CHAPTER III

EXPERIMENT

3.1 Materials

3.1.1 Cassava Starch

Cassava starch was kindly provided by Thai Wah Co., Ltd. This starch has standard specification as follows: 13% maximum moisture content, 0.20% maximum ash, 0.20% maximum pulp, pH value of 4.00-7.00 and maximum viscosity of 550 Brabender unit. It was dried in an oven at 60°C for 24 hours and kept in a desiccator until use.

3.1.2 Chemicals

Methyl methacrylate monomer (MMA), commercial grade, was kindly provided by Sumipex (Thailand) Co., Ltd. It was kept in a refrigerator at 4°C and was used without further purification.

Benzoyl peroxide (BPO), commercial grade, was purchased from AJAX Chemicals. It was kept in a refrigerator at 4°C and was used without further purification.

Acetone, analytical reagent grade, was purchased from Labscan Asia Co., Ltd. It was used without further purification.

Methanol, analytical reagent grade, was purchased from Labscan Asia Co., Ltd. It was used without further purification.

Hydrochloric acid 37% (HCl), analytical reagent grade, was produced by Labscan Asia Co., Ltd. It was used without further purification.

Tetrahydrofuran, (THF), analytical reagent grade, was produced by Labscan Asia Co., Ltd. It was used without further purification.

Sodium hydroxide (NaOH), pellets grade for analysis, was produced by Merck, Germany. It was used as received.

3.2 Synthesis of PMMA Reference

100 cm^3 of distilled water was poured into a 500 cm^3 four-necked round bottom flask placed in a heating mantle and equipped with a mechanical stirrer, a condenser, a thermometer and a nitrogen inlet. It was stirred at room temperature under nitrogen atmosphere for 10 min. 5 g of MMA monomer was then added into the flask and stirred for 10 min. After that, a solution of 0.1 g of BPO in 10 cm^3 of acetone was then added. The mixture was stirred for another 10 min and then the temperature was increased to 80°C and the reaction was carried out at this temperature for 2 hours. The reaction mixture was then allowed to cool down to room temperature. After that, it was poured into methanol. The precipitate was filtered, washed with excess methanol, dried in an oven at 60°C for 24 hours, and kept in a desiccator. The obtained PMMA was used as a reference for the further characterization.

3.3 Preparation of Graft Copolymers

Preparation process of cassava starch-*g*-PMMA copolymer could be divided into 3 steps, including grafting of MMA onto cassava starch, removal of homoPMMA by solvent extraction and finally, acid hydrolysis of graft copolymer in order to separate grafted PMMA from starch backbone. The diagram of this experimental procedure was shown in Figure 3.1.
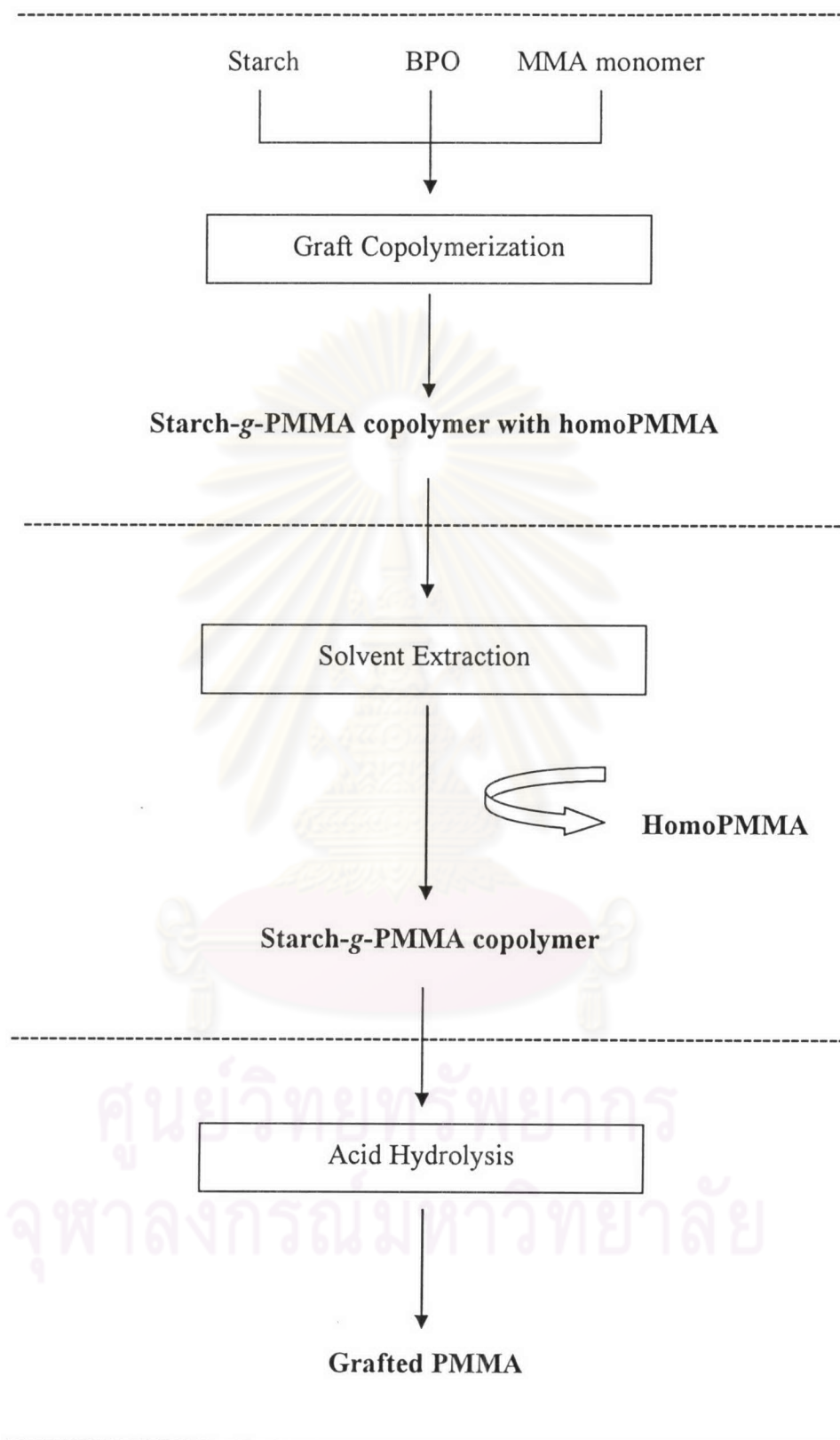
Starch   BPO   MMA monomer

