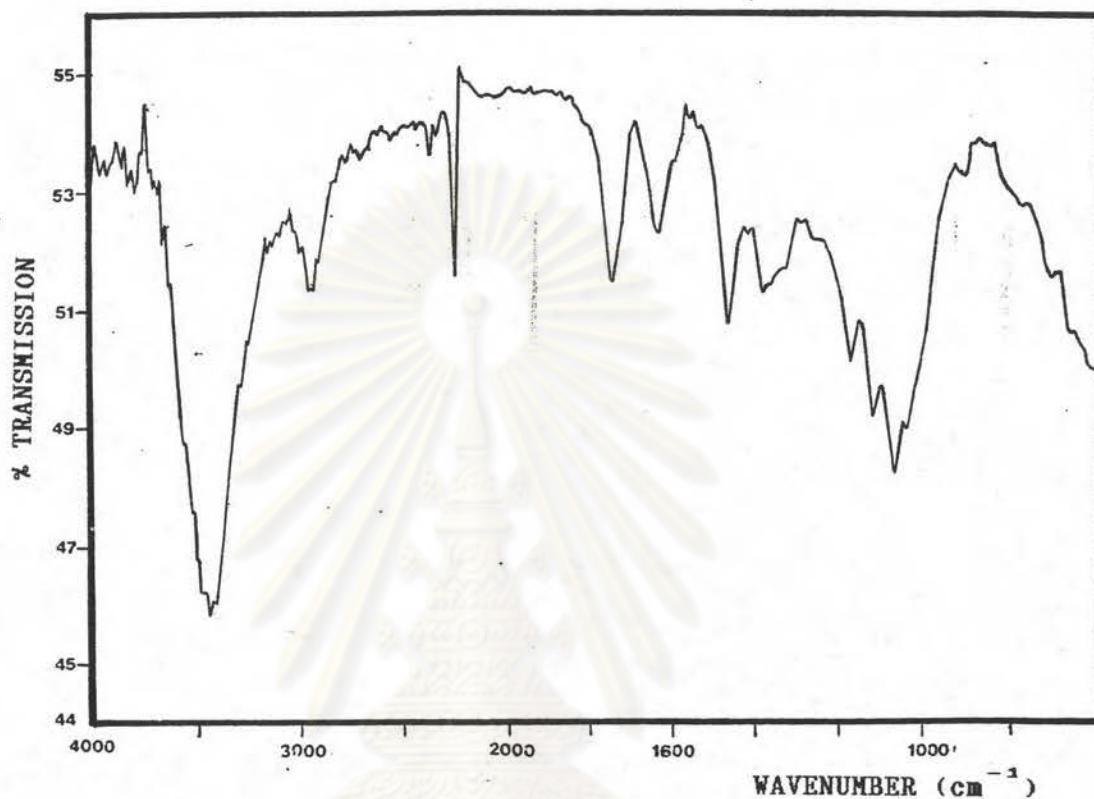


Figure 4.18 Infrared Spectrum (KBr pellet) of Microcrystalline Cellulose-Graft-Poly(Acrylonitrile-co-Acrylic Acid) with Homopolymer

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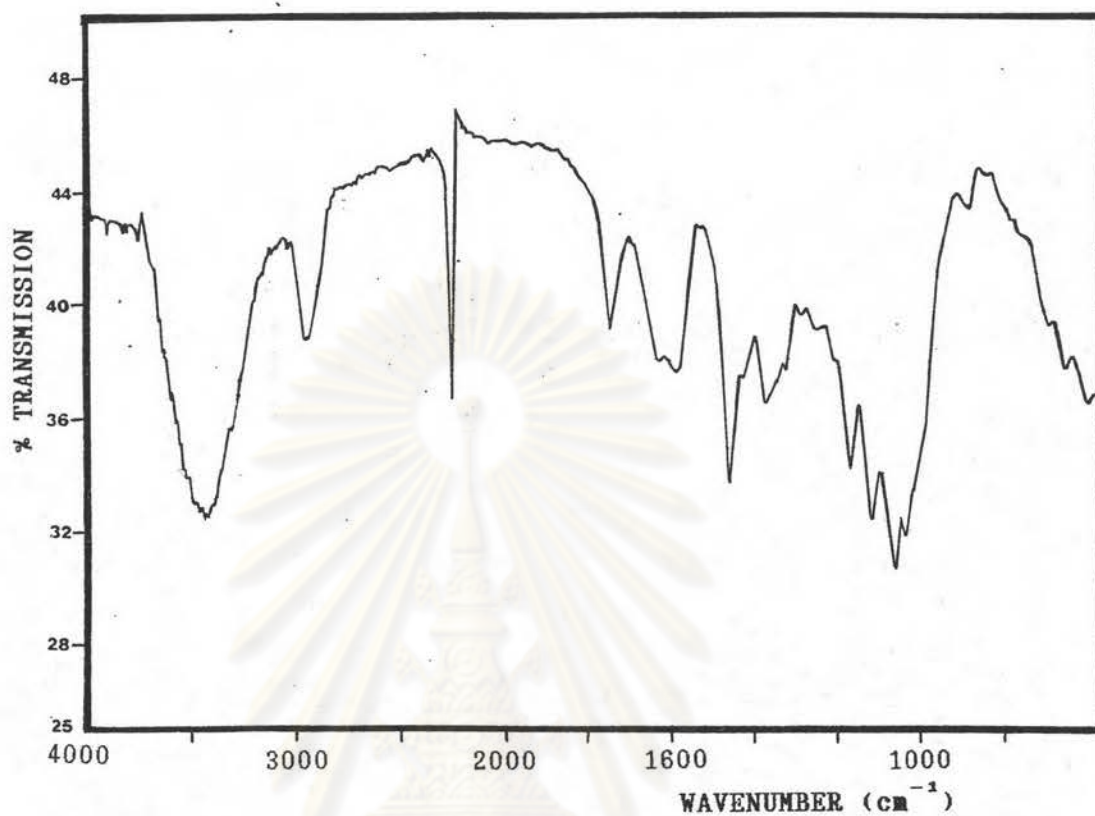


