#### **CHAPTER IV**

# APPLICATION OF ADMICELLAR POLYMERIZATION IN FIBER REINFORCED CONCRETE

## 4.1 ABSTRACT

Admicellar polymerization is the polymerization process of monomers solubilized in adsorbed surfactant aggregates. In this study, modification of polyester surface using admicellar technique for fiber-reinforced concrete applications was investigated. Due to the hydrophobic surface of polyester fabric, the adhesion strength between the fibers and concrete matrix can be improved by modifying the surface of the fabric using admicellar technique with the polar monomer; poly(acrylic acid). The effects of surfactant, acrylic acid, initiator and electrolyte concentration on the polymerization process were determined. The improvement in the hydrophilicity of the fabric was determined by the contact angle of the treated fabric compare with the untreated fabric. The result showed that thin films of poly(acrylic acid) was successfully formed on the surface of the polyester fabric and the contact angle measurement showed a slight decrease in the contact angle of the treated fabric. Flexural test showed that treated polyester fabric reinforced concrete improved the elastic load and flexural deformation by 400%-585% and 175%-250%. The best condition for modifying the fabric was found to be 1.2 mM DSBA, 0.15 M NaCl, 1:15 DBSA: AA ratio, 1:15 AIBN: AA ratio.

Keywords: Polyester fabric, Poly(acrylic acid), Hydrophilicity,

Flexural property, Admicellar Polymerization

#### 4.2 INTRODUCTION

Properties of the fiber/matrix interface are related to the behavior of fiber reinforced cement-based composites. There are several surface modification

techniques to increase the fiber/matrix bonds such as chemical modification<sup>1,2</sup>, corona treatment<sup>3</sup>, surface grafting polymerization<sup>4,5,6</sup> and plasma treatment<sup>7,8,9,10,11</sup> and so on. All of these techniques will improve interfacial strength directly because the processes generate polar or functional chemical groups on the fiber surface. The presences of polar groups enhance the surface reactivity with the matrix in order to promote excellent adhesion. However, these techniques require special equipment and gas phase processing that is difficult to control. Therefore, admicellar polymerization (polymerization of monomer solubilized in adsorbed surfactant aggregates) is a potentially useful process for improving the polymer surface hydrophilic property, especially in the composite material strength. Also, the polymerization is carried out in the liquid phase with no special equipment need.

Admicallar polymerization can be devided into four steps: admicellar formation, monomer adsolubilization, polymer formation, and surfactant removal as illustrated in Fig. 4.1.

# Step 1: Admicellar Formation

The adsorption of surfactant at the solid/liquid interface which forms admicelles (bilayer) is controlled by solution conditions and surfactant concentration.

# Step 2: Monomer Adsolubilization

When organic monomer which sparingly soluble in water is added to the system, it will preferentially partition into the organic interior of the admicelle. Adsolubilization can be done simultaneously with admicelle formation, or subsequent to it.

#### Step 3: Polymer Formation

For free-radical polymerization, an initiator capable of generating radicals is added to the system. Water soluble or water insoluble initiators can be used.

#### Step 4: Surfactant removal

After completing polymerization, accessible surfactant is removed in order to expose the polymer-modified surface.

Admicellar polymerization has been successfully used to coat thin polymeric films on various kinds of substrates for several purposes. Examples are polystyrene on cotton<sup>12</sup>, poly (methyl methacrylate) and polystyrene on aluminium<sup>13</sup>,

poly (tetrafluoroethylene) on alumina<sup>14</sup>, poly (methyl methacrylate) on cellulosic fibers<sup>15</sup> and polystyrene on fiberglass<sup>16</sup>.

Polyester fabric is widely used to as a reinforcing material. However, polyester fabrics have several serious drawbacks in reinforcement applications because of poor adhesion to the polar matrix. To overcome these problems, thin films of polar polymer can be introduced onto polyester fabric using admicellar polymerization technique can increase the adhesion between surface substrate and cement matrix. The surface modification is expected to provide a good wetability and low contact angle (high surface energy) and thus better adhesion between the fiber matrix and continuous concrete phase in order to enhance toughness, the energy absorption capacity of composites. It should also help to reduce the cracking sensitivity of the composite.

