# CHAPTER 3

# EXPERIMENTAL

## 3.1 Materials

1. Colorants (Cyan, Magenta, Yellow, and Black): The pigments provided from Modern Dyestuffs & Pigments Co., Ltd. were used as received as follows: Cyan (MaxNano Jet SPC): C.I. Pigment Blue 15:3, Magenta (MaxNano Jet SPM): C.I. Pigment Red 122, Yellow (MaxNano Jet SPY): C.I. Pigment Yellow 138, and Black (MaxNano Jet SPK): C.I. Pigment Black 7 have been shown in Figures 2.5 – 2.8, respectively. The properties of pigment dispersions are also shown in Table 3.1.

**Table 3.1**: Properties of pigment dispersions

| Color pigment | Color Index of pigment (CI) | Chemical class of pigment | Solid content (wt%) | Particle size (nm) | pH | Viscosity* (mPa s) |
|---|---|---|---|---|---|---|
| Cyan | PB 15:3 | Phthalocyanine | 3.7 | 40 | 8.8 | 8.9 |
| Magenta | PR 122 | Quinacridone | 2.8 | 86 | 8.6 | 8.5 |
| Yellow | PY 138 | Quinophthalone | 12.1 | 77 | 7.8 | 8.8 |
| Black | PBk 7 | Carbon black | 3.4 | 83 | 7.9 | 8.6 |

*The viscosity was measured at a shear rate 310 $s^{-1}$ at 25°C by Brookfield Viscometer.

2. Polymer binders: Mowilith LDM 7668, acrylic acid ester and styrene and surfactants and Printofix Binder 710 a self-crosslinking acrylate-based copolymer dispersion with styrene from Clariant Chemicals (Thailand) Ltd. Both of them are different in molecular weight, particle size, pH, viscosity, and $T_g$.

**Table 3.2**: Physical properties of the binders

| Commercial name | Solid content (wt%) | Particle size (nm) | pH | Viscosity* (mPa s) | $T_g$ (°C) |
|---|---|---|---|---|---|
| Mowilith LDM 7668 | 40 | 70 ± 1 | 8.5 | 47.7 | 9.7 |
| Printofix binder 710 | 40 | 180 ± 4 | 6.5 | 47.5 | -15.5 |

*The viscosity was measured at a shear rate 70 $s^{-1}$ at 25°C by Brookfield Viscometer.

3. Other chemicals

3.1 Deionized water

3.2 Diethylene glycol ($C_2H_6O_2$), analytical grade, $M_w$ = 62.07 g $mol^{-1}$ from Unilab Ajax Finechem Corporation, New Zealand.

3.3 Glycerine, ($C_3H_8O_3$), analytical grade, $M_w$ = 92.10 g $mol^{-1}$ from Univar Ajax Finechem Corporation, New Zealand.

3.4 Urea, analytical grade from Univar Ajax Finechem Corporation, New Zealand.

3.5 Surfactant, Texapon N 70 LST (Sodium lauryl sulfate) from Cognis Thai Co., Ltd.

4. Silk fabric: Plain weave pattern, construction of 88×99 lines/inch, basic weight 0.08 kg $m^{-2}$ from The Thai Silk Co., Ltd, Thailand.

5. Pretreatment compound: chitosan (FL-80: MW 120 kDa with an *N*-deacetylation degree of 88) from Koyo Chemical Co., Ltd., Japan. (see Figure 2.14).

**3.2 Apparatus**

1. Ink jet printer, Epson stylus$_{TM}$ C65, Seiko Epson Corporation, Indonesia
2. Spectrophotometer, X – Rite, SP62, d/8, U.S.A.
3. Spectrodensitometer, X – Rite, 500 series, 45/0, U.S.A.
4. pH meter, pHTestr 20, Oaklon, Eutech instruments, U.S.A.
5. Brookfield viscometer DV III, programmable rheometer, U.S.A.
6. Surface tensiometer, K8, Kruss, Germany
7. Pycnometer, Brand, Germany
8. Differential scanning calorimeter (DSC), 204 F1 Phoenix, Germany
9. Zetasizer nano series, Malvern Instruments Ltd., U.K.
10. Drying stenter, Rapid Labortex Corporation, Taiwan
11. Padding machine, HF-47993, Mathis, Switzerland
12. Optical microscope, DP70, BX51, Olympus, U.S.A.
13. Scanning electron microscope (SEM), JSM 6400, Jeol, Tokyo, Japan
14. Transmission electron microscope (TEM), JEOL, JEM-2100, Japan
15. Crockmeter, AATCC Crockmeter, Atlas Electric Devices Corporation, Chicago, U.S.A.
17. Centilever stiffness tester, Shirley Development Limited, Stockport, England
18. Air permeability tester, Shirley, England
19. Gyro wash, Atlas Electric Devices Corporation, Chicago, U.S.A.

