CHAPTER III

EXPERIMENTAL

Chemicals, Equipment and Glasswares

Chemicals

Cassava Starch was obtained from Thai Wah Co., Ltd. It was produced from tapioca cultivated in summer. It contains 13% moisture, 0.15% ash, pH value of 4.50-7.00 and viscosity of 600.

Acrylonitrile, AN, (98% pure) was provided by Siam Resin & Chemical Co., Ltd. It was purified and fractional distillated at atmospheric pressure and stored under nitrogen gas in a refrigerator.

Styrene, S, was obtained from Siam Resin, which was purified and fractional distillated at atmospheric pressure and was stored under nitrogen gas in a refrigerator.

Methanol, commercial grade from BDH, was also purified by fractional distillation at atmospheric pressure.

Potassium hydroxide, B.P. grade, from Carlo Erba, was used as received.

Other Chemicals, shown below in Table 3.1, which were of analytical grade, were used without further purification.

TABLE 3.1

Chemicals

Chemicals	Source, Company
Ammonium chloride (NH_4Cl)	Merck
Ammonium phosphate dibasic ($(NH_4)_2HPO_4$)	Carlo Erba
N,N - dimethyl formamide (DMF)	Carlo Erba
Magnesium chloride hexa-hydrate ($MgCl_2 . 6H_2O$)	Carlo Erba
Potassium chloride (KCl)	Merck
tri-Potassium phosphate-tri-hydrate ($K_3PO_4.3H_2O$)	Merck
Sodium chloride (NaCl)	Carlo Erba
Aluminium tri-chloride tri-hydrate ($AlCl_3.6H_2O$)	JT. Baker
Methyl Ether Hydroquinone ($C_7H_8O_2$)	TCI
Nitric acid (HNO_3)	Merck
Sulphuric acid (H_2SO_4)	Merck
Urea ($(NH_2)_2CO$)	Carlo Erba

Equipment and Glasswares

3-necked round bottom flask, beakers, funnel, erlenmeyer flask, condenser, hot plate and magnetic stirrer, mechanical stirrer, heating mantle, motor stirrer, water bath circulator, reactor, analytical balance, grinder, cobalt-60 source (Gamma Cell 220 of 24,480 curies from NORDIAN International Inc., Canada) and other general laboratory glasswares and equipment.

Procedure

1. Gelatinization of Cassava Starch

Into a 500 ml reactor, 10 g of cassava starch was mixed with 200 ml of distilled water. The system was stirred at 400 rpm and heated at around 85° ± 3°C at the same time for one hour under the nitrogen atmosphere to form a paste-like slurry.

2. Grafting of Acrylonitrile onto Cassava Starch by Simultaneous irradiation

The gelatinized starch was then cooled at room temperature. 20 ml of acrylonitrile was added into the gelatinized starch within 5 minutes. The mixture was stirred at 400 rpm under nitrogen atmosphere at room temperature for 30 minutes. The gelatinized starch-acrylonitrile mixture was removed into the 250 ml tube covered the inner wall with aluminium foil, and purged with nitrogen gas for 20 minutes. It was closed tightly with foil and parafin film, and then irradiated under gamma ray at various total doses. The reaction product was isolated by filtration, washed with methanol, and dried at 65°C for 24 hours. Percentage yield was also calculated.

To obtain a good yield of copolymer with a high water absorption rate and a high absorption value, important effects on graft copolymerization were carried out as follows:

2.1 Effect of Total Dose (kGy) on Graft Copolymerization

At a fixed dose rate of 0.25 kGy/min, various quantities of total dose of 2, 2.5, 3, 3.5, 4, 5 kGy of gamma ray irradiated to the mixture of the gelatinized starch-acrylonitrile as described in Section 2 were investigated. The dried samples were inspected with an IR spectrometer and water absorption capacity was consequently measured. The higher water absorption value indicates the appropriate total dose for the graft copolymerization of this system. Homopolymer quantity was also calculated.

2.2 Effect of The Metal Sheet on Reduction of Homopolymer

Based on the technical information of the optimum total dose (Section 2.1) and the appropriate amount of AN (Section 2.2), various types of thin metal sheet or film, for instance, aluminium foil, lead sheet, zinc and copper plates, were covered the inner wall of the reaction tube to observe their effects on homopolymer reduction.

