CHAPTER IV
RESISTIVITY OF CONDUCTIVE POLYMER-COATED FABRIC

Abstract

Preparation of conductive polymer-coated fabrics was carried out by admicellar polymerization. By this method, a thin layer of conductive polymers, namely, polypyrrole, poly(*N*-methylpyrrole), polyaniline, and polythiophene was formed on cotton and polyester fabrics via 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 increase in monomer concentration in the range 5-15 mM. There is not much change in resistivity when oxidant to monomer ratio was changed from 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 having resistivity around 10^6 ohm. SEM micrographs of the treated fabric surface showed film-like polymer coating confirming that the fabrics have been successfully coated by admicellar polymerization.

Key words: Conductive fabric; Polyaniline; Polypyrrole; Poly(N-methylpyrrole); Polythiophene; Admicellar polymerization, Cotton fabric, Polyester fabric

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[1]To whom correspondence should be addressed

E-mail address: nantaya.y@chula.ac.th; Tel. (66)-2-2184110-1;Fax. (66)-2-2184459

1. Introduction

Conducting polymers have been widely investigated because of their excellent electrical and optical properties. The most commonly used conducting polymers are polypyrrole (PPY), polythiophene (PTH), polyaniline (PANI) and their derivatives. The important distinguishing features of these chemicals are the conjugation of π-electrons, which are formed by the overlaping of carbon p-orbitals along the backbone. High electrical conductivity is acheived after doping by adding dopants which introduces the charge carriers to move along the polymer chain.

Conducting 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, non-motor vehicle transportation, and awning and canopies markets. These fabrics are mainly used for industrial applications like filters, as well as products for home and business including electrostatic dissipating and electromagnetic interference (EMI) shielding materials for personal computers and electronics devices, flooring, ceiling materials, de-electrifying cloths, and dust and germ-free clothing. They also can be used in the fields where their microwave absorption characteristics are highly desirable, which is the case for military applications like camouflage and radar cross-section reducing 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 conducting polymer onto different kinds of fibers and textiles,-and their properties and applications after deposition have also been investigated [1-12]. One of these techniques, admicellar polymerization can be used to form a very thin layer of polymer on a surface via a surfactant template. In this process a polymer is formed with the assistance of surfactant adsorbed on the surface. Admicellar polymerization is a 4-step process as shown in Figure 1. In the first step, admicelles are formed on the hydrophillic(hydrophobic) 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 admicelles. Initiator is then added to promote the polymerization reaction. When the polymerization reaction is completed, the upper layer of surfactant is removed to expose the polymeric film on the surface. This process has been successfully used to coat polystyrene and poly (3,4-dichloro-1-butene) on cotton [10,11]. By admicellar polymerization and other techniques, various polymers have been successfully coated on many substrates such as polystyrene on alumina [12], silica [13], and glass fiber [14] and poly(tetrafluoroethylene) on alumina [15] and polypyrrole on natural rubber latex [16].

In this study, the admicellar polymerization technique is used for coating cotton and polyester fabrics with polyaniline, polypyrrole, poly (*N*-methylpyrrole) and polythiophene to increase the electrical conductivity of the fabrics. Conductivity of modified fabric is reported in terms of apparent volume and surface resistivity.

2. Experimental

2.1 Materials

Aniline (An; Merck) and pyrrole (Py;98%, Aldrich) were purified by vacuum distillation and kept cool in the dark prior to use. Thiophene (Th;99+%, Aldrich) was used as received. *N*-methylpyrrole (Nmp;99%, Aldrich) was filtered through basic alumina (Sigma) several times. Ammonium peroxydisulfate (Sigma) was selected as oxidant for aniline and the oxidant ferric chloride (Aldrich) was used for pyrrole, *N*-methylpyrrole and thiophene. Dodecylbenzene sulfonic acid (DBSA), sodium salt, tech. (Aldrich) was used as surfactant. Hydrochloric acid and sodium chloride were purchased from Merck and Alex Chemicals, respectively. Plain weave cotton and polyester fabrics were washed in a washing machine at 95°C several times until they were free from any remaining surfactant before use.

2.2 Admicellar polymerization of monomer on fabrics

The admicellar polymerization of monomer on fabrics was carried out using aqueous DBSA solution at the critical micelle concentration (1.2mM,[17]) and pH 4 using various types of monomer and with varying monomer concentration, amount of salt, and oxidant:monomer ratio. The 8×8 cm^2 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 hours to allow time for admicellar formation and monomer adsolubilization into the admicelle. Then oxidant was added into the test tube and polymerization was allowed to take place at 30°C for 4 hours. Conditions used in this part were summarized in Table 1. Following polymerization, the treated fabric was washed by stirring in tap water two times and dried at 65°C in an oven overnight prior to testing.

3. Testing and Characterization

3.1 Surface morphology of the treated fabric

Surface morphology of the treated fabric was examined by Scanning Electron Microscope (SEM). Specimens were sampled at random from different sections of the fabric and sputter coated with gold prior to imaging. Magnifications used was 3500×

3.2 Volume and surface resistivity measurements of the treated fabric

The resistivity of the treated fabric was measured at 70±5 % relative humidity, 22±2°C. The specimens were kept in this condition for more than 24 hours before testing. Resistivity chamber, KEITHLEY Model 6105, was used for all conductivity measurement. A DC voltage of 500 V was applied by a Picoammeter/Voltage Source KEITHLEY Model 487 for 60 seconds and the resulting current was then measured by Programmable Electrometer/Source KEITHLEY Model 617. Representative measurements are shown in Figure 2. The volume resistivity is measured by applying a voltage (V) across the sample and measuring the resulting current (I). The resistivity is calculated from the geometry of

the electrodes and the thickness of the sample (t). The surface resistivity is measured by applying a voltage across the surface of the sample. This procedure was adapted from the ASTM D-257 standard, 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 resulting current is measured and the resistivity is calculated from the following equation:

Volume resistivity,

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

Surface resistivity,

$$\rho_s = \frac{53.4V}{I} \text{ ohms}$$

4. Results and Discussion

4.1 Effect of monomer type and monomer concentration

In this section, admicellar treated fabrics using four different types of monomers, which are pyrrole, *N*-methylpyrrole, aniline and thiophene are compared at the same conditions.

After adsorption and adsolubilization for 15 hours, oxidants were added and polymerization was carried out for 4 hours. The color of the fabric changed to black, dark brown, yellow green and light yellow in the cases of polypyrrole, poly (*N*-methylpyrrole), polyaniline and polythiophene, respectively, indicating that the polymers were successfully coated on the fabric surface. Increase in monomer concentration resulted in a corresponding decrease in the surface and volume resistivity as confirmed by the resistivity measurements shown in Figure 3(a), (b) for cotton and Figure 4(a), (b) for polyester fabric. Polypyrrole coated fabrics show the lowest surface and volume resistivity in the range 10^5–10^6 ohms and ohm-cm when the pyrrole concentration of 15 mM was used. The conductivities are comparable to the result obtained when pyrrole was grafted to fabric by D. Tessier *et al.*[18].

4.2 Effect of fabric type

In the present work two distinctively different fibers were used: cotton and polyester. Effect of fabric type on the surface and volume resistivity is shown in Figure 5. It is interesting to see that the difference in the surface resistivity between the two types of fabrics has been reduced to less than an order of magnitude. This result clearly shows that both types of fabric have been successfully coated and the electrical properties of the coated fabrics is determined mainly by the conductive polymer coated on their surface. The results also show that polypyrrole can coat on polyester fiber better than on cotton. This behavior is a result of the fact that pyrrole molecules and their oligomers adsorb very well not only into the adsorbed surfactant aggregates but also onto polyester fiber, which is more hydrophobic than cotton. Thus, the polypyrrole on the coated polyester fabric was produced by admicellar and in-situ polymerization resulting in lower resistivity.