20. Fourier Transform Infrared spectrometer (FT-IR), Perkins Elmer System 2000, U.K.

21. Drying oven, Rapid Labortex Corporation, Taiwan

22. Atomic Force Microscope (AFM), Seiko, SPI 4000, Japan

## 3.3 Procedure

### 3.3.1 Preparation of pigmented inks

The inks were prepared from two different sizes of copolymer of styrene/acrylate binders (Mowilith LDM 7668 and Printofix Binder 710) in which the average particle sizes were 70 and 180 nm. The other ingredients in the formulation are nano-size pigments, diethylene glycol, glycerol, urea, and surfactant. The formulations were prepared at 1:1 and 1:2 pigment-to-binder ratios (Tables 3.3 and 3.4). Each component was added individually to avoid any unfavorable inhomogeneity in the solution. After the mixing, the inks were filtered to prevent any coarse particles from clogging the orifice of the printer.

**Table 3.3**: Ink recipe containing a 1:1 pigment-to-binder ink formulation

| | wt% of the component | | | |
|---|---|---|---|---|
| Ingredient | Cyan | Magenta | Yellow | Black |
| Pigment dispersion | 40.5 | 50.0 | 30.6 | 44.1 |
| Binder | 3.8 | 3.5 | 9.3 | 3.8 |
| Diethylene glycol | 10 | 10 | 10 | 10 |
| Glycerol | 10 | 10 | 10 | 10 |
| Urea | 5 | 5 | 5 | 5 |
| Surfactant | 0.05 | 0.05 | 0.05 | 0.05 |
| Water | 30.65 | 21.45 | 35.15 | 27.05 |

**Table 3.4**: Ink recipe containing a 1:2 pigment-to-binder ink formulation

| Ingredient | wt% of the component | | | |
|---|---|---|---|---|
| | Cyan | Magenta | Yellow | Black |
| Pigment dispersion | 40.5 | 50.0 | 30.5 | 44.1 |
| Binder | 7.5 | 7.0 | 18.5 | 7.5 |
| Diethylene glycol | 10 | 10 | 10 | 10 |
| Glycerol | 10 | 10 | 10 | 10 |
| Urea | 5 | 5 | 5 | 5 |
| Surfactant | 0.05 | 0.05 | 0.05 | 0.05 |
| Water | 26.95 | 17.95 | 25.85 | 23.35 |

### 3.3.2 Characterization of physical properties of the pigmented inks

**1. pH**

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

**2. Viscosity**

Brookfield viscometer was used to measure the viscosity of the pigment dispersions and the formulated inks at 25°C at a shear rate 310 $s^{-1}$, spindle no.18.

**3. Particle size distribution of the dispersed pigments and pigmented ink jet inks**

Dynamic light scattering was used for the analysis of the particle size of ink formulation. The particle size distributions of the ink formulations were measured at various times (1 day, 1 month, and 3 months) to investigate the stability of the inks.

**4. Pigment charge by Zeta-potential**

The inks were diluted with deionized water before measuring the charge on the pigment surface of the inks by dynamic light scattering. The charge on pigment surface was evaluated at 25°C.

**5. Ink surface tension by tensiometer**

The inks were measured for their surface tensions by Nouy Ring method using the surface tensiometer (K8, Kruss, Germany) measured at room temperature.

**6. Density**

Densities of the inks were measured in a 25-ml pycnometer. The preweighed pycnometer was filled with the ink to the mark at the meter. The cap of the meter was tightly closed. The meter was then weighed to obtain the weight of the ink. The density of the ink was then calculated by Equation (3.1) as follows:

$$D = m/V \qquad (3.1)$$

where D = density, g $cm^{-3}$; m= mass, g; V = volume, $cm^3$.

**7. Glass transition temperature by differential scanning calorimetry**

This technique was used to measure the glass transition temperature of both binders, and related film property and bending stiffness of the printed silk fabrics. The temperature range was varied from –50 to 200°C, with the heating rate at 10°C $min^{-1}$ under liquid nitrogen.

**8. Particle morphology and particle size distribution by transmission electron microscopy**

Transmission electron microscope was used to view the particle morphology and particle size distribution of the pigment dispersions.

**9. Surface of the binder by Atomic Force Microscopy**

This technique was used to study smoothness of the film of binders.

### 3.3.3 Preparation of the silk fabrics

Plain weave silk fabric is constructed by 88 × 99 lines $inch^{-1}$, with a basic weight of 0.08 kg $m^{-2}$ were washed with soap solution, then cleaned with de-ionized water and dried at ambient atmosphere. The fabric was cut into a rectangle shape with a dimension of 21 cm × 29 cm. Then, the silk fabrics were ironed to have a flat and smooth surface.

