

# CHAPTER III

## EXPERIMENTAL

### 3.1 Chemicals

- 1) Acrylamide, (AM) (99% pure) from Siam Resin & Chemical Co., Ltd.

$C_3H_5NO$ , clear, colorless solid, m.p.  $84.5^\circ C$ , b.p.  $87^\circ C$  (2 mmHg)

$M = 71.08 \text{ g mol}^{-1}$

- 2) Itaconic acid, (IA) analytical grade from Merck (Buchs, Switzerland)

$C_4H_6O_2$ , clear, colorless solid,  $M = 86.09 \text{ g mol}^{-1}$

- 3) Ammonium persulphate, (APS) analytical grade from Merck

(Hohenbrunn, Germany),  $(NH_4)_2S_2O_8$ , solid,  $M = 228.2 \text{ g mol}^{-1}$

- 4) *N,N'*-methylenebisacrylamide, (N-MBA) analytical grade from Fluka

(Buchs, Switzerland),  $C_7H_{10}N_2O_2$ , solid,  $M = 154.17 \text{ g mol}^{-1}$

- 5) *N,N,N',N'*-tetramethylethylenediamine, (TEMED) analytical grade from

Sigma-Aldrich (St. Louis, U.S.A.)

$(CH_3)_2NCH_2CH_2N(CH_3)_2$ , liquid,  $M = 116.21 \text{ g mol}^{-1}$ ,  $D = 0.775 \text{ g cm}^{-3}$

- 6) Mica (Wako Pure Chemical Industries, Osaka, Japan), the average particle

size =  $3 \mu m$

- 7) Methyl alcohol, BDH (Bangkok, Thailand)  
 $\text{CH}_3\text{OH}$ , liquid, b.p. 64-65°C,  $M = 32.04 \text{ g mol}^{-1}$ ,  $D = 0.791 \text{ g cm}^{-3}$
  
- 8) Sodium chloride, analytical grade from Ajax Finechem (New South Wales, Australia),  $\text{NaCl}$ , Solid,  $M = 58.44 \text{ g mol}^{-1}$
  
- 9) Potassium chloride, analytical grade from APS Finechem (New South Wales, Australia),  $\text{KCl}$ , Solid,  $M = 74.55 \text{ g mol}^{-1}$
  
- 10) Sodium citrate, analytical grade from J.T. Baker (U.S.A.)  
 $\text{HOC}(\text{COONa})(\text{CH}_2\text{COONa})_2 \cdot 2\text{H}_2\text{O}$ , Solid,  $M = 294.10 \text{ g mol}^{-1}$
  
- 11) Sodium sulphate, analytical grade from Ajax Finechem  
(New South Wales, Australia),  $\text{Na}_2\text{SO}_4$ , Solid,  $M = 142.04 \text{ g mol}^{-1}$
  
- 12) Magnesium sulphate, analytical grade from Unilab (Auburn, Australia)  
 $\text{MgSO}_4$ , Solid,  $M = 156.40 \text{ g mol}^{-1}$
  
- 13) Sodium dihydrogenphosphate, analytical grade from Ajax Finechem  
(New South Wales, Australia),  $\text{NaH}_2\text{PO}_4$ , Solid,  $M = 156.01 \text{ g mol}^{-1}$
  
- 14) Potassium Bromide, analytical grade from APS Finechem (New South Wales, Australia),  $\text{KBr}$ , Solid,  $M = 119.00 \text{ g mol}^{-1}$

- 15) Sodium thiosulphate, analytical grade from Ajax Finechem (New South Wales, Australia),  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , Solid,  $M = 248.18 \text{ g mol}^{-1}$
- 16) Dimethyl phthalate, analytical grade from Across Organics (New Jersey, U.S.A.),  $\text{C}_{10}\text{H}_{10}\text{O}_4$ , colorless liquid,  $D = 1.190 \text{ g/cm}^3$ ,  
 $M = 194.19 \text{ g mol}^{-1}$
- 17) Ethyl acetate, analytical grade from Ajax (Seven Hills, Australia)  
 $\text{C}_4\text{H}_8\text{O}_2$ , liquid,  $M = 88.11 \text{ g mol}^{-1}$
- 18) n-Heptane, analytical grade from J.T.Baker (New Jersey, U.S.A.)  
 $\text{C}_7\text{H}_{16}$ , colorless liquid, b.p.  $96.0^\circ\text{C}$ ,  $D = 0.684 \text{ g/cm}^3$