4.3 Effect of salt

Effect of NaCl salt on the fabric resistivity was determined as a function of NaCl concentration in Figure 6 and 7. When the amount of salt increased, both surface and volume resistivity decreased very steeply until 0.5M NaCl, after which it increased slightly. This gives an indication that adding salt can reduce the repulsion between head groups of surfactant and causes the surfactant molecules to come closer together, hence admicelle formation is enhanced and more monomers can diffuse into the admicelle. Similar results were obtained by Funkhouser[19], Pongprayoon *et al.*[11] and Wu *et al.*[12], who show that the addition of NaCl gives greater adsorption of surfactant on fiber surface. Nevertheless, additional salt above 0.5M fails to decrease the resistivity further, possibly because the admicelle was already saturated by the optimum amount of salt.

4.4 Effect of oxidant:monomer ratio

Effect of oxidant:monomer ratios at 1:1 and 2:1 was investigated using a DBSA concentration of 1.2 mM, a NaCl concentration of 0.5 M and a monomer concentration of 15 mM. Ammonium peroxydisulfate (APS) was selected as oxidant for aniline and the oxidant ferric chloride ($FeCl_3$) was used for pyrrole, *N*-

methylpyrrole and thiophene. The oxidant:monomer ratio is an important factor in admicellar polymerization.If the amount of oxidant which acts an initiator to the reaction is too low, not all monomer available will be polymerized. On the other hand, an excess amount of oxidant may lead to the unwanted solution polymerization. Figure 8 and 9 compare the surface and volume resistivity of cotton and polyester fabric obtained from the use of oxidant:monomer ratios of 1:1 and 2:1. There is a slight decrease in both surface and volume 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 this work the optimum oxidant:monomer ratio for pyrrole based monomers was found to be higher than those for aniline and thiophene. This may be because pyrrole monomer can diffuse more into the bilayer as compared with other monomers. Such a phenomenon was also reported by S.N.Tan *et al.*[20] for a polypyrrole coated cotton thread by vapour-phase chemical polymerization in which the thickness of the polypyrrole formed increased with increasing concentration of $FeCl_3$ as depicted by the change of the color from greyish to totally dark.

4.5 SEM micrographs of admicellar treated fabrics

Figures 10 and 11 show SEM micrographs of untreated and admicellar-treated cotton and polyester surface. It is clearly showed film-like coating on both cotton and polyester with some particle deposition. These particles may come from solution polymerization which is quite possible when both monomer and oxidant presented in the aqueous phase. However, the conductive property of the fiber is believed to come mainly from the film-like coating. The SEM micrographs further confirm that admicellar polymerization has been successfully carried out on the fiber surface.

4.6 Fabric quality

Fabric quality can be directly determined using human touch. For untreated fabrics, they have a soft touch and less stiffness, which are the characteristics of cotton and polyester fabrics. After modification using admicellar polymerization

technique, the treated fabrics with the thin films retain the soft touch and there is very little difference in fabric feel when compared with the untreated fabrics. One of the potential benefits of admicellar polymerization may be that we can form conducting polymer on a non-conducting substrate with better control of film thickness and uniformity in the presence of surfactant, as previously reported by W.L.Yuan *et.al.*[21].

5. Conclusions

This work indicates that deposition of conducting polymer on fabrics can be produced by the method of admicellar polymerization resulting in the surface and volume resistivity as low as 10^5 ohms and ohm-cm. This result showed that increase in the monomer concentration and the amount of NaCl salt resulted in lower resistivity. Addition of salt helps to reduce the repulsion of surfactant that can give the greater adsorption of surfactant on fiber surface. The surface morphology of coated fabric showed deposition of conducting polymer on fabric. In polymerization, the type of monomer has a significant influence on the resistivity of the coated fabrics. At the same condition, polypyrrole gave the lowest resistivity to the fabrics. The lowest resistivities obtained were 6×10^5 ohms and 4×10^5 ohm-cm for apparent surface and volume resistivity, respectively.

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Table 1 Admicellar polymerization conditions

Table 1

Experimental Conditions	Type of Monomer			
	Pyrrole	*N*-methylpyrrole	Aniline	Thiophene
Surfactant concentration (mM)	1.0, 1.2, 1.4	1.2	1.0, 1.2, 1.4	1.0, 1.2, 1.4
Monomer concentration (mM)	5,10,15	5,10,15	5,10,15	5,10,15
Oxidant Type	$FeCl_3$	$FeCl_3$	APS	$FeCl_3$
Oxidant:monomer ratio	1:1, 2:1	1:1, 2:1	1:1, 2:1	1:1, 2:1
NaCl concentration (M)	0, 0.15, 0.5, 1, 1.5	0, 0.15, 0.5, 1, 1.5	0, 0.15, 0.5, 1, 1.5	0, 0.15, 0.5, 1, 1.5

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Figure 9	Effect of oxidant:monomer ratio on (a) surface and (b) volume resistivity of polyester fabric
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Figure 11	SEM micrographs of untreated and treated polyester fabric using different types of monomers with 1.2 mM DBSA, 10 mM monomer, 0.5 M salt and oxidant:mononer ratio 1:1

