CHAPTER III

EXPERIMENTAL

3.1 Chemicals, Equipment and Glasswares

3.1.1 Chemicals

Cassava starch was obtained from Thai Wah Co. Ltd. It was produced from tapioca cultivated in summer. It contains 12.80 % moisture, 0.07 % ash, 32.57 ppm. SO_2, pH value of 5.80 and viscosity at 66-70°C of 780 BU.

Acrylonitrile, AN, (98% pure) was provided by Siam Resin & Chemical Co.Ltd. It was purified by fractional distillation at atmospheric pressure through a 14-inch vigreux column and stored in the refrigerator under nitrogen gas.

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

Potassium hydroxide, B.P. grade, from Carlo Erba.

Other chemicals, shown below which were of analytical grade, listed in Table 3.1, 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
Sulphuric acid (H_2SO_4)	Merck
Sodium Chloride (NaCl)	Carlo Erba

3.1.2 Equipment and Glasswares

4-necked round bottom flask, 3-necked round bottom flask, hot plate and magnetic stirrer, mechanical stirrer, heating mantle, water bath circulator, reactor, cobalt-60 source(Gammacel 650 units from Atomic Energy of Canada Co. Ltd.), analytical balance, beakers, mortar and pestle, filtering system, and other general laboratory glasswares and equipment.

3.2 Procedure

It should be mentioned before hand that all the experiments followed below were carried out at least twice in order that accuracy of each method was confirmed.

3.2.1 Gelatinization of Cassava Starch

Into a 1,000 ml 3-necked round bottom flask, 10g of cassava starch was mixed with 200 ml of distilled water. The system was heated at around 85°±3°C for one hour under the nitrogen atmosphere to form a paste-like slurry.

3.2.2 Grafting of Acrylonitrile onto Cassava Starch

Gamma radiation was used to induce graft copolymerization of acrylonitrile onto cassava starch. Two techniques: simultaneous irradiation, and preirradiation of cassava starch were employed.

3.2.2.1 Simultaneous Irradiation Technique

The gelatinized starch was then cooled to about 35°C. Two portions of 5 ml acrylonitrile were added into gelatinized starch. The mixture was stirred under nitrogen atmosphere at room temperature for 20 minutes. The gelatinized starch-acrylonitrile mixture was then under gamma irradiation. Reaction temperature was controlled at about 30°C by a water-bath circulator. The reaction product was isolated by filtration, washed with water and ethanol, and vacuum dried at 65°C for 24 hours.

3.2.2.1.1 Reduction of Homopolymer

Various amounts of cupric sulphate of 0.2, 1.0, 2.0, and 4.0 g were added to each of the mixture of gelatinized starch-acrylonitrile. The mixture was then irradiated by gamma radiation. Dose rate at the center of the chamber of the unit was 56.2 gray/min and total dose was 5.058 kgy. The reaction products were measured for the quantity of the homopolymer, PAN.

Likewise, lead nitrate and aluminium nitrate were mixed separately with the gelatinized starch-acrylonitrile mixture by repeating the above experimental methods.

With another set of the gelatinized starch-AN mixture, a piece of aluminium foil was inserted in the reactor to cover its inner wall of the reaction vessel to observe the effect of the vessel material on graft copolymerization.

3.2.2.1.2 Effect of Total Dose (kgy) on Graft Copolymerization.

At a fixed dose rate of 56.2 gray/min, various quantities of total dose of 1.686, 2.529, 3.372, 4.215, 5.058, 5.901, 6.744, and 8.430 kgy of gamma ray irradiated to the mixture of the gelatinized starch-acrylonitrile as described in Section 3.2.2.1. Stability of the dose rate of this source was frequently checked by Fricke dosimetry method and nylon thin film as the secondary dosimeter (appendix A). The reaction steps were repeated as mentioned in Section 3.2.2.1. 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.

3.2.2.1.3 Effect of Dose Rate on Graft Copolymerization.

The total dose obtained would be used for further investigations. Various quantities of the dose rate of 11.09, 14.33, 18.80, 22.10, 26.50, 32.80, 41.40, 56.20, and 87.60 gray/min obtained from the souce were used to irradiate the mixture of gelatinized starch-acrylonitrile as described in Section 3.2.2.1. Total dose at the center of the chamber was obtained from the optimum total dose in Section 3.2.2.1.1. The dried samples were inspected with the IR spectrometer and the corresponding water absorption capacity was carried out for the study on dose rate effectiveness.

Likewise, the appropriate dose rate at which the water absorption capacity was maximum would be used for the subsequent experiments.

3.2.2.1.4 Effect of Starch(g)/AN(ml) Ratios on Graft Copolymerization

Various amounts of AN of 5, 10, 15, 20, 25, 30, 35, and 40 ml were added to each of the

10 g of cool gelatinized starch. The reaction mixture was stirred mechanically for 20 minutes. Irradiations were carried out at the optimum total dose obtained from Section 3.2.2.1.2 and the optimum dose rate obtained from Section 3.2.2.1.3. The dried samples were inspected with the IR spectrometer and water absorption capacity was then determined.

3.2.2.2 Preirradiation Technique

3.2.2.2.1 Effect of Total Dose (kgy) on Graft Copolymerization.

Equal amount of the cool gelatinized starch was each irradiated by the gamma rays at a fixed dose rate at the center of the chamber of 56.2 gray/min to various quantities of total dose of 1.686, 2.529, 3.372, 4.215, 5.058, 5. 901, 6.744, and 8.430 kgy. The temperature of reaction was at about 30°C. After the irradiation, a fixed amount of acrylonitrile was immediately added to each sample of the induced the preirradiated gelatinized starch which still contained radiation induced free radicals. The reaction mixture was stirred mechanically for 2 hours under nitrogen atmosphere. The reaction product was subsequently precipitated with methanol, filtered, and washed with methanol again before being dried at 65°C for 24 hours.

