CHAPTER IV

THE EFFECT OF DOPANTS ON THE RESISTIVITY OF POLYANILINE COATED ON POLYESTER FABRIC BY ADMICELLAR POLYMERIZATION

ABSTRACT: Polyaniline was coated on polyester fabric using admicellar polymerization technique. The effects of dopant type including, benzene sulfonic acid (BSA), p-toluenesulfonic acid (PTSA) and (+)-camphor-10-sulfonic acid (β) (CSA), and of dopant concentration were studied. Two methods of doping were also investigated. The results showed that the surface and volume resistivity decreased with increasing dopant concentration over the range examined. The resistivity of doped fabric improved by five to six orders of magnitude over the undoped, modified fabric. The lowest resistivity obtained was with BSA, followed by PTSA and CSA, with resistivity around 10^8 ohm. SEM micrographs of the coated fabric confirm that a very thin film of polyaniline has been successfully deposited by admicellar polymerization.

Keywords: Polyaniline, Admicellar polymerization, Polyester fabric, Dopant, Sulfonic acid

INTRODUCTION

Conductive polymers have been known for more than two decades. They consist of conjugated polymer chain with π- electrons delocalized along the backbone. There are a number of polymers that are stable under ambient conditions such as polypyrrole (PPY), polythiophene (PTH), and polyaniline (PANI). These polymers can be prepared by the oxidative polymerization of their respective monomers. Among these polymers, polyaniline is one of the most extensively studied due to its environmental stability, cheapness and ease of synthesis. Moreover, protonic acid doping of the emeraldine form yields good conductivity. Thus polyaniline has been applied to insulating materials used for many purposes.[1-3]

With the demand for high strength, high flexibility and the wide range of conductivity available with conductive materials, various techniques for deposition of polyaniline onto different kinds of fibers and textiles have been examined.[4-10] Conductive textiles have many potential applications, such as electromagnetic interference shielding materials, heating elements, the dissipation of electrostatic charge, and special purpose clothing such as dust and germ-free apparel. Their application depends on the conductivity of such materials. In addition, the degree of conductivity and stability of conductive fabric strongly depend on dopant.[11-12] Therefore, dopant is one of the most important factors governing the resistivity of coated fabric.

Researchers recently applied admicellar polymerization (AP) to produce a thin film of polymer on textile substrates.[13-14] This technique has been successfully used for producing a thin layer of polyaniline on polyester and cotton fabrics.[15] AP consists of four main steps as shown in Figure 1. The first step is admicelle formation. In the second step, an organic monomer is added which in turn will diffuse into the admicelle. Polymerization occurs when initiator (or oxidant) is added in the third step. The final step is the removal of the upper layer of surfactant to expose the polymeric film coated on the substrate surface.

In this study, polyaniline coated fabric is obtained by admicellar polymerization and the effect of dopants including benzene sulfonic acid (BSA), p-toluenesulfonic acid monohydrate (PTSA), and (+)-camphor-10-sulfonic acid (β) (CSA) on resistivity was investigated. Two methods of doping were compared. One involves immersing the coated fabric in a solution of dopant (i.e. doping after film formation). Another is immersing the untreated fabric in the mixed solution of monomer, dopant salt and surfactant at the step of admicelle formation (i.e. doping in conjunction with the first step). The electrical properties of the treated fabrics were compared and reported in terms of apparent surface and volume resistivity.

EXPERIMENTAL

Materials

Aniline (Merck) was purified by vacuum distillation and kept cool in the dark prior to use. Ammonium peroxydisulfate (Sigma) was selected as the oxidant. Dodecylbenzene sulfonic acid (DBSA), sodium salt, tech (Aldrich) was used as the surfactant. The dopants include benzene sulfonic acid (BSA) from Aldrich, p-toluenesulfonic acid monohydrate (PTSA) from Sigma, and (+)-camphor-10-sulfonic acid (β) (CSA) from Fluka. Hydrochloric acid and sodium chloride were purchased from Merck. A plain weave polyester fabric (fabric weight 180 g/sq.m) was washed in a washing machine at 95 °C several times until it was free from any remaining surfactant before use.

