CHAPTER 3

Experimental

3.1 Materials

1) Cotton fabric: Bleached and unmercerized plain woven fabric was used through out this research.
2) Chemicals: The chemicals used in this research were laboratory reagent grade excepted AIBN, which was commercial grade. The chemical details are given in Table 3.1

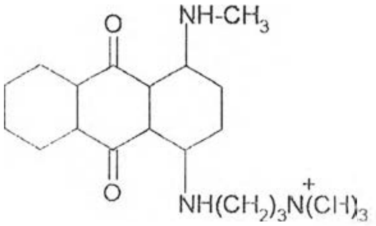
Table 3.1 List of chemicals used in this work.

Chemicals	Formula	Manufacturer
Cetyltrimethylammonium bromide (CTAB)	$C_{19}H_{42}BrN$	Fluka
Sodium dodecyl sulfate (SDS)	$C_{12}H_{25}SO_4Na$	Fluka
2-Propanol	C_3H_7OH	Merck
Benzene	C_6H_6	Fluka
2,2'-Azobisisobutyronitrile (AIBN)	$(CH_3)_2C(CN)NN(CN)C(CH_3)_2$	SCI
Methacrylic acid	C_3H_5COOH	Fluka
Potassium persulfate	$K_2S_2O_8$	Fluka
Ethanol	C_2H_5OH	Fluka
Nonionic detergent	Unavailable	U.N.T. Chemical Co.,Ltd.

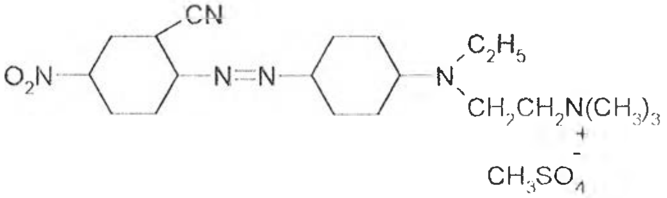
3) Dyes: Two types of basic dyes from Dystar were used as follows:

Commercial name	C.I. Generic name	C.I. Constitution number
Astrazon Blue FGLN 200%	C.I. Basic Blue 22	61512
Astrazon Red 5BL	C.I. Basic Red 24	11088

C.I. Basic Blue 22 (Bright blue)



C.I. Basic Red 24 (Dull Blurish Red)



3.2 Equipment

1. Laboratory dyeing machine, Ahiba Nuance.
2. Macbeth reflectance spectrophotometer, Color-eye 7000
3. Fourier-transform infrared spectrophotometer, Nicolet Impact 400D
4. Light scattering photometer, Malvern 4700
5. Light fastness testing machine, SUGA test instruments Co., Ltd., X75
6. Washing fastness testing machine, ATLAS LEF
7. Oven, Isotemp. model 516G
8. Optical microscope, Olympus, model BH-2
9. Magnetic stirrer, Framo-Geratetech model M21/1
10. Magnetic bar
11. Glasswares e.g. three-necked round bottom flask, condenser, conical flasks, beakers and pipettes
12. Hygrometer, BARICO.

3.3 Preparation of Oil-in-Water Stock Microemulsion Solution

3.3.1 Microemulsion Base on CTAB-Benzene/Propanol-Water System

An amount of 1.75 g. of CTAB and 1.25 g. of 2-propanol were dissolved in 95.75 g. of distilled water. The mixture was stirred vigorously to obtain clear solution. A solution of AIBN (0.125 g.) and benzene (1.125 g.) was then added drop wise to the above solution meanwhile the solution was stirred on a magnetic stirrer at the speed of 1400 rpm until the solution mixture became transparent (about 5 minutes). The transparent solution obtained was stored overnight before use.

3.3.2 Microemulsion Base on SDS-Benzene/Propanol-Water System

For comparison purpose, the anionic surfactant, SDS, was employed to replace CTAB. An amount of 1.75 g. of SDS and 1.25 g. of 2-propanol were dissolved in 95.75 g. of distilled water. The mixture was stirred vigorously to obtain clear solution. A solution of AIBN(0.125 g.) and benzene(1.125 g.) was then added drop wise to the above solution meanwhile the solution was stirred on a magnetic stirrer at the speed of 1400 rpm until the solution mixture became transparent (about 5 minutes). The transparent solution obtained was stored overnight before use.

