

## CHAPTER III EXPERIMENTAL

### 3.1 Material

#### 3.1.1 Monomer

Acrylic acid ( 99% purity ), which is abbreviated as AA, was purchased from Italmar.

#### 3.1.2 Initiator

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

#### 3.1.3 Surfactant

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

#### 3.1.4 Fabric

A plain weave polyester fabric was used as a substrate for admicellar polymerization. Prior to use the fabric was washed several times in hot water at 80°C until it was free from any remaining lubricants and finishes.

#### 3.1.5 Solvent (for monomer)

Ethyl alcohol AR grade was purchased from Lab scan.

### 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, Shimadzu, Model 2550
- FTIR-spectroscopy, Nicolet, Model Nexus 670
- Total Organic Carbon Analyzer, Shimadzu, Model TOC 5000A

- Instron Universal Testing Machine Tensile and flexural tests of the composite samples were carried out by an Instron Universal Testing Machine model 4206.

### 3.3 Methodology

#### 3.3.1 Determination of Equilibrium Adsorption Time

The solution of DBSA of the desired concentration and pH was first prepared ([DBSA] = 5mM, pH = 4). A 25 ml aliquot of the solution was then pipetted into a 32 ml vial containing a piece of polyester fabric. The vial was then placed in a shaker bath at 30°C for a required time. Small amount of supernatant was sampled at various times to determined the equilibrium adsorption time of DBSA on polyester fabrics. The equilibrium DBSA concentration was determined by using the UV-spectrophotometer Shimadzu model 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 carried out to determine 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  $9.524 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  from the calibration curve.

#### 3.3.2 Determination of Surfactant Adsorption Isotherm

The adsorption of DBSA on polyester fabric with and without electrolyte were obtained by exposing 0.4 g piece of polyester fabric to 25 ml of DBSA solution of known initial concentration at pH = 4. The mixture was equilibrated at 30°C for 15 hours in a 32 ml vial. The amounts of DBSA in supernatant were measured by a UV spectrometer at 224 nm. The initial DBSA concentrations in this experiment were varied from 10-6,000  $\mu\text{M}$  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, which is known as the surfactant adsorption isotherm was conducted.

### 3.3.3 Determination of Monomer Adsolubilization Isotherm

Stock acrylic acid-in-surfactant and surfactant solution were used to prepare samples containing constant DBSA concentration with different acrylic acid concentration. The acrylic acid/DBSA solution of various ratios was added to 0.4 g of polyester fabric in 24 ml vials sealed with paraffin. The mixture was kept at 30° C and allowed to equilibrate for 15 h in a shaker bath. The acrylic acid concentrations before and after equilibration were measured by using a Total Organic Carbon analyzer (TOC). Adsolubilization of acrylic acid was calculated by simple mass balance. The adsolubilization isotherm was plot between adsolubilization of acrylic acid on polyester fabric ( $\mu\text{mol/g}$ ) and equilibrium concentration of acrylic acid solution (M)

### 3.3.4 Study of Admicellar Polymerization

Polymerization of AA on polyester fabric was carried out using 1.5 mM DBSA at pH 4 (adjusted by using HCl) with the required amount of NaCl, DBSA:monomer molar ratio, initiator:monomer molar ratio and polymerization time of 24 hours. DBSA: AA molar ratios were varied in the range of 1:2, 1:5, 1:10, to 1:15. Initiator: monomer molar ratios were varied in the range of 1:5, 1:10, 1:15, to 1:20. A 5 x 5 cm<sup>2</sup> polyester fabric was placed in a 32 ml vial containing 30 ml solution of DBSA, required amount of monomer and initiator, and 0.15 M NaCl. The vials were then sealed with aluminium foil and the lids were screwed on and sealed with paraffin film. The vials were placed into a 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 removed from the vials and washed 3 times in distilled water at 80°C for 30 min, to remove the upper layer of DBSA and leave the polymer exposed. Finally, the fabrics were placed in an oven 65°C overnight to remove any remaining water on the surface as well as any residual non-polymerization monomer.

### 3.3.5 Testing and Characterization

#### 3.3.5.1 *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 polymer 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.