In this research work, a thin film of poly(acrylic acid) (PAA) was introduced onto the hydrophobic polyester fabric surface. After the polymerization reaction, the PAA-coated polyester fabric introduces carboxylic groups to the surface of the fabric to improve the hydrophilicity of the polyester fabric. The study will be focused on the optimum solution conditions and surfactant concentration, adsorption isotherm, morphology of surface, and interaction between the thin film surface on the polyester fabric and cement matrix.

#### 4.3 EXPERIMENTAL

#### 4.3.1 Materials

Acrylic acid (99% purity, Italmar). 2, 2'-Azobisbutyronitrile (AIBN) (97%, Aldrich) was used as the initiator. Dodecylbenzenesulfonic acid (DBSA), sodium salt, tech., used as the surfactant, was purchased from Aldrich. Absolute ethyl alcohol AR grade, (Lab scan) was used as received. Polyester fabric was washed several times at 80°C until it was free from any remaining surfactant prior to use. Concentrated hydrochloric acid (37%), sodium chloride were acquired from Carlo Erba Reagenti.

## 4.3.2 <u>Determination of Equilibrium Adsorption Time</u>

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 determine 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 9.524×10<sup>4</sup> L mol<sup>-1</sup> cm<sup>-1</sup> from the calibration curve.

# 4.3.3 Determination of Surfactant Adsorption Isotherm

The adsorption of DBSA on polyester 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  $\mu$ 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 the surfactant adsorption isotherm.

# 4.3.4 <u>Determination of Monomer Adsolubilization Isotherm</u>

Stock acrylic acid-in-surfactant and surfactant solution were used to prepare samples containing constant DBSA concentration with and without 0.15 M NaCl and different acrylic acid concentration. The acrylic acid/DBSA solution of various ratios was added to 0.4 g of polyester in 24 ml vials sealed with paraffin. The mixtures were kept at 30° C and allowed to equilibrate for 15 h in a shaker bath. The acrylic acid concentration 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 (µmol/g) and equilibrium concentration of acrylic acid solution (M).

# 4.3.5 Study of Admicellar polymerization process

Polymerization of AA on polyester fabric was carried out using 1.2 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 cm² polyester fabric is placed in a 32 ml vial containing 30 ml solution of DBSA, required amount 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 evaporate the remaining water on the surface as well as any residual non-polymerization monomer.

# 4.3.6 Characterization of the coated film

FTIR and SEM were used to characterize the poly (acrylic acid) film of coated polyester fabric. The coated film on treated polyester fabric was extracted by boiling in ethyl alcohol. After the solvent was evaporated off, the remaining polymer was analyzed on a FTIR spectrometer (Nicolet model Nexus 670). The surface of the coated polyester fabric was characterized by SEM using a Jeol SEM model JSM 5200-2AE.

# 4.3.7 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°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  $\mu$ L of test liquid with a 10- $\mu$ 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.

## 4.3.8 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 4.2). 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 by an Instron Universal testing machine, Model 4206, at room temperature. Figure 4.3 shows the dimension of the flexural test sample.

#### 4.4 RESULTS AND DISCUSSION

## 4.4.1 <u>Determination of Equilibrium Adsorption Time</u>

Equilibrium adsorption time of DBSA on polyester fabric was carried out to establish the required time for DBSA to adsorbed on the fabric. The plot of adsorption against time (see Figure 4.4) show that DBSA adsorbs immediately on to polyester fabric at 30°C and pH 4. The initial DBSA concentration used was 5mM, which was well above CMC of DBSA which is around 1.2 mM. The adsorption of the surfactant was found to increase gradually until about 14 h after which it started to slow down and become constant at 15 h at 18 μmole/g of polyester. Therefore, in subsequent experiments, the adsorption step was carried out for 15 h to ensure that equilibrium adsorption time was established.

