Modification of Polyester Fabric Properties by Surfactant-Aided Surface Polymerization

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ABSTRACT: Poly(methyl methacrylate) (PMMA) was applied to polyester fabric using a surface analog of emulsion polymerization. The admicellar polymerization was carried out using 1.5 mM dodecylbenzenesulfonic acid (DBSA) at pH 4 with 0.15M NaCl, 1 : 8 DBSA:monomer, and 1 : 10 initiator:monomer molar ratio. The PMMA film, which was formed, was characterized by SEM and FTIR. Hydrolysis of the PMMA film on polyester fabric was carried out to introduce carboxylic acid groups to the polyester surface to increase its hydrophilicity. The results show that a PMMA thin film was successfully formed on the polyester fabric. The water contact angle of the PMMA-coated polyester fabric after hydrolysis by 10M H$_2$SO$_4$ for 5 h was reduced from 117.3° to 0° and there was a significant increase in the moisture-regain value of the treated fabric. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 4059–4064, 2007

Key words: polyester fabric; poly(methyl methacrylate); hydrophilicity; moisture regain; admicellar polymerization; hydrolysis

INTRODUCTION

Polyester fabric, poly(ethylene terephthalate), is a hydrophobic polymer with very low moisture absorption. Its standard moisture regain is around 0.4%[1] making it uncomfortable to wear when used as an apparel. Comfort and wear properties of polyester fabric can be enhanced by increasing the hydrophilicity of the fabric.[2]

Various methods have been developed to increase the hydrophilicity of polyester fabric, such as chemical modification,[3,4] corona discharge,[2] plasma treatment,[5–7] surface grafting polymerization,[8–10] and so on. Some of these methods have disadvantages because of high cost of the equipment, limited practical use, and elevated production cost. The use of surfactant-based methods, however, like admicellar polymerization to improve the hydrophilicity of the polyester fabric, has never been examined in the literature.

Admicellar polymerization is a method that can be used to create a thin polymeric film on a substrate surface. There are three basic steps to admicellar polymerization, as shown in Figure 1. In the first step, surfactant molecules, typically in the form of a bilayer, are adsorbed on the substrate surface, driven by the electrical charges generated on the substrate above or below the point of zero charge. In step two, at equilibrium, the monomer in aqueous solution diffuses into the hydrophobic interior of the admicelle. Thus, the surfactant layer acts as a two-dimensional solvent at the substrate-solution interface to concentrate the insoluble monomer. In the final step, free radical initiators, such as organic azocompounds are introduced into the solution to start the polymerization of the monomer in the admicelle to form a thin polymeric film on the substrate surface. After the polymerization is completed, the outer layer of the surfactant is removed, by washing with water, to leave the polymer film exposed.

Admicellar polymerization has been successfully used to coat thin polymeric films on various kinds of substrates for several purposes. Examples are polystyrene on cotton,[11] poly(methyl methacrylate) (PMMA) and polystyrene on aluminum,[12] poly(tetrafluoroethylene) on alumina,[13] poly(methyl methacrylate) on cellulosic fibers,[14] and polystyrene on fiberglass.[15] In this research work, PMMA is coated onto a polyester fabric surface. After the polymerization reaction, the PMMA-coated polyester fabric was hydrolyzed by acid to introduce carboxylic groups to the surface to improve the hydrophilicity of the polyester fabric (Fig. 2). The moisture regain of the hydrolyzed PMMA-coated polyester fabric was then studied.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) (99% purity, Merck) was purified by 5% NaOH to remove the inhibitor. 2,2'-

