

CHAPTER III

EXPERIMENTAL

3.1 Materials

- Sample**
- Bleached cotton knitted fabric, yarn count 20/1, single jersey structure, weigh 0.54 g. / 100 cm².
 - Bleached cotton knitted fabric, yarn count 50/1, single jersey structure, weigh 0.27 g. / 100 cm².
 - Bleached cotton woven fabric, plain structure, weigh 0.26 g. / 100 cm².
 - Bleach cotton woven fabric, satin structure, weigh 0.59 g. / 100 cm².
- Dye**
- Direct Dye, Benzopurpurine 4B, supplied by Tokyo Chemical Industry Co., Ltd., Japan
- Chemicals**
- All chemicals used in this experiment are laboratory reagent grade (see Table 3.1).

Table 3.1 Chemicals used in this experiment.

Chemical	Company
Sodium hydroxide pellets 98%	Fluka
Formic acid purum 98%	Fluka
Ammonia gas	Unique Gas & Petrochemicals Public Co.,Ltd
Acetone	BDH Laboratory Supplied
Dry ice	Praxair
Cupriethylenediamine hydroxide solution	CARLO ERBA
Nitrogen gas	Praxair

3.2 Equipment

- Hydraulic diaphragm bursting strength tester (SDL Co., Ltd. Model P-1000)
- Tensile strength tester, machine type 5566 Instron
- Laboratory dyeing machine (Fong's ®)
- Macbeth reflectance spectrophotometer, Color-Eye 7000
- X-ray diffractometer (Phillips PW 3710)
- Immersion circulator
- Ubbelohde viscometer, glass capillary type size100
- Precision balance
- Ice bath
- Thermometer
- Transparent water bath (50x35x35 cm³)
- Stop watch
- Oven
- Glasswares

3.3 Preparations of Cellulose Samples

The objectives of this work are to study the transformation of cellulose polymorphs (cellulose I, cellulose II, cellulose III and cellulose IV) in cotton woven and knitted fabrics via chemical treatments, and to determine some properties of these cotton substrates at various stages of cellulose polymorphs.

3.3.1 Preparations of Cellulose I Samples

Native cellulose or cellulose I samples were bleached cotton substrates. They consisted of two woven fabrics and two knitted fabrics. Woven fabrics had plain and satin structures. Knitted fabrics had a single jersey structure with yarn counts 20/1 and 50/1.

Cellulose I samples were also prepared by immersing cellulose I or cellulose II sample in liquid ammonia for 1 minute. Then it was removed from liquid ammonia and immersed in a water bath for an ammonia removal at room temperature until it was freed of ammonia.

All samples were tested for stage of cellulose polymorph, degree of polymerization, tensile or bursting strength and dye absorption.

3.3.2 Preparations of Cellulose II Samples

Cellulose II samples were prepared by immersing cellulose I or cellulose III sample in 20% sodium hydroxide solution for 30 minutes at 20°C. Then it was rinsed with water, neutralized with 1% formic acid and dried.

All samples were tested for stage of cellulose polymorph, degree of polymerization, tensile or bursting strength and dye absorption.

3.3.3 Preparations of Cellulose III Samples

Cellulose III samples were prepared by immersing cellulose I or cellulose II sample in liquid ammonia, condensed from a tank of anhydrous ammonia, for 1 minute at -33.35°C. Then it was kept in a hood for an ammonia evaporation until freed of ammonia.

All samples were tested for stage of cellulose polymorph, degree of polymerization, tensile or bursting strength and dye absorption.

3.3.4 Preparations of Cellulose IV Samples

Cellulose IV sample could be prepared in two ways as follows :

1. Cellulose IV samples were prepared by immersing cellulose I or cellulose II sample in glycerol. Then heated at 260°C for 30 minutes and washed successively with water and acetone.

2. Cellulose IV samples were prepared by heating cellulose I or cellulose II sample in water at 190°C for 2 hours. Then cooled to room temperature, washed successively with water and acetone and dried.