# 4.4.2 Determination of Surfactant Adsorption Isotherm

The adsorption isotherms of DBSA on polyester fabric at pH 4 are presented in Fig. 4.5. It can be observed that the adsorption of DBSA on polyester fabric conforms to the S-shaped adsorption isotherm for an ionic surfactant on neutral substrate. The amount of DBSA adsorbed on polyester fabric was found to sharply increase initially with an increase in DBSA concentration. As the DBSA concentration increased further, the slope started to become more gradual leading eventually to a constant value. In admicellar polymerization process, the concentration of surfactant in the system should be just below or near its CMC to avoid the emulsion polymerization. From the adsorption isotherm, a concentration of

1.2 mM DBSA, which is closed to the CMC of DBSA, was chosen for subsequent polymerization reactions.

## 4.4.3 Determination of Monomer Adsolubilization

Adsolubilization of acrylic acid in the admicellar, with and without added salt, were carried out. Initial concentration of DBSA used for the study was 1.2 mM at pH 4 with no salt or 0.15 M NaCl (see Fig. 4.6). The results show that when the equilibrium concentration of acrylic acid increases, the amount of adsolubilized acrylic acid increases. A similar effect was also reported by Pongprayoon and co-workers [12] for dodecylbenzenesulfonic acid, sodium salt adsorption in the presence of NaCl. An increase in the salt concentration caused a decreased in the surfactant head group area. The addition of salt augments counterion binding, which mitigates electrostatic repulsion between the surfactant head group ions. The decrease in the electrostatic repulsion between surfactant head group ions allows surfactants to pack more closely on the surface of polyester fabric, decreasing the effective head group area to permit more DBSA adsorption and in turn more acrylic acid adsolubilization.

# 4.4.4 Study of Admicellar Polymerization

Results from the earlier experiments were used in establishing the condition for conducting the admicellar polymerization of acrylic acid (AA) on the polyester fabric substrate. For admicellar polymerization of AA on the polyester fabric, the initial concentration of DBSA was fixed at 1.2 mM and the DBSA:AA molar ratios and initiator:monomer molar ratios were varied as shown in the Table 4.1.

# 4.4.4.1 Identification of the Coated Film by FTIR

Ultra-thin polymer, poly(acrylic acid), films were coated on polyester fabric by admicellar polymerization process. This was confirm by FTIR and SEM. The IR spectrum of the extracted PAA film on polyester fabric is presented in Figure 4.7. The results are present in absorbance arbitrary units. It can be observed that the extracted PAA from the admicellar-treated sample show a broad peak at 3436 cm<sup>-1</sup> belong to O-H stretching and sharp peak at 1725 cm<sup>-1</sup>, which

corresponds to the carbonyl stretching of carboxylic acid. An absorption band in the rang of 1500-700 cm<sup>-1</sup> comes from the C-O stretching vibration (1270-990 cm<sup>-1</sup>), C-H stretching (2962-2835 cm<sup>-1</sup>), C-H bending vibration (1450-1350 cm<sup>-1</sup>) and CH<sub>2</sub> rocking vibration (810 and 750 cm<sup>-1</sup>). These results suggested that the polymer film extracted from the treated fabric was PAA.

# 4.4.4.2 SEM micrographs of the treated fiber surface

SEM image of untreated and treated polyester fabric are present in figure 4.8 (a) and (b) respectively. SEM micrograph of the untreated polyester fabric shows a clear and relatively smooth fiber surface. Figure 4.8(b) shows the presence of PAA on the treated polyester fabric surface The SEM image shows that the PAA films are rough and covered most of the surface of the polyester fibers used for making the fabric. These observations were in agreement with the FTIR results and confirmed that the PAA films had been coated on the treated polyester fabric by admicellar polymerization. However, it can also be observed that the polymer are not uniformly and do not cover the entire fiber surface.

