



## CHAPTER III

### EXPERIMENTAL

#### 3.1 CHEMICALS AND INSTRUMENTS

Lists of materials, chemicals, instruments and equipment employed in this research work are tabulated below:

TABLE 3.1 Detail of materials used

Name of materials	Sources
Raw silk fibres (Bombyx mori)	CHOON THAI SILK (PETCHBOON)
Dyestuff "Supranol Fast Orange GSN 140%"	Bayer
Dyestuff "Kayacyl Sky Blue R"	Sumitomo

TABLE 3.2 Detail of chemicals used

Name of Chemicals	Sources	Remarks
N,N'-methylenebisacrylamide (N,N'-MBA)	FLUKA	ANAL - GRADE
Manganese(III) acetylacetonate (Mn(acac) <sub>3</sub> )	MERCK	ANAL - GRADE
Perchloric acid	BDH	ANAL - GRADE
Glacial acetic acid	BDH	ANAL - GRADE
Sodium laurylsulphate (Natrium dodecylsulfate)	FLUKA	ANAL - GRADE
Acetone		Commercial grade
Pyridine	UNIVAR	ANAL - GRADE
Formic acid	BDH	ANAL - GRADE

TABLE 3.3 Detail of instruments and equipment used

Name of instruments and equipment	Sources
UV-Visible Spectrophotometer	PERKIN ELMER MODEL 550
Infrared Spectrophotometer	SHIMADZU IR - 440
Tensile Strength Tester	INSTRON MODEL 1026
Jet Dyeing Machine	WERNER MATHIS AG
Differential Thermal Analyzer	SHIMADZU DT-30
Scanning Electron Microscope	JEOL MODEL JS M - T20

## 3.2 PREPARATION OF RAW MATERIALS FOR GRAFTING REACTION

### 3.2.1 Purification of Raw Silk Fibres

The raw silk fibres were purified by scouring (degumming) in an aqueous solution containing 8-15% of the weight of fibres (owf) soap solution and sodium carbonate 5-8% owf at 90°C for 2 hours. They were then washed with 0.1% solution of sodium carbonate at 40-50°C for 1/2 hour and rinsed with cool water thoroughly 2-3 times.

### 3.2.2 Purification and Recrystallization of N,N'-methylenebisacrylamide (N,N'-MBA)

1. Dissolved N,N'-MBA with the minimum amount of acetone by adding a small portion of acetone to N,N'-MBA in a round bottom flask equipped with a refluxing condenser. Boiling stones were added to the round bottom flask in order to maintain constant boiling and to avoid superheating and bumping of the liquid solution.

2. Heated the solution to 40°C

3. Added the minimum amount of acetone which contained the dissolved N,N'-MBA through the condenser.

4. Subsequently filtered the clear solution through the fluted filter paper.

5. Allowed the recrystallization to take place by cooling the solution to room temperature. Then cooled the solution in the refrigerator so that the growth of the crystal could occur.