Figure 4.19 Infrared Spectrum (KBr pellet) of Microcrystalline Cellulose - Graft - poly(Acrylonitrile -co- Acrylic acid) without Homopolymer

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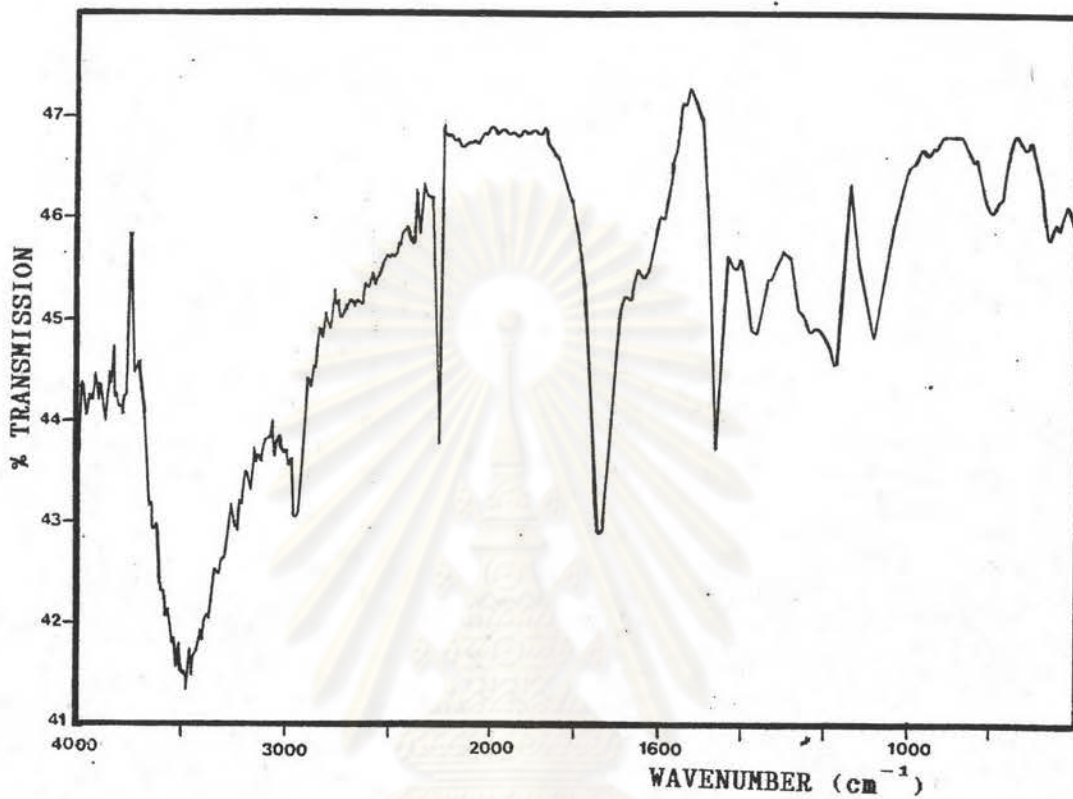


Figure 4.20 Infrared Spectrum (KBr pellet) of Poly(Acrylonitrile-co-Acrylic Acid)

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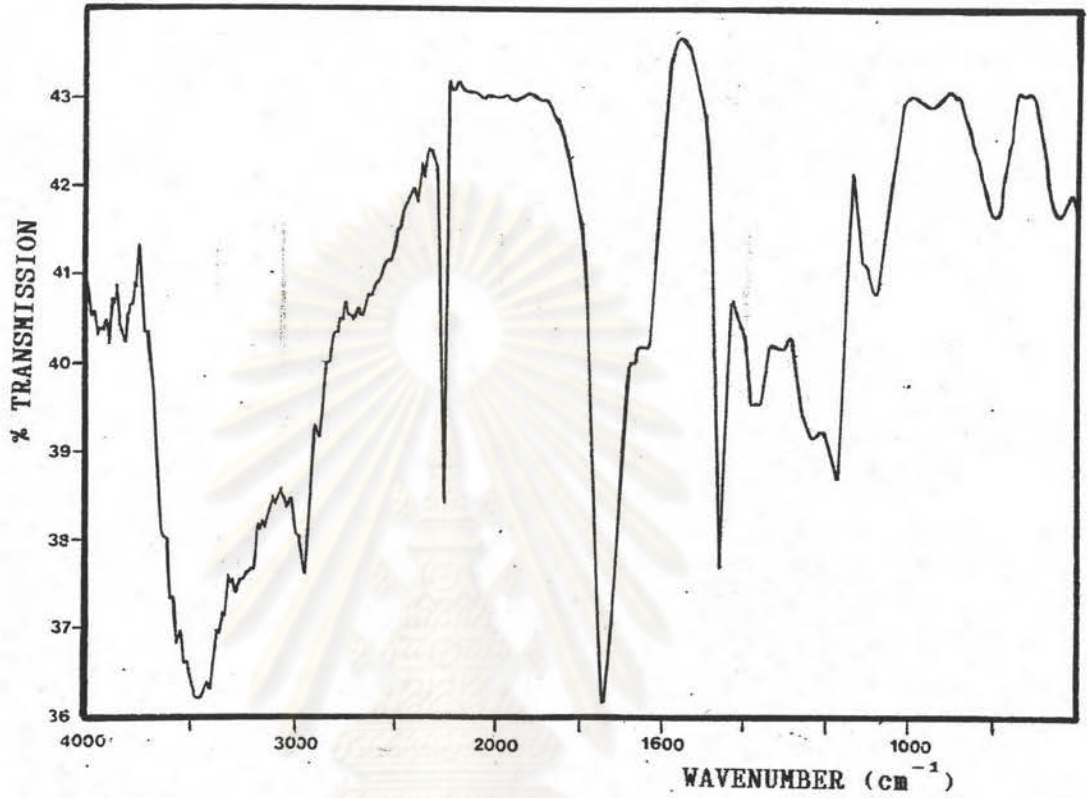