# 4.4.4.3 Effect of monomer concentration

The effect of varying the amount of acrylic acid is shown in the Figure 4.9-4.12. The DBSA concentration was fixed at 1.2 mM while the DBSA:AA ratio was varied from 1:2 to 1:5 to 1:10 to 1:15. For ratio of 1:2, the coating was very thin and rather scattered, when compared to the other ratios of 1:5, 1:10 to 1:15. Matarredona *et al.* [13] proved that thickness of the polymer film increased at high concentration of monomer in the admicelle during the polymerization reaction increased. As the polymerization reaction took place, more monomer could have partitioned into the admicelle and reacted to form addition polymer which can be contributed to the increase of thickness the film.

## 4.4.4.4 Effect of initiator concentration

The effect of initiator and monomer ratio on the treated polyester fabric was also studied (see Figure 4.13). The initiator/monomer ratio seemed to play an importance role on the morphology of the film formed on the fabric. The initiator/monomer ratios were varied from 1:5, 1:10, 1:15 to 1:20. As observed in Fig. 4.13, the highest initiator:monomer ratio resulted in the roughest films on the treated polyester fabric sample. However, when this ratio was reduced,

the roughness of the polyester fabric was also reduced. Pongprayoon and co-workers [12] reported that at high concentrations of initiator in the admicellar polymerization lower molecular weights of polymer with shorter chains forming a patchwise morphology on the fabric surface. On the other hand, the lowest AIBN:monomer ratio led to higher molecular weights in polymer with longer and more entangled chains, resulting in polymer formed coated almost the entire fiber surface with less roughness.

#### 4.4.4.5 Contact Angles Measurement

Contact angle measurement was used to study the hydrophilic characteristic of the obtained treated polyester fabric. Contact angle measurements were carried out on the samples subjected to different polymerization condition. Table 4.2 shows average contact angles obtained from PAA coated samples. Results show that as the amount of monomer increased, the measured contact angles of the fabric decreased. This results corresponded to the improvement of the hydrophilicity of the treated fabric. The untreated polyester fabric has an average contact angle of  $109^{\circ} \pm 0.7$  and the treated polyester fabric exhibited more hydrophilic character, after admicellar polymerization, with contact angle between  $108^{\circ} \pm 0.7$ - $101.4^{\circ} \pm 0.8$ . The treated polyester fabric samples that gave the lowest contact angle, highest hydrophilicity, are those with DBSA:AA molar ratio of 1:15 (see Table 4.2)

## 4.4.4.6 Flexural Test

Flexural tests were also carried to study the hydrophilicity of the treated fabric samples. Treated polyester fabric with the highest hydrophilicity characteristic would provide the highest adhesion between the fabric and the matrix concrete. Flexural test results of plain concrete and untreated polyester reinforced concrete are present in Figure 4.14. Figure 4.14 shows that both plain concrete and untreated polyester reinforced concrete has a relatively similar elastic load characteristic to first cracking at 0.02 kN. However, the untreated polyester reinforced concrete was more flexible than the pain concrete. The untreated fabric reinforced concrete has higher displacement of 280% when compared to the plain concrete. After the first cracking, the plain concrete was sharply broken and the elastic force was reduced to zero. The untreated polyester reinforced concrete remained in the elastic load which is used in ripping polyester fabric from concrete.

shows the load and displacement of the untreated polyester fabric reinforced concrete with the treated polyester fabric reinforced concrete. It was clearly observed that the elastic load and displacement of the treated polyester reinforced concrete was higher than the untreated polyester reinforced concrete. These results indicated that admicellar polymerization was able to improved the hydrophilicity of the polyester fabric and thus able to improve the adhesion between the polyester fabric and the matrix (concrete). The effect of monomer loading on the characteristic of the treated sample was also studied and presented in Figure 4.14. The elastic load of treated polyester reinforced concrete from 1:5 DBSA:AA ratio and 1:15 DBSA:AA ratio respectively was higher than untreated polyester reinforced concrete about 400% and 585% from condition. The elastic load at first cracking of treated polyester reinforced concrete was also increased when the monomer content increased. This results suggested that when ratio of DBSA:AA increased, hydrophilicity of the treated fabric was also increased.