All samples were tested for stage of cellulose polymorph, degree of polymerization, tensile strength or bursting strength and dye absorption.

3.4 Test Procedures

All samples were tested for stage of cellulose polymorph, degree of polymerization, tensile or bursting strength and dye adsorption. The test procedures are described as follows.

3.4.1 Determination of Stage of Cellulose Polymorph

X-ray diffractometer (Phillips PW 3710, see Figure 3.1) using $\text{CuK}\alpha$ radiation was used to investigate the stages of the cellulose polymorphs of samples with a scanning of $0.02^\circ 2\theta$ /min. at 40 kV acceleration voltage and 30 mA. tube current. Each sample was cut to approximately 20 mm. in width and 30 mm. in length. Then it was place on a sample plate for analysis. All sample were scanned from $2\theta = 0^\circ$ to $2\theta = 30^\circ$ and the X-ray diffractograms are shown in section 4.1

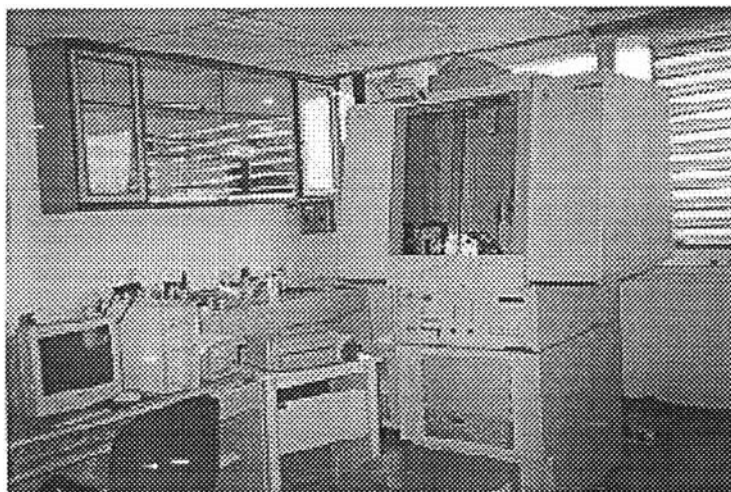


Figure 3.1 X-ray diffractometer (Phillips PW 3710)

3.4.2 Degree of Polymerization Measurement

Cellulose samples were tested for the degree of polymerization according to the standard test method ASTM D 1795⁽⁴⁰⁾ " Intrinsic Viscosity of Cellulose ". This test method covers the determination of the relative viscosity calculated from the ratio of cellulose solution and solvent flow times, and the intrinsic viscosity. Then the intrinsic viscosity was used to calculate for the degree of polymerization. A five-steps experiment was conducted as follows

3.4.2.1 Preparation of Test Sample

Cellulose samples as test samples were cut and ground into powder, and dried at 80°C for 30 minutes.

3.4.2.2 Preparation of Cellulose-Solution

0.03 grams of dried sample was placed in a 50 ml. volumetric flask. Then 20 ml. of 0.5 M. cupriethylenediamine hydroxide solution was added into the volumetric flask. The mixture was flushed with nitrogen gas before closing the flask tightly with a stopper. The flask was shaken vigorously until the sample was completely dissolved.

3.4.2.3 Measurement of Solvent Flow Time (t_0)

10 ml. of 0.5 M. cupriethylenediamine hydroxide solution was filled into a capillary viscometer previously immersed in a constant-temperature bath at 25°C. Then the solution was flushed with nitrogen gas before closing the viscometer tightly with stoppers. The solution was left there for 5 minutes to reach the bath temperature. After 5 minutes, the solution was drawn from the bottom part of the viscometer to the position a little above the top mark of the bulb. Then the solution was let free to flow down and the time required for the solution to flow from the top mark to the bottom mark of the bulb was measured. The measurement was repeated at least twice and the average solvent flow time was calculated (t_0).