Admicellar polymerization of monomer on fabric

The admicellar polymerization of aniline on polyester fabric was carried out using aqueous DBSA solution at 1.2 mM. The pH was adjusted to 4 by using HCl. Monomer concentration used was at 10 mM and oxidant:monomer ratio of 1:1 was used. The amount of NaCl added was 0.5 M. Two methods of doping were employed. For the first method (doping at the last step), the 8×8 cm^2 fabric was placed in the pot of a dyeing machine (Daelim Starlet Model

DL-6000) containing 60 mL of surfactant, monomer and salt solution. Then the pot was placed in the dyeing machine set at 30°C for 15 h with a turning speed of 45 rpm to allow time for admicelle formation and monomer adsolubilization into the admicelle. Then the oxidant was added and polymerization was allowed to take place at 30° C for 4 h. Afterwards, the coated fabric was removed and washed twice in water at 80°C for 30 minutes in a pot before drying at 60°C in an oven overnight. The coated, dried, undoped fabric was placed in 50mL of an aqueous solution containing 20 mM of dopant for 2 h at 30°C and a stirring rate of 45 rpm in the same dyeing unit. At the end of doping time, the doped fabric was taken out from the pot and dried in an oven at 65 °C for 2 h.

To carry out doping concurrently with AP, the untreated polyester fabric was placed in the pot containing 60 mL of solution containing the required amounts of monomer, surfactant, salt and dopant. The procedure otherwise for AP was the same as described above. After polymerization was complete, the coated and doped fabric was rinsed in water to remove any excess monomer. Then the doped fabric was dried in the oven at 60°C for 2 hours. Five dopant concentrations of 1, 2, 4, 6, and 10 mM and three types of dopants, CSA, BSA, and p-TSA, were used.

Surface and apparent volume resistivity measurement of the treated fabric

The resistivity of the treated fabric was measured by using Programmable Electrometer/Source (KEITHLEY Model 6517A). Coated fabric was placed between two electrodes in a procedure adapted from the ASTM D-257 standard test. A DC voltage of 500 V was applied for 60s. For measuring the surface resistivity, voltage was applied across the surface of the sample. The resulting current was measured and the resistivity was calculated from the following equation:

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

For each sample, the surface resistivity of both sides of the fabric was measured and the average was taken.

For measuring the volume resistivity, the voltage (V) was applied across the sample and the resulting current was measured (I). The volume resistivity value can be calculated from the geometry of the electrodes and the thickness of the fabric sample (t) using the following equation:

$$\text{Volume resistivity,} \quad \rho_v = \frac{22.9V}{It} \quad \text{ohm-cm}$$

In this work the fabric thickness (t) = 0.4 mm.

Surface morphology of the treated fabric

Surface morphology of the treated fabric was examined by Jeol SEM model JSM 5200. Specimens were sampled at random from different parts of the fabric and sputter coated with gold prior to image. Magnification used was ×2000 at 10 kV.

RESULTS AND DISCUSSION

Method of doping

In the present work two methods of doping polyaniline-coated fabric were compared, i.e. doping after the last AP step and doping during the first step. The undoped coated fabric obtained from admicellar polymerisation has a dark green colour indicating that polyaniline was successfully coated on polyester fabric. For doping after the final step, after doping with three different types of dopants, BSA, PTSA, and CSA, the color of the doped fabric did not change. For doping with the first step however, the color of the doped fabric changed to a deep bright green colour indicating that emeraldine base form of polyaniline was obtained.[16] Figure 2 (a) and (b) shows the effect of doping method on the resistivity of polyaniline coated fabric when 10 mM of dopant concentration was used. It can be seen that both methods of doping can be used to improve the resistivity of the fabric since the resistivity of the doped fabric was less than the undoped material in all cases. The surface resistivity of doping at the first step was low, in the range 10^9 ohm/sq with all dopants used and the volume resistivity was in the range 10^8 ohm-cm. All three

dopants gave about the same resistivity value. However, for doping at the last step, the resistivity of fabric depended on dopant types, decreasing in the order BSA, CSA, and PTSA. The resistivity was in the range 10^{11}-10^{13} ohm/sq for surface resistivity and 10^{11}-10^{12} ohm-cm for volume resistivity respectively. Therefore, it can be concluded that doping in conjunction with AP is more effective overall while also simplifying the process. The change may also be a result of altered adsorption and adsolubilization during the reaction with the additive.

Dopant type and concentration

To find the suitable dopant concentration, the range of concentration was varied from 1, 2, 4, 6 to 10 mM using the doping with AP method. The effect of dopant concentration on the resistivity of coated fabric can be seen in Figure 3. Generally, values for both surface and volume resistivity were found to decrease as dopant concentration increased. Even when only a small amount of dopant (1mM) was used, the resistivity was decreased by two orders of magnitude compared with the undoped sample. The surface and volume resistivity were $\approx 10^{9}$ ohm/sq and 10^{8} ohm-cm respectively. Resistivity of samples with BSA and PTSA was about the same and slightly lower than CSA. This effect has been attributed to the relatively planar structure of aromatic dopants which permits packing of these molecules between the layers of the conjugated polymer, and thus facilitates electron hopping from chain to chain where defects in the chain occur.[17] In addition, the reproducibility of measurement was good especially with the fabric doped at high dopant concentration.

