

# Resistivity of Conductive Polymer-Coated Fabric

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Received 1 May 2003; accepted 15 November 2003

**ABSTRACT:** Preparation of conductive polymer-coated fabrics was carried out by admicellar polymerization. By this method, a thin layer of conductive polymers (polypyrrole, polyaniline, and polythiophene) was formed on cotton and polyester fabrics by a surfactant template. The effects of monomer concentration, oxidant to monomer ratio, and addition of salt on the resistivity of the resulting fabrics were studied. The results showed that the apparent surface and volume resistivity decreased with an increase in monomer concentration in the range 5–15 mM, but was not strongly dependent on the oxidant to monomer ratio over the range

of 1 : 1 to 2 : 1. Addition of 0.5M salt was found to reduce the resistivity significantly. The lowest resistivity obtained was with polypyrrole-coated fabric, with resistivity around  $10^6$  ohm. SEM micrographs of the treated fabric surface showed a filmlike polymer coating, confirming that the fabrics were successfully coated by admicellar polymerization. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2629–2636, 2004

**Key words:** conductive polymers; admicellar polymerization; cotton; polyesters; surfactants

## INTRODUCTION

Conductive polymers have been widely investigated because of their excellent electrical and optical properties. The most commonly used conductive polymers are polypyrrole (PPY), polyaniline (PANI), polythiophene (PTH), and their derivatives. The important distinguishing features of these polymers are the conjugation of  $\pi$ -electrons formed by the overlapping of carbon  $p$ -orbital along the backbone. High electrical conductivity can be achieved by doping the conductive polymer with an appropriate dopant.

Conductive polymer-coated textiles are part of a family of recently developed composite materials with potential applications in many fields. Demands in coated fabrics are stimulated by growth in many industrial areas. Above-average growth is also expected in the protective clothing, nonmotor vehicle transportation, and awning and canopies markets. These fabrics are used for industrial applications, such as filters, as well as home and business applications, including electrostatic dissipating and electromagnetic interference shielding, flooring, ceiling materials, deelectrifying cloths, and dust- and germ-free clothing. The microwave absorption characteristics of these fabrics are also highly desirable, thus allowing these materials to be used in military applications such as camouflage and radar protective fabrics for stealth technology.

Many methods exist for preparing conductive textiles. One method is to coat conductive polymer on textile substrates such as fibers, yarns, and fabrics. Various techniques have been used to deposit conductive polymer onto different kinds of fibers and textiles and their properties and applications after deposition have also been investigated.<sup>1–9</sup> One of these techniques, admicellar polymerization, can be used to form a very thin layer of polymer on a surface by a surfactant template. In this process a polymer is formed with the assistance of surfactant adsorbed on the surface. Admicellar polymerization is a four-step process, as shown in Figure 1. In the first step, admicelles are formed on the substrate surface. Admicelle formation is controlled by solution conditions (e.g., pH, ionic strength), including a surfactant concentration that is close to or equal to the critical micelle concentration (cmc). In the second step, a hydrophobic monomer is added, which in turn will partition into the admicelle. An initiator is then added to promote the polymerization reaction. When the polymerization reaction is complete, the upper layer of surfactant is removed to expose the polymeric film on the surface. This process has been successfully used to coat various polymers on different types of substrates such as alumina,<sup>10</sup> silica,<sup>11</sup> rubber latex,<sup>12</sup> and glass fiber.<sup>13</sup> More recently the technique has been used to coat thin films of polystyrene on textile fibers.<sup>14,15</sup> In this study, admicellar polymerization was used to coat cotton and polyester fabrics with polypyrrole, polyaniline, and polythiophene to increase the electrical conductivity of the fabrics. The conductivity of modified fabrics is reported in terms of apparent surface and volume resistivity.

