

Experimental Studies on Electro-Conductive Fabric Prepared by *In Situ* Polymerization of Thiophene onto Polyester

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ABSTRACT: This work deals with development, characterization, and performance of an electro-conductive fabric prepared by *in situ* polymerization of thiophene onto polyester. An attempt was made to optimize the polymerization process to achieve highest level of electro-conductivity of this fabric. The essential characteristics of this electro-conductive fabric were examined and

its electromagnetic shielding performance was evaluated. Polythiophene powder was also synthesized and analyzed. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3555–3561, 2010

Key words: electro-conductive textile; *in situ* polymerization; polythiophene; polyester

INTRODUCTION

The amazing discovery of electro-conductive polyacetylene,¹ marking the birth of electro-conductive polymers and resulting in the award of Nobel Prize for chemistry in 2000, has paved the way for development of many electro-conductive polymers such as polyaniline, polypyrrole, polythiophene, and their derivatives. The synthesis of π -conjugated chains in these polymers has been the center of science and technology of electro-conductive polymers. Although these electro-conductive polymers have shown remarkable electro-conductivity, they have limited real-world applications mainly because of their lack of processability and environmental stability.^{2,3} The lack of processability results from the inherent structure of these polymers. A high degree of conjugation along the polymer chain imparts stiffness to the chain which, in turn, leads to intractability from the processing point of view. The lack of environmental stability arises mainly from the formed electro-conductive polymer existing in an energy state that is susceptible to attack by oxygen and other agents such as acids, which results in either chain scission or saturation of some double bonds, thus discontinuing the conjugation path along the polymer chain. In spite of these limitations, there have been some notable efforts to process some of these electro-conductive polymers into fibers, fabrics, and other products.

Work by Gregory et al.⁴ demonstrated that the electro-conductive textiles could be developed by *in situ* polymerization of either aniline or pyrrole on the surface of polyester or nylon fabrics, resulting in electro-conductive fabrics with significant resistance to loss in mechanical properties. Work by Bhat et al.⁵ illustrated *in situ* polymerization of aniline onto cotton fabrics, thereby developing electro-conductive cotton fabrics. Cucchi et al.⁶ developed electro-conductive silk fabrics using *in situ* polymerization of polypyrrole and obtained excellent electro-conductivity with significant resistance to thermal degradation, but with reasonable decay in electro-conductivity when the fabric was exposed to air. Further work by Kunn and Child⁷ showed that high level of electro-conductivity could be obtained and substantial increase in environmental stability could be achieved if the process was correctly carried out and the structure of electro-conductive polymer was suitably modified. Similar observations were made by Bhadani et al.,⁸ Oh et al.,⁹ Kim et al.,¹⁰ and Kutanis et al.¹¹ Work by Nowak¹² and Punyatoya¹³ indicated that there was an interaction between certain substrates and electro-conductive polymers dictating strong adhesion between them. These interactions might eventually form the basis for new solvent systems. The interactions were the strongest on nylon and other polymers with active end groups that interacted as secondary bonding sites. Other substrates like polyester, which did not rely on the same type of secondary bonding force interactions, had a reduced level of adhesion, although this interaction was still reasonably strong due most likely to van der Waals interaction. Besides these studies,

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attempts were also made to investigate the voltage-current characteristics of electro-conductive fabrics. Work by Acqua et al.¹⁴ showed that electro-conductive viscose and lyocell fabrics treated with polypyrrole showed linear voltage-current characteristics; however, Bhat et al.⁵ and Cucchi et al.⁶ observed nonlinear voltage-current characteristics in the case of polyaniline treated cotton fabric and polypyrrole treated silk fabric, respectively. Potential applications of these electro-conductive fabrics in electromagnetic shielding, microwave attenuation, static charge dissipation, flame retardancy, gas sensing, and strain sensor application were pointed out.^{7,15–19} A patented process of polypyrrole deposition onto textiles of all kinds was found out, and a pilot device for the industrial upscaling was set up.²⁰ It has been found that although a substantial amount of research has been made on *in situ* polymerization of polyaniline and polypyrrole onto textiles; however, no such attempt has been reported on polythiophene deposition onto textiles. In this work, we made an attempt to study the development, characterization, and performance of electro-conductive textiles prepared by *in situ* polymerization of thiophene onto polyester.