3.4.2.4 Measurement of Cellulose-Solution Flow Time (t_n)

10 ml. of the cellulose solution prepared from section 3.4.2.2 was filled into the same viscometer as measuring the solvent flow time and the solution flow time was repeatedly measured for 3 times using the same procedure mentioned in section 3.4.2.3. After the measurement, the solution in the viscometer was diluted by adding a known amount of 0.5 M. cupriethylenediamine hydroxide solution, mix well, and measured for flow times. This process was repeated until at least 3-5 different concentrations of cellulose-solution were measured for flow times.

3.4.2.5 Calculation for the Degree of Polymerization

To obtain the degree of polymerization of cellulose sample, the relative viscosity (η_{rel}) was first calculated from the ratio of the cellulose-solution flow time (t) and the solvent flow time (t_0) as follows.

$$\eta_{rel} = t_n / t_0 \quad (\text{Equation 3.1})$$

Where

η_{rel}	=	relative viscosity
t_n	=	flow time of cellulose-solution (second)
t_0	=	flow time of solvent (second)

Then the intrinsic viscosity $[\eta]$ was determined by plotting a straight line relationship of $\log [(\eta_{rel} - 1) / c]$ and c according to the Martin equation shown in Equation 3.2. The interception of the extrapolated line through the axis of $\log [(\eta_{rel} - 1) / c]$ gave $\log [\eta]$.

$$\log [(\eta_{rel} - 1) / c] = \log [\eta] + K [\eta] c \quad (\text{Equation 3.2})$$

Where $[\eta]$ = intrinsic viscosity
 c = cellulose-solution concentration (g/dl)
 η_{rel} = relative viscosity
 K = constant

A reliable approximation of the degree of polymerization of cellulose sample (DP) was calculated by multiplying the intrinsic viscosity by 190 as shown in Equation 3.3

$$DP = [\eta] \times 190 \quad (\text{Equation 3.3})$$

To determine how much damage occurring in the sample after the chemical treatment, the degree of polymerization of cellulose sample was used to calculate for the damage factor (S) as shown in Equation 3.4

$$S = \log \left[\frac{2000 - P_{tx}}{2000 - P_t} + 1 \right] - \log 2 \quad (\text{Equation 3.4})$$

Where P_t = DP of cellulose sample before chemical treatment.
 P_{tx} = DP of cellulose sample after chemical treatment.
 2000 = Reference value.

Table 3.2 Classification of damage factor (S).

Damage factor (S)	Description
0.01-0.2	very good-undamaged
0.21-0.3	Good-very carefully treated
0.31-0.5	satisfactory
0.5-0.75	slightly damaged
0.75	badly damaged

3.4.3 Fabric Strength Measurement

3.4.3.1 Tensile Strength Measurement

Cellulose woven samples were tested for breaking load and breaking elongation by the Standard for Method of Testing for Textile, Volume 9,⁽⁴¹⁾ "Breaking Load and Breaking Elongation of Woven Fabric." This test method covers revealed strip and cut strip test procedures for determining the breaking load and breaking elongation of woven sample.

A tensile strength tester, Machine Type 5566 Instron was used for the task. It was operated at a speed of 100 ± 10 mm./min. The distance between the clamps (gauge length) was set at 20 cm. Each sample was cut to approximately 7cm.in width and 32cm.in length for 3 pieces along the warp direction and for 3 pieces along the weft direction. Yarns along both directions were removed until the sample size was 5 cm.x30 cm. Then the sample was clamped to the tensile strength tester (Figure 3.2) and it was extended until breakage. Breaking load and breaking elongation of the sample were recorded. Three samples for each direction were tested and data were averaged.