#### 4.5 CONCLUSIONS

Formation of poly(acrylic acid) film on polyester fabric by admicellar polymerization has been successfully carried out in this work. The optimum conditions for carried out admicellar polymerization of acrylic acid monomer on polyester fabric are 1.2 mM DBSA, 0.15 M NaCl, 1:15 DBSA:AA ratio, 1:15 AIBN:AA ratio at 75°C for 24 hours. FT-IR spectrum and SEM micrographs confirmed that poly(acrylic acid) thin film was successfully formed on polyester fabric. Hydrophilicity of the PAA-coated fabric as measured by the contact angle was found to decrease when the monomer increased. Ductility of concrete behavior showed that untreated polyester reinforced concrete is more flexural than plain concrete about 280% and the elastic load of treated polyester reinforced concrete was higher than untreated polyester reinforced concrete about 400% and 585% from condition 1:5 DBSA:AA ratio and 1:15 DBSA:AA ratio respectively.

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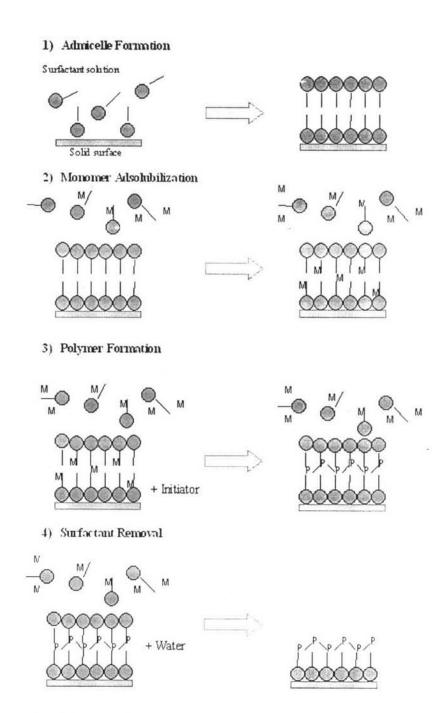


Figure 4.1 Schematic of the steps in the admicellar polymerization.

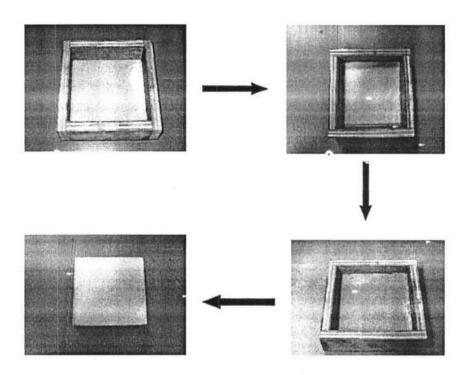


Figure 4.1 Flexural samples preparation.

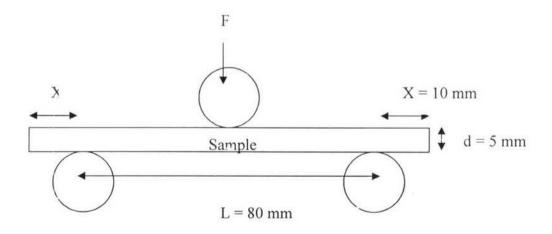


Figure 4.2 Dimension of the flexural test sample.

