CHAPTER III

EXPERIMENTAL

3.1 Chemicals, Equipment and Glassware

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.

Acrylic acid, AA, was provided by Siam Resin & Chemical Co.Ltd. Acrylic acid is a clear, colorless liquid. The molecular weight is 72.06. The melting and boiling points are 14°C and 141°C, respectively. The heat of vaporization is 435 J/g and the heat of polymerization is 76.99 kJ/mol (1.08 kJ/g) (74). Acrylic acid is stabilized with minimum amounts of inhibitors consistent with stability and safty. The monomethyl ether of hydroquinone (MEHQ) is frequently used as an inhibitor (75). MEHQ level of 200 ppm is generally needed for acrylic acid. For most applications, inhibitors do not have to be removed. The low-inhibitor grade of acrylic monomer is particularly suitable for the manufacture of polymers without pretreatment. Removal of inhibitor is best done by adsorption with ion

exchange resins or other adsorbents. Acrylic acid poly-merizes very easily. The polymerization is catalyzed by heat, light, and peroxides. The highly exothermic, spon-taneous polymerization of acrylic acid is extremely violent.
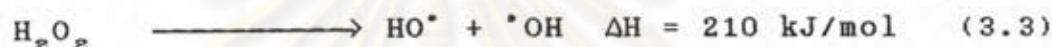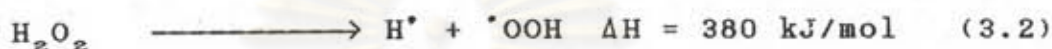
Methanol, commercial grade from BDH, was also purified by fractional distillation at atmospheric pressure.

Hydrogen peroxide (H_2O_2) 35%, analytical grade, from Merck. The relative densities of this H_2O_2 solution at 0, 20, and 25°C are 1.441, 1.1312, and 1.1282 g/cm^3, respectively. The molecular weight of hydrogen peroxide is 34.02. The heat of vaporization at 25°C is 1,519 J g^{-1} K^{-1}. The decomposition of H_2O_2 occurs with disproportionation, as shown in equation 3.1 (76). The heat of decomposition is 98.3 kJ/mol (23.47 kcal/mol).

$$H_2O_2 \ (l) \longrightarrow H_2O \ (l) + 1/2 \ O_2 \ (g) \tag{3.1}$$
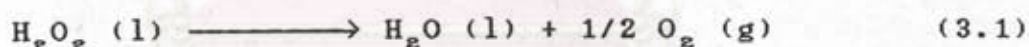
This reaction is extremely important in handling during storage and in the laboratory. This reaction is highly exothermic and takes place in the presence of small amount of catalyst even in aqueous solution. In the absence of catalyst, it occurs only in the gas phase at high tempera-ture. The decomposition can be catalyzed both homogeneously by dissolved ions (especially of the heavy metals) and heterogeneously by suspended oxides and hydroxides. In addition, agitation or contact with rough surfaces or many other substances accelerates decomposition. The decomposi-

tion also proceeds at a rate that increases approximately 2.2 times for each 10 degree rise in temperature over the range of 20-100°C (77). Hydrogen peroxide can form free radicals by homolytic cleavage of either an O-H bond or an O-O bond, as shown in equations 3.2 and 3.3, respectively.

$$H_2O_2 \longrightarrow H^\bullet + {}^\bullet OOH \quad \Delta H = 380 \text{ kJ/mol} \quad (3.2)$$

$$H_2O_2 \longrightarrow HO^\bullet + {}^\bullet OH \quad \Delta H = 210 \text{ kJ/mol} \quad (3.3)$$

Equation 3.3 predominates in uncatalyzed vapor-phase decomposition and photochemically initiated reactions. In catalytic reactions, especially in solution, the nature of the reactants determines which reaction is predominant. Hydrogen peroxide is a strong oxidant and most of its uses depend on this property. It oxidizes a variety of organic and inorganic compounds.

L(+) Ascorbic acid, B.P. grade, from Carlo Erba. Ascorbic acid is a white, odorless, crystalline solid with a sharp acidic taste. The molecular weight is 176.13. The degradation of Ascorbic acid in aqueous solution depends on many factors, e.g., pH, temperature, presence or absence of oxygen, likewise, of metals. In aqueous solution, it is more sensitive to alkalies than to acids; it is most stable at pH 4-6. Ascorbic acid is sensitive to heat, and in the presence of oxygen and heat, it is oxidized at a rate

proportional to the temperature rise (78).

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
Calcium oxide	Merck
Ammonium chloride (NH_4Cl)	Merck
Ammonium phosphate dibasic	Carlo Erba
(($NH_4)_2HPO_4$)	
Magnesium chloride hexa-hydrate	Carlo Erba
($MgCl_2.6H_2O$)	
Potassium chloride (KCl)	Merck
tri-Potassium phosphate tri-	Merck
hydrate ($K_3PO_4.3H_2O$)	
Sulphuric acid (H_2SO_4)	Merck
Sodium chloride (NaCl)	Carlo Erba
Sodium nitrate ($NaNO_3$)	Carlo Erba
Hydrochloric acid (HCl)	Merck

3.1.2 Equipment and Glassware

4-necked round bottom flask, 3-necked round bottom flask, hot plate and magnetic stirrer, mechanical stirrer, heating mantle, water bath circulator, analytical balance, beakers, mortar and pestle, filtering system, and other general laboratory glassware and equipment.

3.2 Procedure

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

3.2.1 Gelatinization of Cassava Starch

30 g Cassava starch was mixed with 300 cm^3 of distilled water in a 1,000 cm^3 4-necked round bottom flask. The system was stirred mechanically at 400 rpm under heating within the range of $80°\pm2°C$ for one hour under the nitrogen atmosphere to form a slurry.