3.3.3 Particle Size Distribution Measurement

Light scattering photometer (Malvern 4700) was employed to measure particle sizes of oil in water microemulsion droplets as well as determine their size distribution. Measurement was performed at λ= 488 nm and θ= 90°. The measured data were analysed using Photon Correlation Spectroscopy (PCS).

3.4 Polymerization of Methacrylic Acid inside Cellulose in Oil-in-Water Microemulsion System

Bleached, unmercerized cotton fabric was boiled in ethanol for 30 minutes and stored overnight at 80°C in weighing bottle and then allowed to stay at room temperature in a vacuum desiccator until constant weight was obtained (37).

3.4.1 Effect of Immersion Times on Percent Add-on of in-situ Polymethacrylic Acid

Cotton fabric was immersed in the oil-in-water cationic microemulsion solution prepared earlier. Fabric to liquor ratio of 20:1 was used. Duration of immersion times was varied from 30, 60, 90, 120, 180, and 240 minutes, respectively. The cotton fabric should be submersed under water to avoid stirring which may interrupt the microemulsion system. Oil phase droplet containing AIBN initiator was allowed to diffuse into amorphous region of cellulose through electrostatic interaction between the positive charge oil droplet and the negative charge of fiber surface. After that the cotton fabric was transferred to a conical flask containing 4% (w/w) methacrylic acid solution (liquor ratio 40:1). The conical flask was placed in an oven at temperature of 80°C for 3 hours. Then the cotton fabric was removed and washed in tap water before allowing drying at room temperature. Extraction of surface homopolymer was carried out by refluxing the sample in boiled ethanol for 6 hours. Finally, the treated fabric was stored in an oven at temperature of 80°C for overnight before weighing until a constant weight was obtained. Percent add-on of in-situ polymethacrylic acid was measured.

3.4.2 Effect of Suitable Time and Concentration for Polymerization of Methacrylic Acid

Cotton fabric was immersed into oil in water cationic microemulsion stock solution in liquor ratio of 20:1 for 2 hours. Then the cotton fabrics were sunk in different concentrations of monomer solution from 0.5 to 5.0 % (w/w) in liquor ratio of 40:1 in conical flask. There were varied polymerization times (from 1 to 4 hours) in each concentration. Next, these 24 samples were placed in an oven at temperature of 80°C. After the time of polymerization, the cotton fabric was removed from oven and rinsed in tap water before drying at room temperature. Then the samples were extracted in boiled ethanol for 6 hours and dried in an oven at 80°C for overnight before weighing until a constant weight was obtained. Percent add-on of polymethacrylic acid was calculated.

3.4.3 Effect of Liquor Ratio in Polymerization Step on Percent Add-on

After the first step, cotton fabric was immersed in microemulsion stock solution liquor ratio 20:1 for 2 hours, the cotton fabric was sunk in conical flask that contained 4% (w/w) methacrylic acid solution in different liquor ratio 20:1, 30:1, and 40:1. Then these conical flasks were placed in an oven at the temperature of 80°C for 3 hours. After that, the fabrics were removed from the conical flask and washed in tap water before allowing drying at room temperature. Next, treated fabrics were extracted in boiled ethanol for 6 hours and dried in oven at temperature of 80°C for overnight before weighing until a constant weight was obtained. Percent add-on of polymethacrylic acid was calculated.

3.4.4 Effect of Different Stock Solution on Percent Add-on

For the comparison, cotton fabric was immersed in the oil in water anionic microemulsion stock solution, which prepared in the section 3.3, in liquor ratio of 20:1 for 2 hours for the diffusion of microemulsion to the amorphous region of cotton fabric. Then the cotton fabric was removed and put in a conical flask that contained 4% of methacrylic acid at liquor ratio of 40:1. The time of polymerization was varied from 1 to 4 hours in an oven at 80°C. After that, the fabric was removed from the conical flask and washed in tap water before allowing to dry at room temperature. To remove the loosely attached homopolymer on the fiber surface, the fabric was extracted by refluxing in boiled ethanol for 6 hours. Next, the fabric was dried in oven at temperature of 80°C for overnight before weighing until a constant weight was obtained. Percent add-on of the remained polymethacrylic acid was computed.