2.3 Effect of The Inhibitor on Graft Copolymerization

Various amounts of methyl ether hydroquinone inhibitor for acrylonitrile of 0.00125, 0.0025, 0.005, 0.01, 0.02 % wt (or 1.25, 2.5, 5, 10, 20 ppt) based on the monomer were added to each of the optimum amount of AN, which was derived from Section 2.2. The AN solution was then added to the gelatinized starch and it was irradiated at the optimum total dose obtained from Section 2.1.

2.4 Effect of The Mineral Acid on Graft Copolymerization

Ten ml of 0.1 M HNO_3 was added to the gelatinized starch before mixing with acrylonitrile to investigate the effect of acid on graft copolymerization. After gamma irradiation, the product was filtered and washed with methanol until the neutralized starch-g-polyacrylonitrile was obtained.

2.5 Effect of The Comonomer on Graft Copolymerization

Styrene was used to study the effect of comonomer on graft copolymerization. After adding AN into the gelatinized starch, 5 ml of styrene was added and the procedure of Section 2 was followed. Irradiations for each of the experiments were carried out at the total dose of 3.5, 7 and 10 kGy. The dried product was extracted in a Soxhlet by toluene to remove polystyrene homopolymer. The product was filtered, washed with methanol and dried at 65 °C for 24 hours.

2.6 Effect of The Amount of AN on Graft Copolymerization

Various amounts of AN of 10, 15, 20, 25 ml (or 0.7547, 1.1321, 1.5094, 1.8868 M) were added to each of the gelatinized starch. The reaction mixture was stirred mechanically for 30 minutes. Irradiations were carried out at the optimum total dose obtained from Section 2.1. The dried samples were inspected with the IR spectrometer and water absorption capacity was then determined.

3. Homopolymer Extraction by N,N-Dimethylformamide

In a 2,000 ml erlenmeyer flask, the total dried product (about 20 g) derived from Section 2, ground previously into a powder form, was stirred in 1,000 ml DMF at room temperature for 24 hours.

The extracted product was filtered, washed with methanol and dried at 65°C for 24 hours and weighed to determine the amount of the homopolymer, polyacrylonitrile. All products were detected with the FT-IR spectrometer.

4. Copolymer Characterization

4.1 Saponification of Starch-g-PAN

A suspension of 5.0 g of DMF-extracted starch-g-polyacrylonitrile was added to 100 ml of 8.5% potassium hydroxide solution. The mixture was stirred with a mechanical stirrer at 400 rpm and the saponification was carried out at 100°C for 2 hours. One could observe a deep red solution developed at the early stage and the color changed to light yellow at the later stage. It was then allowed to cool to room temperature. The product was isolated by precipitation with methanol, filtered and washed thoroughly with methanol until pH 7 was reached. The resulting product was dried in 65°C oven for 24 hours. The dried product was ground into a powder form.

4.2 Determination of Percent Add-On

In a 500 ml erlenmeyer flask equipped with a condenser, 4.00 g of the starch-g-polyacrylonitrile was stirred in 400 ml of 2 M H_2SO_4 and the mixture was refluxed for 90 minutes. The water-insoluble polymer was filtered, then washed until the pH of the washed solution was 7, and then it was dried. The weighed percentage polyacrylonitrile in the graft copolymer or the so called "percent add-on"was computed from the weight difference between the graft copolymer and the insoluble starch which was removed by acid hydrolysis.

4.3 Determination of Percent Conversion

The experimental procedures described in Sections 1 through 2 were carried out. The weight of the graft copolymer along with homopolymer was regarded as the total amount of polymer obtained from the weight of monomer charged. Percent conversion was subsequently calculated.

4.4 Determination of Homopolymer Formation

The weight obtained from Section 3 was the amount of polyacrylonitrile produced as a by-product.

4.5 Determination of Grafting Efficiency

The experimental procedures of Sections 2 through 3, which gave the weight difference between the total weight of polymer and the weight of homopolymer produced were carried out to determine percentage grafting efficiency.