6. Then filtered the crystallized solid through a Büchner funnel.

7. Dried the filter cake at 50°C for 1-2 hours.

### 3.3 GRAFT COPOLYMERIZATION OF N,N'-MBA ONTO SILK FIBRES BY MANGANESE(III) ACETYLACETONATE

1. Weighed the purified silk fibres of  $W_1$  grams and added them in the reaction flask.

2. Dissolved  $Mn(acac)_3$  in glacial acetic acid. To this acidic solution was added distilled water.

3. Added sodium laurylsulfate solution into the above solution and then stirred thoroughly.

TABLE 3.4 Formula used in the grafting reaction of N,N'-MBA onto silk fibres

Formula	Mn(acac) <sub>3</sub> (mole-l <sup>-1</sup> )	glac.acetic <sup>^</sup> a (mole-l <sup>-1</sup> )	N,N'-MBA (mole-l <sup>-1</sup> )
1A	0.5 x 10 <sup>-3</sup>	5(0.5 x 10 <sup>-3</sup> )	2.5 x 10 <sup>-3</sup>
1B	1.5 x 10 <sup>-3</sup>	5(1.5 x 10 <sup>-3</sup> )	2.5 x 10 <sup>-3</sup>
1C	2.5 x 10 <sup>-3</sup>	5(2.5 x 10 <sup>-3</sup> )	2.5 x 10 <sup>-3</sup>
2A	0.5 x 10 <sup>-3</sup>	5(0.5 x 10 <sup>-3</sup> )	5.0 x 10 <sup>-3</sup>
2B	1.5 x 10 <sup>-3</sup>	5(1.5 x 10 <sup>-3</sup> )	5.0 x 10 <sup>-3</sup>
2C	2.5 x 10 <sup>-3</sup>	5(2.5 x 10 <sup>-3</sup> )	5.0 x 10 <sup>-3</sup>
3A	0.5 x 10 <sup>-3</sup>	5(0.5 x 10 <sup>-3</sup> )	7.5 x 10 <sup>-3</sup>
3B	1.5 x 10 <sup>-3</sup>	5(1.5 x 10 <sup>-3</sup> )	7.5 x 10 <sup>-3</sup>
3C	2.5 x 10 <sup>-3</sup>	5(2.5 x 10 <sup>-3</sup> )	7.5 x 10 <sup>-3</sup>
4A	0.5 x 10 <sup>-3</sup>	5(0.5 x 10 <sup>-3</sup> )	10.0 x 10 <sup>-3</sup>
4B	1.5 x 10 <sup>-3</sup>	5(1.5 x 10 <sup>-3</sup> )	10.0 x 10 <sup>-3</sup>
4C	2.5 x 10 <sup>-3</sup>	5(2.5 x 10 <sup>-3</sup> )	10.0 x 10 <sup>-3</sup>
5A	0.5 x 10 <sup>-3</sup>	5(0.5 x 10 <sup>-3</sup> )	15.0 x 10 <sup>-3</sup>
5B	1.5 x 10 <sup>-3</sup>	5(1.5 x 10 <sup>-3</sup> )	15.0 x 10 <sup>-3</sup>
5C	2.5 x 10 <sup>-3</sup>	5(2.5 x 10 <sup>-3</sup> )	15.0 x 10 <sup>-3</sup>

Weight of silk = 1 gm; [HClO<sub>4</sub>] = 7.5 X 10<sup>-3</sup> mole-l<sup>-1</sup>;

[NaLS] = 2.0 X 10<sup>-3</sup> mole-l<sup>-1</sup>; Temp = 50°C; Time = 2 hrs

Liquor ratio = 100 : 1 (Liquor ratio is the ratio by weight of the dyebath to the material to be dyed).

4. Poured the solution mixture from 3) into the reaction flask immediately under the flow of nitrogen gas with a rate of 120 drops per minute. The reaction was started by stirring mechanically at 250 rpm with heating within the range  $50^{\circ} \pm 1^{\circ} \text{C}$ .

5. Then added  $\text{HClO}_4$  after the nitrogen gas was passed through the reaction flask and subsequently the nitrogen gas was passed through again for 30 minutes into which the solution of N,N'-MBA was poured.

6. It is noted that all the grafting reactions were carried out under a nitrogen atmosphere at the temperature of  $50^{\circ} \text{C}$  for 2 hours.

7. At the end of the reaction, filtered the reaction solution and then washed the silk fibres together with the homopolymer on the filter paper thoroughly three to four times with water. The solid substances were dried in a vacuum oven at  $60^{\circ} \text{C}$  until constant weight; they were then placed in a desiccator over silica-gel for 30 minutes, and weighed as  $W_2$  grams.

8. Washed the grafted silk fibres from 7) thoroughly again with water until the clear filtrate was achieved.

9. Dried the washed and air-dried grafted silk fibres in the oven at 60°C to achieve a constant weight, kept in a desiccator over silica-gel for 30 minutes, and weighed as  $W_3$  grams.

From the weights of the graft copolymer on the silk fibres, the percent grafting and the percent of homopolymer were calculated by the following equations.

$$\text{percent grafting} = \frac{(W_3 - W_1)}{W_1} \times 100 \dots\dots\dots(3.1)$$

$$\text{percent homopolymer} = \frac{(W_2 - W_3)}{W_1} \times 100 \dots\dots\dots(3.2)$$

where

$W_1$  = the weight of ungrafted silk fibres

$W_2$  = the weight of grafted silk fibres before extracting the homopolymer.

$W_3$  = the weight of grafted silk fibres after extracting the homopolymer.

### 3.4 CHARACTERIZATION OF N,N'-MBA GRAFTED SILK FIBRES

#### 3.4.1 Infrared Spectroscopy

The infrared spectra of ungrafted silk fibres, N,N'-MBA and N,N'-MBA grafted silk fibres were measured with an infrared spectrophotometer using KBr pellets.



### 3.5 DETERMINATION OF PHYSICAL PROPERTIES SIGNIFICANTLY RELEVANT TO GRAFT COPOLYMERIZATION OF N,N'-MBA ONTO SILK FIBRES

#### 3.5.1 Tensile Strength and Elongation

Tensile tests were performed on the silk fibres by Single Strand Test conditioned at  $21 \pm 2^{\circ}\text{C}$  and 65% RH in accordance with the standard test method of JIS L 2310 - 1979 R [Appendix A].

An Instron machine model 1026 was used with a gage length of 50 cm and a crosshead speed of  $300 \text{ mm}\cdot\text{min}^{-1}$ . Typically, 10 specimens were tested with a maximum load of 500 gm. The tensile properties, namely tensile strength and elongation which were of significant importance to this work, were calculated.

