

CHAPTER III

EXPERIMENTS AND RESULTS

3.1 Chemicals

1. Acetic acid (Pro analysi grade, Merck)
2. Acetone (Analyticals grade, Carloerba)
3. Acrylic acid monomer (commercial grade)
4. Acrylonitrile monomer (Commercial grade, Siam Resin Chemical Co.,Ltd.)
5. Allyl chloride (Commercial grade)
6. Ammonium chloride (Pro analysi grade, Merck)
7. Carboxymethylcellulose
8. Ceric ammonium nitrate (Analyticals grade, Carloerba)
9. Ethanol (Commercial grade)
10. Hydrochloric acid (Analar grade, BDH)
11. Methanol (Commercial grade)
12. Microcrystalline cellulose ; AVICEL pH 101
13. N,N-dimethylformamide (Analyticals grade, Carloerba)
14. Nitric acid (Analyticals grade, Carloerba)
15. Nitrogen gas (Analar grade)
16. Potassium bromide (Analyticals grade , Carloerba)
17. Potassium sulphate (Analar grade , BDH)
18. Sodium chloride (Pro analysi grade, Merck)
19. Sodium hydroxide (Analytical grade , Carloerba)
20. Sodium standard solution (Pro analysi grade, Merck)

21. Sodium sulfite anhydrous (Pro analysi grade, Merck)
22. Sulfuric acid (Analar grade, BDH)
23. Urea (Commercial grade)



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3.2 Apparatus

1. Differential Scanning Calorimetry, Du Pont, model 910
2. Flame Emission Photometer, Corning, model 400
3. Gel Permeation Chromatography, Water 600 E system controller, Detector, Water 470 Differential refractometer
4. Infrared Spectrophotometer, Perkin-Elmer, model Perkin-Elmer 781
5. Inductively Coupled Plasma Emission Spectrometer, model Perkin-Elmer PLASMA-1000
6. Magnetic stirrer, Heidolph, MR 200
7. pH meter, Orion research, model 701A/digital Ionalyzer
8. Thermogravimetric Analysis, Du pont, model 2950
9. Vacuum Oven, Forma Scientific, Inc., model 6515 S/N 60432-43
10. Viscometer, Brookfield , model RVTDV-I

3.3 Procedure

3.3.1 Preparation of Microcrystalline Cellulose

The sheeted bleached alpha-cellulose was torn as small pieces and dried in vacuum oven at 60°C until constant weight. 0.8 g of the dried bleached alpha-cellulose was placed into 400 mL of 2.5 N hydrochloric acid solution in 500 mL round bottom flask. Then it was refluxed at 105°C with continuous stirring. The reaction was allowed to proceed for 20 minutes. The cellulose was then filtered by vacuum filtration through the filter paper and washed several times with double-distilled water until the water became neutral. After drying in vacuum oven at 60°C until the weight was constant, the white powder microcrystalline cellulose was obtained.

3.3.2 Graft Copolymerization of Cyanoethylated Microcrystalline Cellulose

3.3.2.1 Cyanoetylation of microcrystalline cellulose (20)

3 g of dried microcrystalline cellulose was placed into 12 mL of 4.5 N sodium hydroxide solution in 100 mL round bottom flask. After continuous stirring for 30 minutes at room temperature, 15 mL of acrylonitrile was added to the reaction mixture and then heated to 60 °C with continuous stirring. The reaction was allowed to proceed for 5 minutes. Then excess acrylonitrile was decanted and a portion of acetone was added to the mixture for washing. The product was then filtered and washed several times with

acetone. Finally the product was placed into 100 mL beaker and 5% acetic acid solution was added. After stirring for a few minutes the product was filtered and washed several times with double-distilled water until the washing was neutral, then dried in vacuum oven at 60°C until constant weight was obtained. It afforded the product yield of 8.9987 g. Repeatedly the second and the third experiment yielded the products 9.2310 and 9.1024 g, respectively. IR (KBr) ν (cm⁻¹) : 2240 sharp and strong.

3.3.2.2 Graft copolymerization of acrylonitrile on cyanoethylated microcrystalline cellulose

The graft copolymerization of cyanoethylated microcrystalline cellulose with acrylonitrile monomer was carried out in a 100 mL three-necked round bottom flask. The glass reactor was equipped with condenser, dropping funnel, and gas inlet tube for bubbling the oxygen-free nitrogen.

The reaction solution volume was 40 mL. 1 g of the dried cyanoethylated microcrystalline cellulose was dispersed into 29 mL of 0.4 M nitric acid solution with continuous stirring at 350 rpm. The acid solution was previously prepared by adding 1.11 mL of 65 % nitric acid to 30.89 mL of double-distilled water.

The initiator solution was prepared by adding 0.2193 g of ceric ammonium nitrate to the residue nitric acid solution. After that ceric ammonium nitrate solution was poured into dropping funnel and 8 mL of freshly distilled acrylonitrile monomer

was added to the slurry of the cyanoethylated microcrystalline cellulose. An oxygen-free nitrogen was bubbling through the reaction mixture for 30 minutes at 35°C to yield the oxygen-free mixture. The polymerization was carried out by gradually adding the initiator solution to the reaction mixture and continued stirring at 350 rpm for 3 hours under nitrogen atmosphere. The grafting reaction was stopped by allowing air into the reactor and the stirrer was turn off.

