CHAPTER V

THE EFFECT OF DOPANT ON THE RESISTIVITY OF POLYTHIOPHENE COATED ON POLYESTER FABRIC BY ADMICELLAR POLYMERIZATION

ABSTRACT: Preparation of polythiophene-coated polyester fabric was carried out by admicellar polymerization. The effects of dopant type including, (+)-camphor-10-sulfonic acid (β) (CSA), p-toluenesulfonic acid (PTSA) and 5-sulfosalicylic acid (5-SCA) and of dopant concentration were studied. Two methods of doping were also investigated. The results shown that the surface and volume resistivity decreased with increasing dopant concentration over the range investigated. The resistivity of doped fabric was improved by one to four orders of magnitude over the undoped fabric. The lowest resistivity obtained was around 10^9 ohm. Thin film of polythiophene has been successfully deposited by admicellar polymerization. This was confirmed by SEM micrographs of the coated fabric

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

INTRODUCTION

The main feature of the conductive organic polymers such as polythiophene polyaniline and polypyrrole is that they all contain "π" electron structure extending throughout their configuration. These polymers are generally insulators or semi-conductors in their undoped state but can be made as conductive as metals when they are subjected to a doping process. They are highly conductive in an oxidized state. The conductance process in these polymers is believed to take place by "electron delocalization".[1] These polymers can be prepared by the electrochemical or oxidative polymerization of their respective monomers.

Polythiophene has excellent environmental stability in both its doped and undoped states and good electrochemical properties.[2] However, polythiophene itself is prone to over-oxidation during polymerization.[3] Thus most practical work has been carried out by using synthesis of functionalized thiophene. Recently, polythiophene has been deposited with different types of substrate such as rubber, [4] and silicon, [5] by using electrochemical polymerization. In addition, some composites of polythiophene have also been reported.[6-7]

Conductive polymer-coated textiles are part of developed composites materials that are used in many applications. More recently, conductive polymers were successfully coated on fabric by using admicellar polymerization.[8] This technique consists of four main steps which are admicelle formation, monomer adsolubilization, polymer formation, and surfactant removal, as shown in Figure 1. Because the conductivity of most conductive polymers in their undoped form is low, their application is limited. Thus in order to improve their conductivity and stability, a doping process is required. Many authors [9-11] used various organic sulfonic acids as dopants for doping conductive polymers. Therefore, in this work, various sulfonic acids are used to improve the conductivity of polythiophene coated-fabric. Admicellar polymerization (AP) is used to produce a thin film of polythiophene on polyester fabric. The effects of dopants including (+)-

camphor-10-sulfonic acid (β) (CSA), p-toluenesulfonic acid monohydrate (PTSA), and 5-sulfosalicyclic acids dehydrate (5-SCA) on the resistivity of the coated fabric was investigated. In addition, two methods of doping were compared. One involved immersing the coated fabric in the solution of dopant (i.e. doping after film formation). Another was 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 treated fabrics were compared and reported in terms of surface and volume resistivity.

EXPERIMENTAL

Materials

Thiophene (99+%, Aldrich)) was used as received. Ferric chloride (Aldrich) was selected as oxidant. Dodecylbenzene sulfonic acid (DBSA), sodium salt, tech (Aldrich) was used as the surfactant. The dopants including p-toluenesulfonic acid monohydrate (PTSA) and 5-sulfosalicyclic acids dehydrate (5-SCA) 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 used and it 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 polythiophene 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 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 the dyeing machine (Daelim Starlet Model DL-6000) containing 60 mL of surfactant, monomer, and salt solution. The pot was then 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 before-drying at 60°C in an oven overnight. The coated, dried, undoped fabric was placed in 50 ml of an aqueous solution containing 20 mM of dopant for 2 hours at 30°C, using a turning speed of 45 rpm in the same dyeing unit. At the end of doping time, the doped fabric was removed from the pot and dried in an oven at 65 °C for 2 h.