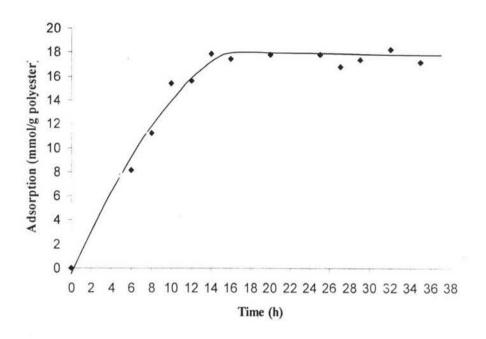
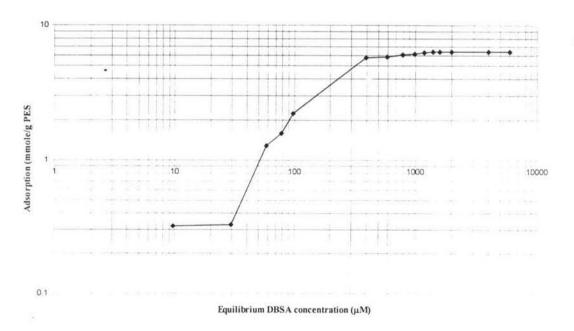


Figure 4.4 Rate of adsorption of DBSA on polyester (temp=30° C, [DBSA]= 5mM).



**Figure 4.5** Adsorption isotherm of DBSA on polyester (Temp. =  $30^{\circ}$  C, time = 16 h, pH 4).

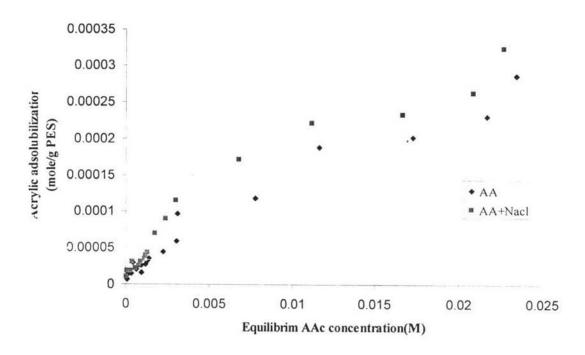


Figure 4.6 The adsolubilization isotherm of Acrylic acid with 0.15 M NaCl and without NaCl.

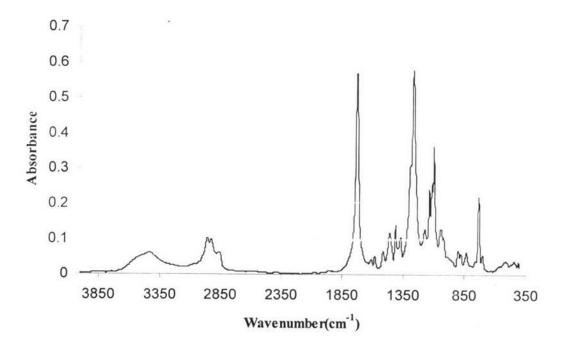
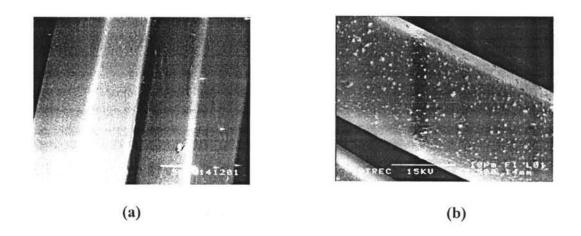
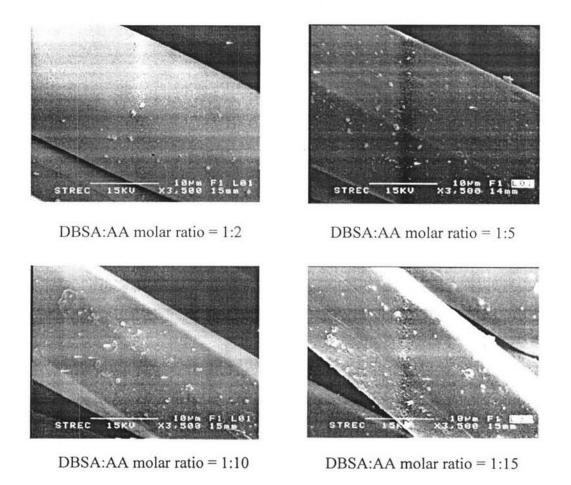