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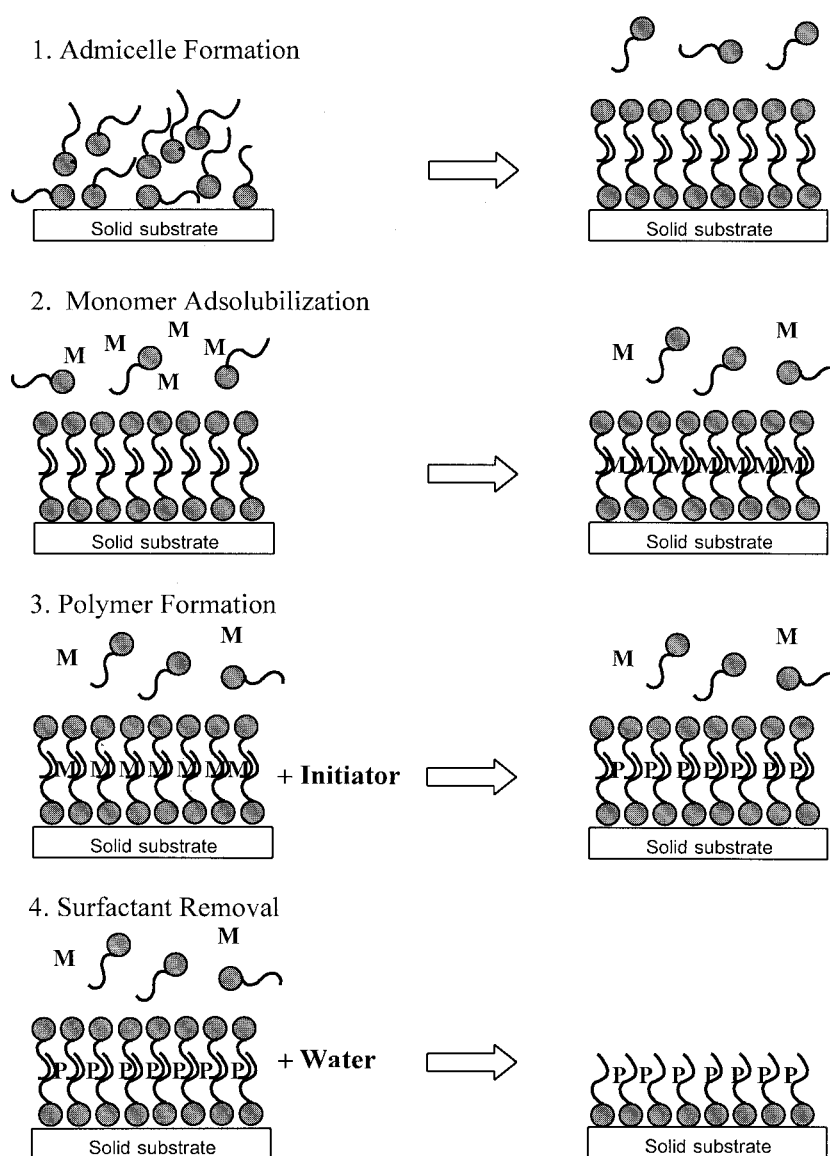


Figure 1 Steps in the admicellar polymerization process.

## EXPERIMENTAL

### Materials

Aniline (Merck, Darmstadt, Germany) and pyrrole (98%, Aldrich, Milwaukee, WI) were purified by vacuum distillation and kept cool in the dark before use. Thiophene (99+%, Aldrich) was used as received. Ammonium peroxydisulfate (Sigma, St. Louis, MO) was selected as oxidant for aniline and the oxidant ferric chloride (Aldrich) was used for pyrrole and thiophene. Dodecylbenzene sulfonic acid (DBSA), sodium salt, tech. (Aldrich) was used as the surfactant. Hydrochloric acid and sodium chloride were purchased from Merck. Plain-weave cotton (fabric weight 150 g/m<sup>2</sup>) and polyester fabrics (fabric weight 180 g/m<sup>2</sup>) were washed in a washing machine at 95°C several times until they were free from any remaining surfactant before use.

### Admicellar polymerization of monomer on fabrics

The admicellar polymerization of monomer on fabrics was carried out using aqueous DBSA solution at 1.0 and 1.2 mM. The pH was adjusted to 4 using HCl. Three types of monomers, pyrrole, aniline, and thiophene, were used at three different concentrations, 5, 10, and 15 mM. Two oxidant : monomer ratios of 1 : 1 and 2 : 1 were used. The amount of NaCl added was 0.5M. The 8 × 8-cm<sup>2</sup> fabric was placed in the test tube containing 80 mL surfactant and monomer solution. Then the test tube was placed in the shaking bath at 30°C for 15 h to allow time for admicelle formation and monomer adsolubilization into the admicelle. An oxidant was then added to the test tube and polymerization was allowed to take place at 30°C for 4 h. After polymerization, the treated fabric was removed from the test tube and washed by stirring in tap water in a

