

CHAPTER 3

EXPERIMENTAL

3.1 Materials

1. Colorants (Cyan, Magenta, Yellow, and Black): surface modified pigments from Cabot Corporation, Japan, were used as follows:

Cyan (IJX 253): C.I. Pigment Blue 15:3;

Magenta (IJX 266): C.I. Pigment Red 122;

Yellow (IJX 273): C.I. Pigment Yellow 74;

Black (CAB-O-JET200): C.I. Pigment Black 7.

Table 3.1 presents the properties of pigment dispersion and binder used in the present research.

2. Polymer binder is NK Vanatex S - 711 (Polyacrylate) from Shin-Nakamura Chemical Co., Tokyo, Japan.

3. Solvents

3.1 Deionized water;

3.2 Diethylene glycol ($C_2H_6O_2$), analytical grade, ($MW = 62 \text{ g mol}^{-1}$),

Unilab Ajax Finechem Corporation, New Zealand;

3.3 Glycerol, ($C_3H_8O_3$), analytical grade, ($MW = 92 \text{ g mol}^{-1}$), Univar

Ajax Finechem Corporation, New Zealand.

Table 3.1: Properties of pigment dispersion and binder

Chemicals	Color Index of pigment (CI)	Chemical class of pigment	Pigment Conc. (wt. %)	Average particle size (nm)	pH	Viscosity (mPa s)
Cyan : C (IJX 253C)	Pigment Blue 15:3	Phthalocyanine	9.45	84	6.9	1.37
Magenta : M (IJX 266D)	Pigment Red 122	Quinacridone	9.96	104	7.6	1.70
Yellow : Y (IJX 273B)	Pigment Yellow 74	Monoazo; Acetoacetyl	9.66	123	6.4	1.43
Black : Bk (CAB-O-JET200)	Pigment Black 7	Carbon black	18.65	166	7.9	3.10
Binder (S-711)	-	Polyacrylate emulsion	50.71	195	5	50.7

4. Other materials

4.1 Urea, analytical grade from Univar Ajax Finechem Corporation, New Zealand;

4.2 pH buffer;

4.3 Sodium hydroxide, analytical grade from Carlo Erba reagent Corporation, Italy;

4.4 Sodium carbonate, analytical grade from Univar Ajax Finechem Corporation, New Zealand;

4.5 Hydrogen peroxide, analytical grade from Peroxythai Corporation, Thailand;

5. Silk fabric: Plain pattern, Local woven, construction of 62×73 threads/inch, a basic weight of 0.11 kg m^{-2} from Srisakate province, Thailand.

6. Pretreatment compounds: four types were used:

6.1 Amino acid

L-Serine, M_w $105.09 \text{ g mol}^{-1}$ from Fluka Biochemika, France;

L-Glycine, M_w 75.07 g mol^{-1} from Fluka Biochemika, Switzerland;

L-Aspartic Acid, M_w $133.10 \text{ g mol}^{-1}$ from Fluka Biochemika, Germany.

Properties of the amino acids used are presented in Table 3.2.

Table 3.2: Properties of the amino acids

Amino acid	Formula	Molecular weight (g mol^{-1})	Structure
Serine	$\text{C}_3\text{H}_7\text{NO}_3$	105.09	$\begin{array}{c} \text{H} \\ \\ \text{HO}-\text{CH}_2-\text{C}-\text{COOH} \\ \\ \text{NH}_2 \end{array}$
Glycine	$\text{C}_2\text{H}_5\text{NO}_2$	75.07	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{COOH} \\ \\ \text{NH}_2 \end{array}$
Aspartic Acid	$\text{C}_4\text{H}_7\text{NO}_4$	133.10	$\begin{array}{c} \text{H} \\ \\ \text{HOOC}-\text{CH}_2-\text{C}-\text{COOH} \\ \\ \text{NH}_2 \end{array}$

6.2 Sericin from Shinano Kenji Company Ltd., Saraburee, Thailand, whose structure is shown in Figure 2.14.

6.3 Chitosan

FM-40: MW 8.5×10^5 Dalton with an *N*-deacetylation degree of 88 from Koyo Chemical Co., Ltd., Japan;

FM-80: MW 3.7×10^5 Dalton with an *N*-deacetylation degree of 87 from Koyo Chemical Co., Ltd., Japan;

FL-80: MW 1.2×10^5 Dalton with an *N*-deacetylation degree of 88 from Koyo Chemical Co., Ltd., Japan.. Chemical structure of chitosan is illustrated in Figure 2.15.

6.4 Sanfix 555 (Cationic acrylate polymer) from Sanyo Chemical Industries, Ltd. Kyoto, Japan, whose structure is illustrated in Figure 3.1.