3.4.5 FT-IR Analysis

Identification of polymethacrylic acid inside cellulose was carried out using FT-IR technique. The method of sample preparation used in this experiment was pressed-disc technique by mixing sample in potassium bromide (KBr). The spectra of polymethacrylic acid were obtained on a Nicolet Impact 400D FT-IR spectrometer and all of spectra were transferred to the computer for further analysis performed by ommic software.

3.4.6 Evaluation of Moisture Regain

Definition

% Moisture regain was defined as the weight of moisture in a material expressed as a percentage of the weight of the completely dry material (28).

$$\% \text{ Moisture regain} = \frac{\text{original weight} - \text{dry weight} \times 100}{\text{dry weight}}$$

$$\% \text{ Moisture content} = \frac{\text{original weight} - \text{dry weight} \times 100}{\text{original weight}}$$

The AATCC method of moisture measurement (AATCC Test Method 20A: 1995(38)) was referred in this research. Weigh the specimen (not less than 1 gram) that inserts in weighing bottle until constant weight and record the constant weight. Place the uncover weighing bottle contains the specimen in an oven maintained at 105 to 110°C for 1.5 hours. At the end of time period, remove the bottle from the oven, immediately replace the cover and put it in the desiccator. When the bottle and content have cooled to room temperature, remove them from the desiccator and reweigh. Repeat the heating and reweigh process for period of 30 minutes until the weight is constant to within 0.001 gram and record the constant weight.

For this research, moisture measurement maintained in the temperature of 23°C and 62% humidity measured by hygrometer, BARICO®.

3.4.7 Measurement of Percent Add-on

All of the cotton fabrics in this research were sewed at four edges before treatment because the plain woven fabric frayed easily. Then the fabric was placed in boiled ethanol for 30 minutes on purpose to substitute ethanol for water in amorphous region. Next, this fabric was put into weighing bottle and placed in an oven at the temperature of 80°C for overnight to be sure that water and ethanol were not presented in amorphous region. After that, this weighing bottle that contained dry fabric was removed to the vacuum dessicator to cool down the fabric and this weighing bottle was removed and weighed until a constant weight was obtained. After the constant weight of the fabric was recorded, this fabric was subjected to the polymerization process. Subsequently, the fabric was weighed again after extraction by the same method. Finally, percent add-on of polymethacrylic acid onto cellulose was calculated using the following formula.

$$\%\ \text{Add-on} = \left[\frac{\text{Final fabric weight} - \text{Initial fabric weight}}{\text{Initial fabric weight}}\right] \times 100$$

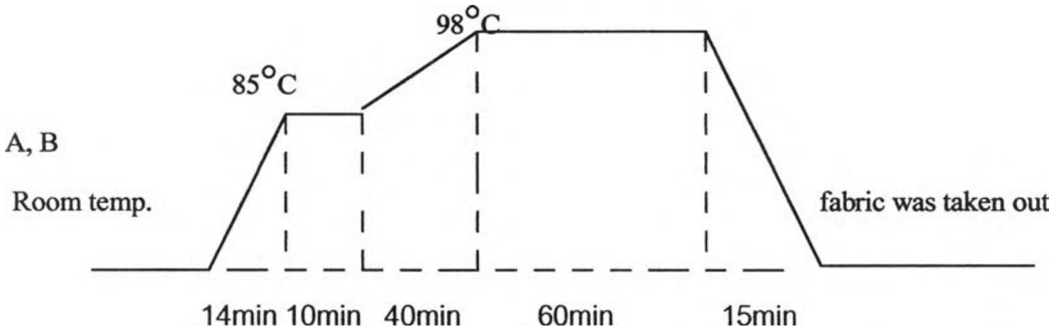
3.5 Graft Polymerization of Methacrylic Acid onto Cellulose Using $K_2S_2O_8$ as Initiator