### 3.2 Glassware

- a) Four-necked round bottomed flask,  $500\text{-cm}^3$
- b) Spiral condenser
- c) Thermometer
- d) Volumetric flask
- e) Other general laboratory glassware
- f) Other general laboratory glassware and equipment: flat bottomed flask, steel wire filtering with 100-mesh aluminium screen, reduced pressure filtering system, four-necked round-bottomed flask, dessicator, porcelain crucible 100 ml.

### 3.3 Equipment

- |   |  |
|---|--|
| a) Flow meter                                     | : Cole Parmer, Illinois, U.S.A.                              |
| b) Stirring type                                  | : Semicircular Teflon Paddle                                 |
| c) Water Bath                                     | : Mammert W 350, Swabach<br>Germany                          |
| d) Oven   | : D7200, Tuttlingen, Germany                                 |
| e) Scanning Electron Microscope (SEM)             | : JOEL JSM-T 220, Tohoku, Japan                              |
| f) Fourier Transform Infrared Spectrometer (FTIR) | : Nicolet Impact 410, Madison,<br>U.S.A.                     |
| f) Transmission Electron Microscopy (TEM)         | : JOEL JEM-2100, Japan                                       |
| h) X-ray diffractometer (XRD)                     | : Bruker AXS Model D8 Discover,<br>U.S.A.                    |
| i) Thermal gravimetric analysis (TGA)             | : Mettler Toledo TGA/SDTA 851e<br>Schwerzenbach, Switzerland |
| j) Furnace  | : Carbolite RSF 1600, Sheffield,<br>England                  |
| k) Rheometer                                      | : ARES Rheometric Scientific, U.S.A.                         |
| l) Pycnometer                                     | : Brand, Germany   |

### 3.4 Procedures

#### 3.4.1 Preparation of Poly[Acrylamide-co-(Itaconic acid)]

Copolymerization: A mixture of 60 cm<sup>3</sup> aqueous solution containing AM, IA monomers and mica was placed in a 500 cm<sup>3</sup> four-necked round-bottomed flask. The system was mechanically stirred at 250 rpm under heating within the temperature

range of  $50 \pm 2$  °C. The ingredients were stirred gently by a small-bladed propeller for 5 min. Next, 20 ml of APS aqueous solution was added and stirred for 5 min. Lastly, 0.2 ml (1.2% mole) of the co-initiator (TEMED) was added. The resulting polymer was dewatered with methanol, cut into small pieces in which they have diameter about 0.5 cm, dried at 50°C for 24 h in a vacuum oven to a constant weight and then milled. All polymerization conditions are shown in Table 3.1.

**Table 3.1:** Polymerization conditions of poly(AM-co-IA) copolymer

Ingredients	Amount
Monomer (AM:IA) ratios (%mol)	100:0, 99:1, 98:2, 97:3, 96:4, 95:5
<i>N,N'</i> -methylenebisacrylamide (%mole)*	0.2, 0.5, 0.7, 0.9
Ammonium persulfate (%mole)*	0.3
<i>N,N,N',N'</i> -tetramethylethylenediamine (%mole)*	1.2 (0.2 ml)
Reaction temperature (°C)	40, 50, 60
Agitation speed (rpm)	250
Reaction time (min)	30

\* %mole based on the concentration in the monomer

#### 3.4.1.1 The Effect of Itaconic Acid Concentration

The experimental procedure as described above and the formulation as shown in Table 3.1 was carried out with varying the IA mole percents of 0 to 5. The concentration of the crosslinker was fixed at 0.2 %mole.