To carry out doping concurrently with AP the untreated PES fabric was placed in the pot containing 60 mL of solution containing the required amounts of monomer, surfactant, salt and dopant. Then the following steps (monomer adsolubilization and polymerization) were the same as described in the first method. After polymerization was complete, the coated and doped fabric was rinsed with water to remove any excess monomer. Then the doped fabric was dried in the oven at 60°C for 2 h. Four dopant concentrations of 10, 20, 40 and 60 mM and three types of dopants, CSA, PTSA and 5-SCA were used.

Surface and volume resistivity measurements of the treated fabric

The resistivity of the treated fabric was measured by using Electrical Resistance (KEITHLEY Model 6517A). The coated fabric was placed between two electrodes. The procedure was adapted from the ASTM D-257 standard method. A DC voltage of 500 V was applied for 60 seconds. For measuring the surface resistivity, voltage (V) was applied across the surface of the sample. The resulting current (I) was measured and the surface resistivity (ρ_s) was calculated from the following equation:

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

For surface resistivity, the measurements were made on both sides of a sample and the average value was calculated.

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

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

In the present work the thickness of the fabric used 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 randomly 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

Two methods of doping polythiophene-coated fabric were compared, i.e. doping after the last AP step and doping during the first step. For the undoped fabric, after the polymerization was complete, the color of the coated fabric was light orange indicating that the polymer was successfully coated on the fabric surface. For doping after the final step, the color of the coated fabric after doping with CSA and PTSA did not change. However, with the dopant 5-SCA, the color of the fabric changed from yellow to dark pale violet colour. For the doped fabric obtained from doping during the first step, the color of the resulting doped fabric changed to light yellow for all the three dopants. The surface and volume resistivity of all the fabrics are shown in Figure 2. It can be seen that the resistivity of the doped fabric from both doping methods was lower than the undoped fabrics. This shows improvement in the resistivity of the fabric after doping. The resistivity obtained for doping at the first step was in the range 10^{11}-10^{13} ohm/sq for surface resistivity and 10^{10}-10^{13} ohm-cm for volume resistivity, respectively. For doping after the last AP step, the resistivity was in the range 10^{10}-10^{13} ohm/sq for surface resistivity and 10^{10}-10^{12} ohm-cm for volume resistivity, respectively. From the results of resistivity, it can be concluded that doping after the final step of AP is effective for PTSA and 5-SCA, while doping during the first step was suitable for CSA dopant. The effect of doping in conjunction with AP may not be due to just doping, the change may also be a result of altered adsorption and adsolubilization during the reaction with addition of the dopant.

Dopant type and concentration

In this work the range of dopant concentration was varied from 10, 20, 40 to 60 mM using doping after the final step method. The effect of dopant concentration on the resistivity of the coated fabric can be seen in Figure 3. Generally, the surface and volume resistivity values were found to decrease as dopant concentration increased. The lowest surface and volume resistivity were $\approx 10^9$ ohm which was improved by one to four orders of magnitude compared with the undoped materials. The effectiveness of the dopant increased in the order CSA, PTSA, and 5-SCA. Generally, a dopant with a large molecule will be less effective since it will reduce the possibility of charge hoping between chains. In the present work CSA with a molecular weight of 232.3 was found to be less effective than PTSA with a molecular weight of 190.2. However, 5-SCA, which has about the same size as CSA was found to be the most effective among the three dopants. This may be due to the presence of the polar groups OH and COOH which may interfere favourably with the electrical conductivity of the doped fabric.

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 40 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.

The effect of dopant on the conductivity of polythiophene

To enhance the conductivity, polythiophene can be doped by many dopants such as iodine, $FeCl_3$, $NOPF_6$ and $NOSbF_6$. Films of doped polythiophene formed electrochemically have a conductivity in the oxidized form of approximately 10^{-4} S/cm (or a resistivity of 10^4 ohm-cm), the doping anion being PF_6^-.[12] In addition, films of polythiophene obtained by plasma polymerization displayed a conductivity of 1.8×10^{-4} S/cm (or a resistivity of 10^4 ohm-cm) after doping with iodine.[13] The surface resistivity was also reported in the range 10^6-10^9 ohm/sq for films of polythiophene obtained with similar method.[14] The conductivity and thermal stability of conductive fabric have been found to be strongly dependent on the type of fabric and dopant.[15-17] In the present work polythiophene coated on polyester fabric obtained by admicellar polymerization and doped with sulfonic acid dopant achieved the lowest resistivity of about 10^9 ohm (Figure 4). The advantage of this technique is that a very thin film of polymer is formed and hence the soft touch of the fabric remained unchanged after coating.