Figure 4.21 Infrared Spectrum (KBr pellet) of Poly(Acrylonitrile-co-Acrylic Acid) After Acid Hydrolysis at Optimum Condition

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4.8 Physical Testing

4.8.1 Water Retaining Value at Various % Add-on and Grafting Ratio

The water retention value of water-retaining material was determined from the weight increase of water-absorbed polymer with respect to dry weight of polymer which was calculated from following equation,

$$\text{water retention value (g water/g polymer)} = [B-A]/A$$

A : dry weight of polymer

B : weight of the water- absorbed polymer

The water retention capacity of cellulosic materials is generally thought to result from the interaction through hydrogen bonding of the hydroxyl groups on cellulose with water molecules. The effect of introducing of vinyl monomer on cellulose backbone by grafting reaction on water retentive ability would depend on the frequency of interposition of the grafted polymer, the nature of grafted polymer, and the fibre-fibre cohesion of the substrate (34).

The frequency of interposition of the grafted polymer was shown as the grafting ratio and the % add-on. The result of this experiment were shown in table 3.19 and Figure 4.22 and 4.23.

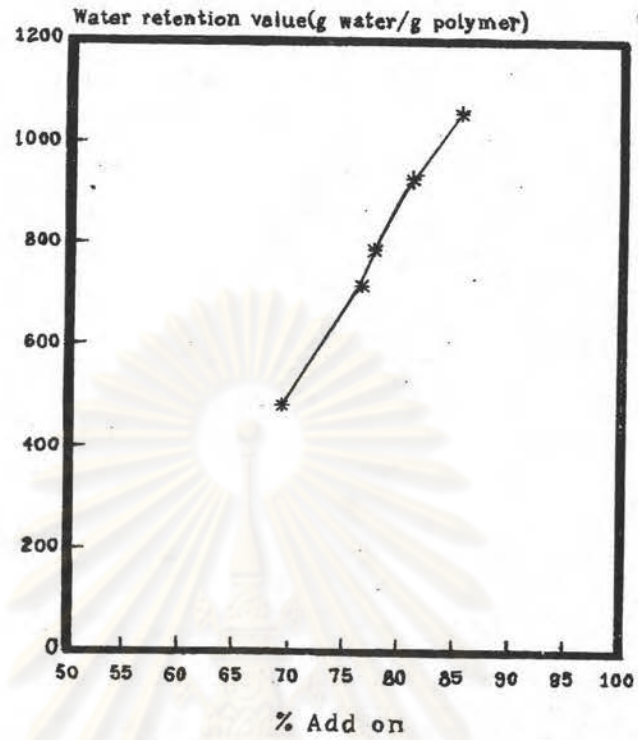


Figure 4.22 Effect of % Add-On on Water Retention Value of Water-Retaining Material

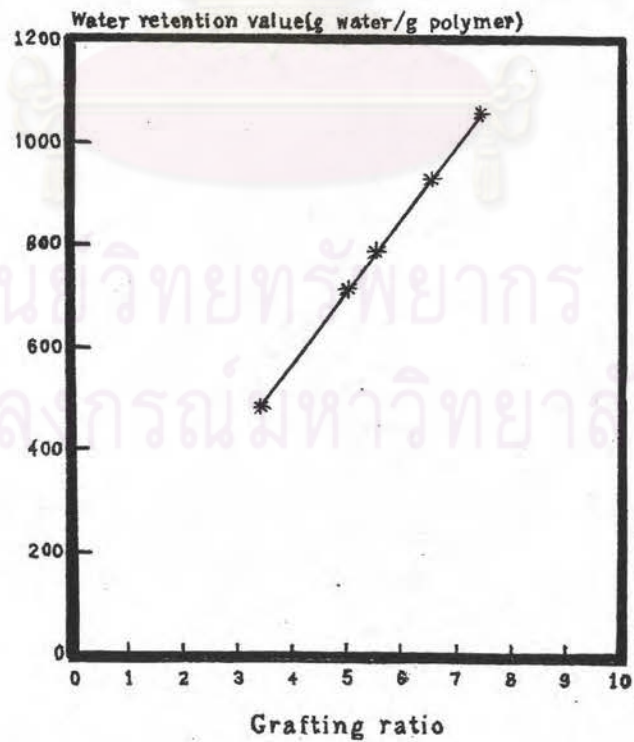


Figure 4.23 Effect of Grafting Ratio on Water Retention Value of Water-Retaining Material

It was found that the increase of the percent add-on and grafting ratio increased water retention values.