#### 3.4.1.2 The Effect of *N,N'*-methylenebisacrylamide Concentration

The ratio of AM/IA was fixed at 99:1, 97:3 and 95:5. The content of crosslinking agent was varied from 0.2 to 0.9 % mole, based on the monomer concentration. The preparation of poly(AM-*co*-IA) and poly(AM-*co*-IA)/mica nanocomposite was carried by following the basic procedure in Section 3.4.1 and other reaction conditions in Table 3.1.

#### 3.4.1.3 The Effect of the Reaction Temperature

The solution of monomers of AM and IA was prepared in three different compositions (AM/IA mole percent ratios at 99/1, 97/3 and 95/5). The concentration of the crosslinking agent (N-MBA), initiator (APS), and co-initiator (TEMED) were fixed at 0.2% mole, 0.3% mole, and 1.2 % mole (0.2 ml), respectively. These solutions were synthesized by varying reaction temperatures at 40, 50, and 60 °C.

### 3.4.2 Preparation of Poly[Acrylamide-*co*-(Itaconic acid)]/mica Superabsorbent Nanocomposites

Copolymerization: A mixture of 60 cm<sup>3</sup> aqueous solution containing AM, IA monomers and mica was placed in a 500 cm<sup>3</sup> four-necked round-bottomed flask. The system was mechanically stirred at 250 rpm under heating within the temperature range of 50±2 °C. The mixture was stirred by a small-bladed propeller for 2 h for intercalation. Then, 20 ml (0.2% mole) of N-MBA aqueous solution was added within 5 min. The mixture was purged with N<sub>2</sub> gas to get rid of oxygen in the solution and the reaction. Next, 20 ml of APS aqueous solution was added and stirred for 5 min. Lastly, 1.2% mole (0.2 ml) of the co-initiator (TEMED) was added. The solution

polymerization was continued for 30 min. The resulting polymer was dewatered with methanol, cut into small pieces in which they have diameter about 0.5 cm, dried at 50°C for 24 h in a vacuum oven until a constant weight. Then, it was milled and screened through a 100-mesh screen, particles of the superabsorbent composite were obtained. All polymerization conditions are shown in Table 3.2.

**Table 3.2:** Polymerization conditions of poly(AM-co-IA)/mica nanocomposites

Ingredients	Amount
Monomer (AM:IA) ratios (%mol)	99:1, 98:2, 97:3, 96:4, 95:5
Mica (%wt)	2, 5, 10, 15
<i>N,N'</i> -methylenebisacrylamide (%mole)*	0.2, 0.5, 0.7, 0.9
Ammonium persulfate (%mole)*	0.3
<i>N,N,N',N'</i> -tetramethylethylenediamine (%mole)*	1.2 (0.2 ml)
Reaction temperature (°C)	40, 50, 60
Agitation speed (rpm)	250
Reaction time (min)	30

\* %mole based on the monomer concentration

#### 3.4.2.1 The Effect of Itaconic Acid Concentration

The experimental procedure as described above and the formulation in Table 3.2 were carried out by varying the IA mole percents of 1 to 5. The mica

contents were 2, 5, 10 and 15 %wt. The concentration of the crosslinking agent was fixed at 0.2 % mole.

#### **3.4.2.2 The Effect of Mica Content**

The ratios of AM/IA were 99:1, 98:2, 97:3, 96:4 and 95:5. The content of mica was varied from 2 to 15% wt, based on monomer concentration. The concentration of the crosslinking agent (N-MBA), initiator (APS), and co-initiator (TEMED) were fixed at, 0.2% mole, 0.3% mole, and 1.2% mole.

#### **3.4.2.3 The Effect of *N,N'*-methylenebisacrylamide Concentration**

The ratios of AM/IA were fixed at 99:1, 97:3 and 95:5. The concentration of the crosslinking agent was varied from 0.2 to 0.9% mole, based on the monomer concentration. The mica contents were 5 and 15 % wt. The preparation of poly(AM-*co*-IA)/mica composite was carried following the basic procedure in Section 3.4.2 and other reaction condition in Table 3.2.