Comparison of the surface and volume resistivity

Surface resistivity is important for static charge removal along the surface whereas volume resistivity is important for charge dissipation across the fabric thickness. In the present work both the surface and volume resistivities of the fabric doped with 10 mM of dopant concentration were compared in Fig 4. It can be seen that volume resistivity was reduced in the same way as the surface

resistivity in all types of dopants. This clearly shows that the coating is not confined only to the exterior surface but uniform throughout the mass of the fabric. In addition, the volume resistivity of doped fabric was improved more than the surface resistivity when compared with undoped, coated material. For the undoped fabric, the volume resistivity was slightly less than the surface resistivity but after doping, the volume resistivity was less than the surface resistivity by one order of magnitude. The surface resistivity was 6×10^{14} ohm/sq for the undoped fabric and was about 8×10^{9} ohm/sq for the doped fabric respectively. The volume resistivity was 4×10^{14} ohm-cm for the undoped fabric and was about 5×10^{8} ohm-cm for the doped fabric respectively.

The effect of dopant on the conductivity of the treated fabric

The conductivity and thermal stability of the conductive fabric strongly depend on a substrate of fabric and dopant.[18-20] Kim[11] reported that the dopant mixtures of HCl and sulfonic acid induced high conductivity and thermal stability. Jin[4] obtained PANI-PET fiber and PANI-Nylon fabric doped with HCl, PTSA, DBSA and 5-sulfosalicyclic acid having a conductivity as high as 10^{-1}-10^{-3} S/cm (or a resistivity of 10^{1}-10^{3} ohm-cm). In the present work the resistivity of polyaniline coated polyester using admicellar polymerization was decreased by 5-6 orders of magnitude when only 10 mM of dopant was used. The lowest resistivity obtained was about 10^{8} ohm, sufficient for preventing problems arising from static charge.[21] In admicellar polymerization, the film thickness is in the nanometer range [22], hence there a limit in the extent to which resistivity might be lowered. While the thickness of the films does impose a limit on conductivity, they provide the benefit of a soft touch of fabric after coating.

SEM micrographs of the treated fiber surface

SEM micrographs of the coated fiber surface are shown in Figure 4. The micrographs of coated polyester show very thin film of polyaniline with some particles deposition. These particles may come from solution polymerization given that the monomer and oxidant are present in the aqueous phase and the surfactant concentration used is approximately the critical micelle concentration (cmc)[15]. For the micrograph of the doped fabric (c), it also shows very thin film of polyaniline with slightly more particles deposition than the coated one. This is probably due to a shift in the cmc with the additive. However, these excess particles are not expected to affect the conductivity significantly, since they do not form a coherent film on the surface. The SEM micrographs confirm that admicellar polymerization has been used successfully to coat a thin polyaniline film on the fiber surface.

CONCLUSIONS

Admicellar polymerization technique was used to produce polyaniline-coated polyester fabric. The resistivity of the doped fabric was improved by five to six orders of magnitude compared to the undoped, coated fabric. Two types of doping method were compared. Doping during the first AP step was found to be a more effective method resulting in much lower resistivity. The lowest value obtained for the doped fabric was around 10^8 ohm using 10 mM of dopant. SEM micrographs of the coated fabric confirm that a very thin film of polyaniline has been successfully coated by admicellar polymerization.

ACKNOWLEDGEMENTS

Tidarat Wongpun is grateful for the partial scholarship provided by the Petroleum and Petrochemical College, Chulalongkorn University.