4.8.2 Water Retention Value at Different Times

The water retention value of the water-retaining material was determined at various times and the results were shown in table 3.20 and Figure 4.24.

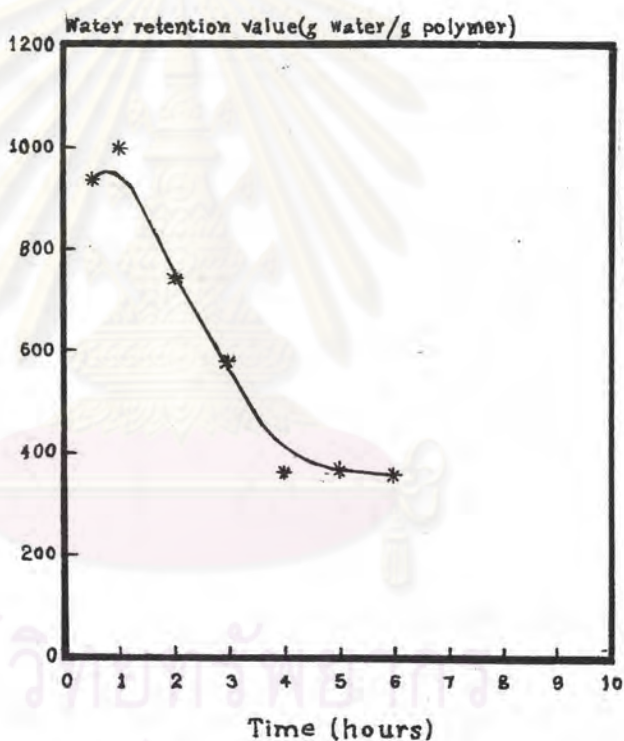


Figure 4.24 The Water Retention Value at Different Times

From Figure 4.24, it was found that the water-retaining material could absorb double-distilled water to maximum value within 1 hour. After that the water retention value gradually decreased until about 354.4 g water/g polymer at 6 hours. This was attributed to the infiltration of the disperse polymer from the sieve 125 mesh stainless steel screen. It was resulted from the continuous stirring

of magnetic bar while absorptive test was done for a long time. Thus the polymer which has a smaller size than the sieve 125 mesh could slip from the sieve and resulted in the decrease of water retention value.

In addition, the water retention value at different swelling times may be determined in a short time interval at the beginning.

4.8.3 Water Releasing at Different Times

The water releasing of the water-retaining material at different times was studied and the result was shown in table 3.21 and Figure 4.25. It was found that in the first hour of open air exposure at 30°C, the water was released from the water-retaining material with high rate of about 182.0 g/hour. During the subsequent hour, the rate of releasing was slow down until absolute 24 hours and the rate of releasing was about 13.5 g per two hours at the last period. Similar observation has also been reported by Miss Vanida Plumpirom in 1990.

The result of water releasing of water-retaining material was shown in Figure 4.25.

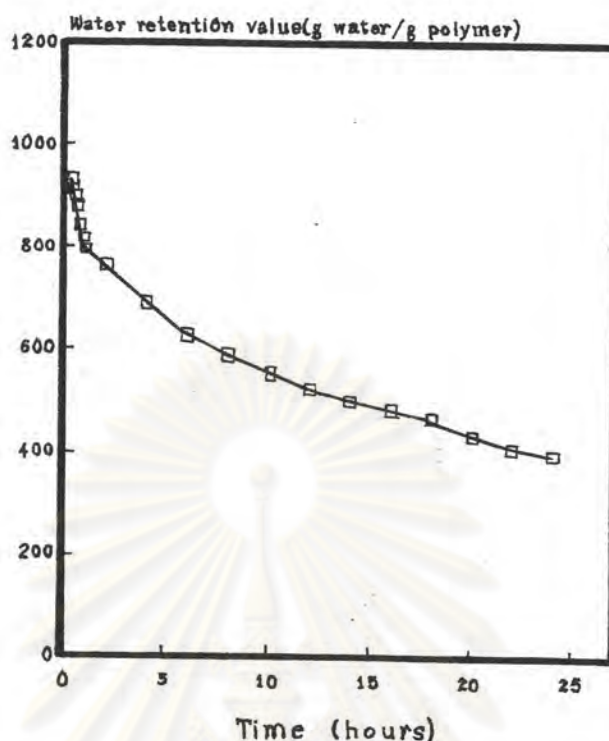


Figure 4.25 The Water Releasing of Water-Retaining Material at Different Times

4.8.4 Water Retention Value at Various Conditions

4.8.4.1 The water retention value at various pH

The suitable range of pH for using the water-retaining material was studied by determining the water-retention value at various pH. The pH was in the range of 4-12 and the result was shown in table 3.24. It was found that the maximum water retention value about 1021.3 g water/g polymer was obtained at the pH 4 and after that when the pH increased the trend of water retention value decreased until the minimum value about 273.7 g water/g polymer was reached at the pH 12. Thus it was expected that the water-retaining material could be used in the range of pH 4-11 or in the weak acid,

neutral, and weak base condition but it could not be effective for water absorption at strong base condition. The similar observation has also been reported by Miss Vanida Plumpirom in 1990 (1).