Graft Copolymerization

Starch-*g*-PMMA copolymer with homoPMMA

Solvent Extraction

HomoPMMA

Starch-*g*-PMMA copolymer

Acid Hydrolysis

Grafted PMMA

Figure 3.1 Preparation process of cassava starch-g-PMMA

3.3.1 Graft Copolymerization [37]

90 cm^3 of distilled water was poured into a 500 cm^3 four-necked round bottom flask placed in a heating mantle and equipped with a mechanical stirrer, a condenser, a thermometer and a nitrogen inlet, as shown in Figure 3.2. It was stirred at room temperature under nitrogen atmosphere for 10 min. Cassava starch was then added into the flask and stirred for 30 min. A solution of BPO in 10 cm^3 of acetone and 5 cm^3 of distilled water were respectively added to the starch slurry. After continuously stirring the mixture for 10 min, MMA monomer and 5 cm^3 of distilled water were added respectively, and the mixture was stirred for another 10 min. It was then heated up to 80°C and the reaction was carried out at this temperature throughout the reaction time. After the reaction finished, the mixture was poured into excess methanol. The precipitate was filtered, washed with methanol, dried in an oven at 60°C for 24 hours, and kept in a desiccator.
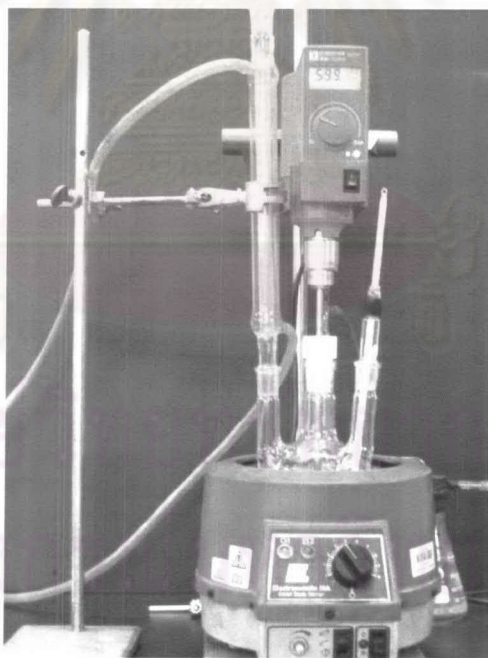
Figure 3.2 Graft copolymerization apparatus