The polymer was washed several times with double-distilled water and the washing water was decanted and finally it was filtered. The product was washed again with double-distilled water and then the polymer was dried in vacuum oven at 60°C to get a constant weight and monitored by Infrared Spectroscopy. It afforded the product yield of 6.2483. Repeatedly, the second and the third experiments yielded the products 6.0998 and 6.1757 g, respectively. IR (KBr) (cm^{-1}): 2240 sharp and strong.

Extraction of polyacrylonitrile from the polymer product 1 g was done by using 100 mL of N,N-dimethylformamide with a continuous stirring at room temperature for 24 hours. The clear and colorless solution was obtained.

3.3.3 Cyanoethylation of Microcrystalline Cellulose Grafted Copolymer

3.3.3.1 Graft copolymerization of acrylonitrile on microcrystalline cellulose

The graft copolymerization of microcrystalline cellulose with acrylonitrile monomer was carried out by using the method mentioned in section 3.3.2.2, but microcrystalline cellulose was used instead of cyanoethylated microcrystalline cellulose. The reaction afforded the product yield of 5.8986. Repeatedly, the second and the third experiments yielded the products of 5.9102 and 5.9217 g, respectively.

The ungrafted polyacrylonitrile homopolymer was extracted from the grafted polymer by using N,N-dimethylformamide as mentioned in the procedure in section 3.3.5.2. Each gram of the polymer product of each experimental attempt yielded pure graft copolymer of 0.9301, 0.9226, and 0.9276 g. The grafted microcrystalline cellulose formation was monitored by Infrared Spectroscopy. IR (KBr) ν (cm^{-1}) : 2240 sharp and strong.

3.3.3.2 Cyanoethylation of grafted product

The cyanoethylation of graft copolymerization product was carried out by using the method mentioned in section 3.3.2.1, but microcrystalline cellulose grafted copolymer was used instead of microcrystalline cellulose. The reaction afforded the

product yield of 1.0045. Repeatedly the second and the third experiments yielded the products of 1.0109 and 1.0220 g, respectively. The product was monitored by Infrared Spectroscopy. IR (KBr) ν (cm^{-1}) : 2240 sharp and strong.

3.3.3.3 The grafted microcrystalline cellulose after cyanoethylation as water-retaining material

The grafted cyanoethylating product was hydrolyzed in 2 M NaOH using the same procedure as section 3.3.8. The hydrolyzed product was then subjected to the water absorption testing as section 3.3.8.1. It could absorb water 392.2 g water/g polymer.

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

3.3.4.1 Synthesis of sodium allyl sulfonate (21)

Sodium allyl sulfonate was synthesized by dissolving 15 g of sodium sulfite in 30 mL of double-distilled water in 100 mL round bottom flask. Allyl chloride 10 mL was poured into the flask and continuously stirred with magnetic stirrer. The reaction was allowed to proceed for 4 hours at 40°C and the clear solution was obtained. After that the solvent and residual allyl chloride were evaporated by rotary evaporator. The white powder was obtained and recrystallized from ethanol as the white powder and monitored by Infrared Spectroscopy and ^1H NMR spectroscopy. It afforded the product yield of 3.4862. Repeatedly, the second and the third experimentals

yielded the products 3.9546 and 4.1772 g, respectively.

IR (KBr) ν (cm^{-1}) : 1048 sharp and strong.

1160-1600 medium.

^1H NMR δ (PPM) : 3.45, 5.20, and 5.70.

3.3.4.2 Graft copolymerization of microcrystalline cellulose with acrylonitrile and sodium allyl sulfonate

The graft copolymerization of acrylonitrile and sodium allyl sulfonate on microcrystalline cellulose was carried out by using the apparatus as mentioned in section 3.3.2.2.

The reaction solution volume was 40 mL. 1 g of the dry microcrystalline cellulose was dispersed into 0.4 M nitric acid solution 29 mL with continuous stirring at 350 rpm. The acid solution had been previously prepared by adding 1.11 mL of 65% nitric acid to 30.89 mL of double-distilled water. The residual nitric acid solution was used to dissolve 0.1535 g of ceric ammonium nitrate for preparing initiator solution. After that ceric ammonium nitrate solution was poured into dropping funnel. 8 mL of freshly distilled acrylonitrile and 4.3344 g of pure sodium allyl sulfonate were added to the slurry of the microcrystalline cellulose. An oxygen-free nitrogen was bubbled through the reaction mixture for 30 minutes at 35°C to yield the oxygen-free mixture. The polymerization was carried out by gradually adding the initiator solution to the reaction mixture and stirring continued at 350 rpm for 4 hours under nitrogen atmosphere.

The grafting reaction was stopped by allowing air into the reactor and the stirrer was turned off. The polymer was washed several times with double-distilled water and the washing water was decanted and finally it was filtered. The product was washed again with double-distilled water and then the polymer was dried in vacuum oven at 60°C to get a constant weight. It afforded the product yield of 5.6911. Repeatedly, the second and the third experiments yielded 5.7171 and 5.7224 g, respectively.