For comparison, graft polymerization of methacrylic onto cellulose was carried out using $K_2S_2O_8$ as initiator. The 0.205 % (w/w) of potassium persulfate solution was employed at liquor ratio of 20:1 for 2 hours for the diffusion and interaction of $K_2S_2O_8$ on cellulose substrate. Then the fabric was removed to immerse in conical flask that contained 4% of methacrylic acid at liquor ratio of 40:1. Graft polymerization was conducted at the temperature of $80^{o}C$ for 3 hours (in an oven). Extraction was necessary to remove the loosely attached homopolymer. The treated fabric was extracted in boiled ethanol for 6 hours. After that, the treated fabric was dried in an oven at the temperature of $80^{o}C$ for overnight before weighing until a constant weight obtained. Percent add-on of the remained polymethacrylic acid was measured.

3.6 Dyeing of Polymethacrylic Acid Modified Fabrics with Basic Dyes in the Absence of Auxiliaries Using Exhaustion Dyeing Method

The polymethacrylic acid modified fabric and unmodified fabric were dyed with ASTRAZON BLUE FGLN 200% at a depth of shade of 1, 2, 3 and 4 % o.w.f. , Excepted sample 5, ASTRAZON RED 5 BL 2% o.w.f. was used. Dyeing was carried out in an Ahiba Nuance® laboratory dyeing machine at liquor ratio of 20:1. All dyeing were commenced at room temperature. The temperature was raised to $85^{o}C$ over 14 minutes ($4^{o}C$/min) and continued at this temperature for 10 minutes. Then, the temperature was raised to $98^{o}C$ in 40 minutes and held at this temperature for 60 minutes. Then, the temperature was reduced to room temperature within 15 minutes. Next, the dyed fabrics was taken out and rinsed thoroughly in running tap water. Finally, dyed fabrics were immersed into the boiled solution of 5 g/l nonionic surfactant in liquor ratio 50:1 for 30 minutes (Dye bath preparation and dyeing method were conducted accordingly to the manufacture's literature(29)).

The dyeing process diagram of basic dye may be illustrated in Diagram 3.1



A: treated or untreated fabric

B: Basic dye (2% o.w.f.)

Diagram 3.1 the dyeing process diagram of basic dye.

3.7 Measurement of Colour Strength

The colour strength of the dyed fabrics were expressed as K/S values calculated by the Kubelka-Munk equation (33)

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

R is the reflectance of an infinitely thick layer of material illuminated with light of a known wavelength (λmax)

K is the absorption coefficient

S is the scattering coefficient

The absorption characteristics for range of dyes on a specific substrate were performed spectrophotometrically by instrumental colour system (I.C.S.) spectrophotometer, which was employed to measure the reflectance values of the coloured samples in the visible wavelength (400-700 nm).

The K/S value was directly proportional to the concentration of colorant in the substrate. Therefore, the percentages of covalent fixation of the dye on the substrates were calculated by comparing the K/S values of the dyed samples before and after washing.

Each dyed sample was divided into two parts. The first was soaped in soaping solution that contained 5 g/l of nonionic detergent at boil for 30 minutes in a 50:1 liquor ratio for removing any unfixed dye and then rinsed for 15 minutes in running water. After drying, the soaped sample was measured by I.C.S. Macbeth reflectance spectrophotometer to obtain K/S values at λ max. The measurement parameters were as follows: 10° observer; D65 illuminant; specula reflectance included; UV reflectance included; large aperture; and average times.

For second part of dyed sample was treated as same as the first but before measuring by I.C.S. Macbeth reflectance spectrophotometer. This part was kept for further test for color fastness to washing by ISO 105-C01 standard test method (35).

The degree of dye fixation (%F) was calculated from the following equation:

$$\%F = \frac{(K/S)_1 X100}{(K/S)_0}$$

$(K/S)_1$ is the K/S value of dyed sample after washing test

$(K/S)_0$ is the K/S value of dyed sample before washing test

The degree of dye fixation (%F) describes the amount of exhausted dye, which was fixed covalently, thus giving an indication of the amount of unfixed dye, which was removed during a washing test process to achieve maximum wet fastness properties.