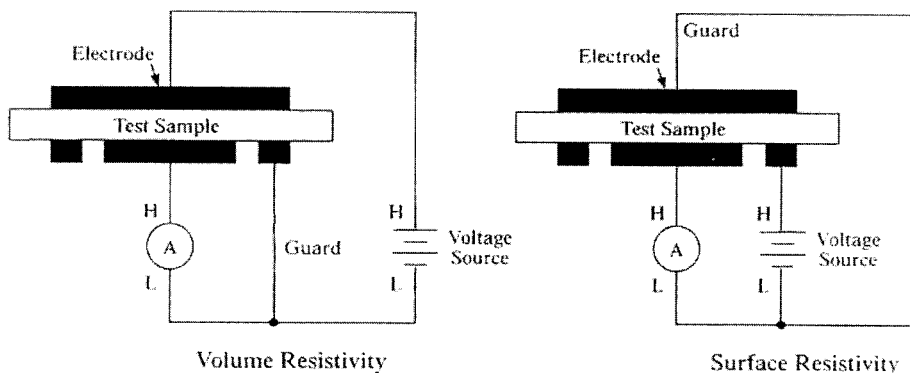


Figure 2 Resistivity measurements.

beaker two times. The fabric was finally dried at 65°C in an oven overnight before testing.

**Surface and volume resistivity measurements of the treated fabric**

A resistivity chamber (Model 6105; Keithley, Taunton, MA) was used for all resistivity measurements. A dc voltage of 500 V was applied by a picoammeter/voltage source (Keithley Model 487) for 60 s and the resulting current was then measured by a programmable electrometer/source (Keithley Model 617). The surface resistivity was measured by applying a voltage (V) across the surface of the sample, whereas in volume resistivity measurements, the voltage was applied across the sample. The resulting current (I) was then measured. Figure 2 shows the flow of current of the two types of measurements. The resistivity was calculated from the geometry of the electrodes and the thickness of the sample (t). This procedure was

adapted from the ASTM D-257 standard method, which is specific to flat, continuous sheets of material, not bundles of cylinders like a fabric. The calculations assumed a flat sheet of material instead of a fabric, and hence we view these resistivities as apparent rather than actual. The resistivities were calculated from the following equations:

$$\text{Surface resistivity, } \rho_s = \frac{53.4V}{I} \text{ ohm}$$

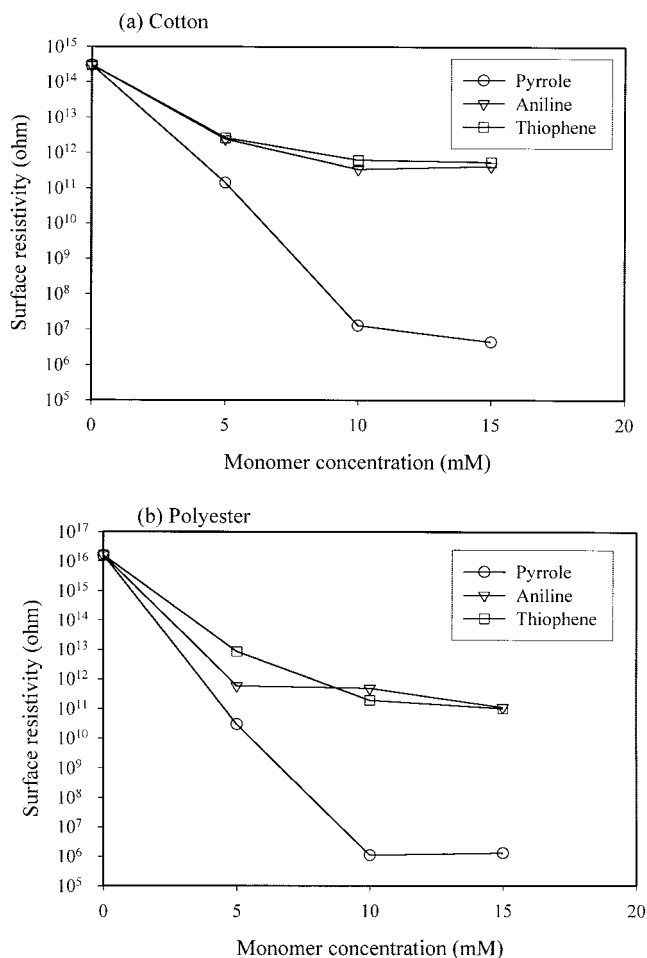
$$\text{Volume resistivity, } \rho_v = \frac{22.9V}{tI} \text{ ohm-centimeter}$$

**Surface morphology of the treated fabric**

Surface morphology of the treated fabric was examined by SEM model JSM 5200 (JEOL, Tokyo, Japan). Specimens were sampled at random from different

**TABLE I**  
**Effect of Surfactant Concentration and Salt Addition on the Resistivity of (a) Cotton Fabrics and (b) Polyester Fabrics Treated with Different Monomers Using 5 mM Monomer and Oxidant : Monomer Ratios of 1:1 and 2:1**