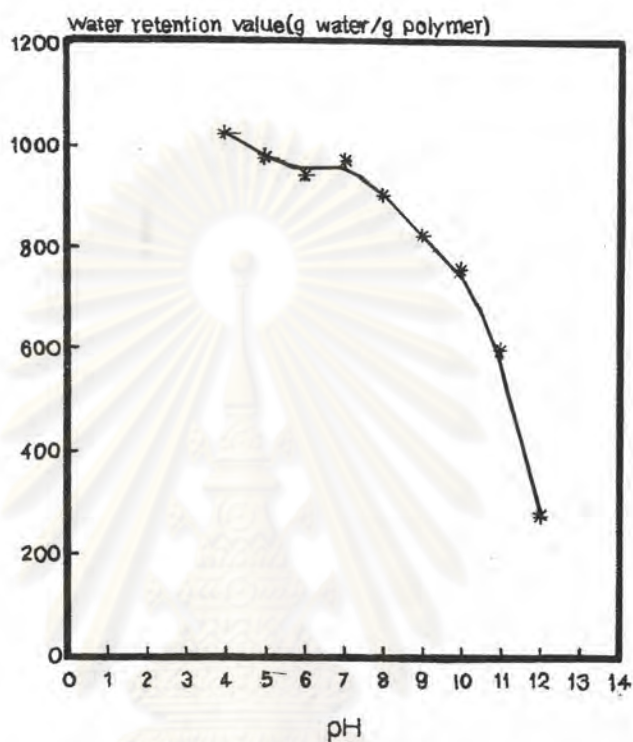


Figure 4.26 The Water Retention Value at Various pH

4.8.4.2 The water retention value of the water-retaining material at various temperatures

The suitable temperature for using the water-retaining material was also studied by determining of water retention value at various temperatures. The temperature was varied from 20°C to 80°C. The result was shown in table 3.25 and it was found that the water retention value increased when temperature was increased from 20°C to 30°C and the maximum absorption about 1035.7 g water/g polymer was obtained at 30°C and beyond 30°C the water retention value decreased until the minimum value of about 458.3 g water/g polymer

was reached at 80°C. Thus the optimum temperature for using the water retaining material was 30°C but in the range of 20-80°C it could also be used. The result of the water retention value of the water-retaining material at various temperatures were shown in Figure 4.27.

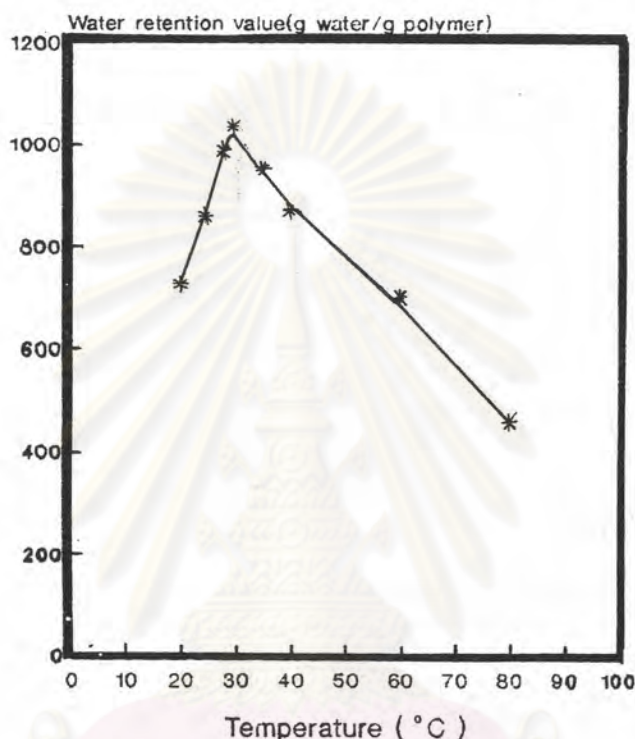


Figure 4.27. The Water Retention Value of Water-Retaining Material at Various Temperatures

4.8.4.3 Water Retention Value at Various Electrolyte Solutions and one of non-electrolyte solution

The swelling of grafted cellulose gel is considered to be caused by differential osmotic pressure resulting from a difference in concentration of mobile ions between the interior of the gel and the exterior solution. The fundamental feature within the gel, bringing about the unequal distribution, is the presence of ionizing carboxylate groups attached to the macromolecular network.

Proctor suggested that the important characteristic of many gel is the presence of ionizable groups attached to the macromolecular network. When such a gel is placed in an ionic solution, an exchange of mobile ion take place between the gel and the solution. As the acidic groups cannot move out of the gel, the solution within the gel is regarded as separated from the external solution by semipermeable membrane which confines the acidic groups but gives free passage to water and all simple ions. Because of the presence of the bound groups, the mobile ions are unevenly distributed so the gel contained the higher concentration. Thus the gel swells as the result of the entry of water in an attempt to reduce the osmotic pressure differential resulting from the difference in concentration. Swelling, he proposed, continues until the osmotic pressure differential equal to the resistance to further expansion brought about by the cohesive forces of the macromolecular network (35).

In the polyanionic gel such as polyacrylate-polyacrylamide cellulose-graft-copolymer, there would be the excess of cations in the gel and excess of anions in the medium solution. Thus the gel swelled to reduce the osmotic pressure. The results of these experiments were shown in table 3.26 and Figure 4.29, 4.30, and 4.31.

In addition, the only one sample of non-electrolyte solution, urea, was also studied and it was found that at high concentration of urea, water retention value decreased. By the principle of diffusion, this phenomena can be explained that water in dilute urea solution diffuse into the polymer gel better than in higher concentration of urea. The result was shown in table 4.28.