REFERENCE

1. A. Malinauskas, *Polymer*, **42**, 3960-3963(2001).
2. K.F. Schoch, Jr., W.A. Byers and L.J. Buckley, *Synth. Met.*, **72**, 13(1995).
3. S. Konagaya, K. Abe and H. Ishihara, *Plast. Rubber and Composites*, **31**, 201(2002).
4. X. Jin and K. Gong, *J. Coated Fabrics*, **26**, 36(1996).
5. H.H. Kuhn, J. Kimbrell and C. William, US Patent 4975317(1990).
6. R. Anbarasan, N. Muthumani, T. Vasudevan, A. Gopalan and T. Wen, *J. Polym. Sci.*, **79**, 1283(2001).
7. S.K. Dhawan, N. Singh and S. Venkatachalam, *Synth.Met.*, **125**, 389(2002).
8. R. Hirase, M. Hasegawa and M. Shirai, *J. Appl.Polym.Sci.*, **87**, 1073(2003).
9. K.W. Oh, K.H. Hong and S.K. Kim, *J. Appl. Polym. Sci.*, **74**, 2094(1999).
10. K.W. Oh, S.K. Kim and E.A. Kim, *J. Appl. Polym. Sci.*, **81**, 684(2001).
11. S.K.Kim, J.H. Seong and K.W. Oh, *J. Appl. Polym. Sci.*, **83**, 2245(2002).
12. K.W. Oh and K.H. Hong, *J. Textile Res.*, **71**, 726(2001).
13. T. Pongprayoon, N. Yanumet and E.A. O'Rear, *J. Col.Interf.Sci.*, **249**, 227(2002).
14. S. Boufi and A. Gandini, *Cellulose*, **83**, 303(2002).
15. P. Lekpittaya, N. Yanumet, B.P. Grady and E.A. O'Rear, *J. Appl. Polym. Sci.*, **92**, 2629(2004).
16. M.A. Habib, in "*Conductive Electroactive Polymers*", 2nd Edition, G.G. Wallace, G.M. Spinks, Leon A.P. Kane-Maguire and P.R. Teasdale, Ed., Boca Raton, New York, 2000, Chapter 5.

17. H.H. Kuhn, *Text. Chem. and Col.*, **29**, 17 (1997).

18. H.Q. Xe, Y.M. Ma, D.S. Feng, *European Polymer J.*, **36**. 2201 (2000).

19. H.H.Kuhn, J. Kimbrell and C. William, *Synth. Met.*, **71**. 2139 (1995).

20. R. V. Gregory, W. C. Kimbrell and H. H. Kuhn, *Synth. Met.*, **28**. 823 (1989).

21. H.H. Kuhn and A.D. Child, in "*Handbook of Conducting Polymer*", 2nd Edition, T.A. Skotheim, R.L. Elsenbaumer, and J.R. Reynolds, Ed., Macel Dekker, New York, 1998, Chapter 35.