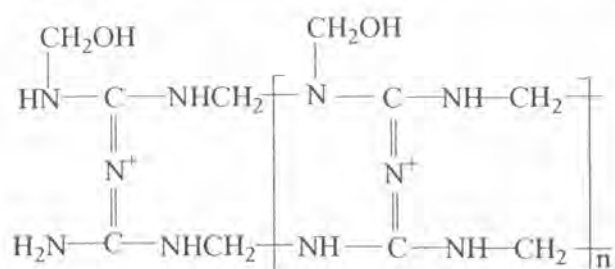


Figure 3.1: Chemical structure of Sanfix 555

3.2 Apparatus

1. Inkjet printer, Epson Stylus™ C65, Seiko Epson Corporation, Indonesia
2. Spectrophotometer, X – rite, SP62, d/8, U.S.A.
3. Spectrophotometer, Gratag-Macbeth, spectrolino, 45/0, Switzerland.
4. Spectrodensitometer, X – rite, 500 series, 45/0, U.S.A.
5. pH meter, pHTestr 20, Oaklon, Eutech instruments, U.S.A.
6. Brookfield viscometer DV III, programmable rheometer, U.S.A.
7. Surface tensiometer, K8, Kruss, Germany.

8. Laser Particle Size Distribution Analyzer, Malvern laser scattering analyzer model Mastersizer S long bed Ver. 2.11, U.K.
9. Differential Scanning Calorimetry (DSC), 204 FI Phoenix, Germany.
10. Transmission Electron Microscope (TEM), JEOL, JEM-2100, Japan.
11. Zeta-potential, Zetasizer Nano Series, Malvern Instruments Ltd., U.K.
12. Drying oven, Rapid Labortex Corporation, Taiwan.
13. Padding machine, Laboratory, Tsuji Dyeing Machine Mfg, Osaka, Japan.
14. Image analyzer, DP70, BX51, Olympus, U.S.A.
15. Scanning Electron Microscope (SEM), JSM 6400, JEOL, Tokyo, Japan.
16. Crockmeter, AATCC Crockmeter, Atlas Electric Devices Corporation, Chicago, U.S.A.
17. Cantilever Stiffness Tester, Sherley Development Limited, Stockport, U.K.
18. Gyro wash, Atlas Electric Devices Corporation, Chicago, U.S.A.
19. Fourier Transform Infrared spectrometer (FT-IR), Perkin Elmer System 2000, U.K.
20. Fourier Transform Infrared - Attenuated Total Reflectance (FTIR-ATR), Spectrum one, Perkin Elmer, U.K.
21. Microscope Laser Raman spectroscopy, Renishaw RM100, U.K.
22. UV-Visible spectrophotometer, UV-2550, Shimadzu, Kyoto, Japan.

3.3 Procedure

3.3.1 Preparation of pigmented ink jet inks

The four-process color of pigmented ink jet inks comprised surface-modified copper phthalocyanine blue pigment (IJXTM 253, C.I. Pigment blue 15:3),

quinacridone red pigment (IJXTM 266, C.I. Pigment red 122), monoazo yellow pigment (IJXTM 273, C.I. Pigment yellow 74), and black pigment (CAB-O-jet 200, C.I. Pigment black 7). A commercial binder (S-711) is a polyacrylate base. The pigmented ink jet formulation is shown in Table 3.3. The pigment/binder ratio was prepared at 1/2, which is a typically selective ratio used in ink jet formulation [8]. The rest of the ingredients including sodium hydroxide, diethylene glycol, glycerol, and urea were used as received. Each component was added individually to avoid any unfavorable inhomogeneity in the solution. Then, a dilute NaOH solution was added to the ink in order to adjust the pH in the range 7 to 9. After mixing, the inks were filtered to prevent any coarse particles from clogging the orifice of the printer.

Table 3.3: Pigmented Ink formulation

Ingredient	Weight (%)
Pigment dispersion	8.0
Diethylene glycol	10.0
Glycerol	12.0
Urea	5.0
Binder	10.0
Water	55.0
Total	100

3.3.2 Characterization of pigmented ink jet inks

1. pH of the inks

pH of the ink was adjusted to the suitable range for printing and measured by pH meter at room temperature.

2. Viscosity

Brookfield viscometer was used to measure the viscosity of the pigment dispersion and of the formulated inks at 25°C.

3. Particle Size Distribution of Dispersed Pigments and Pigmented inkjet Inks

Laser particle size distribution analyzer was used for the particle size analysis of the pigment dispersions and formulated inks. The particle size distributions of the ink formulations were measured at various storage periods (1 day, 1 month, 10 months, and 1 year) to confirm the stability of the inks.

4. Surface Tension

The surface tension of the inks was measured by surface tensiometer using Nouy Ring Method. The measurement was performed at room temperature.