EXPERIMENTAL

Material and chemicals

A polyester fabric of 65 g m^{-2} weight, $15 \text{ cm} \times 15 \text{ cm}$ area, and 0.16 mm thickness was chosen for this study. The chemicals used were sodium carbonate, sodium hydroxide, methanol, tetrachloro ethane, acetonitrile, iodine, phosphorus pentoxide (Qualigence Chemical, India), nonionic detergent lissapol N (HR Chemical, India), thiophene, methylene chloride (Spectrochem, India), ethanol (Changshu Yanguan Chemical, China), ferric chloride, ammonium peroxydisulphate (Rankem, India), and *p*-toluene sulphonic acid (Lobal Chemie, India). All the chemicals used were of laboratory grade and they were used as received.

Preparation of electro-conductive fabric

The polyester fabric was first scoured with 3 gpl sodium carbonate and lissapol N at 70°C for 1 h , keeping the material-to-liquor ratio as $1 : 40$. After scouring, the fabric was hydrolyzed by treating with 10% sodium hydroxide at 90°C for 20 min , keeping the material-to-liquor ratio as $1 : 30$ (Our initial observation showed that the electrical resistivity of the electro-conductive fabric prepared by *in situ* polymerization of thiophene onto nonalkali-treated polyester was five times higher than that prepared by *in situ* polymerization of thiophene onto alkali-treated polyester.). Then a two-step *in situ* polymerization of thiophene onto this fabric was followed. In the first

step, the scoured and hydrolyzed fabric was immersed into thiophene solution at room temperature for 30 min . Different concentrations of thiophene were taken and different solvents were used. In the second step, the thiophene-enriched fabric was immersed into 1M ferric chloride solution so as to initiate polymerization onto the fabric. The polymerization was done at different temperatures for different time periods using different dopants. Afterward, the fabric was washed thoroughly with deionized water and then dried in an oven at 60°C for 40 min . The fabric was finally stored in a control chamber over phosphorous pentoxide environment for 24 h before any testing was carried out.

Measurement of surface resistivity of electro-conductive fabric

Surface resistivity of electro-conductive fabric was measured inside a control chamber at about 0% relative humidity by concentric ring electrode configurations with 10-mm outer radius of the inner ring electrode and 25-mm inner radius of the outer ring electrode. The testing procedure is described in ASTM standard D-257.²¹

Measurement of electromagnetic shielding of electro-conductive fabric

The electromagnetic shielding measurement on the electro-conductive fabric was carried out in an anechoic chamber. The transmitting antenna was connected to an electromagnetic wave source and the receiving antenna was connected to a spectrum analyzer. The distance between these antennas was kept constant at 1.2 m and the operating frequencies were chosen as 2.4 , 6 , and 8 GHz . The electromagnetic shielding effectiveness (EMSE) was calculated from the following formula: $\text{EMSE}_{(\%)} = 10 \log(P_{1(\text{dB})}/P_{2(\text{dB})})$, where P_1 denotes the electromagnetic power received by the antenna in absence of the electro-conductive fabric and P_2 indicates the electromagnetic power received by the antenna in presence of the electro-conductive fabric. This measurement was performed in two modes: in one mode, the fabric was earthed, and in the other mode, the fabric was not earthed.

Measurement of voltage-current characteristic of electro-conductive fabric

The voltage-current characteristic of the electro-conductive fabric was obtained by using Scientific triple power supply equipment (HM 5040). Direct voltage, ranging from 0 to 30 V with an increment of 1 V , was applied to the fabric. As a result of this, the current flow was recorded.

Measurement of voltage-temperature characteristic of electro-conductive fabric

The voltage-temperature characteristic of the electro-conductive fabric was obtained by applying direct voltage to a strip of the electro-conductive fabric, which was wrapped on a thermometer bulb. The temperature rise in the fabric was recorded by applying different voltages for different time periods (1 min, 3 min, and 5 min).

Scanning electron microscopy imaging of electro-conductive fabric

In this work, we used Zeiss EVO 50 scanning electron microscopy system. The electro-conductive fabric sample was mounted on a standard sample holder and no coating of the sample was carried out. The images of the fabrics were taken at a 10 K magnification in order to visualize the deposition of electro-conductive polymers onto the fabric.

Synthesis of polythiophene powder

The polythiophene powder was chemically synthesized to find out the intrinsic property of the pure polythiophene polymer. It was prepared by mixing a solution of thiophene with a solution of ferric chloride, keeping monomer-oxidant molar ratio as 2 : 1. The polymerization was allowed to proceed in air at room temperature for 24 h. The precipitate was then collected by filtration, thoroughly rinsed with ethanol and distilled water, and finally dried in an oven at 60°C temperature for 30 min. The powder thus obtained was characterized.