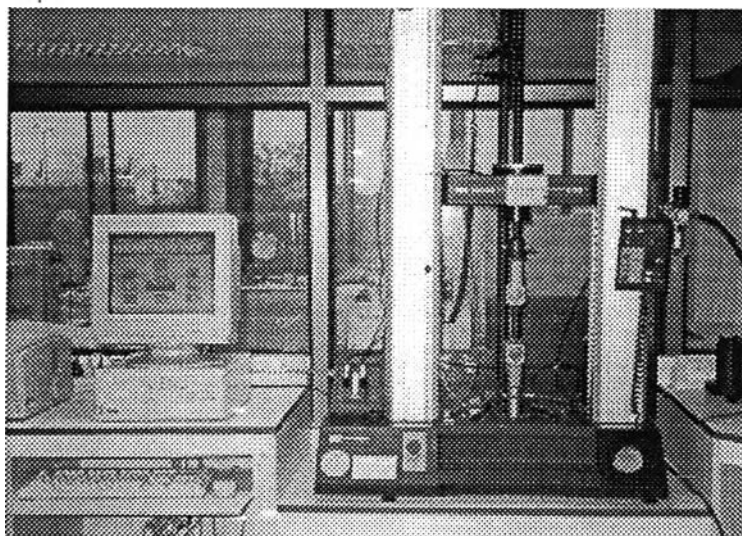


Figure3.2 Tensile strength tester (Machine Type 5566 Instron)

3.4.3.2 Bursting Strength Measurement

Bursting strength of knitted fabric was measured using the Standard for Method of Testing for Textile, Volume 19⁽⁴²⁾ "Hydraulic Bursting of Knitted Goods and Nonwoven Fabrics-Diaphragm Bursting Strength Tester Method." This test method covers the determination of the bursting strength of knitted fabric. Each fabric sample was clamped over a rubber diaphragm expanded up to the sample by a fluid pressure. When the machine was operated, the diaphragm was pushed up to the sample and expanded the sample to the point of rupture. The difference between the total pressure required to rupture the sample and the pressure required to inflate the diaphragm was reported as the bursting strength of the sample. Each sample was tested for at least 10 times and the results were averaged. A hydraulic diaphragm bursting strength tester was shown in Figure 3.3.

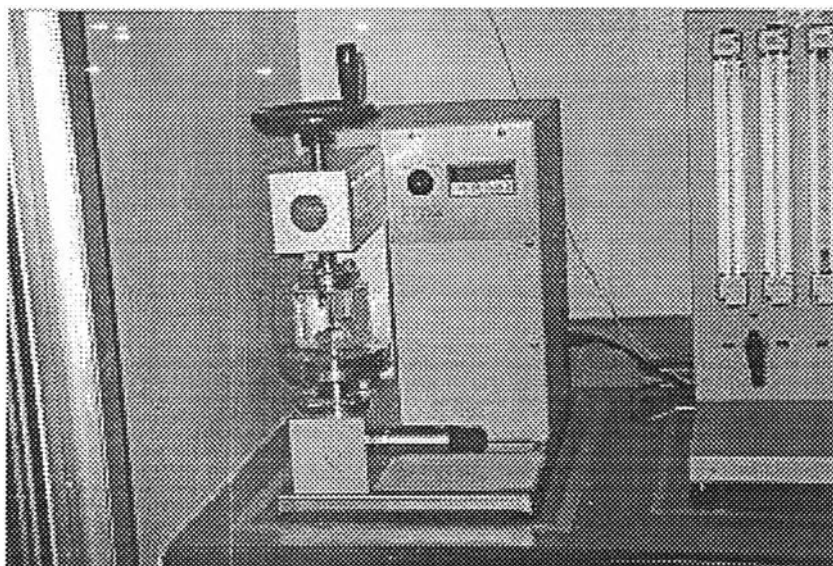


Figure 3.3 Hydraulic diaphragm bursting strength tester (SDL Co., Ltd. Model P-1000)

3.4.4 Dye Absorption Measurement

Cellulose woven and knitted samples were dyed with a direct dye, Benzopurpurine 4B 1% o.w.f. (of weight of fabric) in a laboratory dyeing machine (Figure 3.4) at a liquor ratio of 30 : 1. The dyeing process was commenced at room temperature, raised to 95°C (4°C/min.) and maintained at this temperature for 45 minutes. The dyed fabrics were then removed from dyed solution, rinsed thoroughly in running tap water, squeezed and dried. The dyeing process was illustrated in diagram 3.1.