5. Differential scanning calorimetry

This technique was used to measure the glass-transition temperature of binder (S-711). The temperature range was from -50 to 50°C, using the heating rate at 10°C/min under liquid nitrogen.

6. Scanning electron microscope and Transmission electron microscope

The morphology and particle sizes of the pigment dispersions were viewed by TEM. The ink samples after 1-year storage were diluted and dropped on a cover-glass to evaporate the solvents. The ink samples were also observed by SEM and TEM.

7. Zeta-potential

The inks were diluted in deionized water before measuring the zeta-potential by nanosizer. The charges on pigment surface were evaluated at 25°C.

8. Optical density

A solid tone pattern was printed on the non-treated and treated silk fabric. The optical density of the printed fabrics was measured with a spectrodensitometer (X – rite, 500 series, 45/0, USA) and the average was calculated from 10 measurements.

3.3.3 Preparation of the silk fabrics

Plain weave silk fabric constructs of 62 × 73 threads/inch, and its basic weight is 0.11 Kg m⁻². The fabric was cut into a rectangle shape with a dimension of 22 cm × 31 cm. Then the silk fabrics were bleached by hydrogen peroxide, a mild oxidizing agent at pH 10.5, temperature of 100°C for 1 hours. The bleaching formulation, shown in Table 3.4, is composed of hydrogen peroxide, sodium carbonate and water at 1:50 silk fabric/solution ratio. The bleached fabrics were washed with water several

times to remove the remaining oxidizing agent on the fabric. Then, the fabrics were dried at 50°C for 4 hrs.

Table 3.4: Bleaching formulation for silk fabric

Ingredient	g/L
Hydrogen peroxide	2.0
Sodium carbonate	10.0
Weight of fabric/volume of liquor	1/50

3.3.4 Preparation of the pre-treating solutions

1. Amino acids:

1.1 Serine solutions were prepared at 2.5, 5 and 10% w/v.

1.2 Aspartic acid solutions were prepared at 1, 2, and 5% w/v.

1.3 Glycine solutions were prepared at 5, 10, 15, and 20% w/v.

2. Sericin solutions were prepared at 5, 10, 15, and 20% w/v.

3. Sanfix 555 emulsion was prepared at 10% w/w (Table 3.5).

Table 3.5: Sanfix 555 solution

Ingredient	Weight (%)
Sanfix 555	10
Urea	10
Water	80
Total	100

Each chemical was individually dissolved in deionized water and stirred using magnetic stirrer at 60°C, except aspartic acid, which was stirred at 95°C until a clear

solution was obtained. The concentrations of these pre-treating solutions were limited by the solubility of the chemicals.

4. Chitosan:

4.1 FL-80 (MW= 1.2×10^5) was used to prepare the solutions at 0.25, 0.5, 1, and 2% w/v.

4.2 FM-80 (MW= 3.7×10^5) was used to prepare the solutions at 0.25, 0.5, 1, and 2% w/v.

4.3 FM-40 (MW= 8.5×10^5) was used to prepare the solutions at 0.25, 0.5, and 1% w/v.

Each chitosan was prepared at 0.25, 0.5, 1 and 2% w/v, except chitosan at the highest molecular weight (FM-40), which was prepared at 0.25, 0.5 and 1% w/v. The chitosan pre-treating solutions were prepared in 1% v/v acetic acid solution and heated for a certain time at 60°C until homogeneous solutions were obtained. The highest concentration of each pre-treating solution was limited by the soluble capacity of the chemicals and stickiness of the chitosan solution for padding on the fabric.

3.3.4.1 Characterization of the pretreatments

These pre-treating solutions were measured in term of viscosity, surface tension, and zeta-potential. The pre-treating materials were mixed with KBr powder and characterized by FT-IR.

3.3.4.2 Wicking measurement

The wicking property of textile fabric was determined following INDA IST 10.0 – 70 Method 10.3 with a testing setup shown in Figure 3.2. The test measures the distance of water and 2- octanol front on a 25 mm wide strip of the

fabric during an immersion time of 5 min. A longer traveling distance of the liquid indicates a better wicking behavior of such liquid. This measurement can roughly determine the absorption rate of water into the fabric [42].

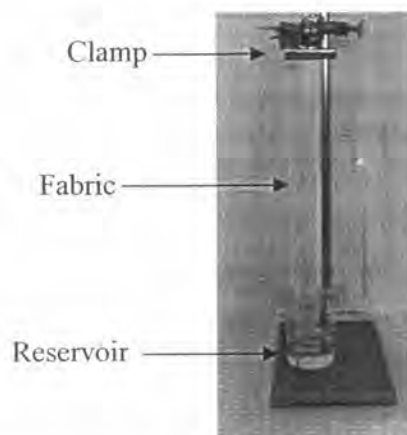


Figure 3.2: Vertical wicking setup

3.3.4.3 Measurement of the pretreated fabrics

The pretreated silk fabrics were measured with FTIR-ATR technique to confirm the pretreatments on the silk fabrics.