Step 1. Admicelle Formation

Step 2. Monomer Adsolubilization

Step 3. Polymer Formation

Step 4. Surfactant Removal

$\s}$ = Surfactant, M = monomer, I = Initiator, P = Polymer
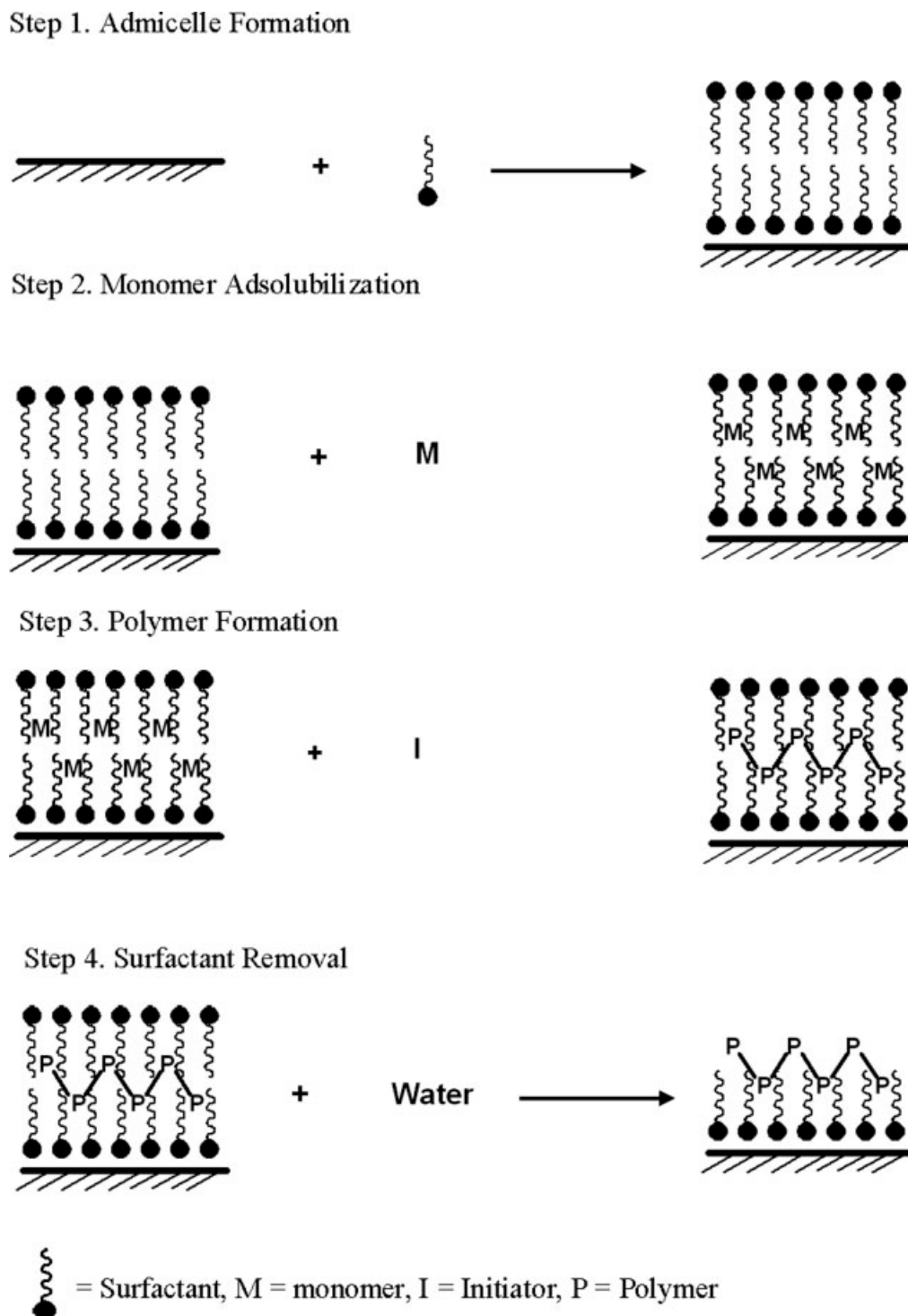
Figure 1 Schematic of the steps in the admicellar polymerization.