SEM micrographs of the treated fiber surface

Figure 5 shows the morphology of the untreated and coated polyester fabrics respectively. The micrographs of coated polyester show very thin film of polythiophene with some particles deposition. These particles may come from solution polymerization given that the monomer and oxidant are present in the aqueous phase. The micrograph of the doped fabric with 20 mM of PTSA also shows very thin film and did not show any different morphology from the undoped fabric. These SEM micrographs confirm that admicellar polymerization has been used successfully to coat a thin polythiophene film on the fiber surface.

CONCLUSIONS

Polythiophene coated-fabric can be obtained by admicellar polymerization technique. The resistivity of the doped fabric was improved by four to five orders of magnitude compared to the undoped fabric. Two types of doping method were employed. Doping after the final step was found to be an effective method for the fabric doped with PTSA and 5-SCA and doping in conjunction with the first step was suitable for the fabric doped with CSA. The lowest resistivity obtained was around 10^9ohm. The lowest resistivity obtained was with 5-SCA followed by PTSA and CSA. The thin film of polythiophene deposited on polyester fabric was confirmed by SEM micrographs.

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LIST OF FIGURES

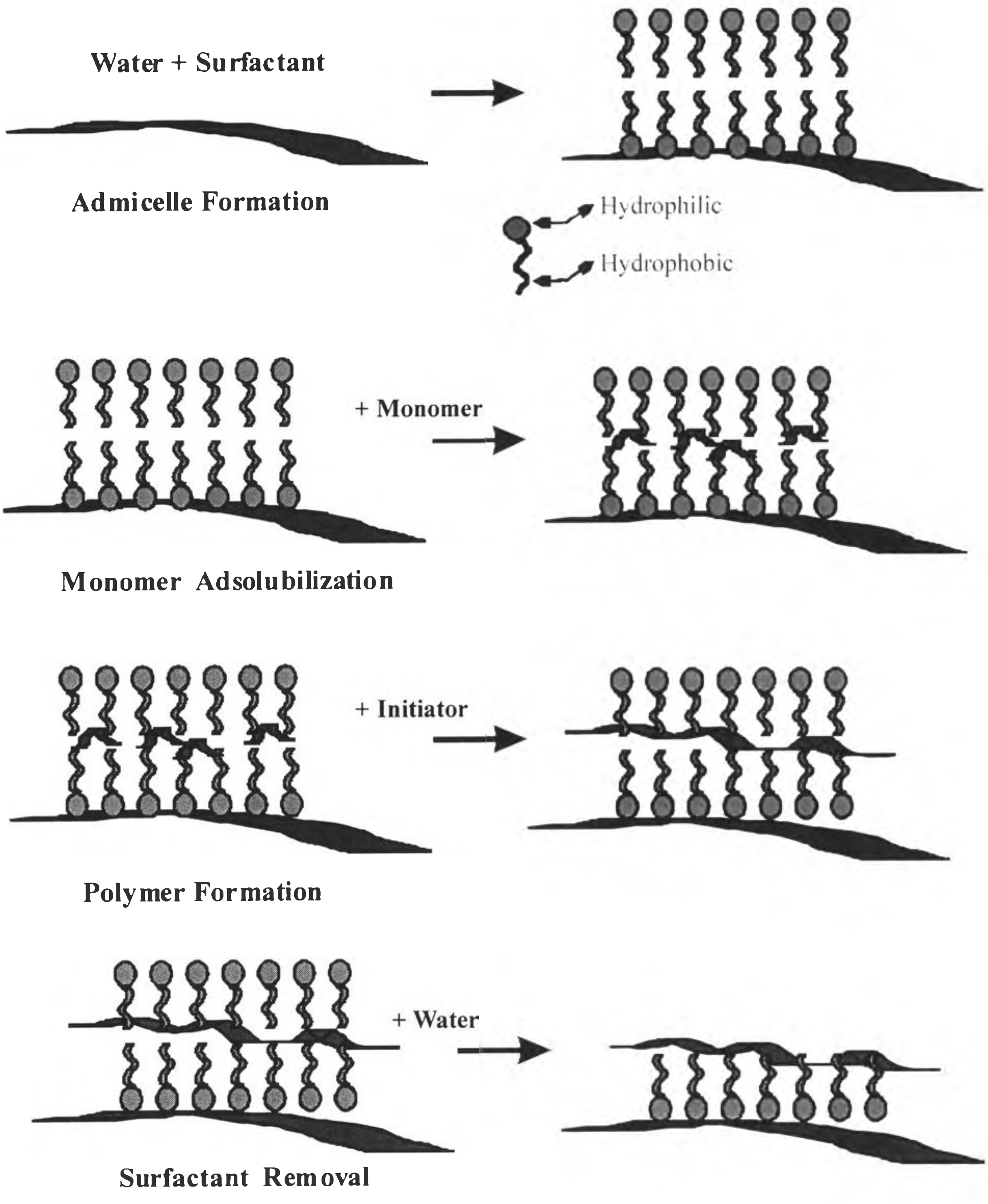
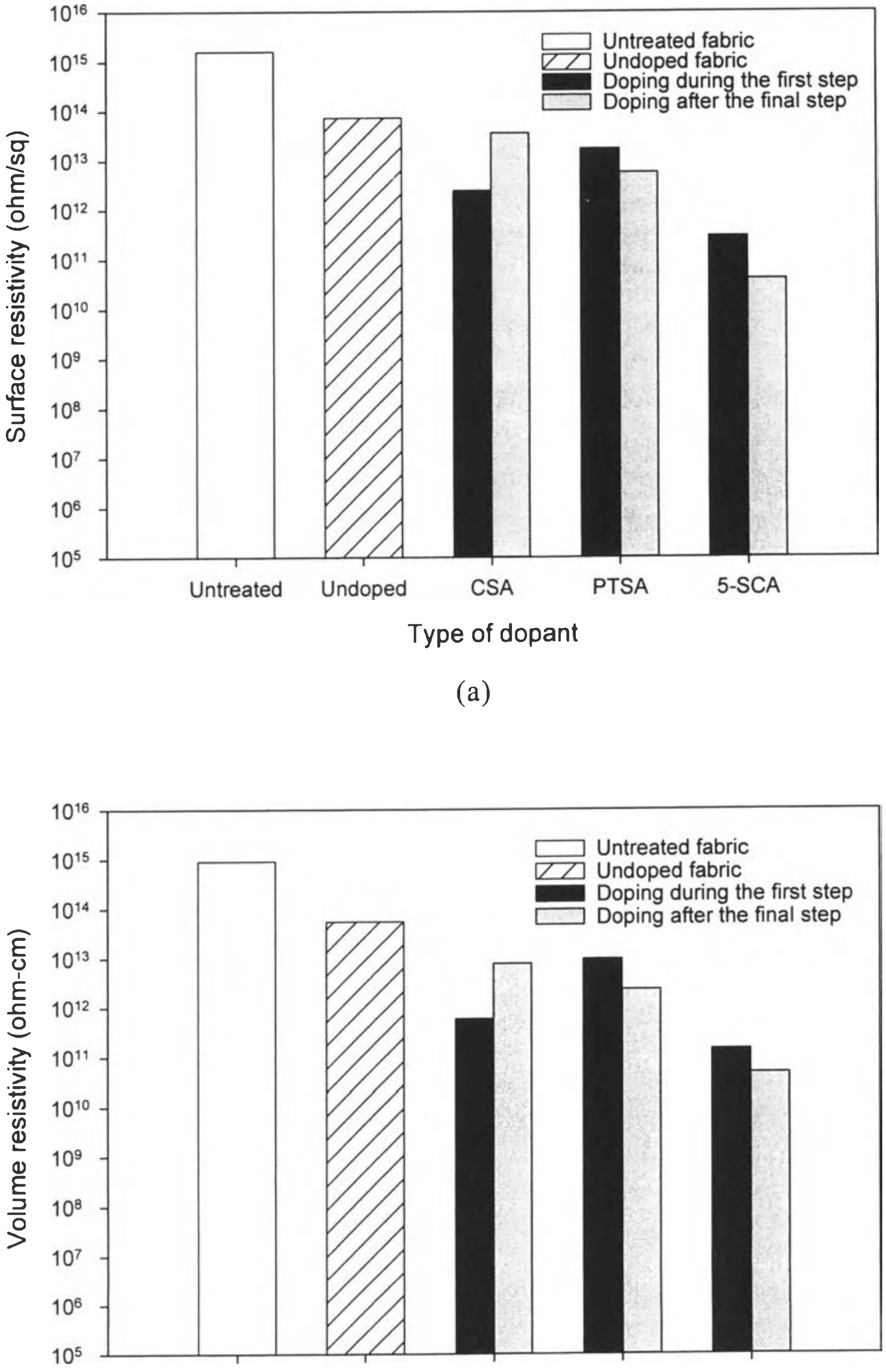