The graft copolymerization was repeated by varying Ce^{4+} concentration and the result was shown in Table 3.1. The ungrafted polyacrylonitrile and polysodium allyl sulfonate homopolymers were extracted from the grafted polymer by using N,N-dimethylformamide as mentioned in the procedure in section 3.3.5.2. Each gram of the polymer product of each experimental attempt yielded pure graft copolymer 0.9632, 0.9640, and 0.9625 g, respectively. The result of graft copolymerization of acrylonitrile and sodium allyl sulfonate by varying Ce^{4+} concentrations was shown in Table 3.1. The grafted microcrystalline cellulose formation was monitored by Infrared Spectroscopy.

IR (KBr) ν (cm^{-1}) : 2240 sharp and strong.

3.3.4.3 The sulphur testing

A dry and clean small pellet of sodium was placed into pyrex test tube 100x10 mm and heated with light flame till sodium was melted. After that Bunsen burner was taken off immediately and

0.2 g of the graft copolymerized product in section 3.3.4.2 was added into the test tube and allowed to react with sodium for 10 seconds. Another small pill of sodium was placed into the mixture and heated the tube violently for 60 seconds. After that the tube was cooled to room temperature and 3 mL of ethanol was added dropwise into the mixture.

The double-distilled water was added into the mixture upto half of the tube and it was poured into the evaporating dish for 2-3 times. After that the mixture was boiled for 10 minutes and filtered through the filter paper. The filtrate or stock solution was kept to test for sulphur by using lead acetate solution, as followed;

2 mL of stock solution was adjusted to be acidic by dilute acetic acid and 10 drops of 1 M lead acetate was added to the solution. The clear and colorless solution was obtained. (The positive test for this method was black precipitate of lead sulphide.) The result of sulphur testing for cellulose-graft-poly(acrylonitrile-co-sodium allyl sulfonate) was shown in Table 3.1.

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Table 3.1 Graft copolymerization of acrylonitrile and sodium allyl sulfonate on microcrystalline cellulose with various Ce^{4+} concentrations and sulphur testing

Ce^{4+} concentration (M)	Product yield (g)	Free-homopolymer (g)	Sulphur testing
0.001	4.4569	0.9674, 0.9679, 0.9666	negative
0.003	4.8933	0.9637, 0.9369, 0.9621	negative
0.005	5.4047	0.9655, 0.9661, 0.9649	negative
0.007	5.7171	0.9632, 0.9642, 0.9625	negative
0.009	5.2947	0.9501, 0.9493, 0.9509	negative
0.011	5.0855	0.9417, 0.9413, 0.9421	negative

3.3.5 The Graft Copolymerization of the Microcrystalline Cellulose

3.3.5.1 Graft copolymerization of acrylonitrile and acrylic acid on microcrystalline cellulose

The graft copolymerization of acrylonitrile and acrylic acid monomers on microcrystalline cellulose was carried out by using the apparatus as mentioned in section 3.3.2.2.

The reaction solution volume was 50 mL. A weighed



quantity of dry microcrystalline cellulose (1 g) was dispersed into 37 mL of 0.3 M nitric acid solution with continuous stirring at 450 rpm by magnetic stirrer. The acid solution had been previously prepared by adding 1.04 mL of 65% nitric acid to 38.97 mL of double-distilled water. The residual nitric acid solution was used to dissolve a definite amount (0.1644 g) of ceric ammonium nitrate for preparing initiator solution. The ceric ammonium nitrate in nitric acid solution was poured into dropping funnel. 8.33 mL and 1.66 mL of freshly distilled acrylonitrile and acrylic acid monomer were added to the slurry of the microcrystalline cellulose. An oxygen-free nitrogen was bubbled through the solution mixture for 30 minutes at 35°C to yield the oxygen-free solution.

After that, the polymerization was carried out under nitrogen atmosphere by gradually adding the initiator solution to the reaction mixture. Polymerization was allowed to proceed for 3 hours with continuous stirring at stirring speed of 450 rpm. The grafting reaction was stopped by allowing air into the reactor and the stirrer was turned off.

The polymer was washed several times with double-distilled water and the washings water was decanted and finally it was filtered. The product was washed again with distilled water and then the polymer was dried in vacuum oven at 60 °C to get a constant weight. It afforded the product yield of 8.7232. Repeatedly, the second and the third experiments yielded 8.7406 and 8.7492 g, respectively.

The ungrafted polyacrylonitrile and polyacrylic acid homopolymer were extracted from the grafted polymer by using N,N-dimethylformamide as mentioned in the procedure in section 3.3.5.2. Each gram of the polymer product of each experimental attempt yielded graft copolymer of 0.9699, 0.9712, and 0.9713 g. The homopolymer content was measured as the decrease in weight of the sample by N,N-dimethylformamide extraction. The grafted cellulose formation was monitored by Infrared Spectroscopy.

IR (KBr) ν (cm^{-1}) : 1710-1760 medium.

2240 sharp and strong.

3.3.5.2 The homopolymer extraction

In the polymerization process as mentioned in section 3.3.5.1, homopolymer of polyacrylonitrile and polyacrylic acid occurred. These two homopolymers were isolated from the grafted cellulose by the following procedure.