#### **3.4.2.4 The Effect of the Reaction Temperature**

The solution of monomers of AM and IA were prepared in three different compositions (AM/IA mole percent ratios, 99/1, 97/3 and 95/5). The concentration of the crosslinking agent (N-MBA), initiator (APS), and co-initiator (TEMED) were fixed at 0.2% mole, 0.3% mole, and 1.2% mole, respectively. The mica contents were 5 and 15 % wt. These solutions were used to synthesize the polymer composites by varying the reaction temperature at 40, 50, and 60 °C.



### **3.4.3 Characterization of the Superabsorbent Nanocomposites**

The synthesized copolymers were characterized as follows:

#### **3.4.3.1 Identification of the Functional Groups of the Synthesized Copolymers**

The functional groups of the copolymers were identified using Fourier-Transform Infrared Spectrometry (FT-IR) (Nicolet Infrared Spectrometer, model Impact 410). The dried sample was ground with the dried KBr powder. The KBr disc was dried again, pressed and subjected to the FT-IR spectrometric technique.

#### **3.4.3.2 Morphology of the Synthesized Copolymers**

The surface morphology of the superabsorbent composites was investigated using scanning electron microscopy [(SEM), model JSM-6400, Japan JEOL] without cross-section. The thickness of gold coating on the copolymer was 25 nm, and SEM was operated with an accelerating voltage of 15 to 20 kV.

#### **3.4.3.3 Transmission Electron Microscopic Analysis of Poly(AM-co-IA)/mica Nanocomposite**

TEM micrographs of samples acquired from JOEL JEM-2100 (Japan) transmission electron microscope at an acceleration voltage of 120 kV. Each sample was dispersed in ethyl alcohol, its suspension was then sonicated for 5 min. Next, the diluted suspension was dropped onto a 300 mesh copper grid, left to dry in a control room atmosphere before the TEM microscopic investigation was carried out.

#### **3.4.3.4 Determination of the Thermal Properties of the Synthesized Poly(AM-co-IA)/mica Nanocomposites**

The superabsorbent composites were investigated with a thermogravimetric analysis for their thermal property. The measurements were carried out over a temperature range of 25 to 800°C with a heating rate of 10°C min<sup>-1</sup>, under the nitrogen flow rate of 60 cm<sup>3</sup> min<sup>-1</sup>, the weight of superabsorbent composites used was 2-4 mg.

#### **3.4.3.5 X-ray Diffraction Analysis**

X-ray diffraction measurements were carried out using a Bruker AXS Model D8 Discover (Cu radiation, 40 kV, 40 mA) scanning from 2-25° at 0.025 °C min<sup>-1</sup>. The dried copolymer powder was mounted on a sample holder with a smooth double-sided adhesive tape.

### **3.4.4 Determination of Swelling Properties of the Synthesized Copolymer**

#### **3.4.4.1 In Distilled Water**

Distilled water 200 g was added to 0.1 g of superabsorbent polymers or its composites in 250 cm<sup>3</sup> glass beaker at room temperature. The composite was allowed to swell for 24 h. The residual water was removed by filtration with a 100-mesh screen for 2 h at room temperature and the swollen gel was weighed. The water absorbency was calculated as shown Equation (3.1):

$$\text{Water absorbency (Q)} = (B - A)/A \quad (3.1)$$

where A = the weight of the dry polymer (g)

B = the weight of the swollen gel (g)

#### 3.4.4.2 In Artificial Urine

The same experimental procedure as described in Section 3.4.4.1 was carried out, except for that artificial reference urine was used instead of the distilled water. The ARU was prepared by mixing equal amounts of the solutions containing 0.1055 M sodium chloride, 0.0323 M sodium dihydrogen phosphate, 0.00321M sodium citrate, 0.00385 M magnesium sulphate, 0.01695 M sodium sulfate, and 0.0637 M potassium chloride. The pH was adjusted to 6.5 using ammonium hydroxide or hydrochloric acid as per requirement (26), in which the artificial has ionic strength  $0.0747 \text{ mol-ion dm}^{-3}$ . The ionic strength of solution is defined by the Equation 3.2 (27):

$$I = \frac{1}{2} \sum (c_i z_i^2) \quad (3.2)$$

where  $I$  = ionic strength ( $\text{mol-ion dm}^{-3}$ )