Water + Surfactant
Admicelle Formation
Hydrophilic
Hydrophobic
+ Monomer
Monomer Adsolubilization
+ Initiator
Polymer Formation
+ Water
Surfactant Removal

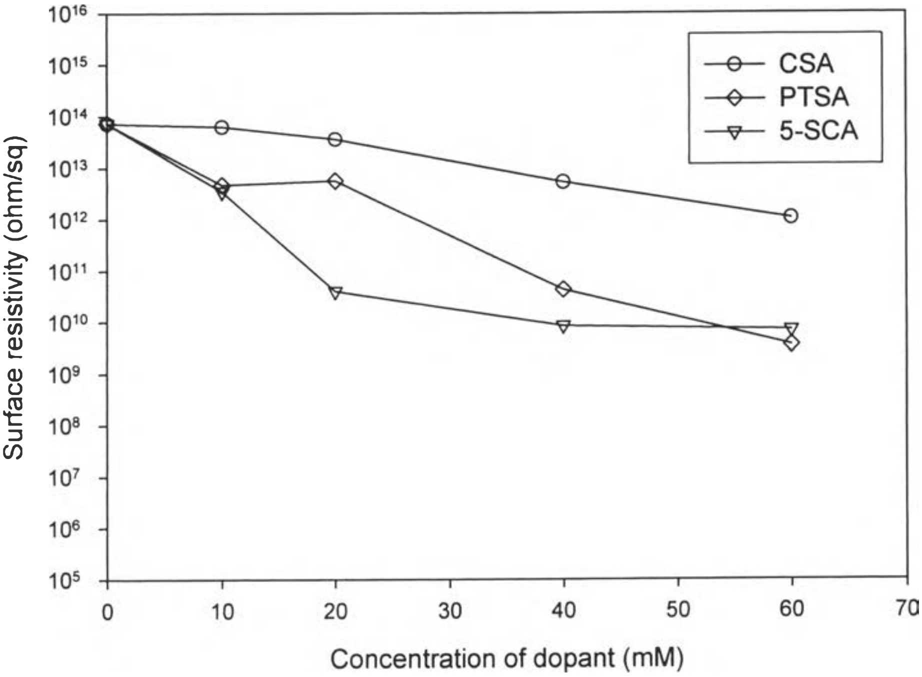
Figure 1


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 (ohm/sq)
Untreated fabric
Undoped fabric
Doping during the first step
Doping after the final step
Untreated
Undoped
CSA
PTSA
5-SCA
Type of dopant
10^{16}
10^{15}
10^{14}
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
Volume resistivity (ohm-cm)
Untreated fabric
Undoped fabric
Doping during the first step
Doping after the final step
Untreated
Undoped
CSA
PTSA
5-SCA
Type of dopant