Surfactant concentration (mM)	Surface resistivity (ohm)					
	Polypyrrole		Polyaniline		Polythiophene	
	Oxidant:monomer ratio		Oxidant:monomer ratio		Oxidant:monomer ratio	
	1:1	2:1	1:1	2:1	1:1	2:1
(a) Cotton fabrics						
(Untreated cotton: surface resistivity = 3.0 × 10 <sup>14</sup> ohm)						
1.0 (< cmc)	2.3 × 10 <sup>12</sup>	3.6 × 10 <sup>11</sup>	3.4 × 10 <sup>12</sup>	3.6 × 10 <sup>12</sup>	3.4 × 10 <sup>12</sup>	3.5 × 10 <sup>12</sup>
1.2 (at cmc)	2.1 × 10 <sup>12</sup>	4.4 × 10 <sup>10</sup>	3.1 × 10 <sup>12</sup>	3.4 × 10 <sup>12</sup>	3.3 × 10 <sup>12</sup>	3.5 × 10 <sup>12</sup>
1.2 + 0.5M NaCl	1.4 × 10 <sup>11</sup>	1.0 × 10 <sup>10</sup>	2.4 × 10 <sup>12</sup>	2.8 × 10 <sup>12</sup>	2.6 × 10 <sup>12</sup>	2.8 × 10 <sup>12</sup>
(b) Polyester fabrics						
(Untreated polyester: surface resistivity = 1.6 × 10 <sup>16</sup> ohm)						
1.0 (< cmc)	2.9 × 10 <sup>12</sup>	3.6 × 10 <sup>10</sup>	6.9 × 10 <sup>13</sup>	7.7 × 10 <sup>13</sup>	7.4 × 10 <sup>13</sup>	7.6 × 10 <sup>13</sup>
1.2 (at cmc)	8.0 × 10 <sup>11</sup>	4.3 × 10 <sup>9</sup>	6.0 × 10 <sup>13</sup>	4.3 × 10 <sup>13</sup>	6.5 × 10 <sup>13</sup>	7.0 × 10 <sup>13</sup>
1.2 + 0.5M NaCl	3.0 × 10 <sup>10</sup>	2.6 × 10 <sup>7</sup>	5.9 × 10 <sup>11</sup>	2.6 × 10 <sup>12</sup>	8.5 × 10 <sup>12</sup>	3.2 × 10 <sup>13</sup>



**Figure 3** Change in surface resistivity with monomer concentration of treated cotton (a) and polyester (b) fabrics using 1.2 mM DBSA, 10 mM monomer, 0.5M NaCl, and oxidant : monomer ratio of 1 : 1.

sections of the fabric and sputter coated with gold before imaging. Magnification used was  $\times 3500$ .

## RESULTS AND DISCUSSION

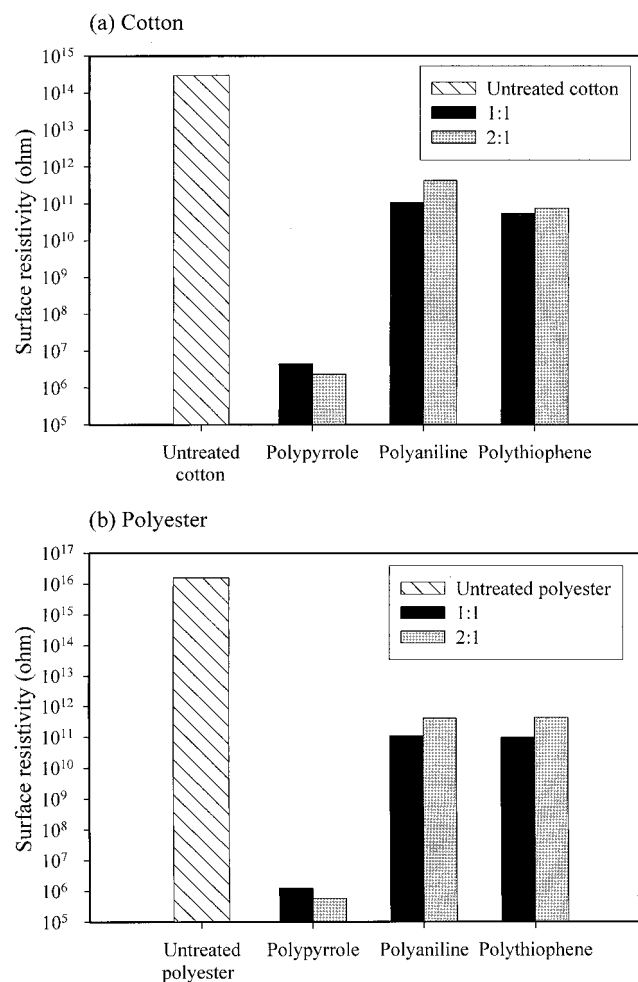
### Role of surfactant and salt

In admicellar polymerization the amount of surfactant molecules adsorbed on the substrate surface to form the admicelle is crucial to the quality of the film formed on the surface. In general the denser the packing of the surfactant molecules in the admicelle, the more monomer will be adsolubilized, leading to better film formation. Table I shows the effect of surfactant concentration below and at the cmc, as well as the effect of added salt. There is a marked decrease in the surface resistivity as the surfactant concentration increased from 1.0 mM, which is below the cmc, to 1.2 mM, which is at the cmc,<sup>16</sup> suggesting increased surfactant adsorption even with this rather small increase in surfactant concentration. Surfactant concentrations