Azobisisobutyronitrile (AIBN) (97%, Aldrich) was used as the initiator. Dodecylbenzenesulfonic acid (DBSA), sodium salt, used as the surfactant, was purchased from Aldrich. Absolute ethyl alcohol (Mallinckrodt) was used as received. Plain weave bleached polyester fabric (fabric weight 184 g/sq m) was washed several times in a washing machine at 95°C until it was free from any remaining surfactant prior to use. Hydrochloric acid (37%), sulfuric acid (96%), nitric acid (65%), methyl alcohol, and sodium chloride were acquired from Carlo Erba Reagenti. Tetrahydrofuran was purchased from Lab-scan.
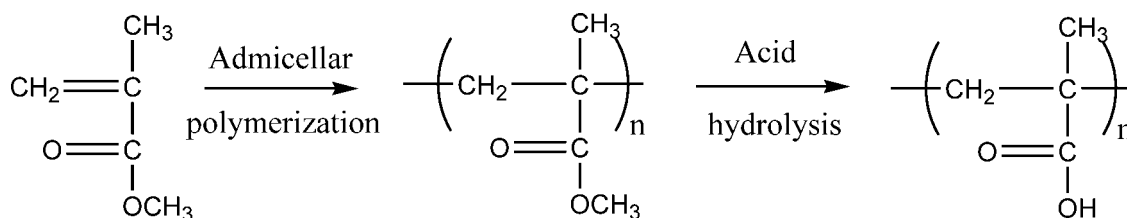
Figure 2 Reaction scheme.

Determination of the equilibration time for DBSA adsorption on the polyester fabric

The solution of DBSA of the desired concentration and pH was first prepared ([DBSA] = 5 mM, pH = 4). A 60-mL aliquot of the solution was then pipetted into a 150-mL dye pot containing a 1-g 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 Shimadzu 2550 UV-spectrophotometer. The adsorbed DBSA on the polyester was calculated by taking the difference between the initial and final concentration of DBSA. A plot of time and the adsorbed surfactant was done to obtain the time for equilibrium adsorption when there was no longer a change in the amount of surfactant adsorbed. The wavelength of maximum absorption for the aqueous solution of DBSA was found at 224 nm with a molar extinction coefficient of 1.155×10^4 L mol^{-1} cm^{-1} from the calibration curve.

Determination of the adsorption isotherm

The adsorption of DBSA on polyester with and without electrolyte was obtained by exposing a 1-g piece of polyester fabric to 60 mL of a DBSA solution of known initial concentration (pH = 4). These are mixed at 30°C for 15 h in a 150-mL dye 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 to 6000 μM, which covered the regions below and above the critical micelle concentration (CMC) of DBSA. A plot of the amount of adsorbed surfactant versus equilibrium supernatant concentration yielded the surfactant adsorption isotherm.

Admicellar polymerization process

Polymerization of MMA on polyester was carried out using 1.5 mM DBSA at pH 4 (adjusted by using HCl) with 0.15M NaCl, 1 : 8 DBSA : monomer molar ratio, and 1 : 10 initiator:monomer molar ratio. The DBSA concentration used was lower than the CMC as shown in the predetermined adsorption isotherm curve in

Figure 5. The 6.5 cm × 6.5 cm polyester fabric weighing 0.8 g was placed in a vertical position with no folding or overlapping in a 24-mL vial containing a 20-mL solution of DBSA, monomer (using ethyl alcohol as a solvent), initiator and NaCl. The vial was then wrapped with aluminum foil and the lid was screwed on and sealed with paraffin film. All vials were placed into a shaker bath set at 30°C for 15 h to allow the DBSA adsorption and monomer solubilization in the admicelle to reach equilibrium, then the temperature was raised to 75°C to initiate the polymerization reaction for 24 h. After polymerization, the vial was cooled and the fabric was removed from the vial and washed in water thrice at 80°C for 30 min to remove the outer layer of DBSA. Finally, the fabrics were dried in an oven overnight at 65°C.