#### 3.5.2 Thermal Properties

The thermal behavior of ungrafted silk fibres and N,N'-MBA-grafted silk fibres was examined under a Differential Thermal Analyzer (DTA).

The thermal curves of ungrafted silk fibres and of N,N'-MBA-grafted silk fibres were recorded on the

DTA instrument at a heating rate of  $10^{\circ}\text{C}/\text{min}$ . The sample weight was 7 mg and was put in a sealable aluminum pan. The sealed aluminum cell was swept with nitrogen gas at the flow rate of 30 ml/min. in a temperature range of  $400\text{-}500^{\circ}\text{C}$ .

### 3.5.3 Surface Characteristics

The surface characteristics of N,N'-MBA-grafted silk fibres were investigated by scanning electron microscopy.

The samples of silk fibres were attached to the SEM stubs by sticky tapes. The samples were then gold coated in 20 nm thickness.

### 3.5.4 Dyeability Property of the Grafted Silk Fibres

The dyeability property of the grafted silk fibres was studied to investigate the extent of grafting efficiency.

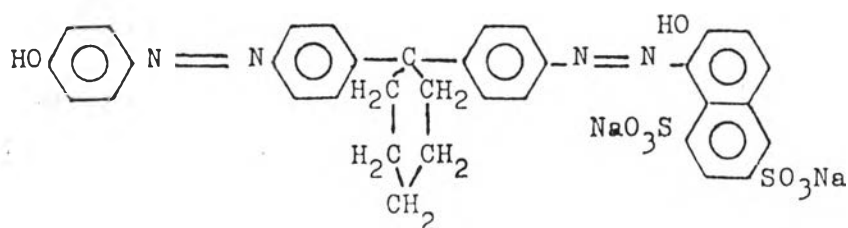
#### 3.5.4.1 Materials

Fibres: The ungrafted silk fibres and 15 samples of the grafted silk fibres were dyed.

Dyestuffs in the dyeing process: The commercial dyestuffs which were used without any further purification were the following:

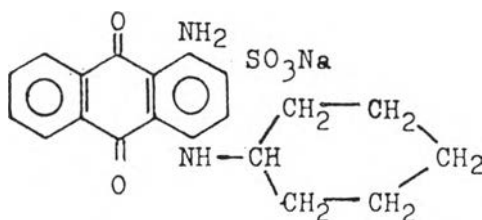
a. Supranol Fast Orange GSN 140% (C.I. Acid Orange 53, C.I. Number = 24780, Milling type).

Its chemical structure is as follows:



b. Kayacyl Sky Blue R with (C.I. Acid Blue 62, C.I. Number = 62045, Levelling type).

Its chemical structure is as follows:



Reagents aiding the dyeing: Acetic acid, formic acid and pyridine were of chemically pure grade.

Solvent for dyeing and soaping:

Distilled water was used for dyeing and soaping.

#### 3.5.4.2 Dyeing Method

The silk fibres were exhaustively dyed using a jet dyeing machine in beaker type (Werner Mathis AG, Switzerland) having a programmable heating and cooling cycle.

The liquor ratio was 50 : 1. The liquor, containing the 2% dyestuff based on weight fibres, was adjusted to a pH value of 5 with the addition of 30% acetic acid for dyeing with Supranol Fast Orange GSN 140%, and was adjusted to a pH value of 4 with the addition of 10% formic acid for dyeing with Kayacyl Sky Blue R.

The dyeing was started at 30°C and the temperature was increased at a rate of 1°C per minute to 90°C. The total dyeing time was 110 minutes. After completion of the dyeing, the samples were washed with cold water until the final wash solution was clear. Then the samples were washed with hot water at 50°C for 15 minutes (Liquor ratio was 75 : 1; 1 gm of the material and 75 ml as the volume of the solution).

They were then rinsed with cold water and dried in air. The detailed dyeing and washing processes were schematically depicted in Figure 3.1.