3.3.4.4 Measurement of the interaction between pre-treating agent and pigment

The pretreatments were mixed with the inks to measure the UV absorption. The serine and glycine solutions were mixed with the cyan ink to evaluate the interaction between pre-treating material and ink. These solutions were evaporated to a solid to observe the spectra by Raman spectroscopic methods.

3.3.5 Pretreatment

The silk fabrics were each padded with the pre-treating solutions at 100% pick up ratio, using a padding machine. The fabrics were steamed to dry the pre-treating solution at 80°C for 5 min and fixed at 110°C for 2 min in an oven.

3.3.6 Printing Process

The silk fabric was supported by a flat plastic sheet using a double sided adhesive tape to give a stable dimension of fabric for jet ink printing. The fabric was printed with the in-house ink jet inks by Epson Stylus™ C65 printer at a resolution of 5,760 × 1,440 optimized dpi. After printing, the printed silk was steamed to fix the printed inks at 100°C for 5 min.

3.3.7 Evaluation of the printed fabric

3.3.7.1 Color gamut

The color test chart of printed fabric was evaluated for CIE L*a*b* (Commission International l'Eclairage), which was measured with a spectrophotometer (Gretag Macbeth Spectrolino, 45/0, Switzerland), using illuminant D50 and the 2° observer, based on CIE 1931 [29]. The equations for CIE 1976 L* a* b* (CIELAB) color space are shown in Chapter 2 (Eq 2.1 – 2.6).

3.3.7.2 Cross-section of pretreated and printed silk fabrics

The printed silk fabrics were cross-cut in the warp and weft directions to observe the depth of the ink penetration. The cross-section of the print was viewed by image analyzer (5x / 0.10).

3.3.7.3 Crock fastness

The crock fastness of the printed fabric was evaluated using AATCC Crockmeter (Atlas Electric Devices Corporation, Chicago, USA), and AATCC Test Method 8 – 2001. The amount of color transferred from the printed surface to the other tested surface by rubbing process, was judged using grey scale (Grey Scale for Staining or the Chromatic Transference Scale). Each printed sample was rubbed with a standard white cotton fabric in back and forth motions for 10 times under both dry and wet conditions. Later, a grade from 1-5 was assigned.

3.3.7.4 Wash fastness

Wash fastness was carried out by Gyrowash, using ISO 105-C06. A specimen of $100 \times 40 \text{ mm}^2$ in contact with the specified adjacent fabric was washed, rinsed, and dried. Each printed fabric, sewed with a multifibre strip, was washed at 40°C for 30 min in liquor containing 4 g of standard detergent (without optical brightener) per litre of water at a liquor volume of 150 ml. The multifibre adjacent fabric (DW) contains wool, acrylic, polyester, polyamide, bleach cotton, and diacetate. A change in color of the staining on the adjacent fabric is compared using the gray scale for staining in accordance with ISO 105 – A03. Moreover, the color difference in the printed fabrics obtained before and after washing was also reported in terms of color strength (K/S) and relative color strength seen in Equations 2.7 and 2.8.

The fabrics were printed as solid tone pattern in four colors (cyan, magenta, yellow, and black). The printed fabrics before and after washing were evaluated by a spectrophotometer, X – Rite (SP62, d/8, U.S.A.). The reflectance of

samples was measured for 5 times to determine K/S values, and then an averaged value was calculated.

3.3.7.5 Air permeability

Standard test method for air permeability of textile fabric is referred from ASTM D 737 – 96. Air permeability of the fabric is indicated by the rate of air flow passing perpendicularly through a known area under a prescribed air pressure differential between the two surfaces of a material. The measurement is generally expressed in SI unit as $\text{cm}^3 \text{ s}^{-1} \text{ cm}^2$.

3.3.7.6 Stiffness

Stiffness is generally regarded as the ability of a material to resist deformation (elongation), and is measured in terms of the bending length. JISL 1096:1999 Stiffness (45° cantilever method) was used to determine the stiffness of the fabric sized 2 x 15 cm. The average bending length in the warp and weft directions obtained from 5 measurements was used to determine the stiffness. The flexural rigidity or stiffness is correlated with the bending length as shown in Equation 3.1 [43].

$$G = W \times C^3 \quad (3.1)$$

Here, G = flexural rigidity, mg cm; W = fabric mass per unit area, mg cm^{-2} ; C = bending length, cm.