One gram of the dried polymer was extracted with 100 mL N,N-dimethylformamide with a continuous stirring at room temperature for 24 hours. The extracted products were filtered by vacuum filtration through the filter paper whose weight was known. The extracted product was rinsed twice with N,N-dimethylformamide, once with methanol, and then ethanol. The free-homopolymer product was then dried in vacuum oven at 60°C until the weight was constant. No homopolymer residue and pure grafted product was obtained. The homopolymer formation was monitored by Infrared Spectroscopy.

IR (KBr) ν (cm^{-1}) : 1710-1760 medium for polyacrylic acid.

2240 sharp and strong for polyacrylonitrile.

3.3.6 Preliminary Study of Graft Copolymerization of the Microcrystalline Cellulose with Acrylonitrile and Acrylic Acid Monomer

3.3.6.1 Variation of the amounts of water

The graft copolymerization of acrylonitrile and acrylic acid monomers on microcrystalline cellulose with various amounts of water were carried out as the same procedure mentioned in section 3.3.5.1. The constant parameters were : 1 g weight of microcrystalline cellulose, 0.16 mol fraction of acrylic acid monomer, 0.4 M concentration of nitric acid, 0.01 M concentration of ceric ammonium nitrate and stirring speed 350 rpm. The polymerization was allowed to proceed for 3 hours at 35°C. The varied amounts of water were in Table 3.2. The grafting was repeated three times with new sample and polyacrylonitrile and polyacrylic acid homopolymers were extracted by N,N-dimethylformamide as mentioned in section 3.3.5.2.

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Table 3.2 Graft copolymerization of the microcrystalline cellulose with various amounts of water

Reaction volume (mL)	Water (mL)	Product yield (g)	* Free-homopolymer (g)
30	18.59	4.9589	0.5157, 0.5182, 0.5127
40	28.59	6.6939	0.5756, 0.5689, 0.5790
50	38.59	8.0548	0.5396, 0.5348, 0.5453
60	48.59	7.5677	0.5524, 0.5448, 0.5381
70	58.59	7.0395	0.5913, 0.5948, 0.5856
80	68.59	6.4208	0.5907, 0.5977, 0.5855

* Repeatedly three times of homopolymer extraction of 1 g of the product

3.3.6.2 Variation of the initiator concentration

In this research, ceric ammonium nitrate was used as the initiator. The graft copolymerization of acrylonitrile and acrylic acid monomers on microcrystalline cellulose with various concentrations of ceric ammonium nitrate were carried out as the same procedure mentioned in section 3.3.5.1. The constant parameters were: 38.58 mL volume of water, 1 g weight of microcrystalline cellulose, 0.16 mol fraction of acrylic acid monomer, 0.4 M concentration of nitric acid solution, and 50 mL reaction volume; 50 mL. The

polymerization was allowed to proceed for 3 hours at 35°C and stirring speed 350 rpm. The varied concentration of ceric ammonium nitrate were in Table 3.3. The grafting was repeated three times with new sample. Polyacrylonitrile and polyacrylic acid homopolymers were extracted by N,N-dimethylformamide extraction as mentioned in section 3.3.5.2.

Table 3.3 Graft copolymerization of the microcrystalline cellulose with various concentrations of ceric ammonium nitrate

Ce ⁴⁺ Concentration (M)	Product yield (g)	* Free-homopolymer (g)
0.001	6.2491	0.1562, 0.1612, 0.1518
0.002	6.6686	0.1867, 0.1900, 0.1833
0.003	7.0604	0.1976, 0.2019, 0.1941
0.004	7.5720	0.2271, 0.2324, 0.2226
0.005	8.1019	0.2673, 0.2730, 0.2608
0.006	8.2859	0.3190, 0.3148, 0.3098
0.007	8.2230	0.3609, 0.3535, 0.3470
0.008	8.2370	0.4810, 0.4777, 0.4744
0.009	8.0734	0.5005, 0.5086, 0.5150
0.010	8.0548	0.5396, 0.5348, 0.5453
0.011	7.4681	0.5436, 0.5377, 0.5309
0.012	7.0024	0.5826, 0.5882, 0.5931

* Repeatedly three times of homopolymer extraction of 1 g of the product.

3.3.6.3 Variation of monomer quantity

The graft copolymerization of acrylonitrile and acrylic acid monomers on microcrystalline cellulose with various quantities of monomers were carried out as the same procedure mentioned in section 3.3.5.1. The quantities of two monomers were shown in the form of mol fraction of acrylic acid monomer. The constant parameters were: 38.58 mL volume of water, 1 g weight of microcrystalline cellulose, 0.4 M concentration of nitric acid, 0.006 M concentration of ceric ammonium nitrate, and 50 mL reaction volume. The polymerization was allowed to proceed for 3 hours at 35°C and stirring speed of 350 rpm. The varied mol fractions of acrylic acid monomer were listed in Table 3.4. The grafting was repeated three times with new sample and polyacrylonitrile and polyacrylic acid homopolymers were extracted by N,N-dimethylformamide as mentioned in section 3.3.5.2.

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Table 3.4 Graft copolymerization of the microcrystalline cellulose with various mol fractions of acrylic acid monomer

Mol fraction of acrylic acid (M)	Product yield (g)	* Free-homopolymer (g)
0.16	8.2859	0.3190,0.3148,0.3098
0.32	8.1866	0.4068,0.4011,0.3954
0.48	7.9464	0.5284,0.5244,0.5205
0.65	7.9306	0.5274,0.5234,0.5194
0.82	7.7437	0.6706,0.6737,0.6768

* Repeatedly three times of homopolymer extraction of 1 g of the product.