$c_i$  = ion concentration ( $\text{mol dm}^{-3}$ )

$z_i$  = charge on each individual ion

#### 3.4.4.3 Absorbency Under Load

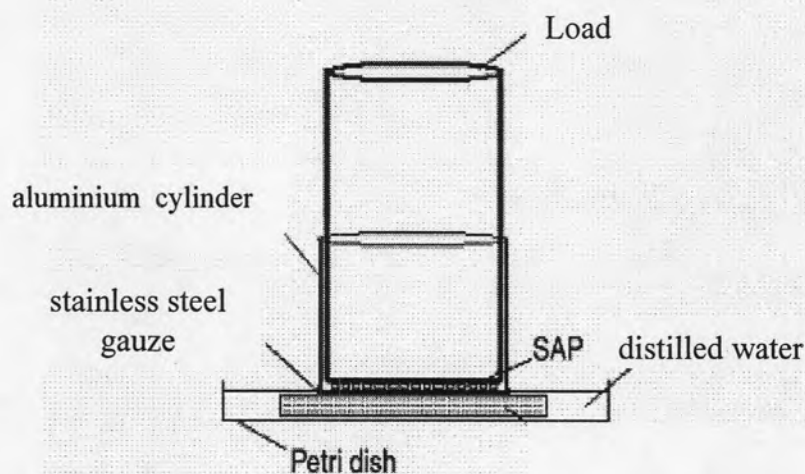
Distilled water (25 ml) was placed in a Petri dish as shown in Figure 3.1. The dried copolymer weighing about 0.16 g was carefully scattered onto the filter screen of the test device (an aluminium cylinder with 100 meshes made of stainless steel cloth at the bottom of the cylinder having a diameter of 26 mm and a

height of 35 mm). A piston assembly, including an additional weight to achieve a load of 0.28 psi (or 0.70 psi) was placed on the top of the dry copolymer. After the assembly device had been weighed, it was placed in the Petri dish, and absorption was allowed to reach an equilibrium swelling for 1 h. After 1 h, the entire device was reweighed. The similar experiments were each carried out for a load of 0.70 psi. The absorbency under load (g of water/g of dry copolymer) was calculated by Equation (3.3):

$$\text{Absorbency under load (AUL) (g/g)} = (B-A)/A \quad (3.3)$$

where A = the weight of the dry samples (g)

B = the weight of the swollen gel (g)



**Figure 3.1** Scheme of the absorbency under load (AUL) tester.

### 3.4.5 Viscoelastic Properties

The rheological measurements were performed in an ARES Rheometric Scientific at 25 °C with a parallel plate geometry. The strains used were chosen to be in a linear viscoelastic (LVE) range where  $G'$  (storage modulus) and  $G''$  (loss

modulus) are independent of the strain amplitude. After a strain sweep test, the test condition for the frequency sweeps was selected to ensure that the test is really carried out in the LVE range. For the LVE determination, approximately 100-110 mg of dried samples with an average particle size of 200-300  $\mu\text{m}$  was dispersed in 200 ml of distilled water for 24 h. The swollen sample was filtered through a weighed 100-mesh screen for 2 h. at room temperature. The swollen gel particles were then placed on the parallel plate of the rheometer, and viscoelastic properties were measured. The effect of shear strain on the measured  $G'$  and  $G''$  at a constant frequency ( $\omega = 1 \text{ rad/s}$ ) was evaluated (17).