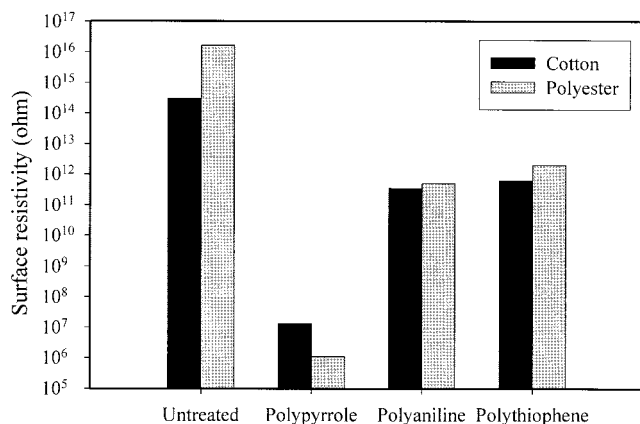
above the cmc are not recommended because emulsion polymerization may occur in the aqueous phase. To increase surfactant concentration in the admicelle, salt can be used to reduce the repulsion between the head groups of the surfactant, leading to an increase in surfactant packing. In the present work the optimum salt concentration was at 0.5M of NaCl. The results in Table I show a significant decrease in surface resistivity in all cases when 0.5M of NaCl is added to the reaction, consistent with more adsorbed surfactant and thus more monomer at the surface available for reaction. A similar effect of salt addition was also obtained by Funkhouser et al.,<sup>17</sup> Pongprayoon et al.,<sup>14</sup> and Wu et al.<sup>10</sup>

### Monomer type and concentration

In the present work three different monomers were used: pyrrole, aniline, and thiophene. After adsorption and adsolubilization for 15 h, oxidants were added and polymerization was carried out for 4 h. The



**Figure 4** Effect of oxidant : monomer ratio on surface resistivity of (a) cotton fabrics and (b) polyester fabrics using 1.2 mM DBSA, 10 mM monomer, and 0.5M NaCl.

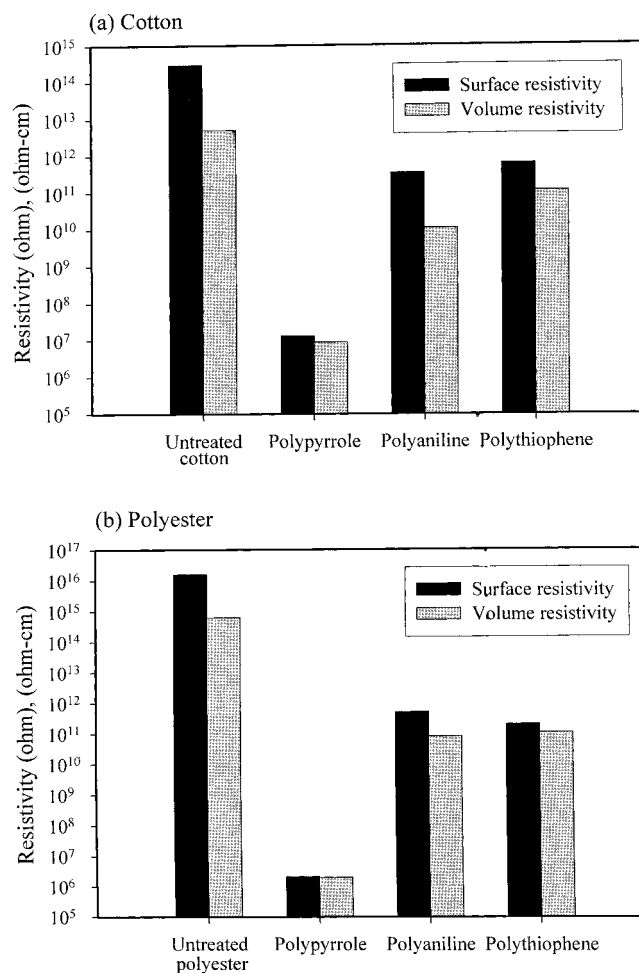


**Figure 5** Comparison of the surface resistivity of cotton and polyester fabrics using 1.2 mM DBSA, 10 mM monomer, 0.5M NaCl, and oxidant : monomer ratio of 1 : 1.