3.3.6.4 Variation of the nitric acid concentration

The graft copolymerization of acrylonitrile and acrylic acid monomers on microcrystalline cellulose with various concentrations of nitric acid solution were carried out as the same procedure mentioned in section 3.3.5.1. The constant parameters were: 1 g weight of microcrystalline cellulose, 0.16 mol fraction of acrylic acid monomer, 0.006 M concentration of ceric ammonium nitrate, and 50 mL reaction volume. The polymerization was allowed to proceed for 3 hours at 35°C and stirring speed 350 rpm. The varied

concentration of nitric acid solution were listed in Table 3.5. The grafting was repeated three times with new sample and polyacrylonitrile and polyacrylic acid homopolymers were extracted by N,N-dimethylformamide as mentioned in section 3.3.5.2.

Table 3.5 Graft copolymerization of the microcrystalline cellulose with various concentrations of nitric acid solution

Nitric acid concentration (M)	Product yield (g)	* Free-homopolymer (g)
0.1	8.4357	0.2345, 0.2277, 0.2210
0.2	8.4703	0.1905, 0.1948, 0.1990
0.3	8.5836	0.2557, 0.2489, 0.2412
0.4	8.2859	0.3190, 0.3148, 0.3098
0.5	7.9376	0.3889, 0.3810, 0.3730
0.6	7.5601	0.3190, 0.3251, 0.3304

* Repeatedly three times of homopolymer extraction of 1 g of the product.

3.3.6.5 Variation of the stirring speed

The graft copolymerization of acrylonitrile and acrylic acid monomers on microcrystalline cellulose with various stirring speed was carried out as the same procedure mentioned in

section 3.3.5.1. The constant parameters were: 38.97 mL volume of water, 1 g weight of microcrystalline cellulose, 0.16 mol fraction of acrylic acid monomer, 0.3 M concentration of nitric acid solution, 0.006 M concentration of ceric ammonium nitrate and 50 mL reaction volume. The polymerization was allowed to proceed for 3 hours at 35°C. The varied stirring speed were in Table 3.6. The grafting was repeated three times and polyacrylonitrile and polyacrylic acid homopolymers were extracted by N,N-dimethylformamide as mentioned in section 3.3.5.2.

Table 3.6 Graft copolymerization of the microcrystalline cellulose at different stirring speeds

Stirring speed (rpm)	Product yield (g)	* Free-homopolymer (g)
150	6.8284	0.3175, 0.3209, 0.3236
250	7.6466	0.3303, 0.3364, 0.3433
350	8.5836	0.2557, 0.2489, 0.2412
450	8.7406	0.2561, 0.2535, 0.2499
550	6.5229	0.4351, 0.4305, 0.4253

* Repeatedly three times of homopolymer extraction of 1 g of the product.

3.3.6.6 Variation of the reaction temperature

The graft copolymerization of acrylonitrile and acrylic acid monomers on microcrystalline cellulose at various reaction temperatures was carried out as the same procedure mentioned in section 3.3.5.1. The constant parameters were: 38.97 mL volume of water, 1 g weight of microcrystalline cellulose, 0.16 mol fraction of acrylic acid monomer, 0.3 M concentration of nitric acid solution, 0.006 M concentration of ceric ammonium nitrate, and 50 mL reaction volume. The polymerization was allowed to proceed for 3 hours and stirring speed of 450 rpm. The varied reaction temperatures were listed in Table 3.7. The grafting was repeated three times and polyacrylonitrile and polyacrylic acid homopolymers were extracted by N,N-dimethylformamide as mentioned in section 3.3.5.2.

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Table 3.7 Graft copolymerization of the microcrystalline cellulose at various reaction temperatures

Temperature (°C)	Product yield (g)	* Free-homopolymer (g)
25	8.2007	0.2279, 0.2214, 0.2156
30	7.9286	0.3829, 0.3806, 0.3789
35	8.7406	0.2561, 0.2535, 0.2499
40	8.0503	0.2785, 0.2737, 0.2680
50	7.7402	0.4760, 0.4798, 0.4837
60	7.1951	0.6166, 0.6115, 0.6058

* Repeatedly three times of homopolymer extraction of 1 g of the product.

3.3.6.7 At the optimum condition

The graft copolymerization of acrylonitrile and acrylic acid monomers on microcrystalline cellulose at the selected condition was carried out as the same procedure mentioned in section 3.3.5.1. The selected condition was: 38.97 mL volume of water, 1 g weight of microcrystalline cellulose, 0.16 mol fraction of acrylic acid monomer, 0.3 M concentration of nitric acid solution, 0.006 M concentration of ceric ammonium nitrate, and 50 mL reaction volume. The polymerization was allowed to proceed for 3 hours at reaction temperature of 35°C and stirring speed of 450 rpm. The grafting was

repeated three times with new sample and polyacrylonitrile and polyacrylic acid homopolymers were extracted by N,N-dimethylformamide as mentioned in section 3.3.5.2.