Characterization of polythiophene powder

Thermo-gravimetric (TGA) analysis of pure polythiophene powder was carried out in Perkin-Elmer TGA 7 instrument at a scanning rate of 20°C/min in a nitrogen atmosphere. X-ray diffraction study of polythiophene powder was carried out by using Philip's Analytical Instrument from 10 to 40° 2 θ range using an X-ray generator with 40 kV voltage and 30 mA current. Fourier transform infra-red (FTIR) spectroscopy of polythiophene powder was carried out using KBr support. Energy dispersive X-ray (EDX) analysis of polythiophene powder was also done to ascertain the elemental composition of the powder.

RESULTS AND DISCUSSION

Finding a suitable solvent for thiophene

To find out a suitable solvent for thiophene, different reagents—methanol, ethanol, methylene chloride, tetrachloroethane, and acetonitrile—were tried and

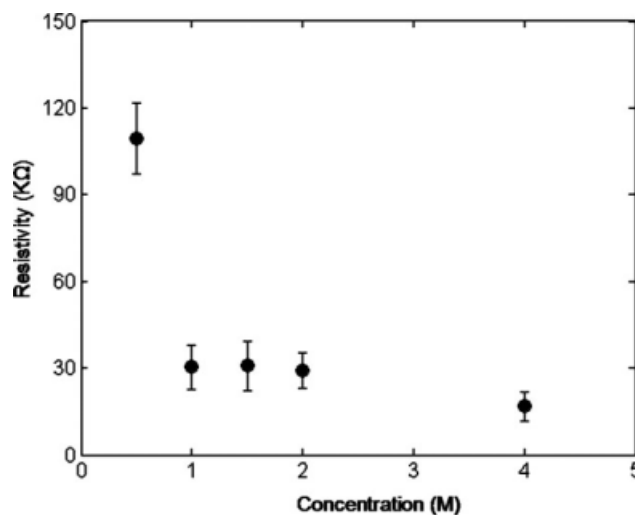


Figure 1 Plot of surface resistivity at different concentrations of thiophene.

the fabrics made thereof were tested for their surface resistivity. It was found that the surface resistivity of the fabric, when acetonitrile was used, was in the order of $10^3 \Omega$, but the same was in the order of $10^7 \Omega$ when the reagents were tetrachloroethane and methylene chloride, and $10^8 \Omega$ when the reagents were methanol and ethanol. This suggested acetonitrile as the best solvent for thiophene among all reagents studied.

Effect of thiophene concentration on surface resistivity

The effect of thiophene concentration on surface resistivity of the electro-conductive fabric was studied by varying the amount of thiophene in the solution of thiophene and acetonitrile. The result is displayed in Figure 1. It can be observed that as the concentration of thiophene increases, the surface resistivity of the fabric reduces and the rate of reduction is faster at lower concentration of thiophene than at higher concentration of thiophene. It is obvious that the fabric “absorbed” more thiophene when it was offered with more thiophene in solution, consequently, the fabric showed less surface resistivity with the increase in thiophene concentration. It is also obvious that the rate of thiophene absorption reduces as the fabric becomes more saturated with thiophene.

Effect of polymerization temperature on surface resistivity

The effect of polymerization temperature on surface resistivity of the electro-conductive fabric was examined. The polymerization was carried out at 5, 15, 25, 40, and 60°C temperatures, and the fabrics made thereof were tested for their surface resistivity. The result is displayed in Figure 2. As shown, the

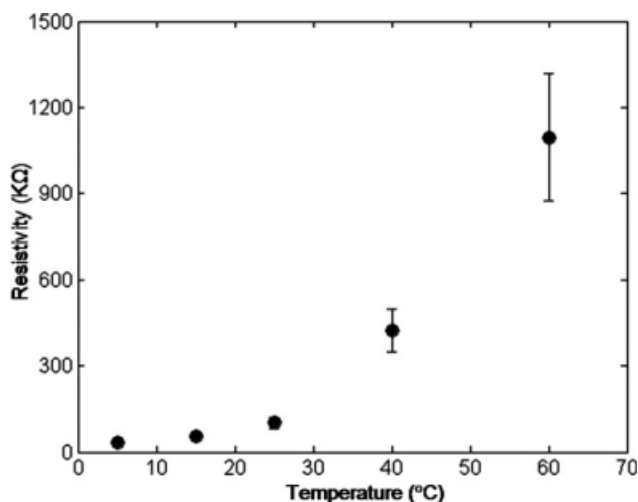


Figure 2 Plot of surface resistivity versus polymerization temperature.

surface resistivity of the electro-conductive fabric increases with the increase in polymerization temperature. This might be due to the fact that the boiling of thiophene is dominant at elevated temperatures; consequently, the deposition of thiophene onto the fabrics is less at elevated temperatures. This was confirmed from the scanning electron images of