3.3.2 Solvent Extraction of HomoPMMA

The total dried product was ground and put in the thimble which was then weighed. This weight was identified as the weight before in equation 3.1. After that, the thimble containing dried product was inserted into Soxhlet extractor (Figure 3.3). 300 cm^3 of acetone, used as the solvent for extracting homoPMMA from the crude product, was poured into a 500 cm^3 round bottom flask equipped with Soxhlet extractor and a condenser. It was heated up to 70°C for 10 hours. Then the thimble was removed from Soxhlet extractor, dried in oven at 60°C for 24 hours and then kept in a desiccator. After its temperature reaching room temperature, the dried thimble was weighed and this weight was identified as the weight after in equation 3.1. The weight of homoPMMA was calculated as shown in the following equation:

$$\text{weight of homoPMMA} = \text{the weight after} - \text{the weight before} \qquad (3.1)$$

Figure 3.3 Soxhlet extraction apparatus

3.3.3 Acid Hydrolysis of Graft Copolymer

In a 250 cm^3 Erlenmeyer flask equipped with a condenser (Figure 3.4), starch-*g*-PMMA copolymer was weighed and stirred in 200 cm^3 of 3 N HCl. The mixture was refluxed for 2 hours. The water-insoluble polymer was filtered and washed with distilled water until its pH was approximately 7. Then it was dried in an oven at 60°C for 24 hours. The product was allowed to cool to room temperature before weighing.
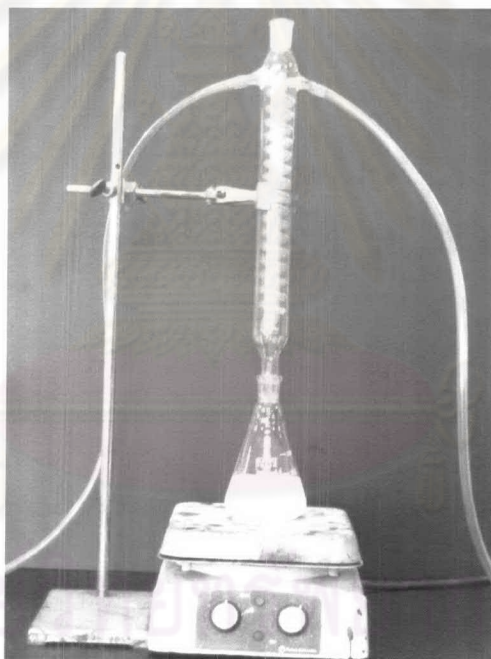
Figure 3.4 Acid hydrolysis apparatus

3.4 Investigation of the Effects of Reaction Parameters

In order to determine the optimum conditions for this graft copolymerization system, the reaction parameters including the amount of BPO, the amounts of cassava starch and MMA monomer and the reaction time were varied.

3.4.1 Amount of Initiator

As described earlier in Chapter I and II that BPO was used as an initiator for this research. It was used in the form of solution by dissolving in 10 cm^3 of acetone. The amount of BPO used were 0.01, 0.1, and 1.0 g, respectively.

3.4.2 Amounts of Reactants

The effects of the amounts of the reactants on grafting characteristics of the graft copolymers were investigated in three cases as follows:

a.) The amounts of two reactants were equal. In this case, 5 g of cassava starch and 5 g of MMA monomer were applied.

b.) The amount of MMA monomer was higher than that of cassava starch. In this case, 2.5 g of cassava starch and 7.5 g of MMA monomer were applied.

c.) The amount of cassava starch was higher than that of MMA monomer. In this case, 7.5 g of cassava starch and 2.5 g of MMA monomer were applied.

3.4.3 Reaction Time

The reaction times were varied from 1, 2, 3, 4, to 5 hours.

3.5 Determination of Grafting Characteristics [8,12,37]

The definitions and the calculations of 6 grafting characteristics determined in this research were present below.

3.5.1 Percent Yield

Percent yield is a representation of an ability of raw materials to form all products that obtained from the reaction. It can be calculated by the following equation:

$$\% \text{ yield} = \frac{\text{weight of starch - } g \text{ - PMMA copolymer with homoPMMA}}{\text{weight of starch} + \text{weight of BPO} + \text{weight of MMA monomer}} \times 100 \quad (3.2)$$

3.5.2 Percent Monomer Conversion

It is used to describe the degree of polymerization of the monomer, which gives graft copolymer and homopolymer. It can be evaluated by the following equation:

$$\% \text{ conversion} = \frac{\text{weight of homoPMMA} + \text{weight of grafted PMMA}}{\text{weight of MMA monomer}} \times 100 \quad (3.3)$$

3.5.3 Percent Homopolymer Formation

It is used to describe the percent of homopolymer formed which is related to grafting efficiency. It can be calculated as:

$$\% \text{ homopolymer formation} = \frac{\text{weight of homoPMMA}}{\text{weight of grafted PMMA} + \text{weight of homoPMMA}} \times 100$$

$$(3.4)$$

3.5.4 Percent Grafting Efficiency

It is defined as the percentage of total synthetic grafted polymer. High grafting efficiency indicates that the formation of grafted polymer is more preferable than the formation of homopolymer. It can be calculated as:

$$\% \text{ grafting efficiency} = \frac{\text{weight of grafted PMMA}}{\text{weight of grafted PMMA} + \text{weight of homoPMMA}} \times 100 \quad (3.5)$$