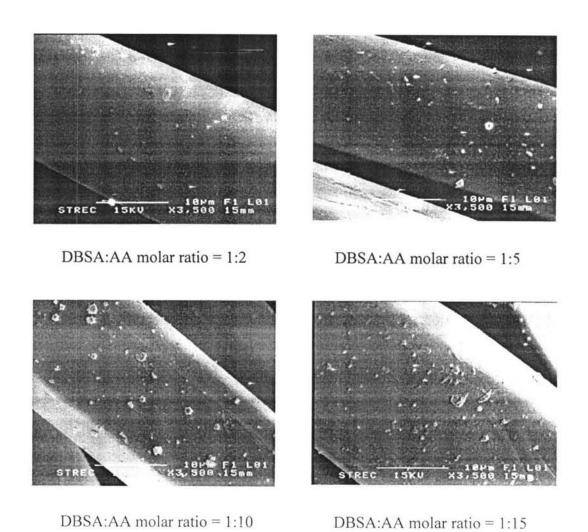
Figure 4.7 FTIR spectrum of extracted PAA.



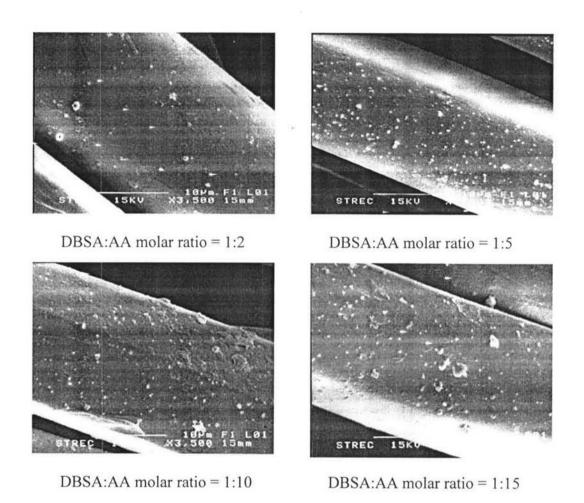
**Figure 4.8** SEM micrograph of (a) untreated polyester fabric and (b) PAA coated polyester fabric (× 3,500).



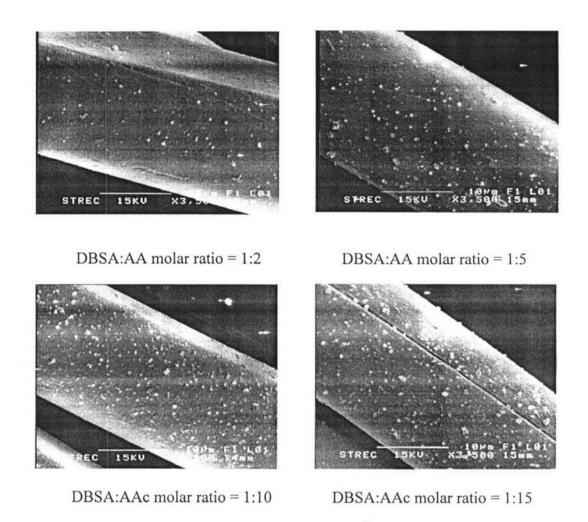
**Figure 4.9** SEM micrographs of treated polyester fabric using different monomer concentration with 1.2 mM DBSA, 0.15 M NaCl and AIBN:AA ratio 1:5.



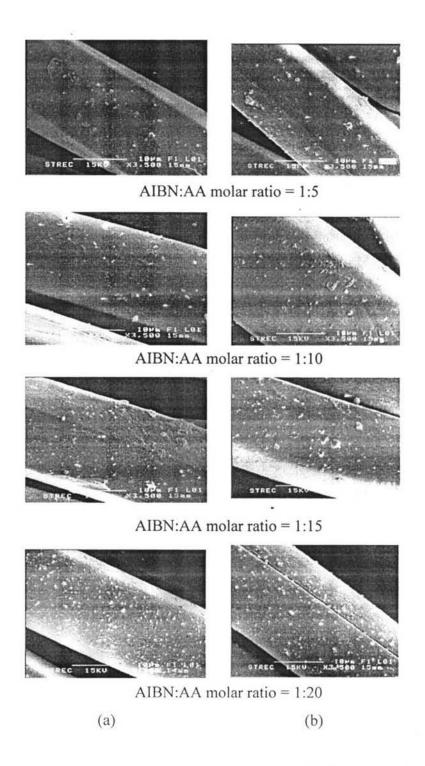
**Figure 4.10** SEM micrographs of treated polyester fabric using different monomer concentration with 1.2 mM DBSA, 0.15 M NaCl and AIBN:AA ratio 1:10.