Table 3.8 Graft copolymerization of the microcrystalline cellulose at the selected condition

Experiment number	Product yield (g)	* Free-homopolymer (g)
1	17.2234	0.9692, 0.9719, 0.9701
2	17.2423	0.9723, 0.9706, 0.9709
3	17.5430	0.9762, 0.9751, 0.9737

* Repeatedly three times of homopolymer extraction of 1 g of the product.

3.3.7 Determination of Molecular Weight of Grafted Side Chain

3.3.7.1 Acid hydrolysis of cellulose-graft-poly(acrylonitrile-co-acrylic acid)

0.5 g of dried grafted product obtained from the experiment as mentioned in section 3.3.6.7, was introduced into 50 mL acid solution which was then refluxed. The various conditions of acid hydrolysis were given in Table 3.9. The product was filtered through

the sintered glass funnel of medium porosity and washed several times with double-distilled water until it was free of acid. Finally, it was rinsed with ethanol, and dried in vacuum oven at 60°C.

Table 3.9 Acid hydrolysis at various conditions of microcrystalline cellulose-graft-poly (acrylonitrile-co-acrylic acid)

Acid	Concentration (M)	Reflux time (hours)
H ₂ SO ₄	3	6, 12, 24
	4	6, 12, 24
	5	6, 12, 24
HCl	3	6, 12, 24
	4	6, 12, 24
	5	6, 12, 24

3.3.7.2 Determination of the molecular weight of grafted side chain by Gel Permeation Chromatography

The polymer product obtained from section 3.3.7.1 was refluxed in N,N-dimethylformamide for 24 hours with continuous stirring. Most of polymer was dissolved while some residue was swelled in N,N-dimethylformamide. After filtration, the clear solution was used to determine the molecular weight of polyacrylonitrile and polyacrylic acid grafted side chain. The determination was done by

comparing with the polystyrene standard solution as shown in Table 3.10. The result indicated that the average molecular weight of grafted side chain was 20489.

Table 3.10 Molecular weight of polystyrene standard solution by Gel Permeation Chromatography

Sample name	Retention time (minute)	Molecular weight
Std 01	7.16	3840000
Std 02	7.53	1090000
Std 03	7.83	70600
Std 04	8.22	355000
Std 05	8.53	190000
Std 06	8.87	96400
Std 07	9.38	37900
Std 08	9.80	18100
Std 09	10.05	9100
Std 10	10.17	5570

3.3.8 Alkaline Hydrolysis of Cellulose-Graft-Poly(Acrylonitrile-co-Acrylic Acid)

1.0 g of the dried grafted cellulose was introduced into 100 mL sodium hydroxide solution which was then heated to 95°C. The

alkaline hydrolysis was allowed to proceed for 2 hours with continuous stirring. The various concentrations of sodium hydroxide for alkaline hydrolysis were given in Table 3.11.

Table 3.11 Alkaline hydrolysis of microcrystalline cellulose-graft-poly (acrylonitrile-co-acrylic acid) at various concentrations of sodium hydroxide solution

Polymer (g)	Sodium hydroxide concentration (M)
1.0003	1
1.0001	2
1.0001	3
1.0002	4
1.0000	5
0.9998	6

Graft copolymer had a red-orange color which then slowly faded to light yellow as the reaction was nearly completed. The mixture was then cooled. The alternation between precipitation in methanol and reswelling in double-distilled water was done twice. Finally the pH of product in double-distilled water was adjusted to 7.0 by neutralization with 5% acetic acid. The product was precipitated again in methanol, rinsed with ethanol and dried in vacuum oven at 60°C.

3.3.8.1 The water absorption of the alkaline-hydrolyzed polymer(water - retaining material) at various alkaline concentrations

500 mL of double-distilled water was added to 0.5 g of dried alkaline-hydrolyzed polymer (A) at room temperature and stirred with magnetic stirrer at 600 rpm. The sample was allowed to swell for 1 hour and after that transferred to 125 mesh stainless steel screen. The swollen sample was drained for 20 minutes by gravitation and then weighed. The weight of the gel (B) was used to calculate the water retention value by following equation.

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

The water retention values of the alkaline-hydrolyzed polymer obtained using various alkaline concentrations were determined and their results were given in Table 3.12.

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Table 3.12 Water retention value of the alkaline-hydrolyzed product at various concentrations of sodium hydroxide

Sodium hydroxide concentration (M)	Water retention value (g water/g polymer)	
1	893.8	2.7
2	910.9	2.8
3	980.3	7.2
4	1056.0	2.3
5	1040.8	2.3
6	1046.6	1.8

3.3.8.2 Determination of the nitrogen residue

The nitrogen residue in the alkaline-hydrolyzed product at various concentrations was determined by Kjeldahl method and the results were shown in Table 3.13.

Table 3.13 Nitrogen residue in the alkaline-hydrolyzed product

Sodium hydroxide concentration (M)	% Nitrogen residue		
	No. 1	No. 2	average
0	18.61	18.37	18.49 ± 0.12
1	5.42	5.51	5.46 ± 0.04
2	5.38	5.38	5.38 ± 0.00
3	4.79	4.78	4.78 ± 0.01
4	4.19	4.21	4.20 ± 0.01
5	4.07	4.00	4.04 ± 0.04
6	3.47	3.46	3.46 ± 0.01

3.3.8.3 Determination of the degradation of the alkaline hydrolysis

0.2 g (dry weight) of the alkaline-hydrolyzed polymer was suspended in 200 mL double-distilled water at room temperature. Then it was stirred for 1 hour. The viscosity was measured by Brookfield Viscometer at room temperature (29 °C).