22. W.L. Yuan, E.A. O'Rear, G. Cho, G.P. Funkhouser and D.T. Glatzhofer, *Thin Solid Film*, **385**, 96 (2001).

LIST OF FIGURES

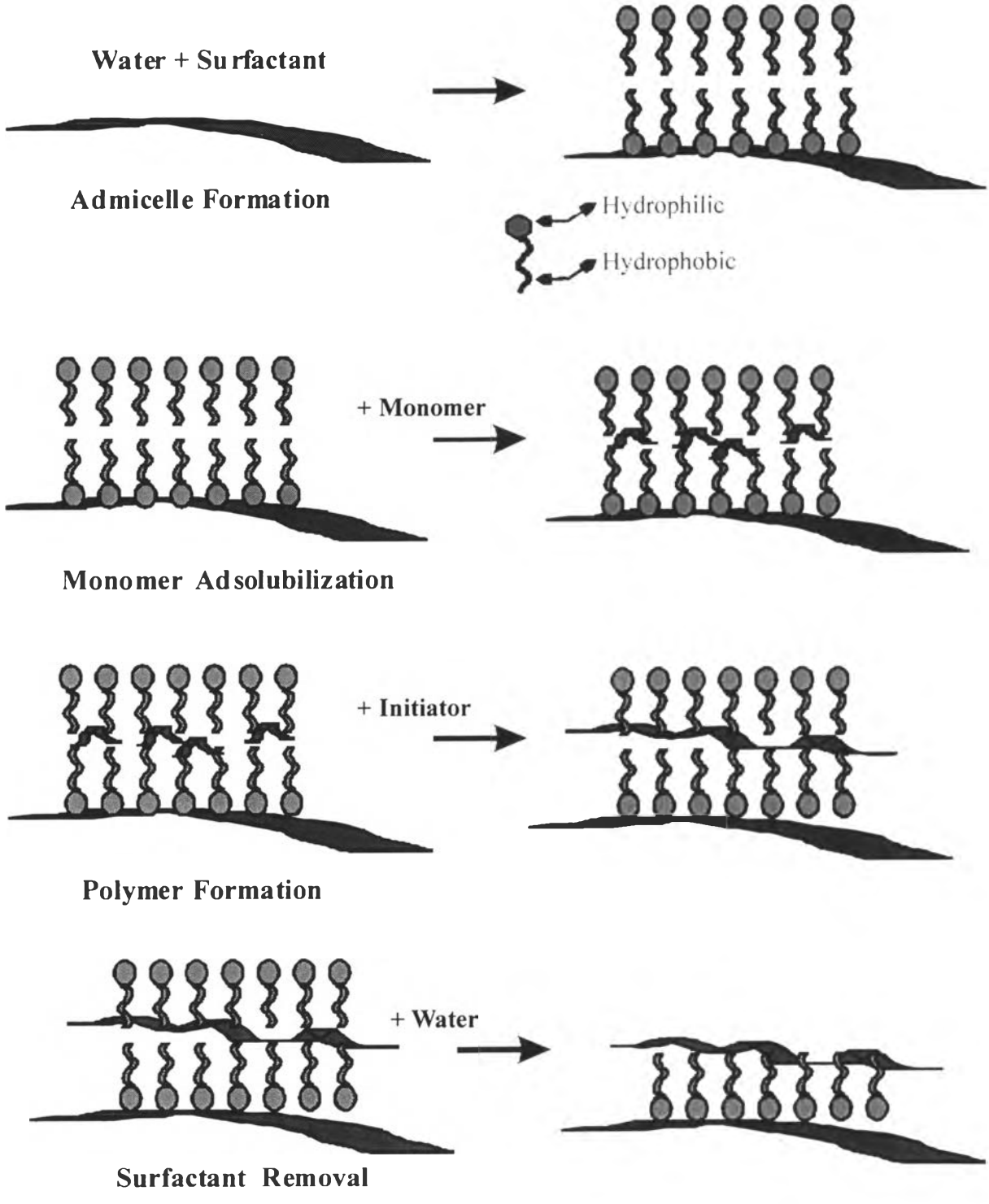
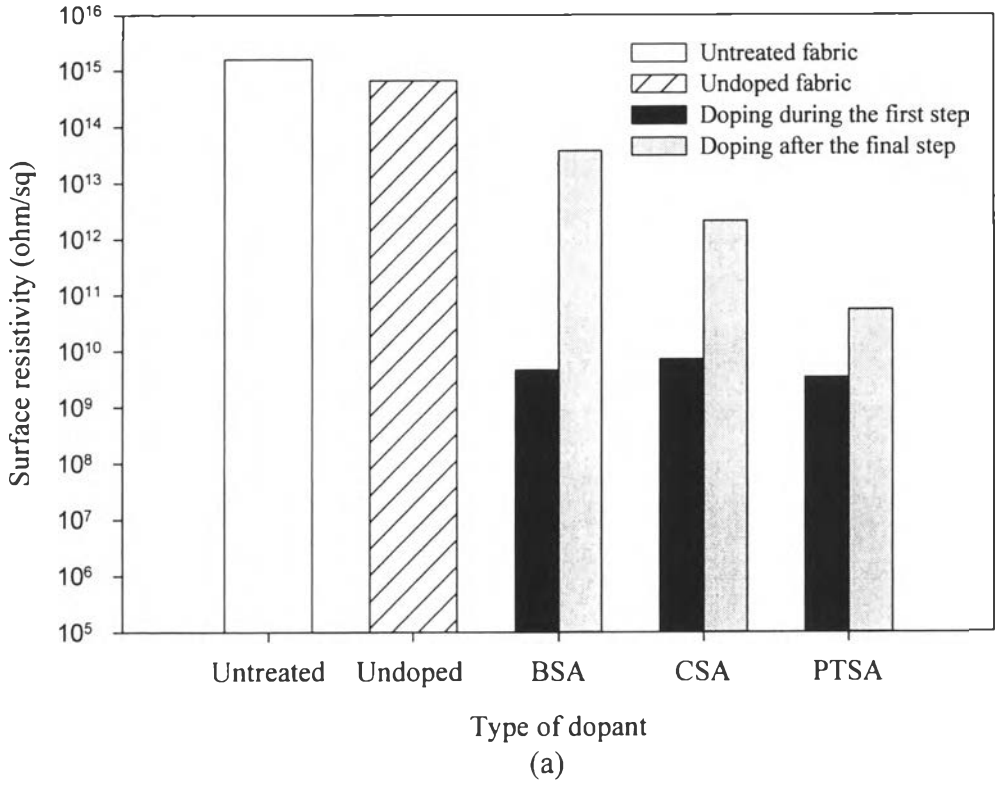
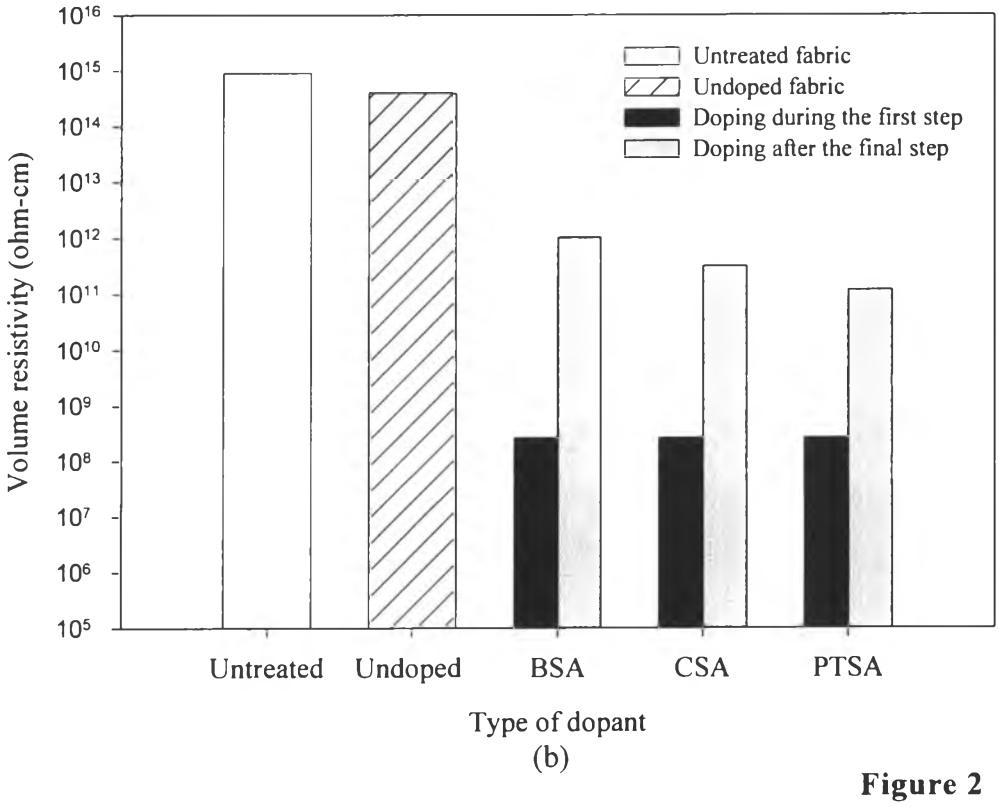