#### **3.4.6 Absorption Kinetics of the Synthesized Copolymer**

Distilled water 200 g was added to 0.1 g of the dried nanocomposites in a 250 ml glass beaker covered with a glass lid. The polymer was allowed to swell first for 1 min. The fully swollen gel was then separated from the unabsorbed water by filtering through a 100-mesh sieve aluminum screen for 2 h at room temperature and the swollen copolymer was then weighed. The similar experiments were carried out for each gel at the swelling times of 1, 5, 10, 30, 60, 180, 300, and 480 min.

#### **3.4.7 Determination of Retained Mica in the Composite**

The dried copolymer nanocomposites weighing  $1.00 \pm 0.01 \text{ g}$  was placed in a 25 ml porcelain crucible. The crucible was placed in the furnace at  $800^\circ\text{C}$  for 10 h or until a complete until combustion of all the remaining white mica powder has been obtained. The crucible was removed from the furnace and cool. The remaining mica content was weighed.

### 3.4.8 Determination of the Unreacted Amounts of Acrylamide Monomer in the Superabsorbent Polymer by Gas Chromatography

The superabsorbent polymer achieved from the polymerization reaction was stirred in 300 cm<sup>3</sup> distilled water at room temperature for 30 min. Then 50 ml of solution was used to determine the trace amounts of acrylamide monomer in the polymerization reaction by Method 8032A. This method is for the bromination of the acrylamide double bond. The reaction product (2, 3-dibromopropionamide) was extracted from the reaction mixture with ethyl acetate, after salting out sodium sulfate. The extract was analyzed by gas chromatography. The detailed procedure of this method (Method 8032A) was described in Appendix A and the polymerization conditions for preparing the superabsorbent polymer are shown in Table 3.3.

**Table 3.3:** Polymerization conditions for poly(AM-co-IA) copolymer

Ingredients	Amount
Monomer (AM:IA) ratios (%mol)	100:0, 99:1, 95:5
<i>N,N'</i> -methylenebisacrylamide (%mole)*	0.2
Ammonium persulfate (%mole)*	0.3
<i>N,N,N',N'</i> -tetramethylethylenediamine (%mole)*	1.2
Reaction temperature (°C)	50
Agitation speed (rpm)	250
Reaction time (min)	30

\* %mole based on the concentration of the monomer

### 3.4.9 Determination of Density of the Synthesized Poly(AM-co-IA)/mica Nanocomposites

The standard method for determination of density of polymer is based on ASTM D 792. A pycnometer was used to determine the densities of mica, poly(AM-co-IA), and poly(AM-co-IA)/mica nanocomposites. Since the density  $\rho$  is defined by:

$$\rho = W_{\text{solid}} / V_{\text{solid}} \quad (3.4)$$

The method involves the use of a pycnometer of known volume which is first weighed empty, then weighed containing the solid sample (mica, poly(AM-co-IA) or polymer nanocomposites) to be studied. The solid sample was analyzed for 0.1 g. The difference gives the weight of the sample,  $W_{\text{solid}}$ . Finally the pycnometer (containing the sample) is filled with n-heptane of known density and reweighed; the weight, and therefore the volume, of n-heptane can be found by difference. Since the total volume of the pycnometer is known, one can then calculate the volume  $V_{\text{solid}}$  which is occupied by the solid sample.

The weight of the solid sample is given by:

$$W_{\text{solid}} = W_2 - W_1 \quad (3.5)$$

where  $W_1$  is the weight of the empty pycnometer and  $W_2$  is that of the pycnometer plus solid sample. The weight of n-heptane contained in the pycnometer,  $W_L$ , is

$$W_L = W_3 - W_2 \quad (3.6)$$

where  $W_3$  is the total weight of the pycnometer, sample, and n-heptane. If the density of the n-heptane is denoted by  $\rho_L$ , it follows from Equation (3.6) that the volume of the solid sample is given by:

$$V_{\text{solid}} = V - V_L = (V + W_2 - W_3) / \rho_L \quad (3.7)$$

It is only necessary to determine  $W_1$ ,  $W_2$ , and  $W_3$  in order to calculate the density of mica, poly(AM-co-IA) or polymer nanocomposites.