Hydrolysis of PMMA-coated film

Hydrolysis of the poly(methyl methacrylate) (PMMA)-coated sample was carried out by using hydrochloric acid and sulfuric acid. Acid concentration was varied in the range of 5–10M. Hydrolysis time was varied at 1, 2, and 5 h at temperatures of 30 and 80°C. After the hydrolysis, the fabrics were taken out and washed thrice with distilled water at 30°C for 15 min to
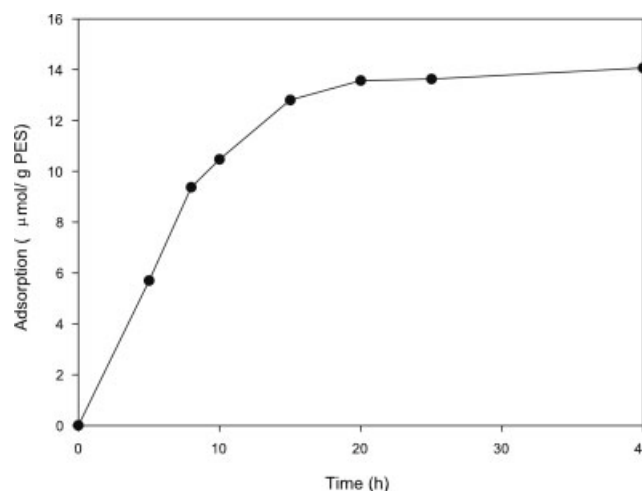

Figure 3 Rate of adsorption of DBSA on the polyester fabric (temp = 30°C, [DBSA] = 5 mM, and pH = 4).
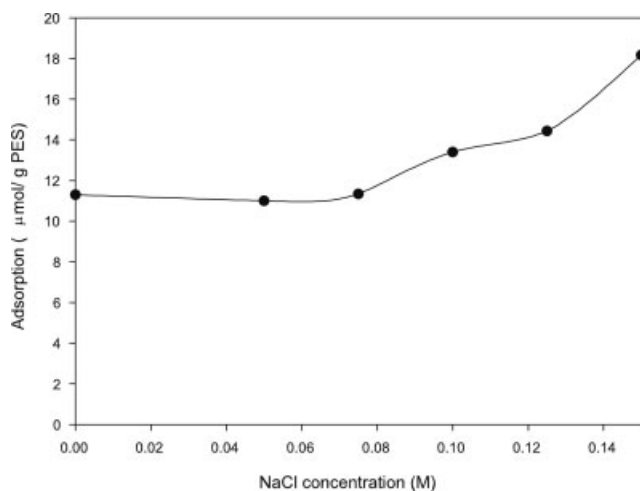
Figure 4 Effect of electrolyte on the amount of DBSA adsorbed on the polyester fabric (temp = 30°C, time = 15 h, [DBSA] = 5 mM, and pH = 4).

remove the acid. Finally, the fabrics were dried in an oven overnight at 65°C.

Characterization of the coated film

FTIR and SEM were used to characterize the PMMA film of the coated polyester fabric before and after hydrolysis. The coated film on the treated polyester fabric was extracted by boiling in THF. After the solvent was evaporated, the remaining polymer was analyzed on an 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.

Contact angle measurement

Static contact angles with water were measured for both sides of the fabric surface using the 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 μL of test liquid with a 10-μL syringe. Contact angle was measured a few seconds after dropping from the syringe. The average value of all measurements was then calculated.

Moisture regain measurement

Moisture regain of the treated fabric was determined based on the standard test method described in AATCC Test Method 20A-1995, RA 24.[16] The fabric samples were conditioned at 22°C and 68% relative humidity for 4 h before weighing using the analytical balance. After that, the fabric samples were placed in an oven at 110°C for 1.5 h before reweighing. The heating and reweighing process was repeated for a period of 30 min until the weight was constant to within ±0.001 g and the constant weight was recorded. The moisture regain values were calculated from the following equation:

$$\text{Moisture regain} = \frac{\left(\begin{array}{c}\text{weight of conditioned fabric (g)} \\ - \text{ weight of dried fabric (g)}\end{array}\right) \times 100}{\text{weight of dried fabric (g)}}$$
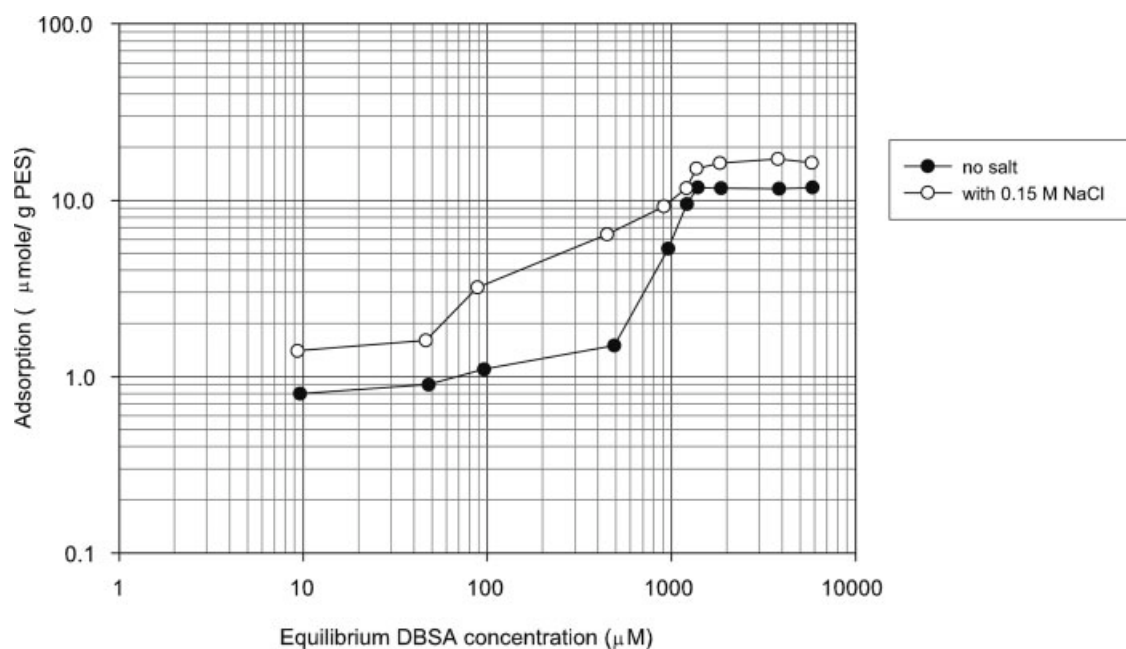

Figure 5 Adsorption isotherms of DBSA on the polyester fabric (temp = 30°C, time = 15 h, and pH = 4).

RESULTS AND DISCUSSION

Determination of the optimum conditions for DBSA adsorption on the polyester fabric

DBSA adsorbs readily on polyester at 30°C and pH 4, as shown in Figure 3. The adsorption was found to increase rapidly until about 10 h, after which the rate slowed considerably. It became constant at 13.0 μmol/ g of polyester after 15 h. Therefore, the adsorption step was carried out for 15 h to ensure the establishment of equilibrium. The amount of DBSA adsorption in the presence of different concentrations of NaCl is shown in Figure 4. The results show that the adsorption of DBSA on the polyester fabric increased with increasing NaCl concentration. Pongprayoon et al.[11] show that the addition of NaCl gives greater adsorption of surfactant on fiber surface. From this finding, 0.15M NaCl was used in subsequent experiments.