**Figure 4.11** SEM micrographs of treated polyester fabric using different monomer concentration with 1.2 mM DBSA, 0.15 M NaCl and AIBN:AA ratio 1:15.



**Figure 4.12** SEM micrographs of treated polyester fabric using different monomer concentration with 1.2 mM DBSA, 0.15 M NaCl and AIBN:AA ratio 1:20.



**Figure 4.13** SEM micrographs of treated polyester fabric using different initiator concentration with 1.2 mM DBSA, 0.15 M NaCl, and DBSA:AAc ratio 1:20.

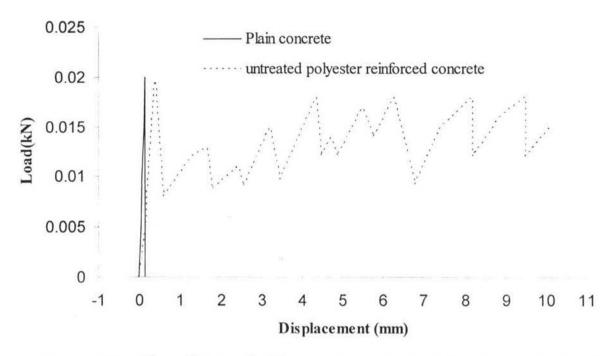
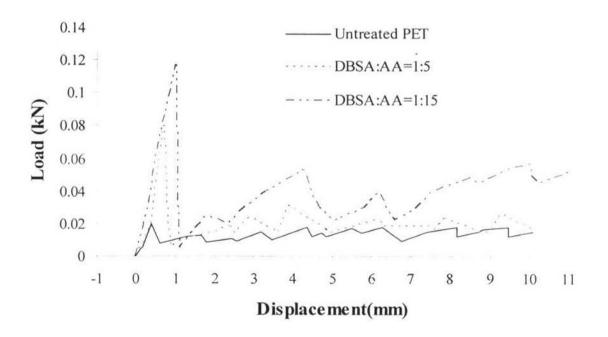


Figure 4.14 Flexural tests of plain concrete and untreated polyester reinforced concrete.



**Figure 4.15** Flexural tests of untreated polyester reinforced concrete and treated polyester reinforced concrete of 1:5 DBSA:AA ratio and 1:15 DBSA:AA ratio.

**Table 4.1** The molar ratio of DBSA:AA and initiator:monomer at 1.2mM DBSA, temp =  $30^{\circ}$  C, pH = 4, 0.15 M NaCl

DBSA: AAc	Initiator: Monomer	
1:2	1:5, 1:10, 1:15, 1:20	
1:5	1:5, 1:10, 1:15, 1:20	
1:10	1:5, 1:10, 1:15, 1:20	
1:15	1:5, 1:10, 1:15, 1:20	

 Table 4.2 Average contact angle of polyester fabric polymerized with acrylic acid

 at different conditions

	Average contact angle (θ)deg  DBSA:AA molar ratio			
AIBN:AA molar ratio				
	1:2	1:5	1:10	1:15
1:5	108.0±0.7	107.3±0.8.	104.8±0.4	102.6±0.4
1:10	108.4±0.3	106.±0.4	105.5±0.2	103.2±0.3
1:15	107.9±0.5	107.0±0.6	104.2±0.1	101.4±0.8
1:20	108.1±0.6	105.8±0.3	104.8±0.4	103.3±0.5