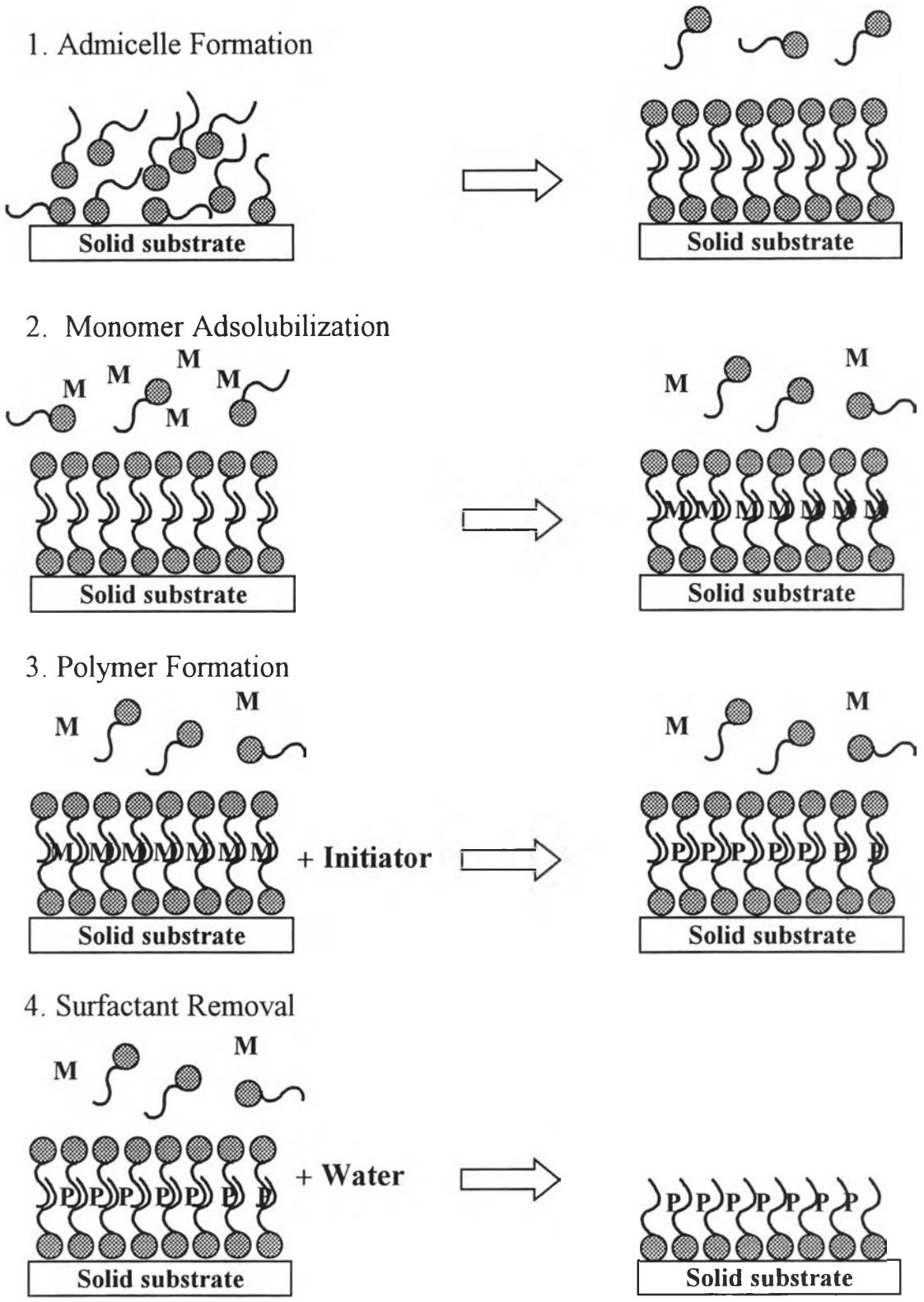

1. Admicelle Formation
Solid substrate
Solid substrate
2. Monomer Adsolubilization
M
M
M
M
M
Solid substrate
M
M
Solid substrate
3. Polymer Formation
M
M
+ Initiator
Solid substrate
M
M
Solid substrate
4. Surfactant Removal
M
M
+ Water
Solid substrate
Solid substrate

Figure 1

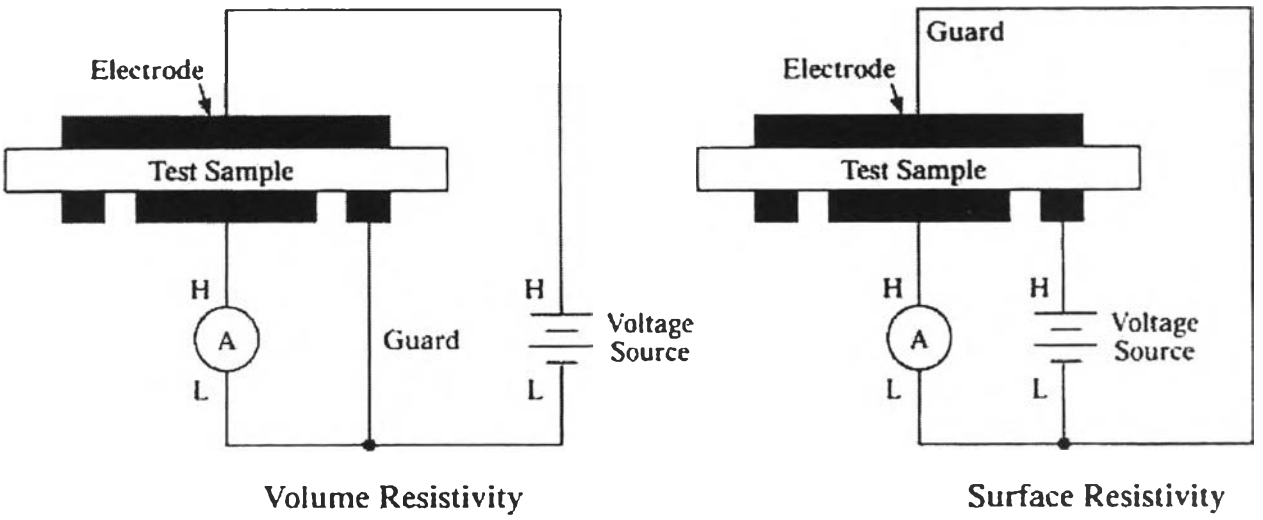


Figure 2

จุฬาลงกรณ์มหาวิทยาลัย

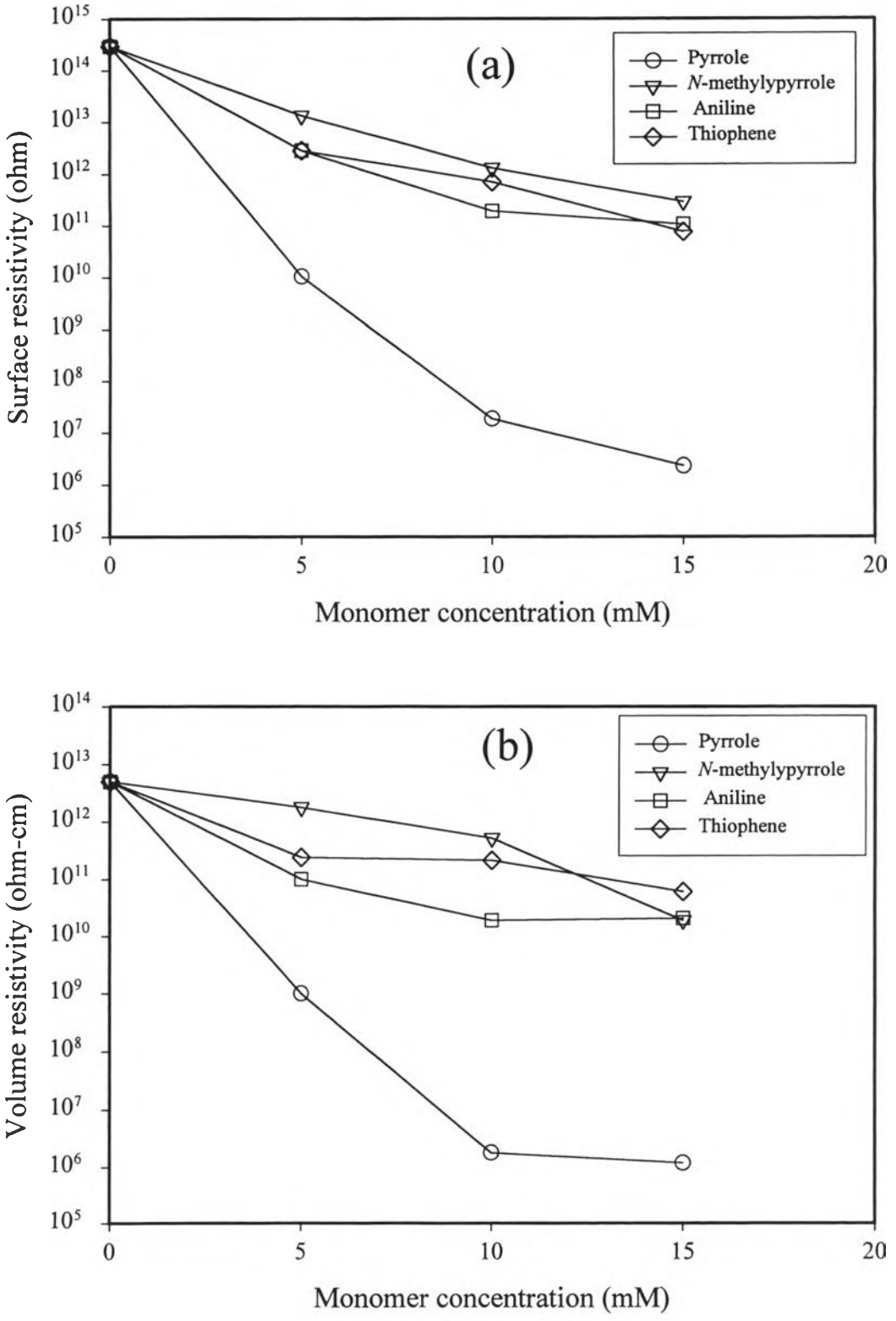

(a)
Pyrrole
N-methylypyrrole
Aniline
Thiophene
Surface resistivity (ohm)
10^15
10^14
10^13
10^12
10^11
10^10
10^9
10^8
10^7
10^6
10^5
0
5
10
15
20
Monomer concentration (mM)
(b)
Pyrrole
N-methylypyrrole
Aniline
Thiophene
Volume resistivity (ohm-cm)
10^14
10^13
10^12
10^11
10^10
10^9
10^8
10^7
10^6
10^5
0
5
10
15
20
Monomer concentration (mM)