3.5.5 Percent Grafting Ratio

It is defined as the percentage of the polymer grafted onto starch with respect to the starch. It can be calculated by the following equation:

$$\% \text{ grafting ratio} = \frac{\text{weight of grafted PMMA}}{\text{weight of starch}} \times 100 \quad (3.6)$$

3.5.6 Percent Add-on

It is referred to the weight percent of synthetic polymer in the pure graft copolymer and it can be determined as follows:

$$\% \text{ add-on} = \frac{\text{weight of grafted PMMA}}{\text{weight of starch-}g\text{-PMMA copolymer}} \times 100 \quad (3.7)$$

3.6 Characterizations of the Graft Copolymers and Their Components

3.6.1 Chemical Structural Analysis

Fourier transform infrared (FT-IR) spectroscopy was performed using a Nicolet Impact 400D Spectrophotometer to characterize chemical structures of the samples. The dried powder samples were mixed with KBr and pressed into the disc form by the hydraulic compression. The samples were scanned at the frequency range of 4000-400 cm^{-1} with 32 consecutive scans and 4 cm^{-1} resolution.

Figure 3.5 Fourier transform infrared spectrophotometer

3.6.2 Molecular Weight Determination

The molecular weight determination was carried out by gel permeation chromatography (GPC) using Waters 150-CV gel permeation chromatograph. The measurements were made using a refractive index detector and a pair column packing with PL gel. PL is a highly crosslinked spherical polystyrene/divinylbenzene gel matrix having molecular weight resolving range as 500-10,000,000. The analytical reagent

grade THF was used as eluent at a flow rate of 1.0 cm^3/min. The operating temperature was 30°C.

The GPC samples were prepared by dissolving PMMA reference, homoPMMA and grafted PMMA in analytical reagent grade THF. 100 µl of the sample solution was injected into GPC for analysis. The molecular weights of samples were obtained by using polystyrene standards calibration, having molecular weights of 5460-1,290,000. The grafting frequency, i.e. AGU/graft, was calculated from the following equation [42]:

$$\text{Grafting frequency} = \frac{(100 - \% \text{ add - on}) \ /162}{\% \text{ add - on} \ / \text{ MW graft}} \tag{3.8}$$

Where AGU/graft is the number of anhydroglucopyranose (formula weight 162) units per grafting point.

Figure 3.6 Gel permeation chromatograph

3.6.3 Morphological Study

Jeol JSM-5410 LV scanning electron microscope (SEM) was used to observe the sample morphology. Prior to test, the sample was dried in an oven at 60°C for 24 hours and kept in a desiccator. Then the sample was mounted on the stub with double sticky tape. The sample was then coated with a thin evaporated layer of gold in order to improve conductivity and prevent electron charging on the surface. The SEM was operated at 15 kV.
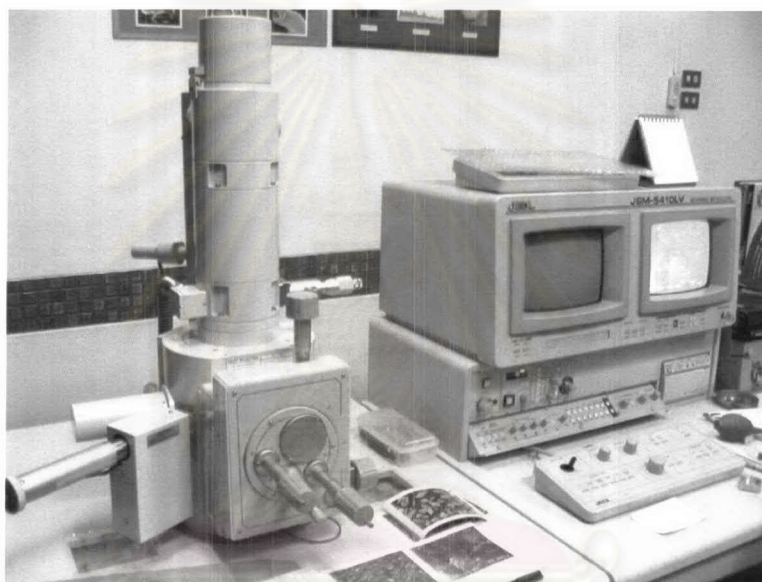
Figure 3.7 Scanning electron microscope