3.2.2 Grafting of Acrylic acid onto Cassava Starch

The gelatinized starch was then cooled to 35°C. 0.5 g Calcium oxide, 0.004 M ascorbic acid , 2 cm^3 (0.055 M) hydrogen peroxide 35%, and 30 cm^3 acrylic acid monomer were added in the reaction. The reaction mixture was stirred mechanically at 600 rpm under heating within the temperature of 35 ± 2 °C under nitrogen atmosphere for 3 hours.

3.2.3   Saponification of starch-g-polyacrylic acid

250 cm^3 of a 25% potassium hydroxide solution was added to the starch-g-poly(acrylic acid) slurry. The mixture was stirred mechanically and the saponification was carried out at room temperature for 1 hour. One could observe an exothermic heat developed during the reaction. It was then allowed to cool to room temperature and was 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.

3.3. Influencing Variables

3.3.1   Effect of Starch (g)/Acrylic Acid (cm^3) Ratios on Graft Copolymerization

All other variables were fixed except acylic acid monomer. Various amounts of acrylic acid of 30, 45, 60, 75, and 90 cm^3 (1.47, 2.21, 2.95, 3.68, and 4.42 M) were added to each of the gelatinized starch. The reaction steps were repeated as mentioned in Sections 3.2.1, 3.2.2, and 3.2.3

The reaction products were then characterized as described in Sections 3.4.1, 3.4.2 and investigated their water absorption capacity. The maximum water absorp-

tion capacity produced by the particular amount of acrylic acid at a fixed quantity of starch indicated the appropriate starch (g)/ acrylic acid (M) ratio.

The starch/acrylic acid ratio at which the water absorption capacity was maximum would be used for the subsequent experiments.

3.3.2 Effect of Hydrogen Peroxide Concentration on Graft Copolymerization

All other variables were fixed except hydrogen peroxide initiator. Various amounts of hydrogen peroxide of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 cm^3 (0.0553, 0.1107, 0.1661, 0.2217, 0.2768, and 0.3322 M, respectively) were added to each of the gelatinized starch. The reaction steps were repeated as mentioned in Sections 3.2.1, 3.2.2 and 3.2.3

The reaction products were then characterized as descriped in Sections 3.4.1 and 3.4.2 and investigation of their water absorption capacity was carried out. The maximum water absorption capacity of the hydrolyzed starch-g-poly(acrylic acid) copolymer indicated the appropriate hydrogen peroxide concentration.

3.3.3 Effect of Reaction Temperature on Graft Copolymerization

In this experiment, the temperature of the grafting raction was understudied as a variable. Various levels of temperature were 45, 55, and 65°C. The reaction

steps were repeated as mentioned in Sections 3.2.1, 3.2.2 and 3.2.3.

The reaction products were then characterized as described in Sections 3.4.1 , 3.4.2 and water absorption capacity was investigated. The maximum water absorption capacity of the hydrolyzed starch-g-poly(acrylic acid) copolymer indicated the appropriate reaction temperature.

3.4 Copolymer Characterization

3.4.1 Infrared Spectroscopy

The infrared spectra of cassava starch, and the hydrolyzed starch-g-poly(acrylic acid) copolymers were measured with an FT-IR spectrophotometer (Perkin Elmer Model 1760X) using KBr pellets.

3.4.2 Determination of the Grafted Polymer Molecular Weight

Gel permeation chromatography was performed with a Millipore Waters HPLC-M600E liquid chromatograph, equipped with an Ultrahydrogel linear column (300x78 mm I.D.), a column thermostat, and a differential refractometer detector M-410, at 35°C .

The mobile phase was 0.1 M sodium nitrate solution, at a flow-rate of 0.1 cm^3/min, and was deaerated by an ultrasonic bath. All samples (prepared by the method in

3.4.2.1) were filtered through a 0.45 micron Millipore Millex [R] -HA Filter prior to injection and carefully deaerated in the ultrasonic bath. The injection volume was 100 microliters. The instrument was accurately controlled and data was processed with a Model M-810 Baseline software data station.

The molecular weight calibration curve was determined and constructed with polyethylene oxide standards (TSK SE-2, SE-4 and SE-5, with molecular weights of 24,000, 46,000 and 85,000) of a narrow molecular weight distribution in distilled water. A 100 microliter of 0.1% solution of each standard was injected.

3.4.2.1 Sample Preparation Technique

In a 250 cm^3 round bottom flask equipped with a condensor, the 0.1 g hydrolyzed starch-g-poly(acrylic acid) copolymer was refluxed in 100 cm^3 of 1.0 N HCl solution for 2 hours to separate the grafted poly(acrylic acid) from polysaccharide backbone.

3.5 Water Absorption/Retention Capacities of the Copolymer

3.5.1 In Deionized Distillated Water

A 100 g of deionized distilled water was added to 0.1 g of dried and saponified starch-g-polyacrylic acid in a 250-cm^3 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-poly(acrylic acid) was culculated as in gram per gram of dry modified starch.

3.5.2 In Sodium Chloride and Magnesium Chloride Solutions

The same experimental procedure as described in Sections 3.5.1 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 and distillated water.

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

The same experimental procedures as described in Sections 3.5.1 and 3.5.2 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 and distillated water.

3.5.4   In Sand Alone and Sand with Saponified Starch-g-Poly(acrylic acid) copolymer

The sand of particle size larger than 100 mesh was mixed with the dried and saponified starch-g-Poly(acrylic acid) copolymer 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-cm^3 glass beaker. A 100 cm^3 deionized and 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 hours 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-poly(acrylic acid) were mixed with the sand by repeating the above experiments.