### 3.3.4 Preparation of the pretreated solutions

Chitosan (FL-80, 120 kDa) was prepared at 0.5, 1 and 1.5% w/v. The chitosan pre-treating solutions were prepared by dissolving the chitosan powder at 0.5, 1 and 1.5% w/v in 1% v/v acetic acid solution and heated for a certain time at 60°C until homogeneous solutions were obtained.

### 3.3.5 Pretreatment by chitosan solution

The silk fabrics were each padded with the 0.5%, 1%, and 1.5% pre-treating chitosan solutions at a 75% pick-up ratio, using a padding machine. The pre-treating substances were fixed at 80°C for 5 min and 110°C for 2 min in a stenter, Rapid Labortex Corporation, Taiwan.

### 3.3.6 Printing process

The untreated and chitosan treated silk fabrics were supported by a flat plastic sheet using a double sided adhesive tape to give a stable dimension of fabric for ink jet printing. The fabric was printed with the in-house formulated ink jet inks by an Epson stylus$_{TM}$ C65 printer at a resolution of 5,760 × 1,440 optimized dpi. After printing, the printed ink on the silk was further fixed at 150°C for 5 min.

### 3.3.7 Evaluation of printed quality

#### 3.3.7.1 Color gamut

The color test chart of printed fabric was evaluated for CIEL*a*b*, which was measured by a spectrophotometer, X-Rite (SP62, d/8, U.S.A.) using illuminant D50 and the 2° observer, measured in terms of X,Y and Z, including UV and reflection component, as mentioned in Section 2.1.9.1.

#### 3.3.7.2 Cross-section of the pretreated and printed silk fabrics

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

#### 3.3.7.3 Crock fastness

The crock fastness of the printed fabric was evaluated using an AATCC Crockmeter (Atlas Electric Devices Corporation, Chicago, USA), by AATCC Test Method 8 – 2001 [25]. The amount of color transferred from the printed surface to the receiving testing surface by rubbing, was judged using a 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 double rubs under both dry and wet conditions. Later, a grade from 1–5 is assigned.

### 3.3.7.4 Wash fastness

Wash fastness was carried out by Gyrowash, using ISO 105-C06 [26]. A specimen of 100 mm×40 mm size in contact with the specified adjacent fabric is washed, rinsed and dried. Each printed fabric, sewed with a multifibre strip, was washed at 40°C for 30 min in a liquor containing 4 g of standard detergent (without an 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 grey scale for staining in accordance with ISO 105 – A03. Moreover, the color difference in the printed fabrics obtained before and after the washing was also reported in terms of color strength (K/S) and relative color strength was already given in Equations 2.7 and 2.8, these equations are presented in page 35.

The fabrics were printed in a solid tone pattern of four-color inks (cyan, magenta, yellow, and black). The ink colors of the printed fabrics before and after washings were evaluated by a spectrophotometer, X-Rite (SP62, d/8, U.S.A). The samples reflectance was measured at 5 different areas to determine an average K/S value.

### 3.3.7.5 Air permeability

ASTM D 737 – 96 (Standard test method, 1996) for air permeability of textile fabric was used to study the effect of padding and printing of the fabrics [27]. 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 an SI unit as $cm^3\ s^{-1}\ cm^2$.

### 3.3.7.6 Bending stiffness

Bending stiffness is generally regarded as an 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 bending stiffness of the fabric sized 2 × 15 cm [28]. The average bending length in the warp and weft directions obtained from 5 measurements was used to determine the average bending stiffness. The flexural rigidity or bending stiffness is correlated with the bending length and is usually expressed as the fabric flexibility as shown in Equation 3.2 [17]:

$$G = W \times C^3 \qquad (3.2)$$

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

### 3.3.7.7 Optical density

A solid tone pattern was printed on the untreated and treated silk fabric. The optical density of the printed fabrics was measured with a spectrodensitometer and the average was calculated from 10 measurements.

### 3.3.7.8 Ink penetration

The penetration of the pastes through the fabric was assessed on printed, dried and cured samples from the difference in reflectance between the face and back of the printed area measured on a spectrophotometer. The percentage penetration of the print was defined as shown in Equation 3.3 [6]:

$$\text{Penetration} = \frac{100(K/S)_b}{0.5[(K/S)_f + (K/S)_b]} \quad (3.3)$$

where the $(K/S)_f$ and $(K/S)_b$ values are for the front and back of the fabric, respectively, K is the absorption coefficient in the Kubelka-Munk analysis of reflectance, and S is the color values taken as the color strength of the printed fabric.

The depth of ink penetration can be observed through the optical microscopic technique. A cross-section of a printed silk yarn was pasted on the slide of the microscope. Its depth of penetration was recorded via a CCD camera coupled with the microscope. A scale bar at the micrograph can be used as a ruler to estimate the depth of ink penetration into the silk yarn.

Applying a simple physical approach for penetration of a liquid flowing under its own capillary pressure, the Lucas-Washburn in Equation (2.9) can be used to reflect the depth or speed of penetration in fabrics [9].