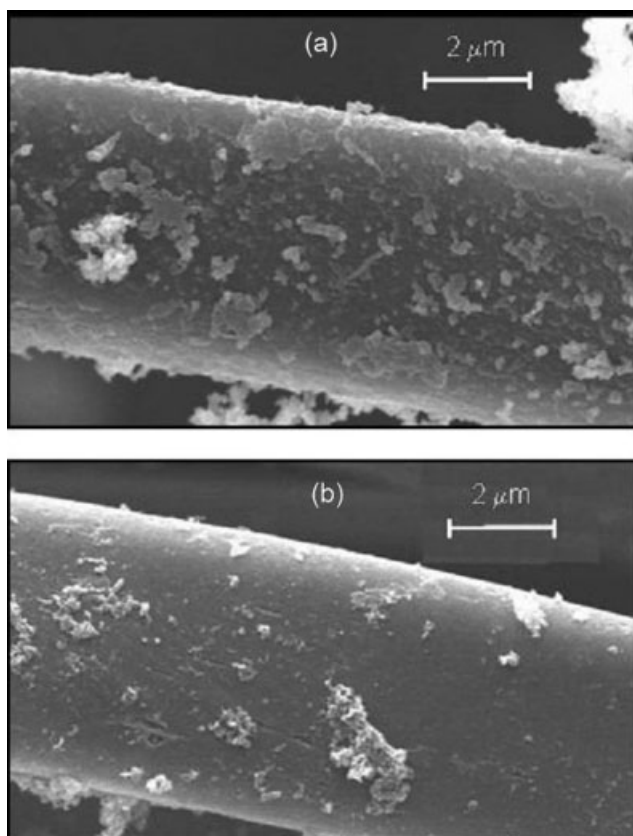


Figure 3 Scanning electron microscopic images of electro-conductive fabrics: (a) Polymerization temperature: 5°C and (b) polymerization temperature: 60°C.

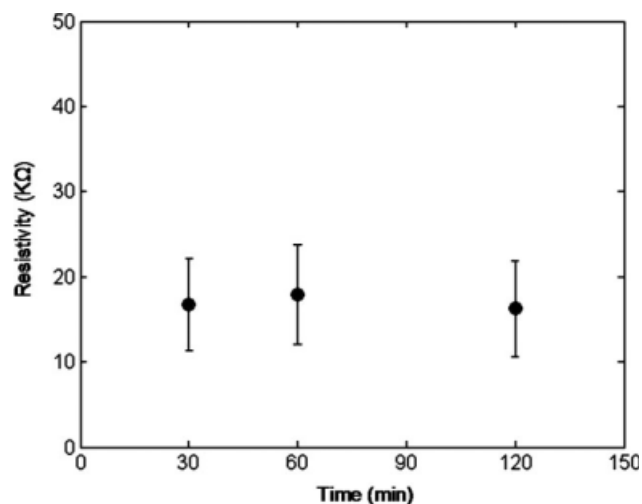


Figure 4 Plot of surface resistivity versus polymerization time.

the electro-conductive fabrics (Fig. 3). This suggests polymerization of thiophene should be carried out at cold temperature.

Effect of polymerization time on surface resistivity

The effect of polymerization time on surface resistivity of the electro-conductive fabric was studied. The polymerization was carried out for 30, 60, and 120 min at 5°C. The result is shown in Figure 4. It can be observed that the surface resistivity of the electro-conductive fabric remains almost unchanged with the time of polymerization.

Finding a suitable dopant for polymerization

An attempt was made to find out a suitable dopant for polymerization of thiophene. Three different dopants—*p*-toluene sulphonic acid (TSA), iodine, and ammonium peroxodisulphate (APS)—were chosen. Concentration 0.5M of each of these dopants was added separately into 1M ferric chloride solution and the polymerization was carried out at 5°C temperature for 30 min. The electro-conductive fabrics thus prepared were tested for their surface resistivity and compared with the electro-conductive fabric prepared without any dopant. The result is shown in Figure 5. It was observed that the surface resistivity of the electro-conductive fabric was reduced by 22% with the addition of TSA, 40% with the addition of iodine, and 64% with the addition of APS. This suggests APS as the best dopant for polymerization of thiophene among all dopants studied.