Table 3.14 Viscosity of the suspended polymer obtained from hydrolysis at various alkaline concentrations

Sodium hydroxide concentration (M)	Viscosity (cps)
1	11.8
2	13.4
3	15.1
4	16.9
5	19.7
6	22.3

3.3.8.4 Determination of the residual sodium ion in the water-retaining material

Residual sodium in the water-retaining material was determined by Flame Emission Photometer. 0.05 g of the water-retaining material was digested by the mixture of conc.HCl and conc.HNO₃. The solution was then diluted with double-distilled water until the volume was 50 mL.

The determination was done by comparing with standard sodium solution at various concentrations. The concentrations of these solutions were 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 ppm. The solution was prepared in 50 mL of volumetric flask and

the result was shown in Table 3.15.

Table 3.15 Relative absorbance of standard sodium solution by Flame Emission Photometer

Concentration of standard sodium solution (ppm)	Relative absorbance		
	First reading	Second reading	Average
10	73.5	73.0	73.3 ± 0.3
20	77.0	76.5	76.8 ± 0.3
30	80.0	80.0	80.0 ± 0.0
40	83.0	84.0	83.5 ± 0.5
50	86.0	86.0	86.0 ± 0.0
60	87.5	87.0	87.3 ± 0.3
70	90.5	91.5	91.0 ± 0.5
80	92.0	92.0	92.0 ± 0.0
90	94.5	96.0	95.3 ± 0.8
100	100.0	100.0	100.0 ± 0.0



Table 3.16 Percentage of residual sodium in the water-retaining material

Polymer (g)	Relative absorbance	Concentration (ppm)	* Sodium	
			(g)	%
0.0501	84.7	47.0	0.0024	4.79
	85.1	48.0	0.0024	4.79
0.0500	86.5	53.0	0.0027	5.40
	87.0	55.0	0.0028	5.60
0.0503	88.0	59.0	0.0029	5.76
	87.5	57.0	0.0028	5.56
0.0502	86.2	52.0	0.0026	5.18
	86.0	51.0	0.0026	5.18
0.0501	85.4	50.0	0.0025	5.00
	85.8	51.0	0.0026	5.19

* The average sodium quantity was $5.24 \pm 0.30\%$.

3.3.8.5 Determination of the residual cerium ion in the water-retaining material

Residual ceric ion in the water-retaining material was determined by Inductive Couple Plasma Emission Spectrometer. 5 g of the water retaining material was digested by mixture of conc. HCl and conc. HNO₃. The solution was then diluted

with double-distilled water until the volume was 50 mL. The determination was done by comparing with standard ceric solution. The result was shown in Table 3.17 and 3.18.

Table 3.17 Intensity of standard ceric solution by Inductive Couple Plasma Emission Spectrometer

Cerium solution	Intensity
Standard 1 (0.2156)	248.2
	220.3
	227.8
	246.8
Average	235.8 ± 12.0
Standard 2 (1.0780)	1081.3
	1104.5
	1064.3
	1069.2
Average	1079.8 ± 15.5

Table 3.18 Concentration of residual cerium ion in the water-retaining material

Testing No.	*Concentration (ppm)
Sample:rep 1	0.6137
rep 2	0.6144
rep 3	0.6108
rep 4	0.6130
Average	0.6130 ± 1.3497

* The average cerium quantity was 0.0006 %.

3.3.9 Physical Testing

3.3.9.1 Water retention value at various % add-on and grafting ratio

500 mL of double-distilled water was added to 0.5 g of sample at room temperature and stirred with magnetic stirrer at 600 rpm. The sample was allowed to swell for 1 hour and after that transferred to 125 mesh stainless steel screen. The sample was drained for 20 minutes by gravitation and then weighed. The calculation of water retention value was done using the same equation in section 3.3.8.1.

Table 3.19 Water retention value of the water-retaining material at various % add-on and grafting ratio parameters

* % Add-on	* Grafting ratio (g PAN and PAA/g cell)	Water retention value (g water / g polymer)
69.40	3.44	481.6 ± 2.0
76.58	5.06	713.7 ± 3.0
77.60	5.58	786.1 ± 2.5
81.09	6.59	927.2 ± 3.0
85.45	7.48	1056.0 ± 2.3

* See appendix A.

3.3.9.2 Water absorption at various swelling times

The testing was performed in the same manner as in section 3.3.9.1, except swelling time was varied as shown in Table 3.20.

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Table 3.20 Water retention value of the water-retaining material at various swelling times

Swelling time (hours)	Water retention value (g water / g polymer)
0.5	934.9 ± 2.3
1	996.3 ± 4.8
2	742.8 ± 4.0
3	579.5 ± 6.2
4	358.9 ± 4.9
5	363.7 ± 3.5
6	354.4 ± 3.2

3.3.9.3 Water releasing

500 mL of double-distilled water was added to 0.5 g of sample at room temperature and stirred with magnetic stirrer at 600 rpm. The sample was allowed to swell for 1 hour and after that transferred to 125 mesh stainless steel screen. The sample was drained for 20 minutes by gravitation and then left in open air at room temperature. It was weighed in a short time interval at the beginning and later in a longer time interval as exhibited in table 3.21.