Water + Surfactant
Admicelle Formation
Hydrophilic
Hydrophobic
+ Monomer
Monomer Adsolubilization
+ Initiator
Polymer Formation
+ Water
Surfactant Removal

Figure 1


Surface resistivity (ohm/sq)
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 fabric
Undoped fabric
Doping during the first step
Doping after the final step
Untreated
Undoped
BSA
CSA
PTSA
Type of dopant

(a)


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 fabric
Undoped fabric
Doping during the first step
Doping after the final step
Untreated
Undoped
BSA
CSA
PTSA
Type of dopant

(b)

Figure 2

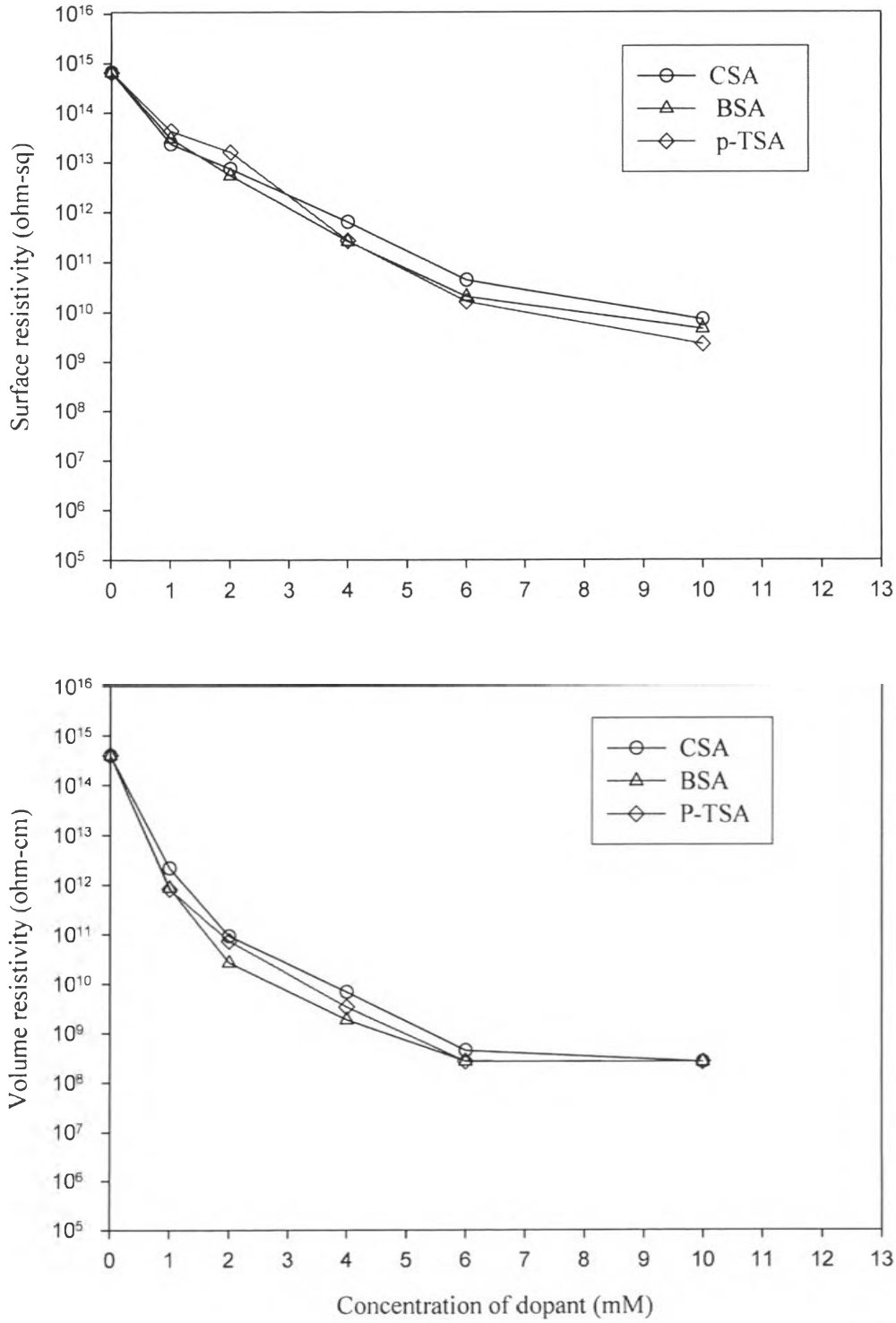

Surface resistivity (ohm-sq)
10^{16}
10^{15}
10^{14}
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
0 1 2 3 4 5 6 7 8 9 10 11 12 13
CSA
BSA
p-TSA
Volume resistivity (ohm-cm)
10^{16}
10^{15}
10^{14}
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
0 1 2 3 4 5 6 7 8 9 10 11 12 13
CSA
BSA
P-TSA
Concentration of dopant (mM)