Figure 3

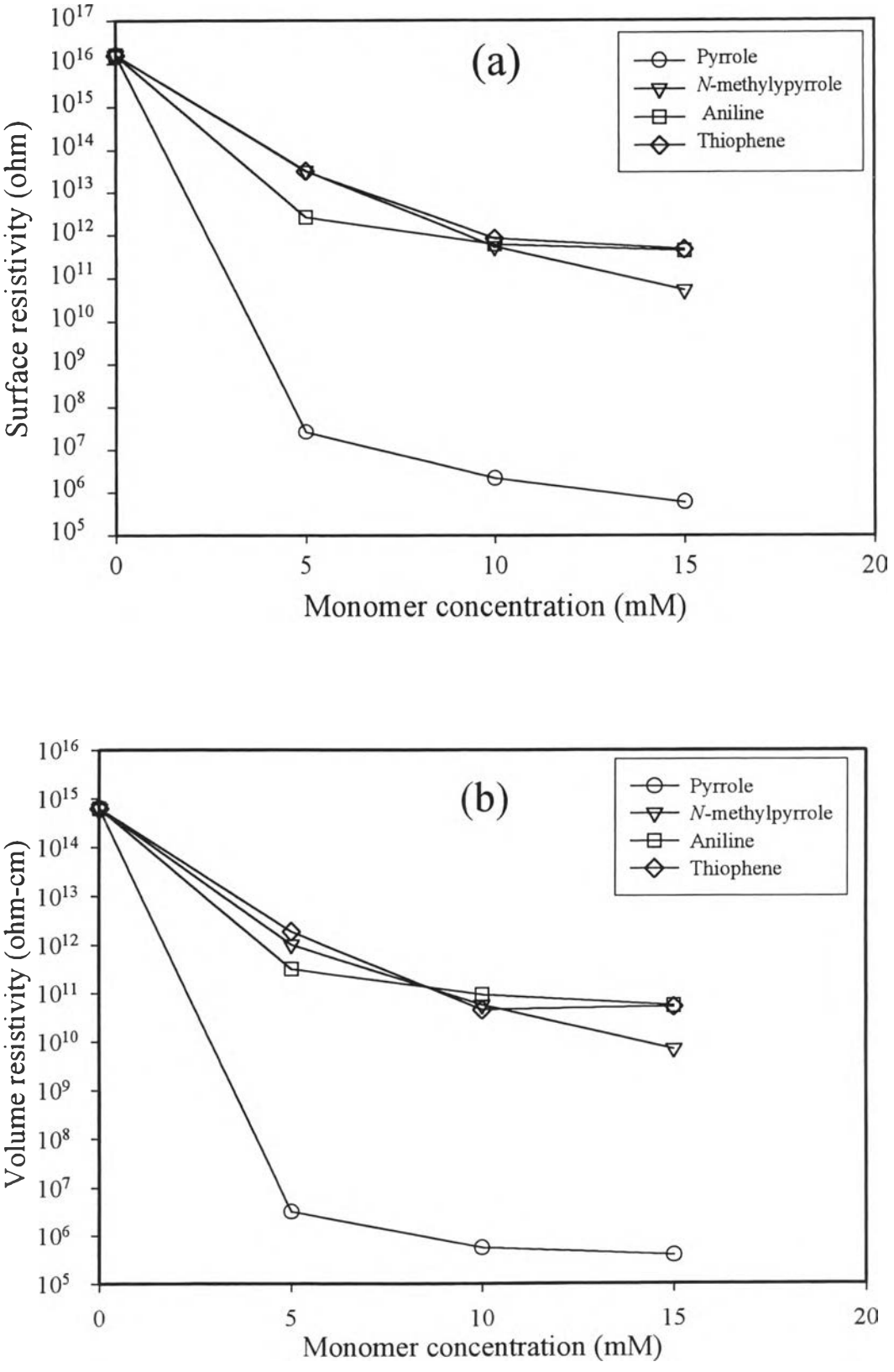

(a)
Pyrrole
N-methylypyrrole
Aniline
Thiophene
Surface resistivity (ohm)
Monomer concentration (mM)
(b)
Pyrrole
N-methylpyrrole
Aniline
Thiophene
Volume resistivity (ohm-cm)
Monomer concentration (mM)

