

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Chemicals, Glassware, Equipment and Materials

##### 3.1.1 Chemicals

Cassava starch was obtained from Thai Wah Co., Ltd. It was product from topioca cultivated in summer. It contained 13.5% moisture, 0.20% ash, pH range 4.00-7.00 and viscosity 550 B.U.

Acrylic acid ( $\text{CH}_2\text{CHCOOH}$ ) was provided by Siam Rasin & Chemical Co., Ltd. It was used as received.

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) 35%, analytical grade, was obtained from Peroxythai, Rayong, Thailand. Hydrogen peroxide is a clear, colorless liquid, which is miscible with water in all proportions. The molecular weight of hydrogen peroxide is 34.02. The melting and boiling temperature are  $-33^\circ\text{C}$  and  $107.9^\circ\text{C}$ , respectively.

Calcium oxide ( $\text{CaO}$ ), analytical grade, was obtained from Ajax Laboratory Chemicals, Auburn, Australia. The molecular weight of calcium oxide is 56.08.

L (+) Ascorbic acid ( $\text{C}_6\text{H}_8\text{O}_6$ ), analytical grade, was supplied from Carlo Erba, Milano, Italy. Ascorbic acid is a white, odorless, crystalline solid with a sharp acidic taste. The molecular weight is 176.13 and melting temperature range is  $190.5\text{-}192^\circ\text{C}$ .

*N,N'*-Methylenebisacrylamide (*N,N'*-MBA), analytical grade, was provided by Nacalai Tesque Inc, Kyoto, Japan. *N,N'*-MBA was used as a crosslinking agent in grafting reaction.

Sodium hydroxide (NaOH), analytical grade, was obtained from Eka Nobel, Bohus, Sweden.

Methanol (CH<sub>3</sub>OH), commercial grade, was supplied from BDH. Methanol was also purified by fraction distillation at atmospheric pressure.

2-ethoxyethanol (C<sub>2</sub>H<sub>5</sub>OCH<sub>2</sub>CH<sub>2</sub>OH), analytical grade, was obtained from Ajax, Auburn, Australia. The molecular weight of 2-ethoxyethanol is 90.12. The density is 0.93 g/ml and the boiling range is 133-136°C. 2-Ethoxyethanol was used in measuring contact angle on plastic film.

Methyl alcohol (CH<sub>3</sub>OH), analytical grade, was provided by J.T. Baker Inc, Philipsburg, U.S.A. The molecular weight of methyl alcohol is 32.04, and flash point is 12°C. Methyl alcohol was used in measuring contact angles on plastic film.

Dyne solution was obtained from Solftal, Tokyo, Japan.

Blue 5380 E that is Phthalocyanine Blue NC Beta form (C.I. Pigment Blue 15:3 No. 74160), was obtained from Dianippon Ink & Chemical (Thailand) Co., Ltd. The beta form of copper phthalocyanine is bright greenish blue, completely resistant to acids, alkalis, solvents, plasticizers, greases, paraffin wax, and soap; also solvent stable, heat resistant, and very lightfast; transparent; strong tinting power; very permanent; slightly weaker than the alpha form.

Nonylphenol alcohol ethoxylate surfactant (Tergitol 15-S-9 surfactant) was supplied from Union Carbide Corporation, Nonthaburi, Thailand. Tergitol 15-S-9 is water-soluble, nonionic surfactant. Its properties are presented in Table 3.1.

**Table 3.1** Typical Properties of Tergitol 15-S-9 Surfactant

Parameter	Property
Cloud Point (1% aqueous solution), °C	60
Pour Point, °C	9
HLB	13.3
Surface Tension, ppm/mN m <sup>-1</sup>	560/30 <sup>a</sup>
Foam Height, initial (5 min) at 25°C of 0.1% aqueous solution, mm	92 (20)
Odor	Low odor
Appearance	Liquid, colorless

<sup>a</sup>CMC/Equilibrium Surface Tension

Other chemicals are listed in Table 3.2

**Table 3.2** Other Chemicals

Chemicals	Source
Sodium bicarbonate (NaHCO <sub>3</sub> )	V.P.C. Group, Bangkok, Thailand
Polyethylene wax	Dianippon Ink & Chemical (Thailand), Co., Ltd
Silicone defoamer	BSA Ink Industry Co., Ltd., Bangkok, Thailand
Non-silicone defoamer	Hi Ink Co., Ltd., Bangkok, Thailand
Blue-colored emulsion	Winco Screen Co., Ltd., Bangkok, Thailand
Sensitizer	Winco Screen Co., Ltd., Bangkok, Thailand
Chlorine	Winco Screen Co., Ltd., Bangkok, Thailand
Stencil hardener	Winco Screen Co., Ltd., Bangkok, Thailand

### 3.1.2 Glassware

Four-necked round bottom flask 2,000 cm<sup>3</sup>, condenser, beaker, funnel, thermometer, desiccator, 100-mesh aluminium screen, semicircular teflon paddle stirrer, blender, and other general laboratory glassware.