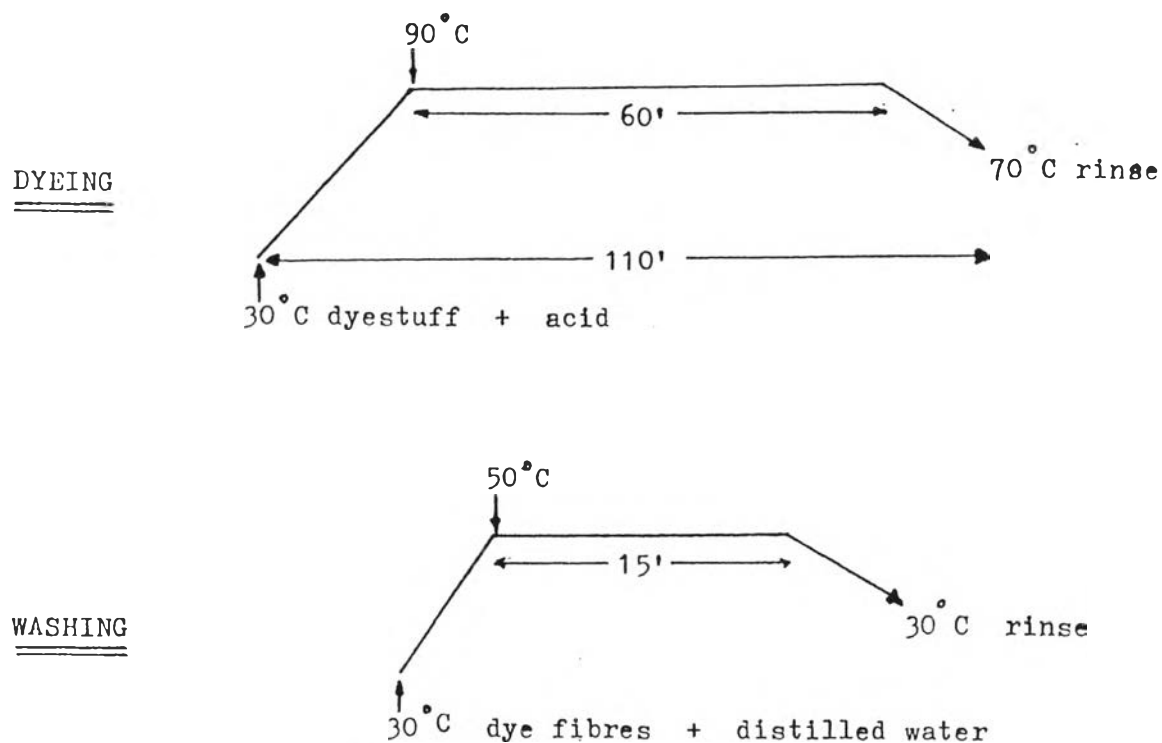


FIGURE 3.1 Schematic diagram of the dyeing and washing processes

#### 3.4.5.3 Calibration Curve for the Dyeing Process

In order to determine the amount of dyestuffs dyed on the silk fibres, a calibration curve of the virgin dyestuff was constructed. The dye deposited on the fibres could be extracted and evaluated accordingly.

a) Concentration of stock solution of acid dyestuffs for the dyeing process

1. The quantities of dyed silk fibres were extracted by 50% aqueous pyridine. After extracting, the dye solution was divided into two parts. 150 ml of the solution was pipetted to a 250-ml beaker.

2. The solution was then evaporated to dryness until the constant weight of the dyestuff was obtained. The concentration of the dye solution in mg/l was computed as shown in Table E.1.

b) Measurement of "Absorbance" of the dye solution at various concentrations

1. The second part of the dye solution from a) was diluted in an appropriate concentration for the measurement of "absorbance" on a visible spectrophotometer at 400-700 nm wavelength. The wavelength at which the dye solution gives the maximum absorbance is the " $\lambda_{\max}$ ". The absorption spectra of dyestuffs used in this experiment are shown in Figures E.1a and E.1b the  $\lambda_{\max}$  of each dyestuff is listed in Table E.1.

2. The dye solution from a) at various concentrations of 0.1, 0.3, 0.5, 0.7, 1.0, 1.2, 1.5, 1.7 and 2.0 ml was pipetted into the volumetric flasks and the total volume of each flask was 10 ml by filling up with 50 wt% aqueous pyridine. The corresponding absorbance was then measured at the maximum wavelength of the dye solution as shown in Table E.1.

#### C. Calibration curve plotting

The calibration curve for each dye was plotted between its various concentrations of standard solutions against its corresponding absorbance. The data for calibration curve preparation are summarized in Tables E.2a and E.2b, the calibration curves are shown in Figures E.2a and E.2b.

#### 3.5.4.4 Measurement of the Fixation of the Dyestuff onto the Silk Fibres.

1.  $40 \pm 0.5$  mg of the dyed silk fibres was subjected to extraction in 50 wt% of aqueous pyridine at  $95^{\circ}\text{C}$ . The solution together with the sample of silk fibres was boiled until no more dyestuff was left in the solution.

2. The solution left from 1) was made up to 25 ml with pyridine in a volumetric flask for spectrophotometric measurement.

3. The absorbance at its corresponding maximum absorption was measured.

#### 3.5.4.5 Measurement of Purity of the Dyestuff

1) A 0.0100 gm of the dyestuff was weighed and dissolved in 50 wt% aqueous pyridine. The final volume was made to 50 ml.

2) 2 ml of the mother liquor from 1) was pipetted to a 10 ml volumetric flask and the final volume was made with 50 wt% aqueous pyridine.

3) The absorbance of the dye solution was measured at the maximum absorption wavelength as for Section 3.5.4.3 b.