

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Monomer

Methyl methacrylate monomer (99% purity), which is abbreviated as MMA, was purchased from Merck.

3.1.2 Initiator

2, 2'-Azobisisobutyronitrile, which is abbreviated as AIBN, was purchased from Aldrich.

3.1.3 Surfactant

Dodecylbenzenesulfonic acid, sodium salt, tech., which is abbreviated as DBSA, was purchased from Aldrich.

3.1.4 Fabric

A plain weave polyester fabric was used. Before use, the fabric was washed several times in a washing machine at 95°C until it was free from any remaining surfactant.

3.1.5 Solvent (for monomer)

Absolute ethyl alcohol was purchased from Mallinckrodt.

3.2 Equipment

- Hot plate and magnetic stirrer
- Air circulating oven
- Shaker water bath
- Scanning Electron Microscope JEOL, model JSM 2590+ (Joel Ltd.,Tokyo, Japan)

- UV-spectrophotometer model Shimadzu 2550
- DSA10 Contact angle measuring instrument, model DSA10-Mk2 TIC (KRÜSS, Germany)
- FTIR-spectroscopy model Nicolet
- BET surface area measurement model Quantachrome Autosorb-1

3.3 Experimental Procedures

3.3.1 Time for Equilibrium Adsorption

The solution of DBSA of the desired concentration and pH was first prepared ([DBSA] = 5mM, pH = 4). A 60-mL aliquot of the solution was then pipetted into a 150-mL dye pot containing a piece of polyester fabric. The dye pot was then placed in a dyeing machine at 30°C for a set time. The supernatant was taken out at various times to find the period needed for equilibration. The equilibrium DBSA concentration was determined by using the UV-spectrophotometer model Shimadzu 2550. The adsorbed DBSA on polyester was calculated by taking the difference between the initial and final concentration of DBSA. A plot of time versus adsorbed surfactant was done to get the time for equilibrium adsorption when there was no longer change in adsorbed surfactant. The wavelength of maximum absorption for aqueous solution of DBSA was found at 224 nm with a molar extinction coefficient $1.155 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ from the calibration curve.

3.3.2 The Effect of Electrolyte on the Adsorption of DBSA on Polyester Fabric

The initial concentration of DBSA was 5 mM and the amount of NaCl was varied over the range of 0-0.15 M. Then, 50-mL of 6 mM DBSA and 10-mL of NaCl were pipetted into 150-mL dyed pot containing a 1-g piece of polyester fabric. The dye pot was then placed in a dyeing machine at 30°C for 15 hours. The equilibrium DBSA concentration was determined by using the UV spectrophotometer at 224 nm. The difference between the final concentration and

equilibrium concentration is called adsorbed DBSA concentration (adsorbed concentration). The plot of NaCl concentration versus the adsorbed surfactant was done to determine the amount of salt, which can be enhancing in DBSA adsorption on polyester fabric.

3.3.3 Surfactant Adsorption Isotherm

The adsorption of DBSA on polyester with and without electrolyte were obtained by exposing a 1-g piece of polyester to 60 mL of DBSA solution of known initial concentration (pH = 4). The mixture equilibrated at 30°C for 15 hours in a 150-mL dyed pot. The amounts of DBSA in supernatant were measured by a UV spectrometer at 224 nm. The initial DBSA concentration in this experiment was varied from 10-6,000 μM which covered the region below and above the critical micelle concentration (CMC) of DBSA. A plot of equilibrium supernatant concentration versus the amount of adsorbed surfactant yielded and it is called the surfactant adsorption isotherm.

3.3.4 Determination of Surface Area of Polyester Fabric

A polyester fabric weighing 1.5 g was cut into very small pieces and degassed at 100°C overnight. Its surface area was then determined by nitrogen adsorption BET measurement on a Quanta Chrome model Autosorb-1.

3.3.5 Admicellar Polymerization

Polymerization of MMA on polyester fabric was carried out using 1.5 mM DBSA at pH 4 (adjusted by using HCl) with the desired amount of NaCl, DBSA:monomer molar ratio, and initiator:monomer molar ratio. Polymerization time was 24 hours. DBSA: MMA molar ratio was varied in the range of 1:2, 1:5, 1:8, to 1:10. Initiator: monomer molar ratio was varied in the range of 1:5, 1:10, to 1:20. The 6.5 x 6.5 cm² polyester fabric is placed in a 32-mL vial containing 30 mL solution of DBSA, monomer, initiator and 0.15 M NaCl. The vial was then sealed with aluminium foil and the lid was screwed on and sealed with paraffin film. The vial was placed into the shaker bath at 30°C for 15 hours, and then the temperature was raised to 75°C to initiate the

polymerization reaction. Following the polymerization, the reaction was quenched by immersion of the vials in an iced bath. The fabrics were then out from the vials and washed in distilled water at 80°C for 30 min, 3 times to remove the outer layer of DBSA and leave the polymer exposed. Finally, the fabrics were placed in an oven 65°C overnight to evaporate the remaining water on the surface as well as any residual non-polymerization monomer.

3.3.6 Hydrolysis

Hydrolysis of PMMA coated-sample was carried out by using hydrochloric acid, sulfuric acid, nitric acid and p-toluenesulfonic acid. The acid concentration was varied in the range of 5-10 M. The treated samples were placed in the beaker containing the solution of acid. The hydrolysis time was varied from 1, 2, and 5 hours at temperatures of 30°C and 80°C. The fabrics were then taken out and washed with distilled water at 30°C for 15 min, 3 times to remove the acid. Finally, the fabrics were placed in an oven at 65°C overnight to evaporate the remaining water on the surface.

3.3.7 Testing and Characterization

3.3.7.1 *Surface Morphology of the Treated Fabric*

Surface morphology of the treated fabric was studied by a JEOL 5200-2AE scanning electron microscope (SEM) to assess the uniformity and coverage of the films. Specimens were sampled at random from different fabric locations and sputter coated with gold prior to observation. Magnification used was in the range of x100-x3500.

3.3.7.2 *Fourier Transform Spectrometer*

FTIR spectra were recorded on a Nicolet Nexus 670 FTIR spectrometer with spectral resolution of 4 cm⁻¹ to confirm the formation of a polymeric thin film on the fabric surface.

3.3.7.3 *Contact Angles Measurement*

Static contact angles with water were measured for both sides of fabric surface using sessile drop method on a DSA10-Mk2 contact angle measuring instrument. Measurements were done at 30°C. For each sample, five drops of liquid were placed in different parts of the sample on both sides. A drop of test liquid was introduced by injecting exactly 10- μ L of test liquid with a 10- μ L syringe. Contact angle was measured at a few seconds after the drop is put down from the syringe. The average value of all measurements was then calculated.

3.3.7.4 *Moisture Regain Measurement*

Moisture regain of the treated fabric were determined according to the standard test method described in AATCC Test Method 20A-1995, RA 24. The 1-g of fabric samples were conditioned at 25°C in a medium having a relative humidity of 65% for 4 hours then weigh the fabric samples using the analytical balance. After that the fabric samples were placed in an oven maintained at 105 to 110°C for 1.5 hours and reweigh the fabric. Repeat the heating and reweighing process for periods of 30 minutes until the weight is constant to within \pm 0.001 g and record the constant weight. The moisture regain value was calculated from the following equation.

$$\text{Moisture regain (\%)} = \frac{A - B}{B} \times 100$$

A = weight of condition fabric (g)

B = weight of dried fabric (g)