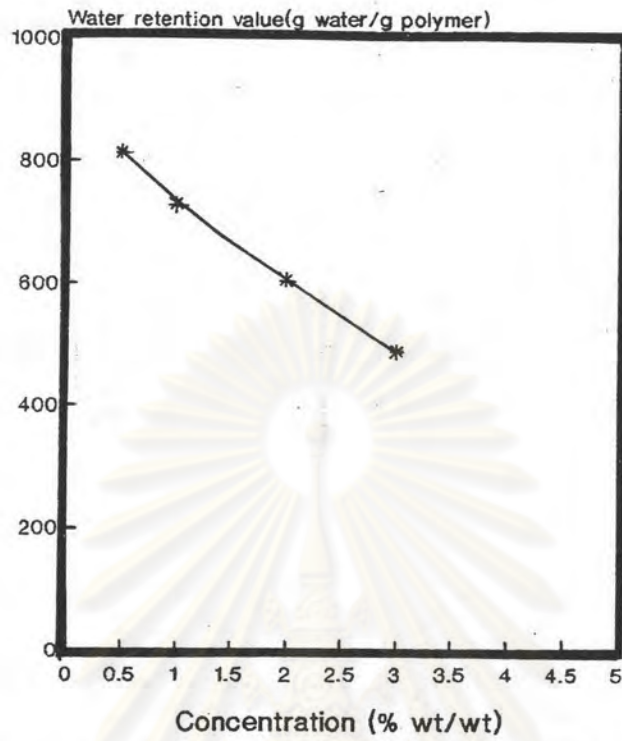


Figure 4.28 The Water Retention Value at Various Concentrations of Urea

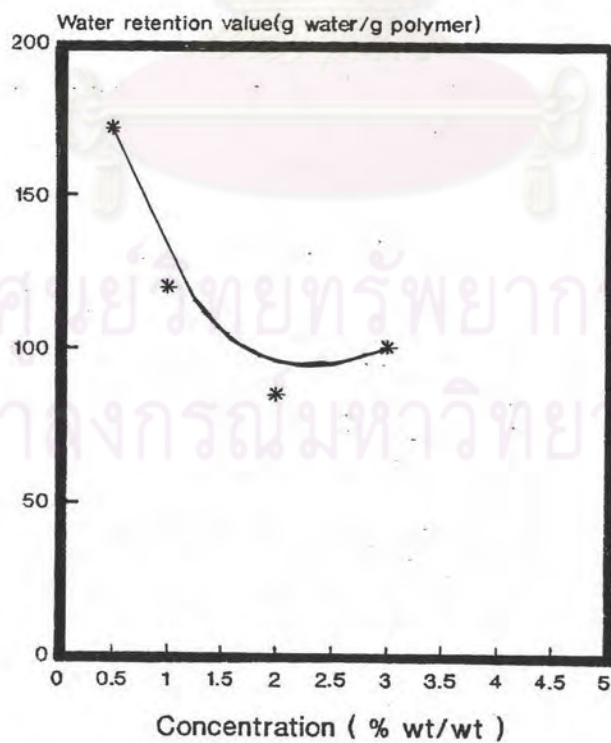


Figure 4.29 The Water Retention Value at Various Concentrations of Potassium Sulphate

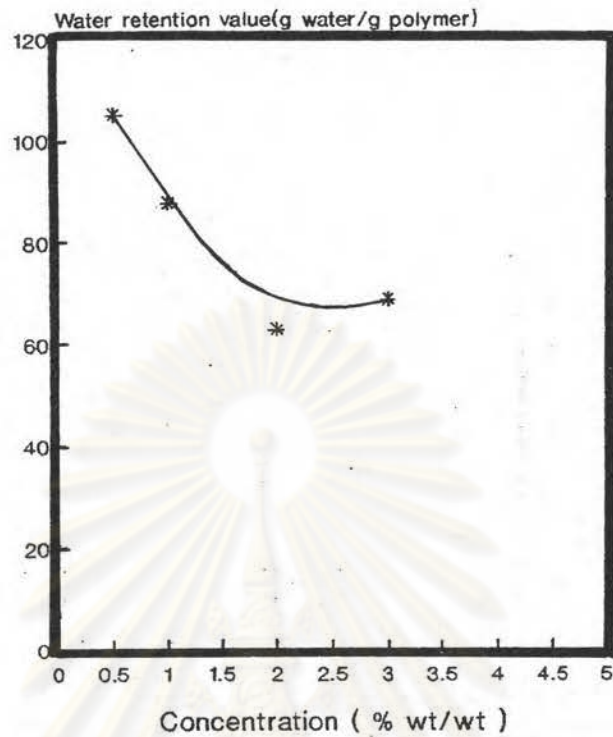


Figure 4.30 The Water Retention Value at Various Concentrations of Ammonium Chloride