Figure 3

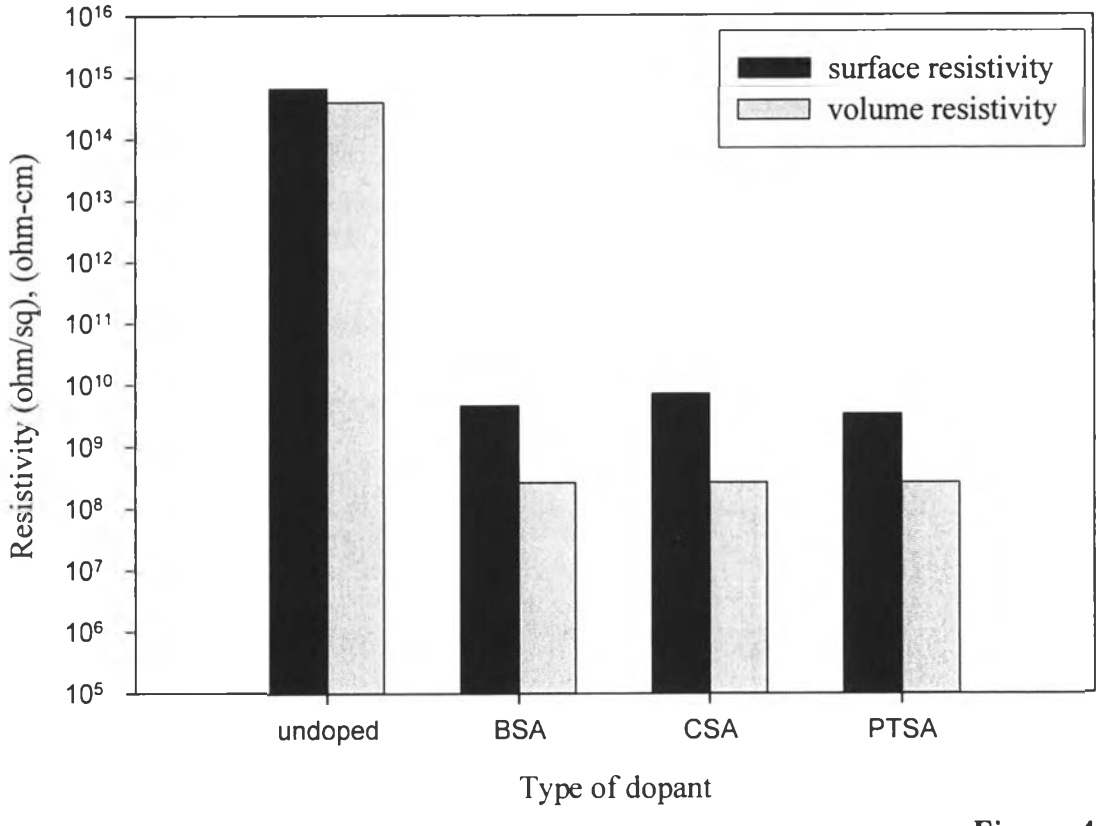
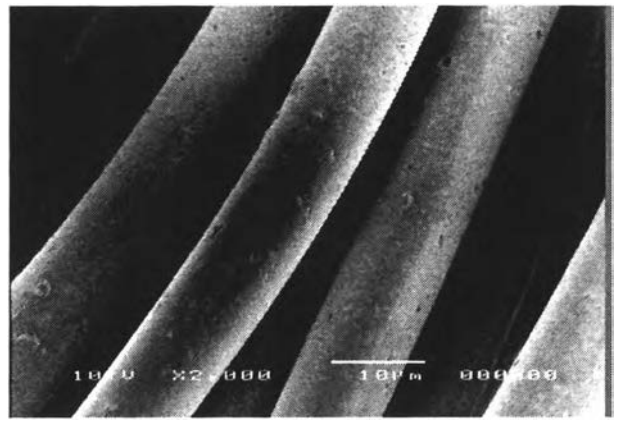
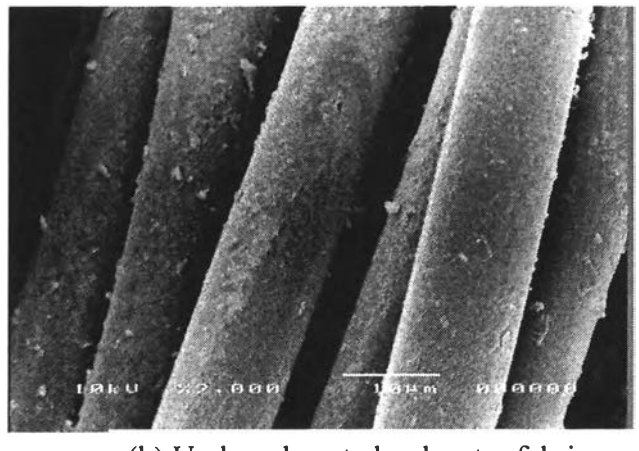

Resistivity (ohm/sq), (ohm-cm)
10^{16}
10^{15}
10^{14}
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
surface resistivity
volume resistivity
undoped
BSA
CSA
PTSA
Type of dopant

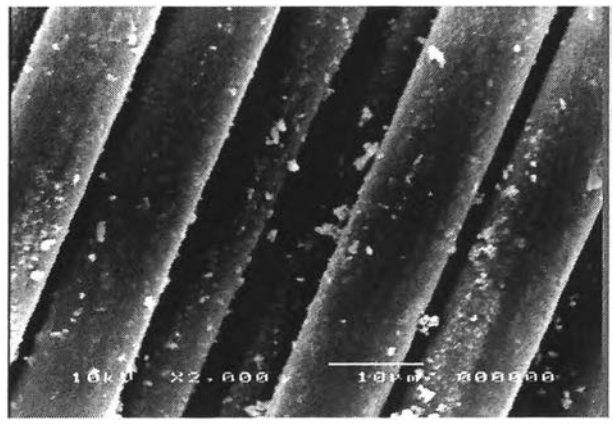
Figure 4



(a) Untreated polyester fabric



(b) Undoped coated polyester fabric



(c) Doped fabric using 10 mM of PTSA

Figure 5