Figure 4

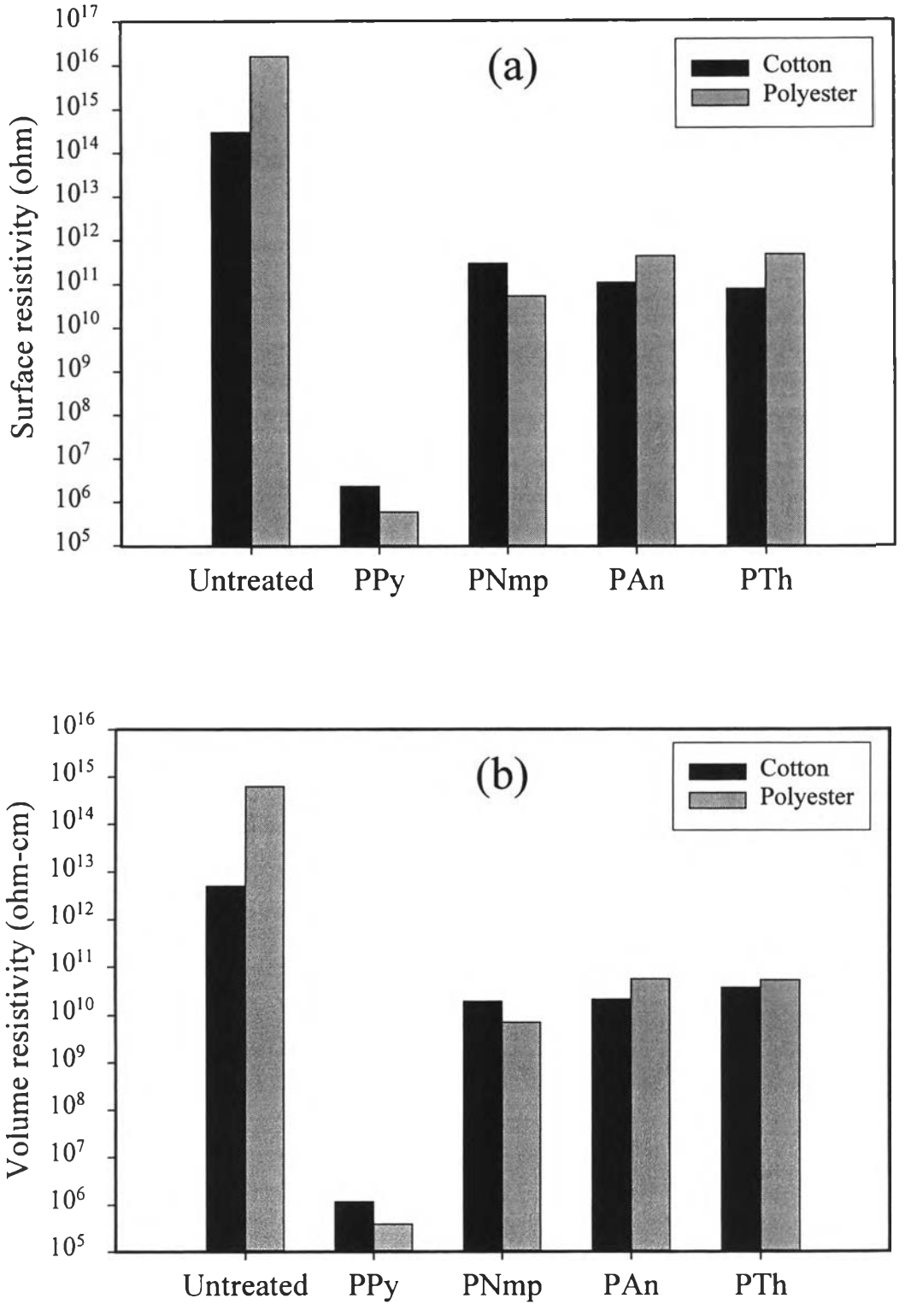
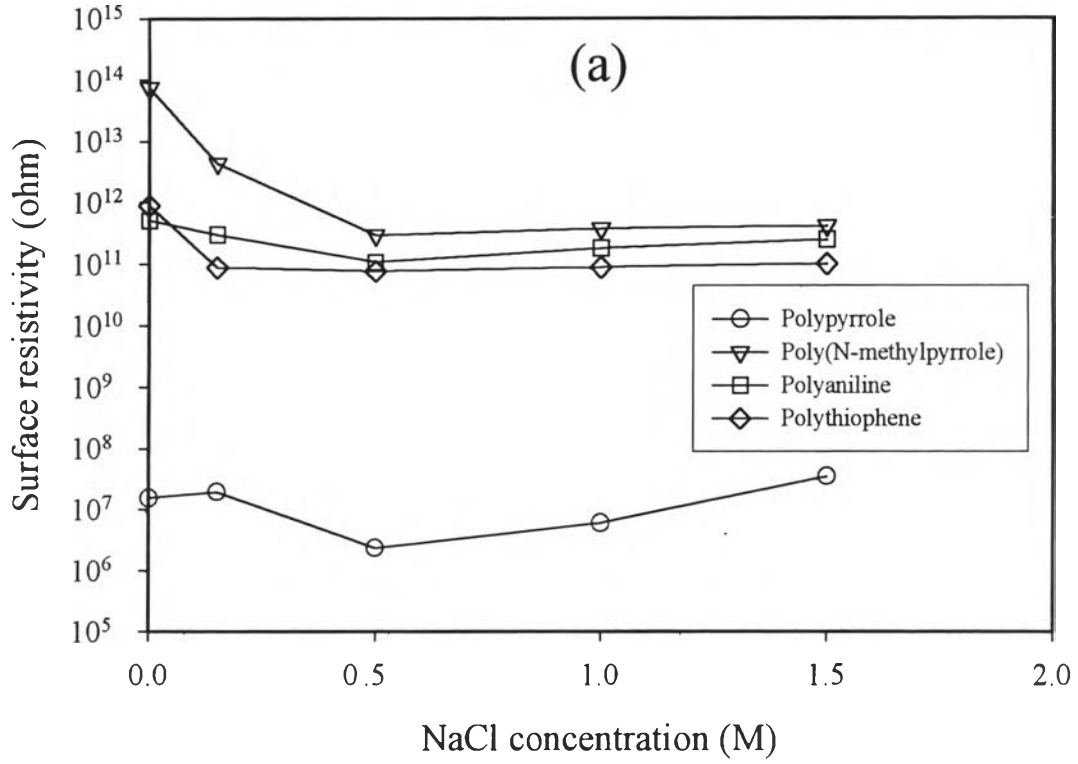

(a)
Cotton
Polyester
Surface resistivity (ohm)
10^{17}
10^{16}
10^{15}
10^{14}
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
Untreated
PPy
PNmp
PAn
PTh
(b)
Cotton
Polyester
Volume resistivity (ohm-cm)
10^{16}
10^{15}
10^{14}
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
Untreated
PPy
PNmp
PAn
PTh

Figure 5


(a)
Surface resistivity (ohm)
10^{15}
10^{14}
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
0.0
0.5
1.0
1.5
2.0
NaCl concentration (M)
Polypyrrole
Poly(N-methylpyrrole)
Polyaniline
Polythiophene

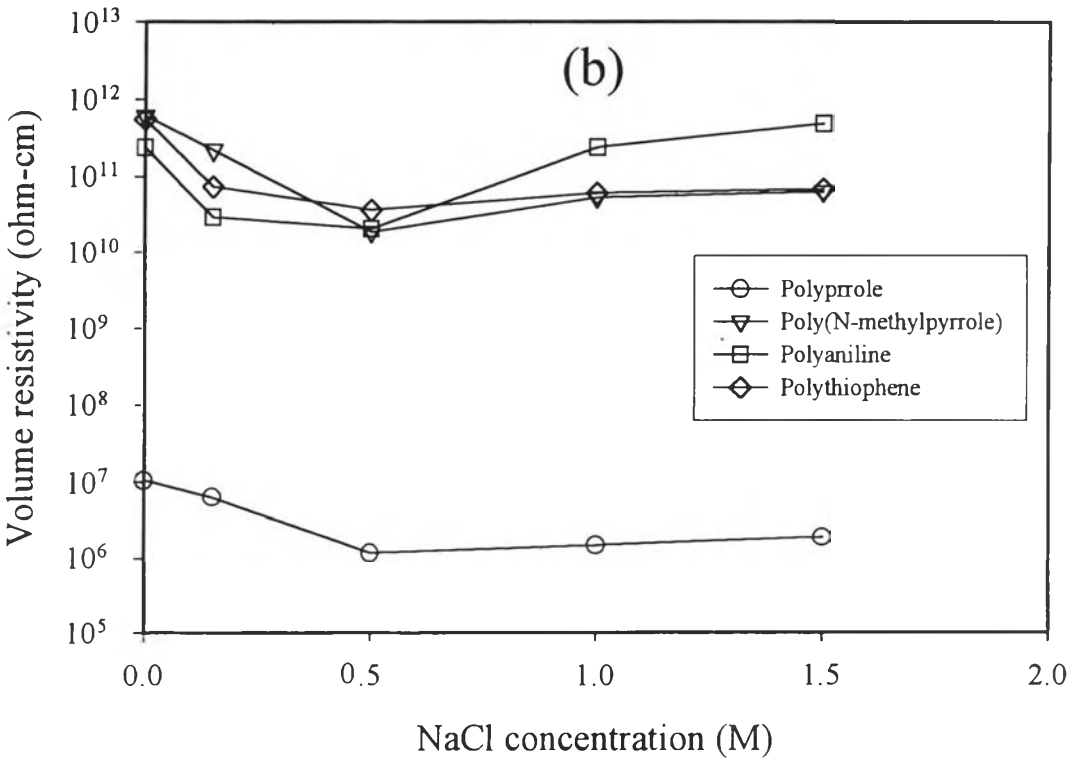
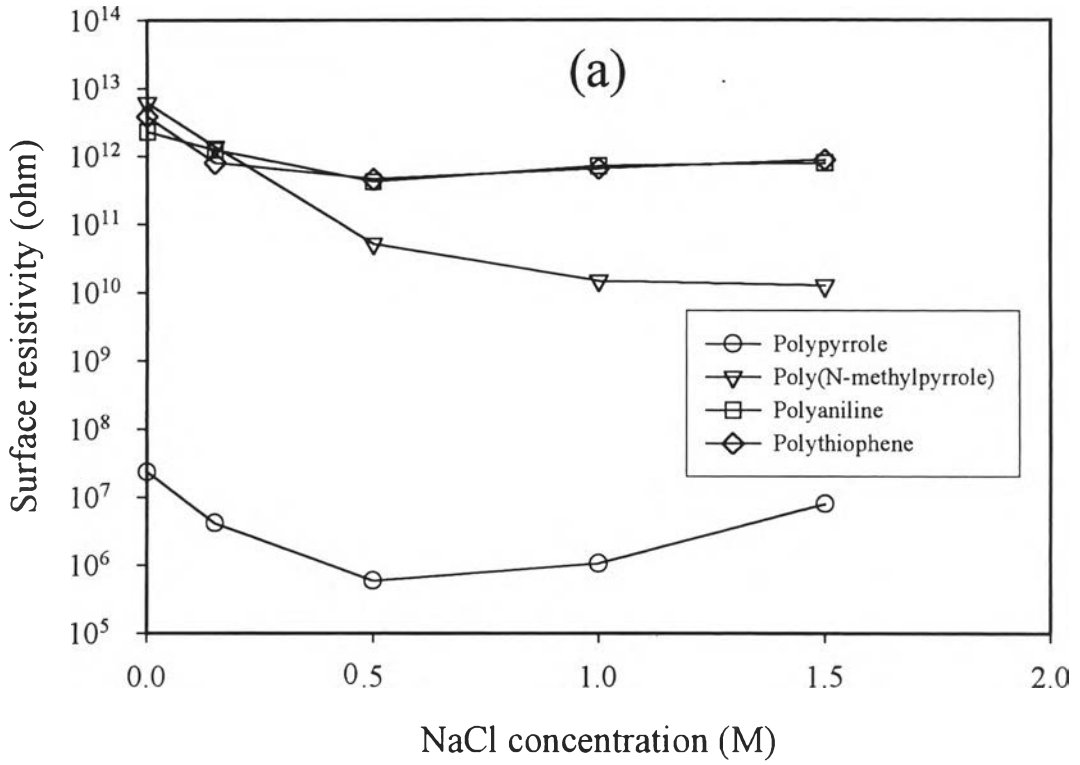