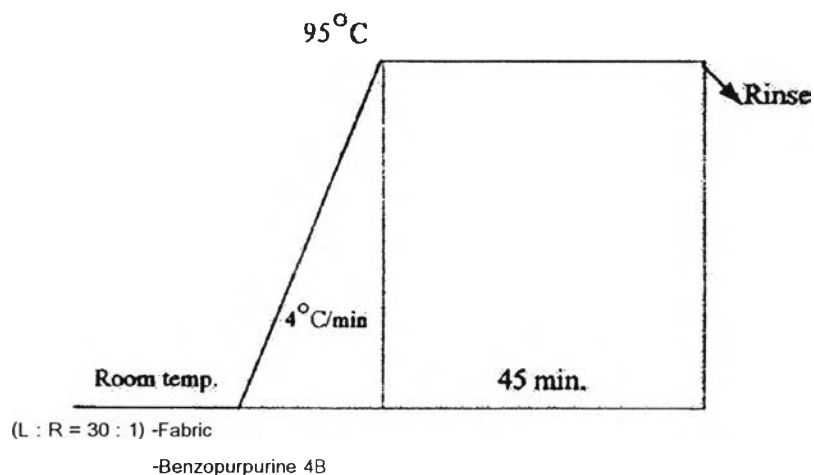


Diagram 3.1 Dyeing process.

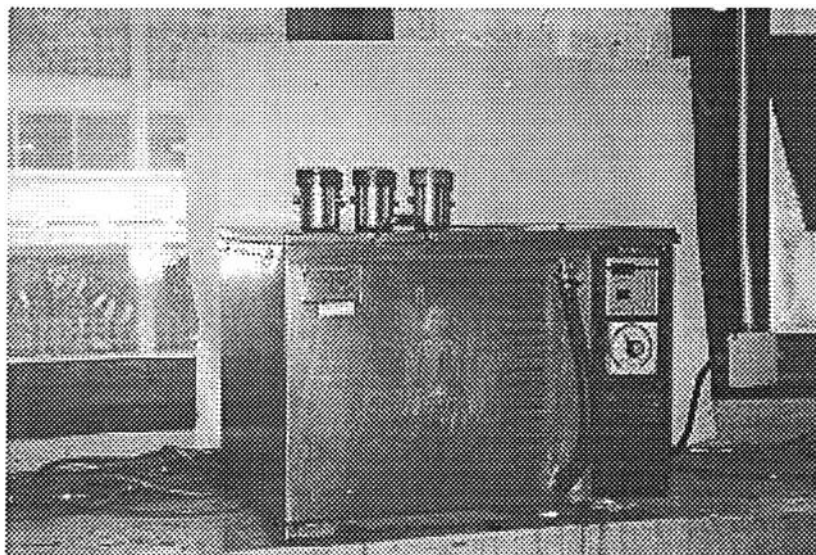


Figure 3.4 Laboratory dyeing machine (Fong's [®])

After dyeing, dyed sample was measured for color strength or color depth at a wavelength of 520 nm. using the Instrumental Color System (I.C.S) Macbeth Reflectance Spectrophotometer (Figure 3.5). The sample with more dyestuff on gave higher color strength than the sample with less dyestuff on. Each sample was measured twice and the average was reported. The color strength of the dyed fabric can be expressed as K/S value calculated by the Kubelka Munk equation shown in equation 3.5

$$K / S = \frac{(1 - R)^2}{2R} \quad \text{(Equation 3.5)}$$

Where

K	=	the absorption coefficient
S	=	the scattering coefficient
R	=	the reflectance of the fabric at the wavelength of maximum absorption (λ_{\max})



Figure 3.5 I.C.I Macbeth spectrophotometer (Color-Eye 7000)