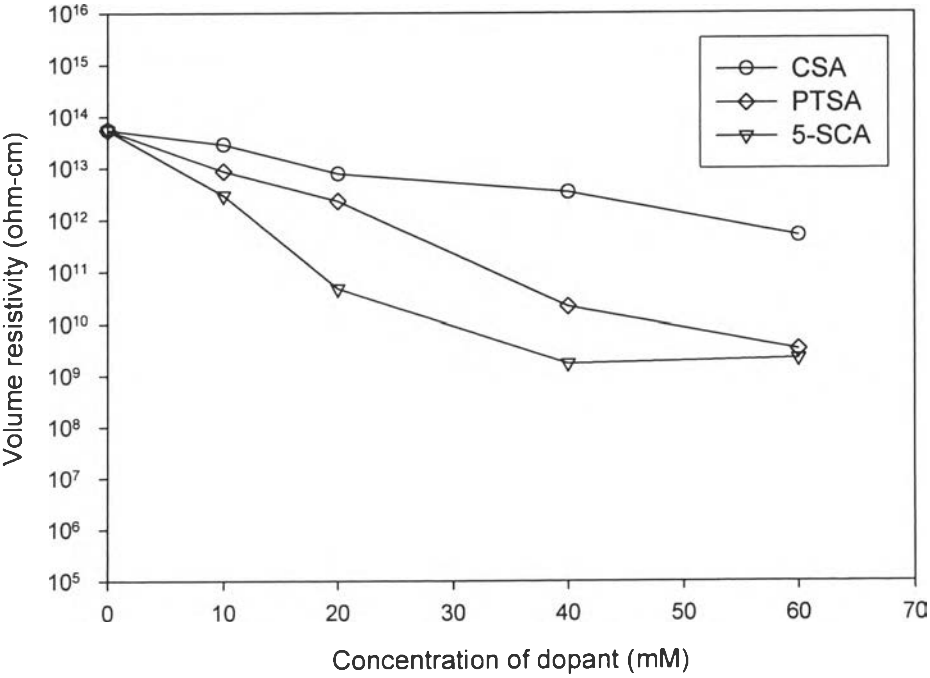
(a)

(b)

Figure 2


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 (ohm/sq)
0
10
20
30
40
50
60
70
Concentration of dopant (mM)
CSA
PTSA
5-SCA

(a)


10^{16}
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10^{14}
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
Volume resistivity (ohm-cm)
0
10
20
30
40
50
60
70
Concentration of dopant (mM)
CSA
PTSA
5-SCA

(b)