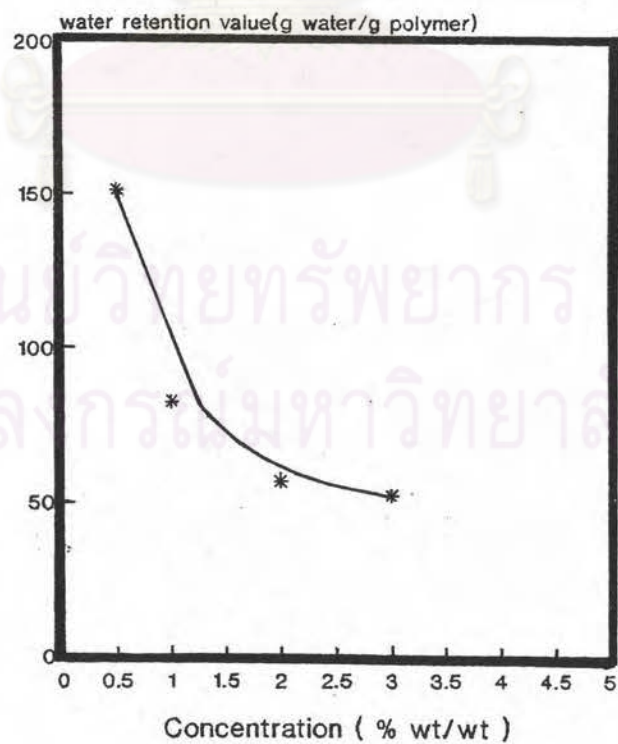


Figure 4.31 The Water retention Value at Various Concentrations of Sodium Chloride

From Figure 4.28, 4.29, 4.30, and 4.31 it was found that at low concentration of electrolyte and one of non-electrolyte solution, the tendency of water retention value was higher than at high concentration.



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4.8.5 The General Properties

The other general properties of the water-retaining material were the absorbing speed and the moisture content. The absorbing speed of the water-retaining material was investigated in 0.9 % by weight of saline solution. The absorbing speed was the period of time since the water-retaining material was added into the vortex until the surface of saline solution became quiet. The result was shown that the high absorbing speed at 12.5 seconds was obtained.

The moisture content of the water retaining material was measured by two methods. The first one was the method mentioned in section 3.3.9.5 and the second method used the Thermogravimetric Analysis (TGA). The results were shown in table 3.23 and it was found that the average moisture content of the first and second method were about 29.85 % and 30.98 % respectively. It was different between the results obtained from these two methods which resulted from the difference in each part of polymer. However it indicated that within 24 hours the water-retaining material could absorb the moisture in air with high content. Accordingly, if it was held in open air for more than 24 hours, it was expected that the water-retaining material could absorb higher moisture content. Thus it was suitable for keeping fruits and vegetables fresh.

4.8.6 Thermal Analysis (36), (37)

Thermal analysis can be defined as the measurement of a property of a sample as a function of temperature. The objectives of

thermal analysis were the determine Kinetics parameters of a polymer sample in the Arrhenius equation such as a pre-experimental factor, an order of reaction, an activation energy, and physical properties of polymer such as temperature transition and weight loss by using Differential Scanning Calorimetric Analysis and Thermogravimetric Analysis.

4.8.6.1 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) is a thermal analysis technique for measuring the amount and rate of change in sample mass as a function of temperature and time. It is used to characterize any material that exhibits weight loss or phase changes as a result of decomposition, dehydration, and oxidation.

In polymer chemistry, Thermogravimetry is mainly applied to the study of the thermal degradation of polymer sample, identification of polymers by analysis thermograms, and determination of moisture etc. In this research the sodium polyacrylate-polyacrylamide cellulose-graft-copolymer or water-retaining material was used to study about the characteristic of the thermogram of this product and determined the moisture content. The thermogram is the plot of mass as a function of temperature which provides both qualitative and quantitative information. In the Thermogravimetric Analysis of the water-retaining material, the mass of the product was recorded continuously as its temperature was increased from ambient to as high as 500°C. The thermograms of water-retaining material were shown in Figure 4.32.

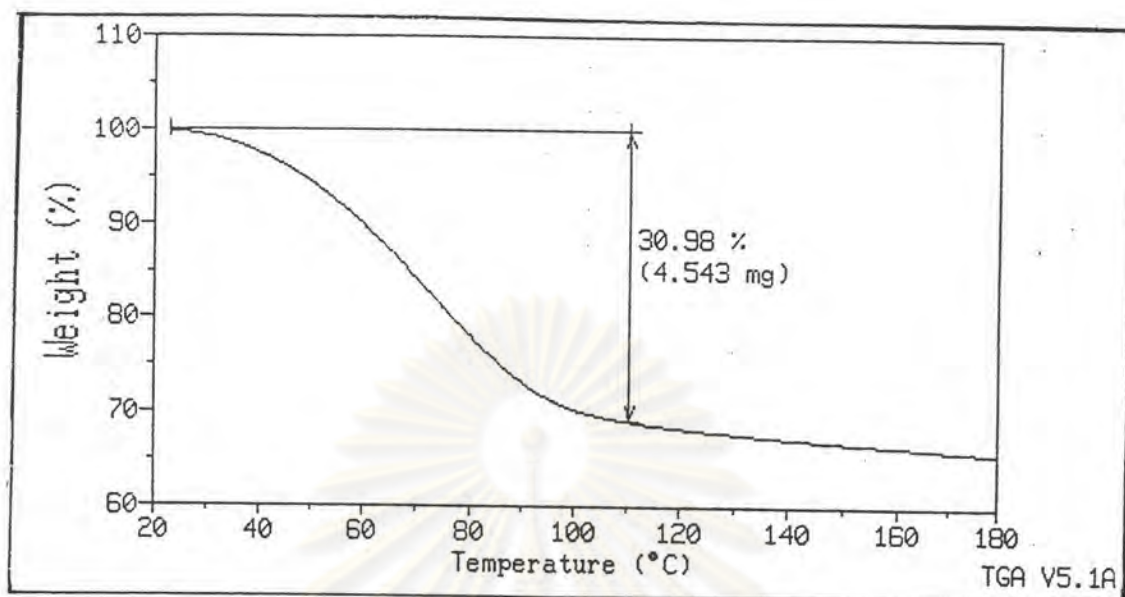


Figure 4.32 The Thermogram of Water - Retaining Material by Thermogravimetric Analysis

From the thermogram, it was found that the weight change in the first step (below 110°C) resulted from the loss of H₂O. The moisture content was about 30.98 % which shows that this product could absorb the high content of moisture within 24 hours. Thus it was expected that the water-retaining material could be used in the application of moisture absorbency.