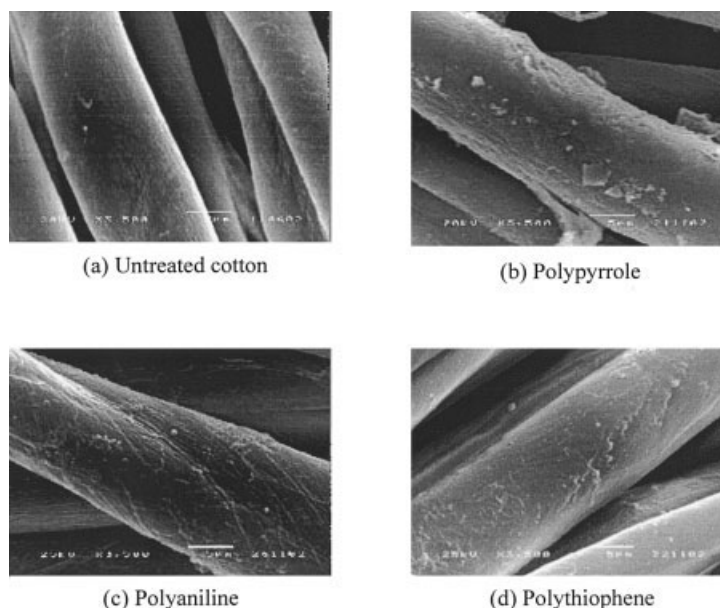
color of the fabric changed to black, yellow green, and light yellow in the cases of polypyrrole, polyaniline, and polythiophene, respectively, indicating that the polymers were successfully coated on the fabric surface. The monomer concentration was varied from 5, 10, to 15 mM and the surface resistivity was found to decrease as the monomer concentration increased in this range, as shown in Figure 3(a) and (b) for cotton and polyester, respectively. Polypyrrole-coated fabrics show the lowest surface resistivity in the range  $10^6$  ohm, whereas polyaniline- and polythiophene-coated fabrics show much higher resistivity in the range  $10^{11}$  ohm. It is interesting to note that other authors, using different coating techniques, obtained much lower resistivity in the range  $10^2$ – $10^4$  ohm.<sup>2,4,7,8</sup> As described earlier, in admicellar polymerization, the nature of the interface where polymerization occurs is changed by the presence of the surfactant bilayer on the fiber surface. Yuan showed that polypyrrole film morphology and thickness were altered by surfactant during deposition on mica and alumina by admicellar polymerization.<sup>18</sup> In this method film thickness is limited because the reaction is confined in the surfactant bilayer, and thus there is a limit in the lowering of surface resistivity that may be obtained. Admicellar polymerization is therefore suitable when very thin film is required, as in the case of fabric coating to preserve the soft handling and flexibility of the fabric. Film thicknesses in the range of 50–60 nm<sup>18</sup> and as thin as 5 nm<sup>19</sup> have been reported for admicellar polymerization. It should also be noted that most of the work where very low resistivity was obtained used dopants. In this work, no dopant was used and thus the conductivity of the fabric might be improved with dopants, although this will be the subject of further investigation.

### Oxidant : monomer ratio

The oxidant : monomer ratio is an important factor in admicellar polymerization. If the amount of oxidant initiator is too low, all the monomer at the surface will not be polymerized. On the other hand, an excess amount of oxidant may exacerbate the unwanted solution polymerization. Figure 4 compares the surface resistivity obtained from the use of oxidant : monomer ratios of 1 : 1 and 2 : 1. There is a slight decrease in surface resistivity at 2 : 1 ratio in the case of polypyrrole, whereas the opposite results were obtained in the cases of polyaniline and polythiophene. The results show that the optimum amount of oxidant is different for different monomers. In any case there is not much difference in the resistivity values obtained from the two different ratios, and thus the 1 : 1 ratio is the more appropriate one to use in practice to minimize possible solution polymerization.



**Figure 6** Comparison of the surface and volume resistivities of treated cotton (a) and polyester (b) fabrics using 1.2 mM DBSA, 10 mM monomer, 0.5M NaCl, and oxidant : monomer ratio of 1 : 1.



**Figure 7** SEM micrographs of (a) untreated fabric and (b)–(d) treated cotton fabrics using different types of monomers with 1.2 mM DBSA, 10 mM monomer, 0.5M NaCl, and oxidant : monomer ratio of 1 : 1.