(b)
Volume resistivity (ohm-cm)
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
0.0
0.5
1.0
1.5
2.0
NaCl concentration (M)
Polypyrrole
Poly(N-methylpyrrole)
Polyaniline
Polythiophene

Figure 6


(a)
Surface resistivity (ohm)
10^{14}
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
0.0
0.5
1.0
1.5
2.0
NaCl concentration (M)
Polypyrrole
Poly(N-methylpyrrole)
Polyaniline
Polythiophene

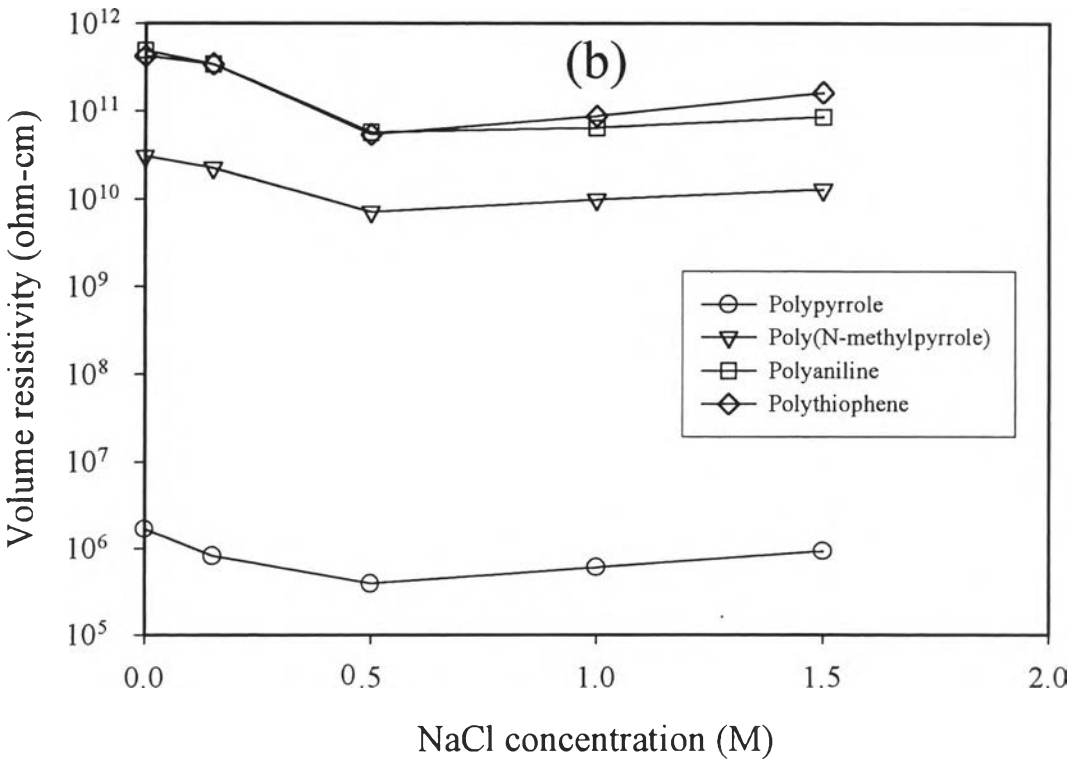
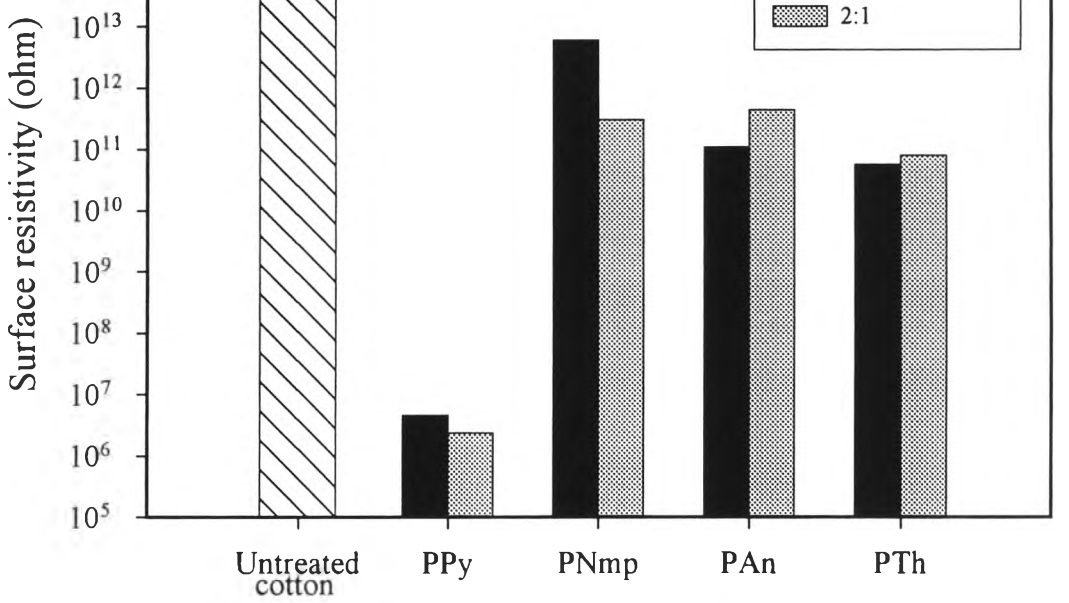
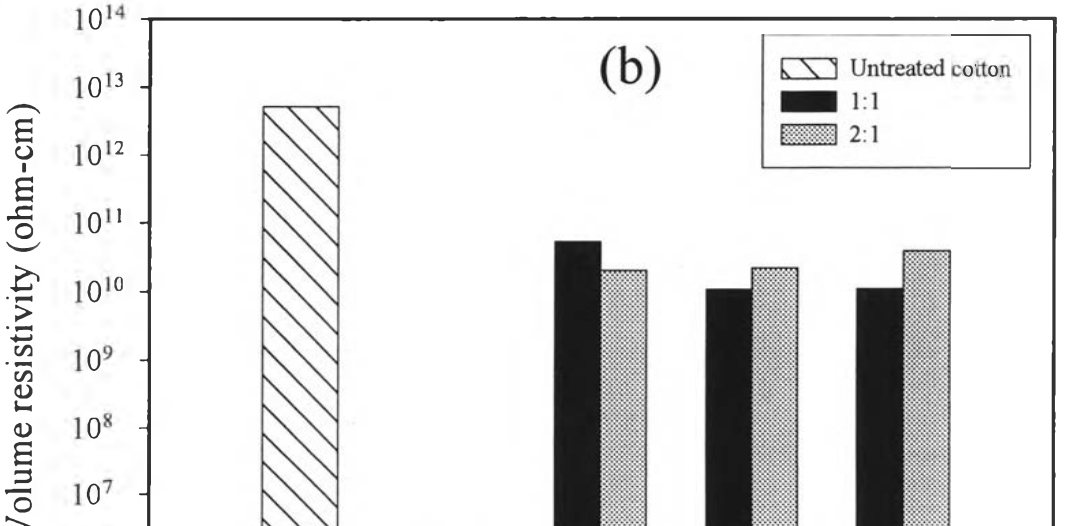