### 3.1.3 Equipment

1. Water Bath Circulator, Model: WBU 45

Memmert, Schwabach, Germany

2. Analytical Balance, Model: 300A

Precisa, Zurich, Switzerland

3. Oven, Model: 173700

Hotpack, Philadelphia, U.S.A.

4. Mechanical Stirrer, Model: RW20

Ika Werker, Staufen, Germany

5. Viscometer, Model: RVT, Spindle and Chamber: SC4-14/6R

Brookfield, U.S.A.

6. Contact Angle Meter, Model: CA-A, Injection tube No.3268, diameter

6.27 mm with needle 22 gauge

Face, Tokyo, Japan

7. Corona Generator 6010

Softal, Tokyo, Japan

8. Interfacial Tensiometer Model: K8

Kruss, Hamburg, Germany

9. Image setter, Model: Linotronic 260  
Linotype-Hell, Germany
10. UV Exposure  
Tashiang, China
11. Screen Printer, Model: Photo Print 2  
Twin star, Bangkok, Thailand
12. Image Analyzer, Model: Luzex-F  
Olympus, Tokyo, Japan
13. Scanning Electron Microscope, JEOL, JSM-6400  
Tokyo, Japan
14. Densitometer, GRETAG D 200-II  
Regensdort, Switzerland
15. Glossmeter, 155 Sheen  
London, England
16. Dryer, Casiko 1500  
Casiko, PRC

#### **3.1.4 Materials**

Cast polypropylene (CPP) plastic film, non-treated surface, was obtained from Print Master Co., Ltd., Bangkok, Thailand. The plastic film thickness is 40 micrometers.

Screen frame, the area of 18 x 25 square inch with the stretched mesh count J 150 line per inch, was supplied by Winco Screen Co., Ltd., Bangkok, Thailand.

610 Scotch Cellophane Tape was produced by 3M, U.S.A.

## 3.2 Procedures

### 3.2.1 Gelatinization of Cassava Starch

Cassava starch 60 g was mixed with 600 cm<sup>3</sup> of distilled water in a 2,000 cm<sup>3</sup> four-necked round bottom flask. The system was stirred mechanically at 360 rpm under heating within the temperature range of 80 ± 2°C for one hour under nitrogen atmosphere to form a slurry-paste.

### 3.2.2 Graft Copolymerization of Acrylic Acid onto Cassava Starch

The gelatinized starch was then cooled to 35°C; 1.0 g calcium oxide, 0.4 g of ascorbic acid, 0.4208 g of *N,N'*-MBA, a mixture of 4 cm<sup>3</sup> of hydrogen peroxide 35%, and 80 cm<sup>3</sup> of acrylic acid monomer were added in the reaction. The reaction mixture was stirred mechanically at 450 rpm under heating within the controlled temperature of 35 ± 2°C under nitrogen atmosphere for 2 hours.

### 3.2.3 Saponification of Starch-g-Poly(acrylic acid)

100 cm<sup>3</sup> of 25% sodium hydroxide solution was added in the starch-g-poly (acrylic acid) slurry at room temperature. The mixture was stirred mechanically. One could observe an exothermic heat developed during the reaction. It was then allowed to cool to room temperature. It was precipitated with methanol, which was added to starch slurry, the mixture was stirred mechanically. The product was then filtered and washed through with methanol until pH 7 was reached. It was dried at 65°C in an oven for 24 hours to remove residual methanol. The dried product was ground into a powder form.

### 3.2.4 Effect of the Crosslinking Agent Concentration on Graft Copolymerization

To obtain a product with the relatively minimum water absorption capacity and an appropriate viscous paste, influence of the crosslinking agent concentration on graft copolymer was investigated. The same reaction procedures as described in Sections 3.2.1 to 3.2.3 were carried out. The concentration of crosslinking agent was varied to 0.4208, 0.8416, 1.2624, 1.6832 and 2.1040 g (0.5, 1.0, 1.5, 2.0 and 2.5% weight based on amount of acrylic acid) while other variables were constant.

Starch-g-poly(acrylic acid) with the crosslinking agent concentration at which the water absorption capacity was minimum and the viscosity at which was appropriate, would be used as an ingredient for water-based screen printing ink formulation.