The dried samples were investigated for its water absorption capacity. The maximum water absorption capacity produced by the particular total dose indicated the appropriate total dose for this system.

3.2.2.2.2 Effect of Dose Rate on Graft Copolymerization.

At a fixed total dose obtained from Section 3.2.2.2.1, various quantities of the dose rate of 11.09, 14.33, 18.08, 22.10, 26.50, 32.80, 41.40, 56.20, and 87.60 gray/min obtained from the source were used to irradiate the cool gelatinized starch. After the irradiation, AN was immediately added to the preirradiated gelatinized starch. The reaction mixture was stirred mechanically for 2 hours under nitrogen atmosphere. The reaction product was subsequently precipitated with methanol, filtered, and washed with methanol again before being dried at 65°C for 24 hours. The maximum water absorption capacity of dried graft copolymer produced by the particular dose rate indicate the appropriate dose rate.

3.2.2.2.3 Effect of Starch(g)/AN(ml) Ratios on Graft Copolymerizatrion

The cool gelatinized starch was irradiated by the gamma rays at a fixed total dose obtained from Section 3.2.2.2.1 and a fixed dose rate obtained from Section 3.2.2.2.2. The temperature of reaction was at about 30°C. After the irradiation, Acrylonitrile was immediately added to the preirradiated gelatinized starch. The reaction product was then characterized as described in Section 3.2.2.2.2. The maximum water absorption capacity produced by the particular amount of AN at a fixed quantity of starch indicated the appropriate starch(g)/ acrylonitrile (ml) ratio.

3.2.3 Homopolymer Extraction by N,N-Dimethylformamide

In a 500-ml erlenmeyer flask, 5.0 g of dried starch-g-polyacrylonitrile, ground into a powder form, was stirred in 250 ml of 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 IR spectrometer.

3.2.4 Copolymer Characterization

3.2.4.1 Soponification of Starch-g-PAN

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

3.2.4.2 Determination of Per Cent Add-On

In a 500 ml 3-necked round bottom flask equiped with a condenser, 4.00 g of the DMF extracted polymer was stirred in 400 ml of 2 M H_2SO_4 and the mixture was refluxed for 90 minutes. Filtered the water-insoluble polymer, then washed until pH of the washed solution was 7, and then dried. The weighed percentage polyacrylonitrile in the graft copolymer or so called "percentage add-on" was computed from the weight difference between the graft copolymer and the insoluble starch which was removed by acid hydrolysis.

3.2.4.3 Determination of Per Cent Conversion

The experimental procedures described in Sections 3.2.1 through 3.2.2 were carried out. The weight of the graft copolymer and homopolymer was regarded as the total amount of polymer obtained from the weight of monomer charged.

3.2.4.4 Determination of Homopolymer Formation

The weight obtained from Section 3.2.2

was the amount of polyacrylonitrile produced as a by-product.

3.2.4.5 Determination of Grafting Efficiency

The experimental procedures of Sections 3.2.2 through 3.2.3, which gave the weight difference between the total weight of polymer and the weight of homopolymer produced were regarded as percentage grafting efficiency.

3.2.4.6 Determination of the Viscosity Average Molecular Weight ($\bar{M}_v$)

The intrinsic viscosity of the grafted polyacrylonitrile was determined in DMF solution using a Cannon-Fenske viscometer No 100. The molecular weight was culculated using the following equation.

$$[\eta] = 3.92 \times 10^{-4} \bar{M}_v^{0.75} \qquad 2.1$$

3.2.4.7 Determination of Grafting Frequency (AGU/chain)

The average number of AGU units, separating each grafted branch, obtained from the experimental procedures of Sections 3.2.4.2 and 3.2.4.6 was calculated, based on the data of percentage add-on and the viscosity average molecular weight of the graft copolymer.

3.2.4.8 Determination of Grafting Ratio

The experimental procedure of Section 3.2.4.2 giving the weight of the polymer in grafts and the weight of substrate was regarded as the percentage grafting ratio.

3.3 Water Absorption/Retention Capacities of the Copolymer

3.3.1 In Deionized Distillated Water

A 150 g of deionized distilled water was added to 0.1 g of dried and saponified starch-g-polyacrylonitrile in a 250-ml glass beaker and allowed to stand for 30 minutes. 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 dry modified starch.

3.3.2 In Sodium Chloride and Magnesium Chloride Solution

The same experimental procedure as described in Section 3.3.1 was carried out, except 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 distillated water.

3.3.3 In Ammonium Chloride, Dibasic Ammonium Phosphate, Potassium Chloride, and tri-Potassium Phosphate tri-hydrate Solutions.

The same experimental procedures as described in Sections 3.3.1 and 3.3.2 were carried out, except a series of ammonium chloride, dibasic ammonium phosphate, potassium chloride and tri-potassium phosphate tri-hydrate solutions of 0.9 % w/w was used instead of deionized distillated water.

3.3.4 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 alone was placed in a 250-ml glass beaker. A 150 ml deionized distillated 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 hour and the drained water was weighed. Calculated the water remained from the drained water.

Likewise, 0.5, 1.0, 2.0, and 3.0 % w/w of saponified starch-g-polyacrylonitrile were mixed with the sand by repeating the above experiments.