### Fiber type

In the present work two distinctively different fibers were used: cotton and polyester. Cotton is a natural fiber with high moisture absorption, whereas polyester is a hydrophobic synthetic fiber with very low moisture. The surface resistivities of untreated cotton and polyester were found to have the values of  $3.0 \times 10^{14}$  and  $1.6 \times 10^{16}$  ohm, respectively. These values are in agreement with those reported in the literature.<sup>9,20</sup> Figure 5 compares the surface resistivity of cotton and polyester after being admicellar treated with polypyrrole, polyaniline, and polythiophene. The difference in the surface resistivity between the two types of fibers has been reduced from two orders of magnitude to less than one order of magnitude. This result clearly shows that both fabrics were coated and the electrical properties of the coated fabrics are determined primarily by the conductive polymer coated on the surface. The results also show that polypyrrole can coat polyester fiber better than cotton because the surface resistivity of polypyrrole-coated polyester is lower than that of polypyrrole-coated cotton.

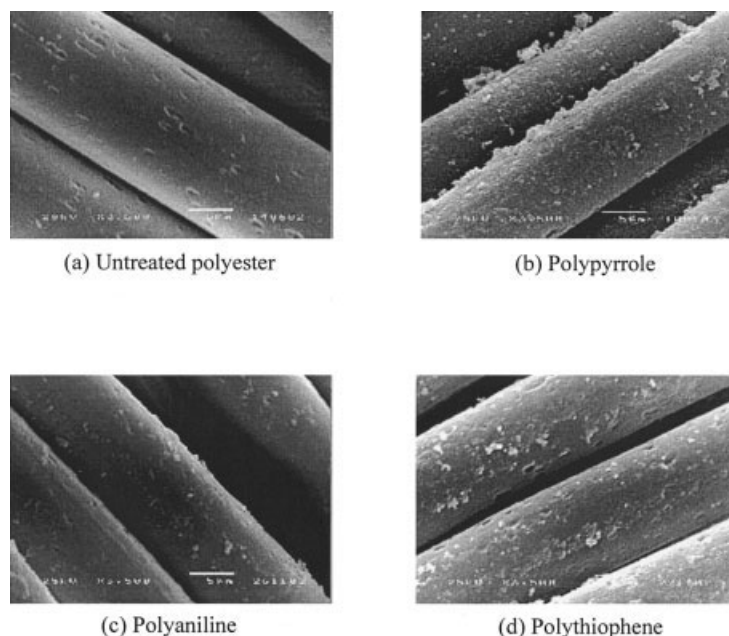
### Fabric properties relating to applications

Antistatic is an important property relating to fiber applications<sup>20</sup> and is related to comfort in wearing and ease of fiber processing. Antistatic is essential in such applications as parachutes, operation gowns, conveyor belts, carpets, and so forth. Schick<sup>21</sup> reviewed the work of several authors and concluded that most static electrical problems arising from the use of textile materials are reduced to manageable levels at a sur-

face resistivity of  $10^{11}$ – $10^{12}$  ohm. Lobel<sup>22</sup> found that charging is highly improbable if the surface resistivity is below  $10^{12}$  ohm and is practically excluded below  $10^{10}$  ohm. In the present work both cotton and polyester coated with polyaniline and polythiophene have surface resistivity in the range  $10^{11}$  ohm, sufficient for preventing problems arising from static charge. Polypyrrole-coated fabrics have even better surface resistivities of  $10^6$  ohm. At this level, the fabric will have excellent static charge dissipation property equivalent to that of carbon-filled fabric.<sup>23</sup> Admicellar polymerization is therefore a technique that can be used to produce antistatic fabric both with cotton and polyester. The advantage of this technique is that a very thin film is the result, and thus the treated fabrics are able to retain soft handling and flexibility. In the present work the feel of the treated fabric remained unchanged after the treatment. One other advantage of this technique is that no blocking of the fiber interstices occurs because the coating is confined strictly to the fiber surface, and thus the fabric retains good air permeability, making the fabric comfortable to wear. Methachan et al.<sup>24</sup> measured the air permeability of cotton fabric before and after admicellar polymerization of styrene and found that the air permeability of the fabric remained practically unchanged. In most other techniques the coating relies on deposition from solution where blocking of the interfiber spaces may occur.

### Comparison of the surface and volume resistivity

Surface resistivity is important for static charge removal along the surface, whereas volume resistivity is



**Figure 8** SEM micrographs of (a) untreated fabric and (b)–(d) treated polyester fabrics using different types of monomers with 1.2 mM DBSA, 10 mM monomer, 0.5M NaCl, and oxidant : monomer ratio of 1 : 1.

important for charge dissipation across the fabric thickness. Both are generally desirable in most applications. In the present work both the surface and volume resistivities were measured and the results are compared in Figure 6. It can be seen that volume resistivity is reduced in much the same way as the surface resistivity in all cases. This clearly shows that the coating is not confined only to the exterior surface but is uniform throughout the mass of the fabric, and both the surface and volume conductivities of the fabric improved after the treatment.