3.8 Determination of Colour Fastness to Artificial Light: Xenon Arc Fading Lamp Test

The ISO 105-B02 colour fastness to light (34) was used to determine the resistance of the colour of textiles of all types and in all forms to the action of an artificial light source. The light fastness of dye is usually assessed against a set of standard dyeing ISO has chosen a set of eight blue dyes which vary in light fastness on wool call "Blue wool." The blue wool references developed and produced in Europe are identified by the numeral designation 1 to 8. These references are cloths dyed with the dyes listed in Table 3.2. They range from 1 (very low light fastness) to 8 (very high light fastness) so that each higher number reference is approximately twice as fast as the preceding one.

Table 3.2: Dyes for blue wool references 1 to 8

Reference	Dye-colour Index Designation
1	C.I. Acid Blue 104
2	C.I. Acid Blue 109
3	C.I. Acid Blue 83
4	C.I. Acid Blue 121
5	C.I. Acid Blue 47
6	C.I. Acid Blue 23
7	C.I. Solubility Vat Blue 5
8	C.I. Solubility Vat Blue 8

Test procedure

The size of the specimen was 1 cm x 4.5 cm (in apparatus of the air-cooled type) when several periods of exposure are made side by side on the same specimen and compressed to give uniform surface and fasten on a card. Each exposed and unexposed are should be not less than 10 mm x 8 mm. The exposure condition was $63\pm1^{\circ}C$ controlled by continuous operation of blower with thermostatic control of the temperature of a constant volume of air whose relative humidity is increased by adding moisture to the air as it pass through the conditioning chamber by means of an electrically operated atomizer. The controls of the apparatus are adjusted so that the relative humidity of the air in the test chamber is $30\pm5\%$.

3.9 Determination of Washing Fastness

The ISO 105-C01 colour fastness to washing test 1(35) was established to determine the fastness to washing of colour textile. In the principle, a specimen in contact with specified adjacent fabric is mechanically agitated under specified condition of time and temperature in a soaping solution, then rinsed and dried the change in colour of the specimen and the stain of the adjacent fabrics are assessed with the gray scales.

Test procedure

Attach a specimen measuring 40 mm x 100 mm to a piece of the multifiber adjacent fabric, also measuring 40 mm x 100 mm, by sewing along one of the shorter side. Then place the composite specimen in the container and add the necessary amount of soap solution, 5 g/l of standard soap in distilled water, liquor 50:1 and heated to 40°C for 30 minutes. Afterward, removed the composite specimen, rinsed in cool water and running tap water for 10 minutes, and squeezed it.

Open out the composite specimen and dry it by hanging it in air at temperature not exceeding 60°C.

The change in color of the specimen and the staining of each type of fiber in the multifiber adjacent fabric were assessed with both the Grey scale and determined as the color difference (ΔE) values by using I.C.S. Macbeth spectrophotometer. The settings on the I.C.S. were as follows: 10° observer; D65 illuminant; specular and UV reflectance included; aperture; average 2 times; and used CIELAB equation.

3.10 Effect of % Add-on of Polymethacrylic Acid on the Dyeability of Treated Fabrics with Basic Dyes

Cotton fabrics modified with different percent add-on of polymethacrylic acid (0.1% - 0.4%) were dyed with 2% o.w.f. ASTRAZON FGLN 200% in Ahiba Nuance® laboratory dyeing machine at liquor ratio 20:1. The condition of dyeing was the same as described in the section 3.6. The K/S values of dyed fabrics were measured.

3.11 Optical Microscopic Analysis of a Cross-section of Dyed Fabrics

The well-prepared cross section of dyed fibers was subjected to optical microscopic analysis (using Olympus optical microscope, model BH 21). In all cases, warp yarn was selected and carefully cut by the cross section test kid. The optical micrograph of fiber cross section was taken at magnifying power of 100 times.