4.7.6.2 Differential Scanning Calorimetry (DSC) (38)

Differential Scanning Calorimetry (DSC) is a method which records the energy necessary to establish zero temperature difference between a substance and a reference material against either time or temperature as the two specimens are subjected to identical temperature conditions in an environment heated or cooled

at a controlled rate.

Differential thermal method find widespread use in determining the composition of naturally occurring and manufactured products. Especially in the polymer research, it has been widely applied to the study and characterization of polymeric materials. In addition, Differential Scanning Calorimetry is used to measure the glass transition temperature (T_g), melting point (T_m), and decomposition temperature (T_d) of the polymer.

In this research, the sodium polyacrylate-polyacrylamide cellulose-graft-copolymer was used to study the characteristic of the thermogram and measure the glass transition temperature and melting point. Thermograms of water-retaining material by Differential Scanning Calorimetry were shown in Figure 4.33.

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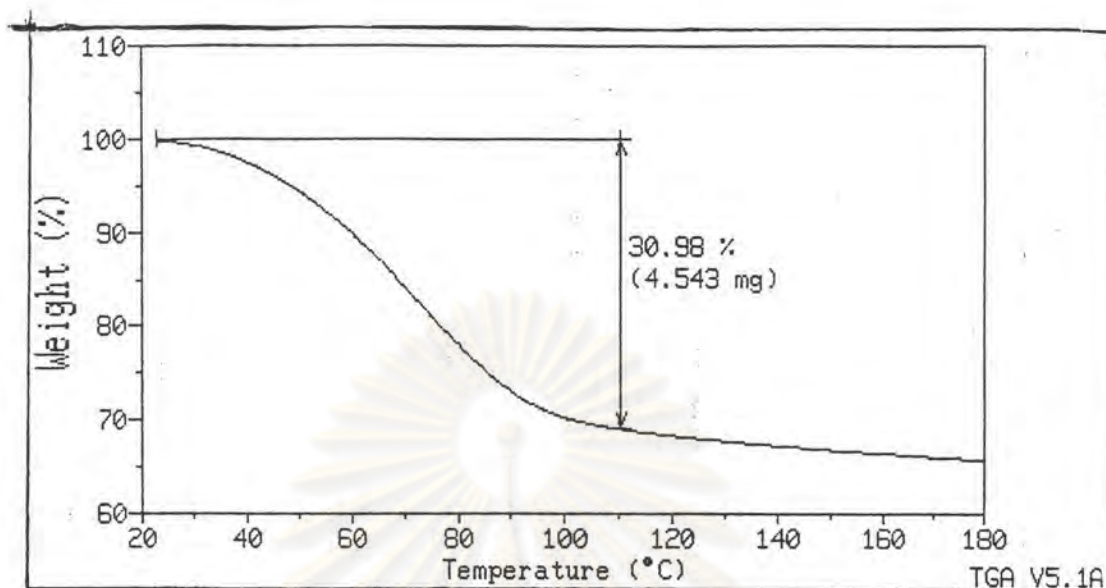


Figure 4.33 The Thermogram of Water - Retaining Material by Differential Scanning Calorimetry

From thermogram it was found that the sharp and high peak corresponds to the characteristic of melting point (T_m). The melting point were about 119.70°C and 129.06°C and from the thermograms it could not indicate the peak corresponds to the characteristic of glass transition temperature of this polymer.

The glass transition temperature depends on the amorphous region of the polymer. So it could be expected that this polymer product has a high crystallinity and from the melting point of this polymer it indicated that the water-retaining material melted at moderate temperature. So it could be used at the temperature below 119.70°C but it must consider the water absorptive ability of this product at various temperatures as mentioned in section 4.8.4.2.

4.8.7 The Application of Water-Retaining Material

Cellulose is the important constituent in cell wall of plants. The improvement of some properties give the graft copolymer product which high water absorbency. The product is biodegradable material and has no or less toxic for user. So this graft copolymer will not pollute the environment when used in many applications. From the advantage of these properties, it can be used for fluid absorbent products as disposable diaper, incontinent underpads, sanitary napkin, and moisture absorbent plate for keeping fruits and vegetables to be fresh. In addition to, it can be used in agriculture as soil condition by mixing with soil which lacking of water absorbent property. The water-retaining material can improve the soil to greatly enhance their retentive ability, increase amount of water, and decrease the density of soil. From the advantage of these properties, it is suitable for growing plants in dry area especial the sand soil area. This area cannot absorb water for a long time when raining because the water will prenetrate through the gap of soil quickly and the minerals are also eluted. Accordingly, it was found that the soil was lack of fertility. Thus this research can help to increase agricultural product and able to use the cellulose from useless, cheap, and available material. So this research is the part of solving problems about agriculture, economics, and social which are the important problems for our country.