(b)
Volume resistivity (ohm-cm)
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
0.0
0.5
1.0
1.5
2.0
NaCl concentration (M)
Polypyrrole
Poly(N-methylpyrrole)
Polyaniline
Polythiophene

Figure 7


Surface resistivity (ohm)
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
2:1
Untreated cotton
PPy
PNmp
PAn
PTh


(b)
Volume resistivity (ohm-cm)
10^{14}
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
Untreated cotton
1:1
2:1

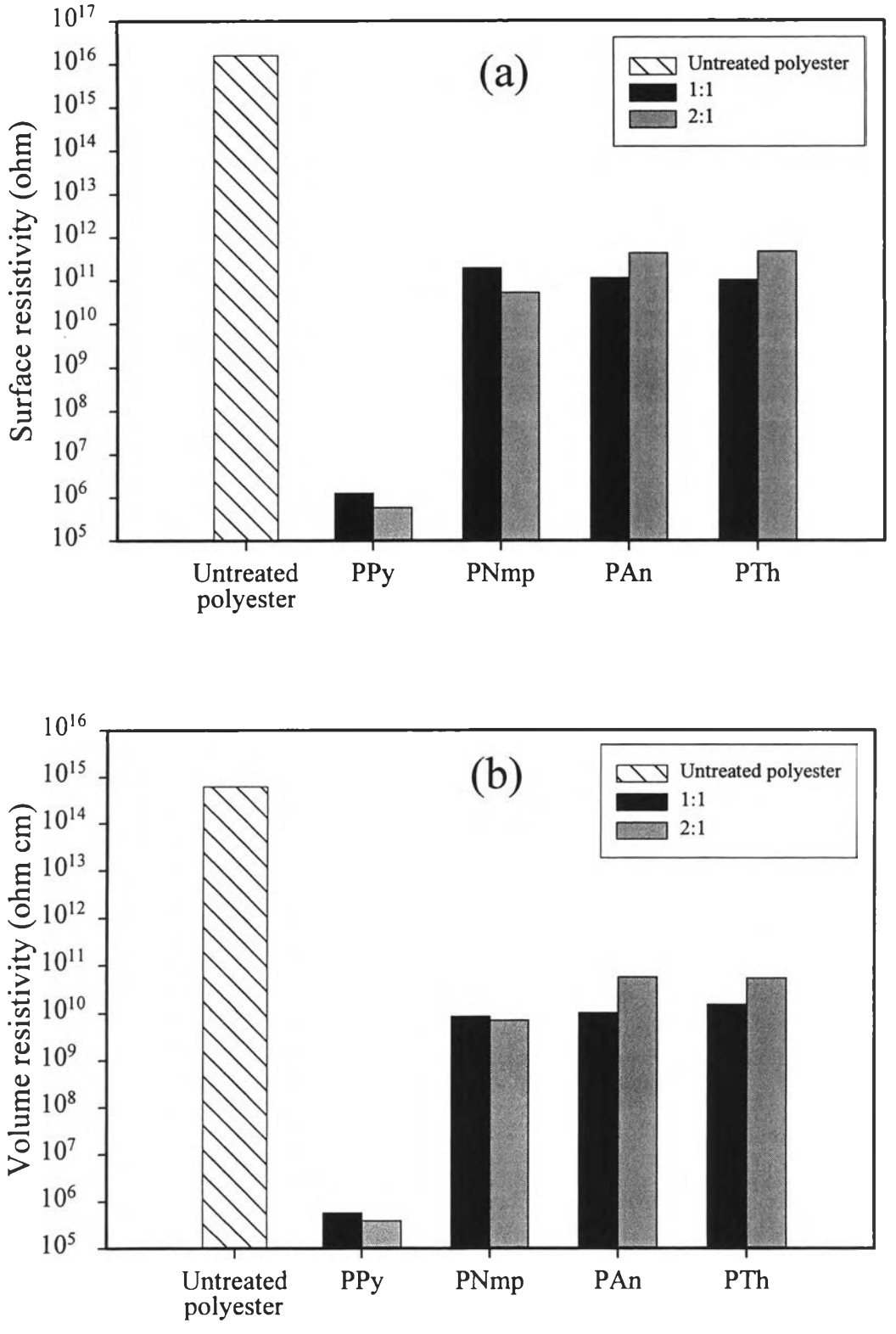
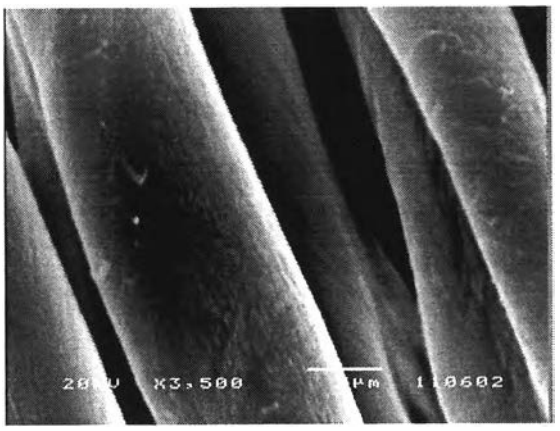
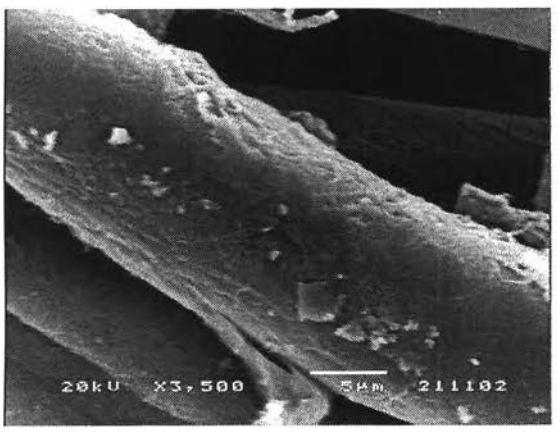