4.6 Determination of the Viscosity Average Molecular Weight (M_v)

The intrinsic viscosity of the grafted polyacrylonitrile was determined in DMF solution using a Cannon-Fenske viscometer No 100 at 35°C. The viscosity-average molecular weight was calculated from the Mark-Houwink equation

$$[\eta] = kM_v^a \qquad (3.1)$$

$$k = 2.78 \times 10^{-4} \text{ dl/g and } a = 0.76$$

4.7 Determination of Grafting Frequency (AGU/chain)

The average number of AGU units, separating each grafted branch, obtained from the experimental procedures of Sections 4.2 and 4.6 was calculated, based on the data of percentage add-on and the viscosity average molecular weight of the graft copolymer.

4.8 Determination of Grafting Ratio

The experimental procedure of Section 4.2 giving the weight of the polymer in grafts and the weight of substrate was regarded as the percentage grafting ratio.

5. Water Absoption/Retention Capacities of the Copolymer

5.1 In Deionized Distillated Water

One hundred gram of deionized, distilled water was added to 0.1 g of dried and saponified starch-g-polyacrylonitrile in a 150 ml glass beaker and allowed to stand for 30 minutes for swelling. The fully swollen polymer was filtered through a 100-mesh aluminium screen for 3 hours and the drained water was weighed. The amount of water retained by the starch-g-polyacrylonitrile was calculated as in gram per gram of the dry modified starch.

5.2 In Sodium Chloride and Magnesium Chloride Solutions

The same experimental procedure as described in Section 5.1 was carried out, except that a series of sodium chloride and magnesium chloride solutions of 0.1, 0.5, 1.0, and 2.0% w/v was used instead of deionized, distilled water.

5.3 In Ammonium Chloride, Dibasic Ammonium Phosphate, Potassium Chloride, tri-Potassium Phosphate-tri-hydrate Solutions, and simulated urine

The same experimental procedure as described in Section 5.1 was carried out, except that a series of ammonium chloride, dibasic ammonium phosphate, potassium chloride, and tri-potassium phosphate-tri-hydrate solutions of 0.9% w/w and simulated urine solution (0.64g $CaCl_2$, 1.14 g $MgSO_4.7H_2O$, 8.20g NaCl, 20.0g urea and 1,000g deionized water (29)) was used instead of deionized, distilled water.

5.4 In Sand Alone and Sand with Saponified Starch-g-Polyacrylonitrile.

The sand of particle size larger than 100 mesh was mixed with the dried and saponified starch-g-PAN at concentrations of 0.5, 1.0, 2.0, and 3.0 % w/w. A 20 g of sand was placed in a 250 ml glass beaker. A 150 ml deionized distilled water was then poured over the above mentioned sand. The sand was then allowed to stand for 30 minutes. The mixture was filtered through a 100 mesh aluminium screen for 3 hours and the drained water was weighed. The water remained from the drained water was calculated.

6. Water Absorption Rate of the Copolymer

The saponified starch-g-PAN before precipitating with methanol was added with the various amounts of aluminium trichloride hexahydrate of 1.5, 0.75, 0.25, and 0 g for comparison of the water absorption rate of the copolymer. The mixture was mixed together for approximately 30 minutes. The product was isolated by precipitation with methanol, filtered and washed thoroughly with methanol until pH 7 was reached. The resulting product was divided into two approximately equal portions. The first portion was dried in 65°C oven for 24 hours and the second portion was freeze dried to remove any residual methanol. The dried product was ground into a powder form for determining the water absorption rate and the water absorption capacity in deionized distilled water.

The equipment for finding water absorption rate was composed of 100-mesh aluminium screen in a funnel that was connected with a graduated buret through a rubber tube. The level of aluminium screen and that of the buret at zero scale were the same. The deionized, distilled water was filled into the buret until the water level was at zero scale. We found that the aluminium screen was thoroughly wet. Then 0.1 g of dried, saponified product was dropped onto the wet aluminium screen and then it swelled immediately. The time required for 0.1 g of the product to fully wet, regarded as the wicking time, was recorded. The amount of water which lessened from the zero level of the buret expressed in gram of water per gram of the product within a specified time needed was the water absorption rate.