Determination of the adsorption isotherm of DBSA on polyester fabric

The adsorption isotherms of DBSA on polyester fabric at pH 4 with no salt and 0.15M NaCl are presented in Figure 5. It can be seen that the adsorption of DBSA on polyester fabric conforms to a S-shaped adsorption isotherm for an ionic surfactant on a neutral substrate.[17] The amount of DBSA adsorbed on the polyester fabric was found to initially increase gradually with an increase in DBSA concentration. It then rose sharply just before the CMC, after which the absorption remained constant. In the admicellar polymerization process, the concentration of surfactant in the system should be just below or near its CMC to ensure significant coverage while avoiding emulsion polymerization. From the adsorption isotherm, a concentration of 1.5 mM DBSA, which is near the CMC, was chosen for the polymerization reaction.
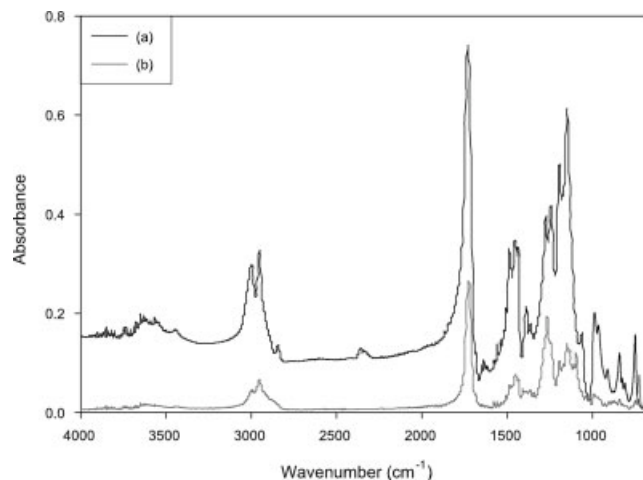

Figure 6 FTIR spectrum of (a) standard PMMA and (b) extracted PMMA from the treated fabric.

TABLE I
Water Contact Angle of Hydrolyzed PMMA-Coated Fabric as a Function of Hydrolysis Time and Temperature

| Time (h) | Contact angle (°) | | | |
| | 10M HCl | | 10M H$_2$SO$_4$ | |
	30°C	80°C	30°C	80°C
1	117.3 ± 3.9	113.6 ± 2.1	112.5 ± 4.3	0
2	116.3 ± 3.4	113.2 ± 2.3	111.6 ± 3.6	0
5	113.3 ± 1.7	112.7 ± 2.4	111.3 ± 3.2	0

Identification of the coated film by FTIR

The IR spectrum of the extracted PMMA film on the polyester fabric is displayed in Figure 6. The results are presented in absorbance arbitrary units. It can be seen that the extracted PMMA from the admicellar-treated sample shows a very intense characteristic peak at 1730 cm^{-1}, which corresponds to the C=O bond of the pendant group (—COOCH$_3$) of PMMA. An absorption band in the range of 1500–700 cm^{-1} comes from the C—O stretching vibration (1270–990 cm^{-1}), C—H bending vibration (1450–1350 cm^{-1}), and CH$_2$ rocking vibration (810 and 750 cm^{-1}). Additionally, when compared with a PMMA standard, there is a match on the fingerprint region. Thus, the FTIR spectra indicated that the PMMA films had been coated on the fabric surface.

Contact angle and moisture regain of the treated fabric

The hydrolysis of the PMMA film resulted in the formation of carboxylic acid groups on the fabric surface.[6] The water contact angle of untreated polyester and PMMA-coated fabric was 110° and 117.3°, respectively. Table I shows that the water contact angle of hydrolyzed PMMA-coated fabric slightly decreased with hydrolysis time. As the hydrolysis temperature increased, the water contact angle decreased due to the improvement of hydrophilicity of the polyester fabric, which corresponded to the increase in the polar carboxylic acid groups on the fabric surface during the hydrolysis procedure. In the case of the fabric hydrolyzed with 10M H$_2$SO$_4$ at 80°C, the water drop-

TABLE II
Moisture Regain Value of Hydrolyzed PMMA-Coated Fabric as a Function of Hydrolysis Time and Temperature