(a)
Surface resistivity (ohm)
10^{17}
10^{16}
10^{15}
10^{14}
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
Untreated polyester
1:1
2:1
Untreated polyester
PPy
PNmp
PAn
PTh
(b)
Volume resistivity (ohm cm)
10^{16}
10^{15}
10^{14}
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
Untreated polyester
1:1
2:1
Untreated polyester
PPy
PNmp
PAn
PTh

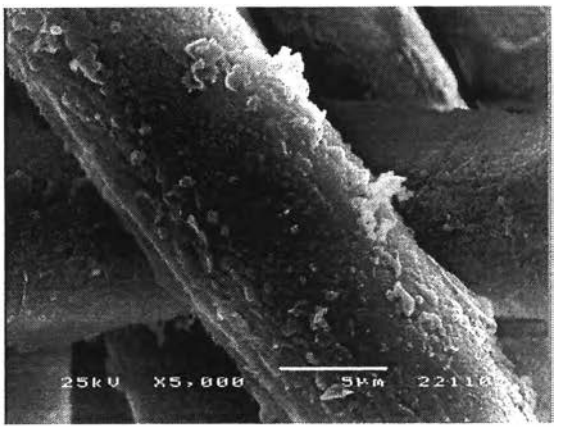
Figure 9



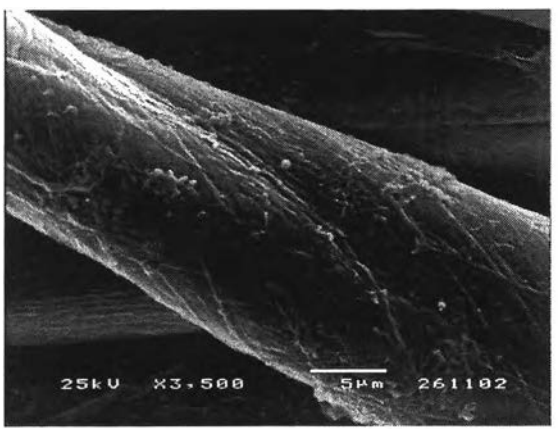
Untreated cotton



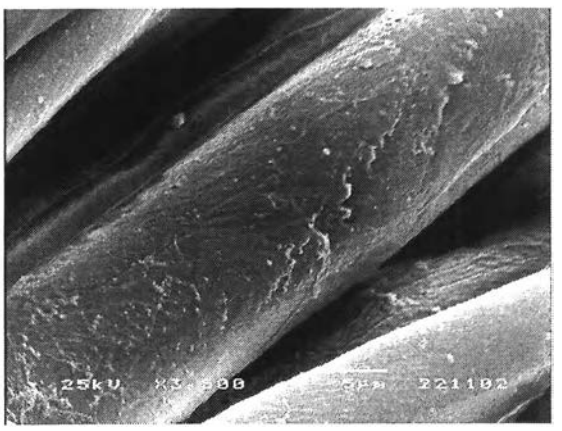
Polypyrrole



Poly(*N*-methylpyrrole)

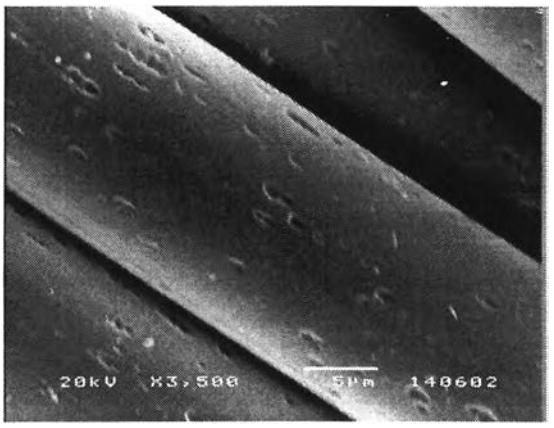


Polyaniline

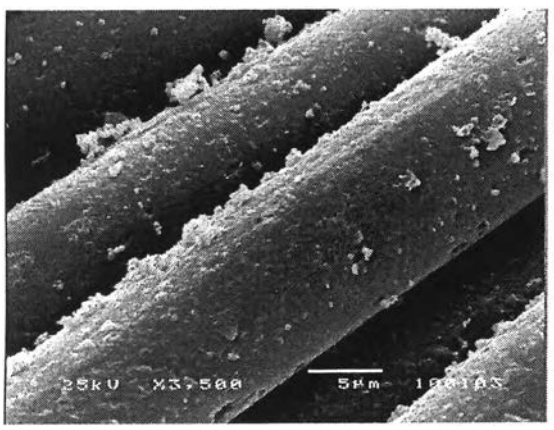


Polythiophene

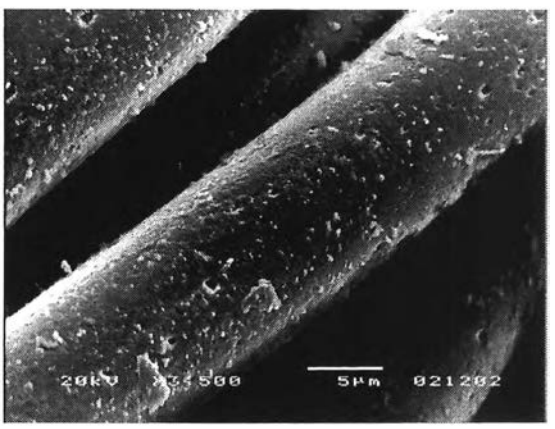
Figure 10



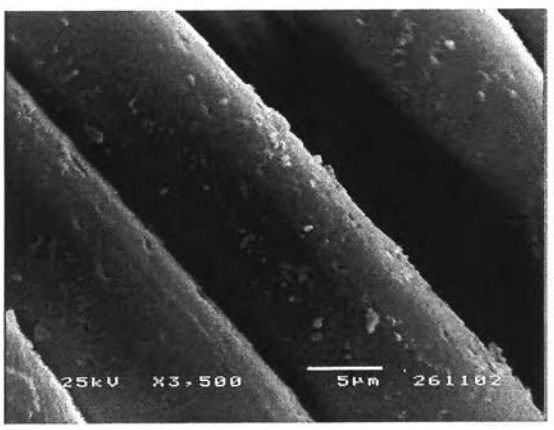
Untreated polyester



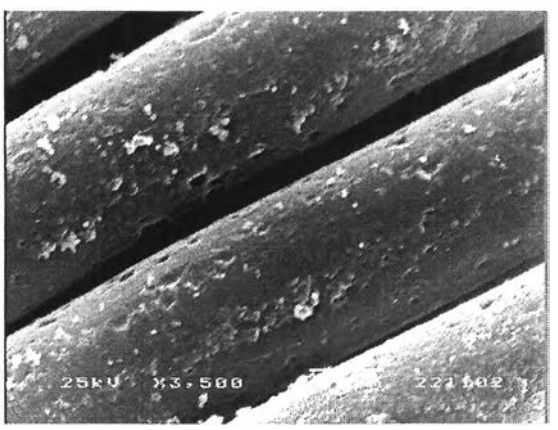
Polypyrrole



Poly(*N*-methylpyrrole)



Polyaniline



Polythiophene

Figure 11