#### 3.3.5.2 *Fourier Transform Spectrometer*

FTIR spectra were recorded on a Nicolet Nexus 670 FTIR spectrometer with spectral resolution of  $4\text{ cm}^{-1}$  to confirm the formation of a polymeric thin film on the fabric surface.

#### 3.3.5.3 *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 carried out at  $30^{\circ}\text{C}$ . 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  $10\text{-}\mu\text{L}$  of test liquid with a  $10\text{-}\mu\text{L}$  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.

#### 3.3.5.4 *Flexural Sample preparation and Experiment Procedure*

Wet cement mortar was poured into a mold, and the untreated and treated polyester fabric was introduced onto the wet cement (see Figure 3.1). After that, another portion of wet cement was introduced to cover another side of the polyester fabrics. The samples were allowed to harden in air for 4-5 day, after which, the flexural tests were carried out. Figure 3.2 shows the dimension of the flexural test samples.

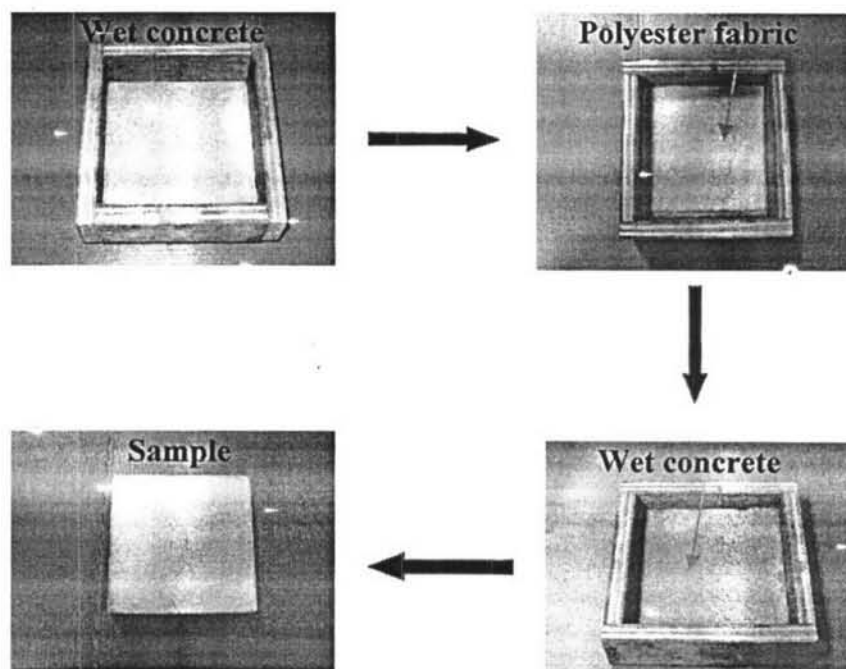


Figure 3.1 Flexural samples preparation.

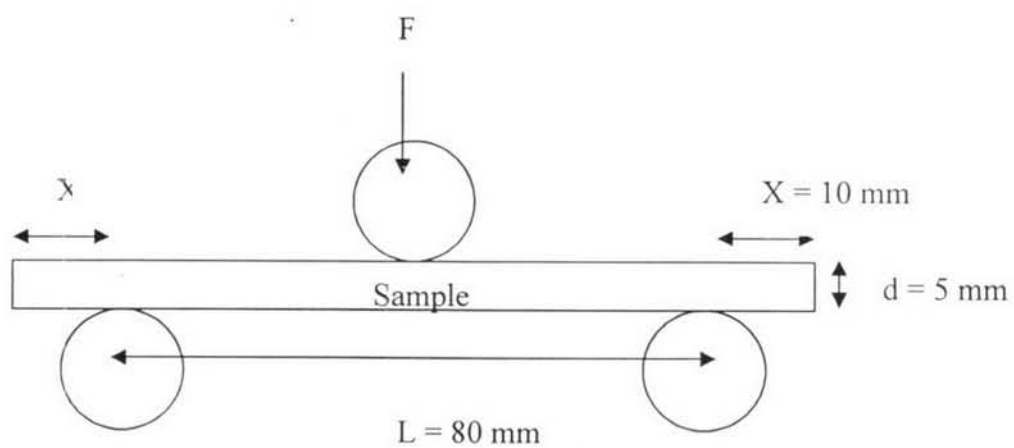


Figure 3.2 Dimension of the flexural test sample.