### 3.2.5 Water Absorption Capacity of Saponified Starch-g-Poly(acrylic acid)

The dried saponified cassava starch-g-poly(acrylic acid) of 0.10 g was soaked in 75 cm<sup>3</sup> of distilled water for 1 hour. The swollen copolymer was filtered through a weighed 100-mesh aluminium screen and allowed to drain for 2 hours. Then it was weighed to determine the weight of water-swollen gel.

The water absorption capacity was calculated in g/g of the dried polymer as follows:

$$\text{Water Absorption Capacity (g/g)} = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \quad (3.1)$$

### 3.2.6 Measurement of the Viscosity of Thickener Solution

Various amounts of the dried saponified starch-g-copolymer of 6%, 8%, 10%, and 12% weight by weight (0.3, 0.4, 0.5, and 0.6 g) were added to 5 g distilled water. The prepared thickener solutions were measured for the viscosity profile.

The viscosity of the above solution of saponified starch-g-poly(acrylic acid) was measured by Brookfield viscometer (model RVT, with a small sample adapter and spindle number 14) at 25°C under various rates: 1, 2, 4, 8, and 20 ( $\text{sec}^{-1}$ ) were calculated by multiplying 0.4 with 2.5, 5, 10, 20, and 50 rpm, respectively.

### 3.2.7 Water-based Screen Printing Ink Formulations

Typical water-based screen printing ink formulations as given in Table 3.3 were prepared.

**Table 3.3** Formulations for Typical Water-Based Screen Printing Ink

Raw Material	% By Weight	
	Formula 1	Formula 2
Phthalocyanine Blue	12.5	12.5
15% Thickener solution	52.0	52.0
Water	28.0	29.0
Sodium bicarbonate	1.5	1.0
Polyethylene wax	3.0	3.0
Tergitol 15-S-9 surfactant	1.5	1.5
Non-silicone defoamer	1.5	-
Silicone defomer	-	1.0
Total	100.0	100.0



The 15% thickener solution was made of 15 g dried saponified cassava starch-g-poly(acrylic acid) obtained from Section 3.2.4, dissolved in distilled water 85 g. The 15% thickener solution was then determined for the viscosity profile.

### **3.2.8 Investigation of Rheological, Dispersion, and Surface Tension Properties of the Water-Based Screen Inks**

The properties of the water-based inks as derived from section 3.2.7 were investigated as follows:

Rheology was investigated with Brookfield viscometer.

Dispersion (fineness of grind) was measured using a grind gauge.

Surface tension was determined using a tensiometer. The inks had been diluted with distilled water as 0.1, 0.5, 1.0, 10, 15, 20 and 25 wt% before their surface tensions were measured.

### **3.2.9 Sampling of Cast Polypropylene Film**

#### **3.2.9.1 Corona Treatment on Cast Polypropylene Film**

22 x 30 cm<sup>2</sup> of each piece of cast polypropylene (CPP) plastic film was treated with a corona generator for 3 seconds. Amount of the output power was varied as 300 and 350 watts.

#### **3.2.9.2 Sampling**

The minimum amount of the non-treated and corona-treated plastic film obtained from Section 3.2.9.1 required for characterization was an approximately 1.5-cm wide and 3.5-cm long sample strip. The number of nine sample strips per (each) piece of the film was prepared in order to determine the contact angles.

### **3.2.10 Characterization of Corona-Treated Cast Polypropylene Film**

The sample film derived in above Section were characterized in order to search for the optimum condition of treatment in subsequent experiments.

#### **3.2.10.1 Determination of Surface Energy of Cast Polypropylene Film**

(a) The dyne solutions were used in the wetting test of the non-treated and corona-treated film surfaces according to ASTM D2578-94, wetting tension of CPP film approximated its surface energy.

(b) The methyl alcohol-water mixtures were applied for advancing and receding contact angle measurements on sample strip surfaces using a contact angle meter. The concentration of the methyl alcohol-water mixtures as shown in Table 3.4 was used for this investigation.

To determine accurate surface tension values of the methyl alcohol-water mixtures, the calibration curve was plotted between the actual surface tension as shown in Table 3.4 and measured surface tension values obtained using the tensiometer. The fitted curve was performed to search the proper results utilized in the Zisman plot.