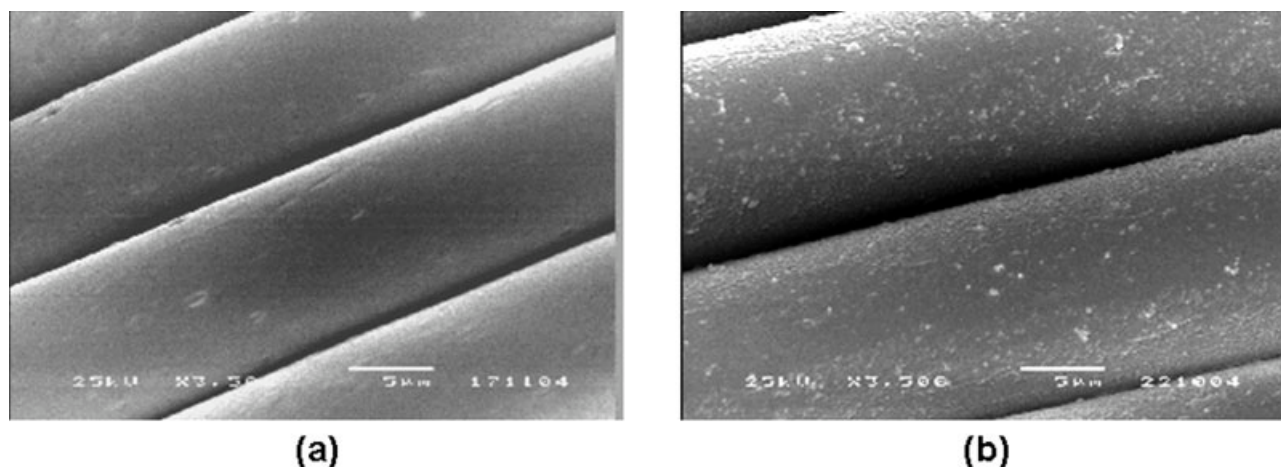| Hydrolysis temperature (°C) | Moisture regain (%) | | | | | |
| | 10M HCl | | | 10M H$_2$SO$_4$ | | |
	1-h	2-h	5-h	1-h	2-h	5-h
30	0.63	0.64	0.60	0.63	0.59	0.62
80	0.62	0.66	0.70	0.70	0.72	0.87

Figure 7 SEM micrographs of (a) untreated and (b) PMMA-coated polyester fabrics (×3500).

let disappeared as soon as it touched the fabric surface, indicating a highly hydrophilic surface. Table II indicates that the moisture-regain value shows a significant increase with hydrolysis time and temperature. When the hydrolysis was carried out by $10M$ sulfuric acid at 80°C for 5 h, the moisture regain of the polyester increased from 0.55% to 0.87%. The increase in the moisture regain, though significant, was not very large. This may be due to the fact that the admicellar polymerization technique produced a thin film with nanoscale thickness[18,19] so it did not affect the bulk properties, such as moisture regain of the polyester fabric, to a great extent.

SEM micrographs of the treated fiber surface

Representative SEM images of untreated and coated polyester fabric are presented in Figure 7. Figure 7(b) shows the presence of PMMA on the polyester fabric surface. The SEM images showed that the PMMA films were rough and covered most of the surface on each filament of the fabric. These observations were in agreement with the FTIR results and confirmed that the PMMA films had been coated on the polyester fabric by admicellar polymerization.

SUMMARY

The formation of an ultrathin PMMA film on a polyester fabric by admicellar polymerization was successfully carried out in this work. The conditions used were 1.5 mM DBSA, 0.15M NaCl, 1 : 8 DBSA : MMA ratio, 1 : 10 AIBN:MMA ratio, and polymerization was carried out at 75°C for 24 h. FTIR results and SEM micrographs confirmed that a PMMA thin film was

successfully formed on the polyester fabric. After hydrolysis by $10M$ H_2SO_4 at 80°C for 5 h, the contact angle of the PMMA-coated polyester fabric decreased from 117.3° to 0° and moisture regain showed a significant increase from 0.55% to 0.87%.

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