#### SEM micrographs of the treated fiber surface

SEM micrographs of the treated fiber surface, as shown in Figures 7 and 8, clearly show a filmlike coating on both cotton and polyester with some particle deposition. These particles may come from solution polymerization, given that the monomer and oxidant are present in the aqueous phase. SEM micrographs further confirmed that admicellar polymerization was successfully carried out on the fiber surface.

#### CONCLUSIONS

This work indicates that coating of conductive polymers on both cotton and polyester fabrics can be produced by the method of admicellar polymerization, resulting in fabrics with good antistatic properties. Polypyrrole-coated fabrics showed the lowest resistivity of  $10^6$  ohm. The results showed that an increase in the monomer

concentration and addition of NaCl salt resulted in lower resistivity. The optimum oxidant : monomer ratio of pyrrole was 1 : 1, whereas for aniline and thiophene, a ratio of 2 : 1 gave a better result. SEM micrographs of the treated surface showed a filmlike coating of the polymer together with a certain amount of small particles.

Pornpip Lekpittaya is grateful for the scholarship provided by Faculty of Engineering, Kasetsart University, Thailand. The authors thank Andrew D. W. Carswell for assistance with resistivity measurements.

#### References

1. Kuhn, H. H.; Kimbrell, J.; William, C. U.S. Pat. 4,975,317, 1990.
2. Bhadani, S. N.; Madhuri, K.; Gupta, S.; Sumanta, K.; Sahu, G. C. *J Appl Polym Sci* 1997, 64, 1073.
3. Collins, G. E.; Buckley, L. J. *Synth Met* 1996, 78, 93.
4. Jin, X.; Gong, K. *J Coated Fabrics* 1996, 26, 36.
5. Kuhn, H. H. *Text Chem Color J* 1997, 29, 11.
6. Anbarasan, R.; Vasudevan, T.; Paruthimal Kalaigan, G.; Gopalan, A. *J Appl Polym Sci* 1999, 73, 121.
7. Oh, K. W.; Hong, K. H.; Kim, S. K. *J Appl Polym Sci* 1999, 74, 2094.
8. Dhawan, S. K.; Singh, N.; Venkatachalam. *Synth Met* 2002, 125, 389.
9. Lian, A.; Dao, L. H.; Zhang, Z.; King, M. W.; Guidoin, R. G. *Polym Polym Compos* 2002, 8, 1.
10. Wu, J.; Harwell, J. H.; O'Rear, E. A. *Langmuir* 1987, 3, 531.
11. O'Haver, J. H.; Harwell, J. H.; Snodgrass, L. J.; Waddelt, W. H. *Langmuir* 1994, 10, 2588.
12. Bunsomsit, K.; Magaraphan, R.; O'Rear, E. A.; Grady, B. P. *Colloid Polym Sci* 2002, 280, 509.
13. Sakhalkar, S. S.; Hirt, D. E. *Langmuir* 1995, 11, 3369.
14. Pongprayoon, T.; Yanumet, N.; O'Rear, E. A. *J Colloid Interface Sci* 2002, 249, 227.

15. Boufi, S.; Gandini, A. *Cellulose* 2002, 8, 303.
16. Rosen, M. J. *Surfactant and Interfacial Phenomenon*; Wiley: New York, 1989.
17. Funkhouser, G. P.; Arevalo, M. P.; Glatzhofer, D. T.; O'Rear, E. A. *Langmuir* 1995, 11, 1443.
18. Yuan, W. L.; O'Rear, E. A.; Cho, G.; Funkhouser, G. P.; Glatzhofer, D. T. *Thin Solid Films* 2001, 385, 96.
19. Yuan, W. L.; O'Rear, E. A.; Grady, B. P.; Glatzhafer, D. T. *Langmuir* 2002, 18, 3343.
20. Brown, D. M.; Pailthorpe, M. T. *Rev Prog Color* 1986, 16, 8.
21. Schick, M. J. *Surface Characteristics of Fibers and Textiles, Part I*; Marcel Dekker: New York, 1975.
22. Lobel, W. *Faserforsch Textil* 1973, 24, 195.
23. Khun, H. H.; Child, A. D. In: *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998; Chapter 35.
24. Methachan, B.; Pongprayoon, T.; Yanumet, N.; O'Rear, E. A. *AATCC Rev* 2002, 2, 53.