The advancing and receding contact angles were obtained by increasing and decreasing the volume of the droplet, respectively, until the three-phase boundary moved on the surface. In this experiment, the volume of each droplet was fixed at  $0.309 \text{ mm}^3$  (calculated using the volume cylinder formula) for advancing contact angle, and a half of  $0.309 \text{ mm}^3$  for receding contact angle. Two contact angle measurements, left and right sides of the droplet on both advancing and receding contact angles were taken. The same experimental procedure was repeated on nine

sample strips of the film surface. The advancing and receding contact angles were averaged and reported. The critical surface energy of CPP plastic film was investigated by the Zisman plot.

**Table 3.4** The Concentration of Methyl Alcohol-Water Mixtures Used in Contact Angle Measurement at 20°C [42]

Water (vol %)	Methyl Alcohol (vol %)	Surface Tension (mN m <sup>-1</sup> )
0	100	22.65
10	90	25.36
20	80	27.26
40	60	32.95
50	50	35.31
75	25	46.38
90	10	59.04
100	0	72.80

To study the effectiveness of corona treatment of the aged plastic film, the aforementioned experiment was reiterated. Various storage times of the corona-treated plastic film for 0, 2, 4, 7, 11, and 14 days on contact angles were measured.

The results obtained were analyzed via Student's t distribution order.

### **3.2.10.2 Determination of Surface Energy Components of Cast Polypropylene Film**

Distilled water and 2-ethoxyethanol, at 20°C, were used to measure the contact angles to determine the polar and dispersion components for surface energy of CPP film. The non-treated and treated films stored for 0, 7, and 14 days

were investigated in order to search for their surface energy components. Surface energy of the film and its components were explored as follows:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s^d \gamma_l^d)^{1/2} - 2(\gamma_s^p \gamma_l^p)^{1/2} \quad (3.2)$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (3.3)$$

and % polarity was calculated as follows:

$$\%Polarity = \frac{100 \times \text{polar component}}{\text{total surface energy}} \quad (3.4)$$

### 3.2.10.3 Film Morphology Characterization

The morphology of the non-treated and corona-treated plastic film was examined with a scanning electron microscopy (JOEL, JSM-6400, Tokyo, Japan).

### 3.2.11 Determination of Work of Adhesion of the Inks on the Corona-Treated Plastic Film

The contact angles of the two inks on the optimally treated plastic films were measured in order to explore the work of adhesion. Each ink diluted with distilled water at 10, 15, 20 and 25 wt%, with known surface tension values derived from experiment procedure in Section 3.2.8, was used for the contact angle measurement. The work of adhesion ( $W_a$ ) could be calculated as follows:

$$W_a = \gamma_l(1 + \cos\theta) \quad (3.5)$$

### **3.2.12 Photo Process Screen Making**

1. 30 line per inch positive film was used out with the image setter.
2. Fabric was cleaned and degreased.
3. Photo process screen making was consisted of the following steps:
  - a) Ratio of blue-emulsion to sensitizer, 5:1, was mixed then it was applied on a screen fabric, and dried.
  - b) Emulsion was exposed to UV radiation through positive images for 40 seconds.
  - c) After exposure, the hardened emulsion become the stencil fixed onto the screen, and the unexposed emulsion was washed away to reveal the image area.
  - d) The stencil was dried properly.

### **3.2.13 Printing Experiment**

The plastic films were treated using the optimum condition obtained from Section 3.2.10. The two water-based inks were printed on the 30 pieces of corona-treated film each stored for 0, 7, and 14 days, respectively, by screen printing process.

### **3.2.14 Print Qualities Measurement**

The printed plastic films (30 pieces) obtained from Section 3.2.13 were evaluated for print qualities. The results obtained were analyzed via Student's t distribution order. The evaluation items for print qualities are given below:

#### **a) % Dot Area and % Dot Gain**

% Dot areas of the original film and the printed plastic film, at 10 to 100% dot, were evaluated by the image analyzer. Dot gain curves were reported.

### **b) Tone Reproduction**

Densities of 0 to 100% dot location of the printed plastic films and the original film were measured. Printing characteristic plot and tone reproduction curve were reported.

### **c) Dot Characteristics**

Dot characteristics were examined using the image analyzer. Dot characteristics of the original film and the printed film were compared.

### **d) Print Contrast**

Print contrast of the printed plastic films was determined as follows:

$$\text{Print contrast} = \frac{D_s - D_t}{D_s} \quad (3.6)$$

where  $D_s$  = density of the shadow area

$D_t$  = density at 70 percent tint

### **e) Gloss**

Gloss of the printed plastic films at solid tone was measured using a glossmeter (155 Sheen).

### **f) Adhesion Test**

A pressure-sensitive tape (3M 610 or equivalent) was applied for investigating the ink film adhesion to the plastic film surface according to ASTM D 3359-97 [43].