Table 3.21 Water releasing of the water-retaining material at various times

Releasing time (hours)	Water retention value (g water / g polymer)
0.25	932.2 ± 5.4
0.33	913.7 ± 4.6
0.42	897.7 ± 3.6
0.50	880.0 ± 6.0
0.67	840.3 ± 4.7
0.83	812.1 ± 5.1
1.00	797.6 ± 5.9
2.00	763.6 ± 5.2
4.00	692.6 ± 4.6
6.00	626.4 ± 4.7
8.00	590.9 ± 2.8
10.00	551.6 ± 3.4
12.00	522.8 ± 2.6
14.00	497.9 ± 2.0
16.00	483.2 ± 2.7
18.00	467.0 ± 2.8
20.00	432.7 ± 2.7
22.00	409.5 ± 1.4
24.00	396.0 ± 3.2

3.3.9.4 Absorbing speed

50 mL of saline solution (0.9 % NaCl by weight) was added to 100 mL beaker and stirred with magnetic stirrer at 600 rpm. 0.5 g of sample was added into vortex and then the time was recorded immediately. When the surface of saline solution became quiet, the time was recorded again. The absorbing speed was the period of time since the sample was added into the saline solution until the surface of saline solution became quiet.

Table 3.22 Absorbing speed of water-retaining material

Testing No.	Absorbing speed (seconds)
1	13.0
2	12.0
average	12.5 ± 0.5

3.3.9.5 Moisture content

The water-retaining material was left in open air for 24 hours and after that the accurately weighed sample (W_1 g) was dried at 110°C in an oven for a constant weight (W_2 g). (The dried

sample was cooled in desiccator before weighing.) The percentage of moisture was calculated by this following equation.

$$\% \text{ Moisture content} = \{ [W_1 - W_2] / W_1 \} \times 100$$

Table 3.23 The moisture content of the water-retaining material

Testing No.	% Moisture content
1	29.70
2	30.01
average	29.85 ± 0.15

The % moisture content was also determined by Thermogravimetric Analysis. It was found to be 30.98%.

3.3.9.6 The water absorbancy at various conditions

3.3.9.6.1 The water absorption at different pH

The testing was performed in the same manner as in section 3.3.9.1, except the aqueous solution with different pHs were used instead of double-distilled water. These solutions were adjusted to the selected pH by sodium hydroxide

and hydrochloric acid solution. Table 3.24 records the water retention value of the water-retaining material at various pH.

Table 3.24 The water retention value of the water-retaining material at various pH

pH	Water retention value (g water / g polymer)
4	1021.3± 5.7
5	974.3± 3.6
6	940.0± 2.8
7	968.6± 4.9
8	900.0± 3.7
9	821.0± 5.3
10	755.0± 4.5
11	596.6± 4.4
12	273.7± 4.2

3.3.9.6.2 The water absorption at different temperatures

The testing was performed in the same manner as in section 3.3.9.1, except double-distilled water at different temperature were used instead of double-distilled water. Table 3.25 records the water retention value of the water-retaining

material at different temperature.

Table 3.25 The water retention value of the water-retaining material at different temperatures

Temperature (°C)	Water retention value (g water / g polymer)
20	725.1 ± 3.4
25	856.5 ± 6.3
28	992.0 ± 5.4
30	1035.7 ± 6.2
35	951.0 ± 4.6
40	869.6 ± 3.5
60	698.1 ± 4.7
80	458.3 ± 6.4

3.3.9.6.3 The water absorption at various electrolyte solutions and one of non-electrolyte solution

The testing was performed in the same manner as in section 3.3.9.1, except the aqueous solution of urea, ammonium chloride, potassium sulphate, and sodium chloride at various concentration were used instead of double-distilled water. The concentration of these solutions were 0.5, 1.0, 2.0, and 3.0 % weight



by weight. Table 3.26 records the water retention value of the water-retaining material at various electrolyte solutions and one of non-electrolyte solution.

Table 3.26 The water retention value of the water-retaining material at various electrolyte solutions and one of non-electrolyte solution

Conc. (%)	Water retention value (g water / g polymer)	Conc. (%)	Water retention value (g water / g polymer)
Urea		Potassium Sulphate	
0.5	813.0 ± 4.4	0.5	171.9 ± 3.8
1.0	726.6 ± 3.4	1.0	119.7 ± 3.7
2.0	604.4 ± 3.5	2.0	84.9 ± 3.4
3.0	486.5 ± 2.2	3.0	100.5 ± 3.0
Ammonium Chloride		Sodium Chloride	
0.5	104.8 ± 2.9	0.5	151.2 ± 3.7
1.0	87.5 ± 2.1	1.0	82.4 ± 1.7
2.0	62.8 ± 2.8	2.0	56.5 ± 3.4
3.0	68.6 ± 3.1	3.0	51.7 ± 2.9

3.3.9.7 Thermal analysis of the water-retaining material

The thermal analysis of the water-retaining material was studied by using Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The results are shown in figure 4.33 and 4.34.



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