Figure 3

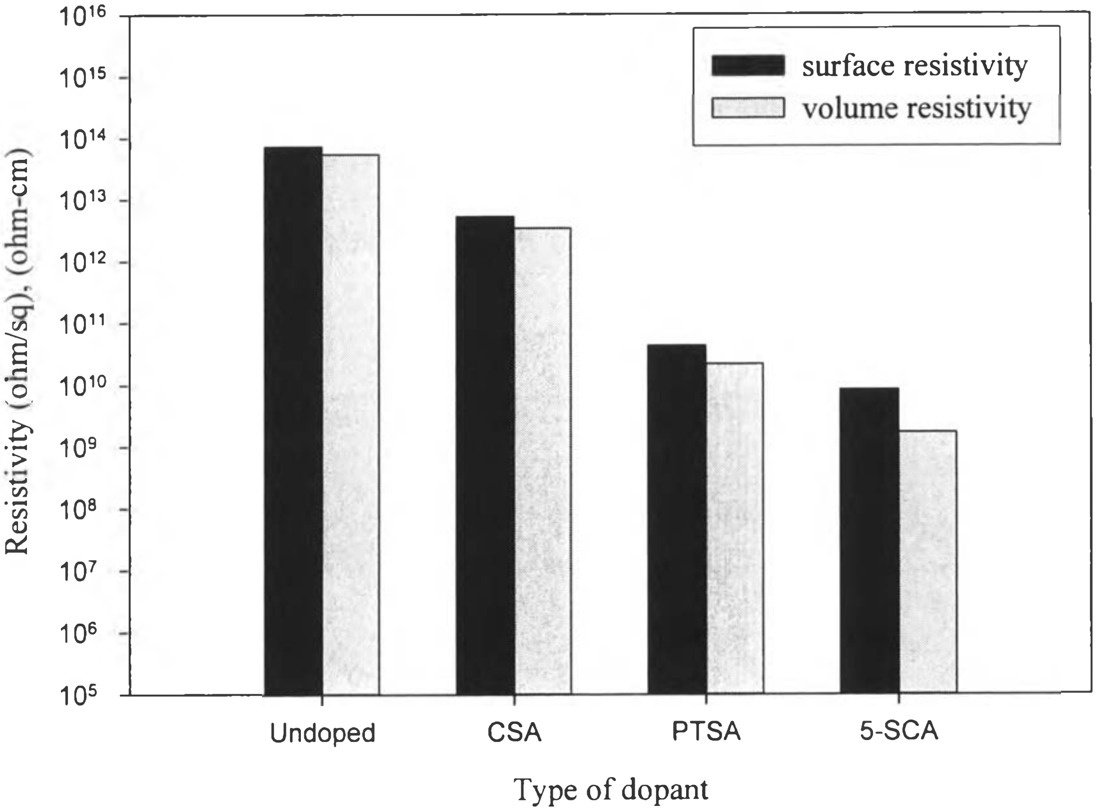
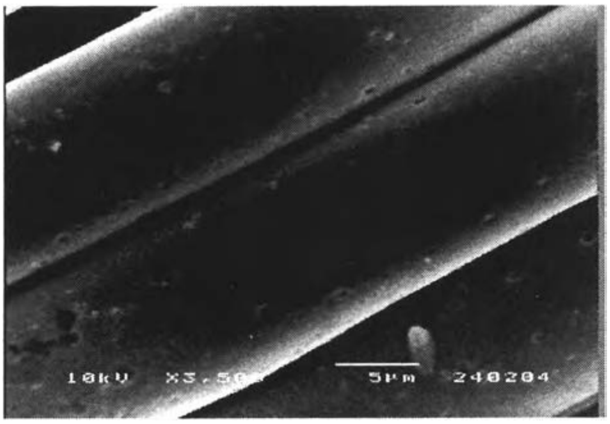
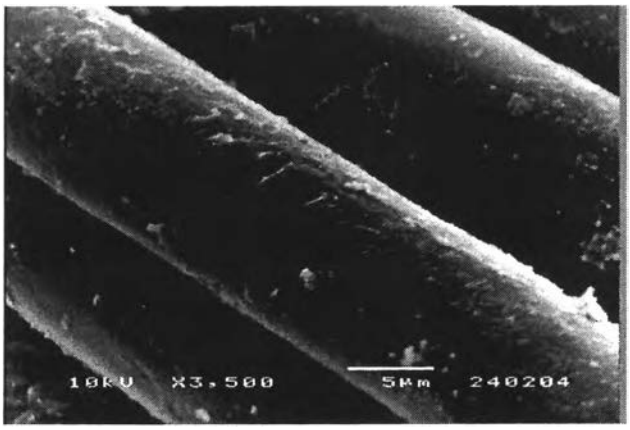

10^{16}
10^{15}
10^{14}
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
Resistivity (ohm/sq), (ohm-cm)
surface resistivity
volume resistivity
Undoped
CSA
PTSA
5-SCA
Type of dopant

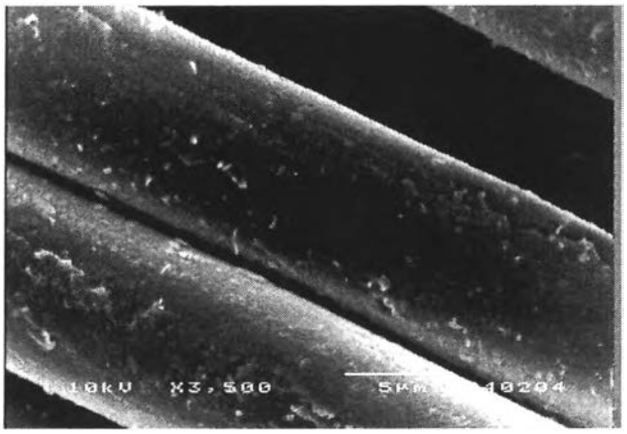
Figure 4



(a) Untreated polyester fabric



(b) Coated polyester fabric



(c) Doped fabric using 20 mM of PTSA.

Figure 5