Electromagnetic shielding behavior of electro-conductive fabric

Figure 6 displays the electromagnetic shielding behaviors of the electro-conductive fabric vis-à-vis

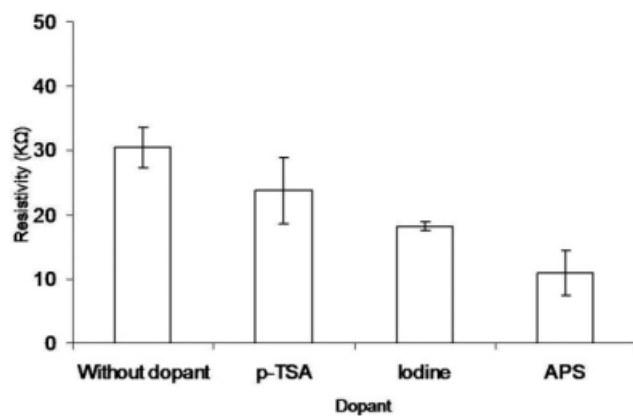


Figure 5 Plot of surface resistivity of fabrics prepared with and without dopants.

the control fabric. As shown, the electro-conductive fabric could shield the electromagnetic waves remarkably better than the control fabric at all frequencies studied, and further improvement in shielding behavior was found when the fabrics were earthed. One can observe that this polythiophene-treated-polyester fabric was able to shield 94% electromagnetic waves radiating at a frequency of 8 GHz.

Voltage-current characteristics of electro-conductive fabric

The voltage-current profile of the electro-conductive fabric is shown in Figure 7. Clearly, the voltage-current behavior of this fabric is non-ohmic. This may be explained due to the growth of the polymer chains in the interconnected regions was so disordered that it behaved like a semiconductor or a

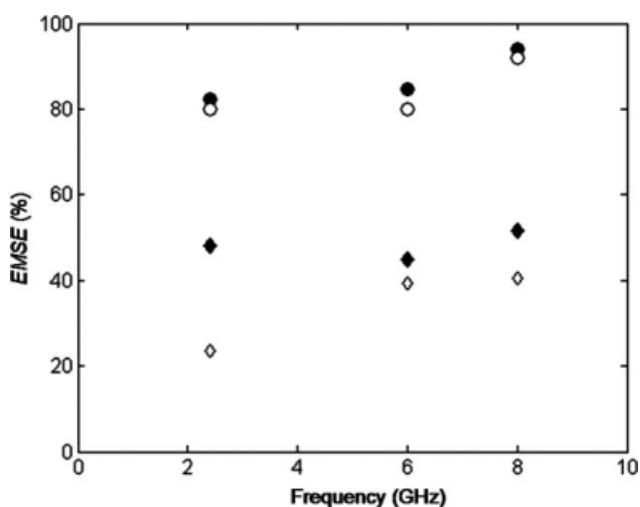


Figure 6 Plot of electromagnetic shielding performance (●, electro-conductive fabric with earthing; ○, electro-conductive fabric without earthing; ◆, control fabric with earthing; and ◇, control fabric without earthing).

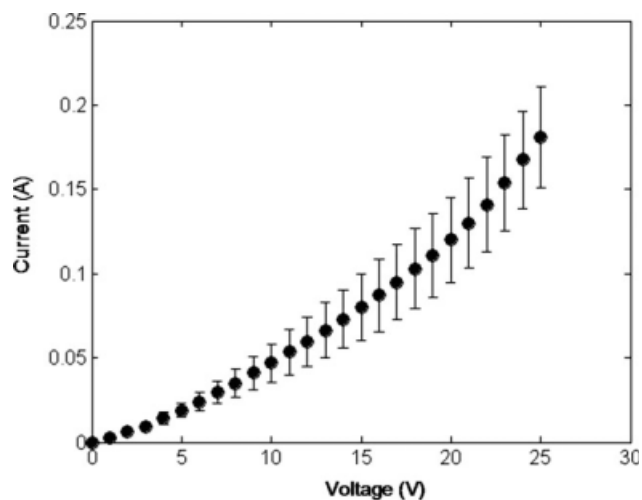


Figure 7 Voltage-current profile of electro-conductive fabric.

metal-semiconductor Schottky junction. A similar conclusion in the case electro-conductive polypyrrole nanotube was made by Saha et al.²² The breakdown voltage of this fabric was found at 28 V.

Voltage-temperature characteristics of electro-conductive fabric

The voltage-temperature profiles of the electro-conductive fabric are displayed in Figure 8. One can see that as the voltage applied across the fabric increases the surface temperature of the fabric rises and this effect is higher with longer duration of voltage applied across the fabric. The voltage-temperature profiles of the electro-conductive fabric were fitted by the following exponential curves: $T = T_0[1 + c_0(1 - e^{c_1 V})]$, where T and T_0 denote the final and initial temperatures of the fabric,

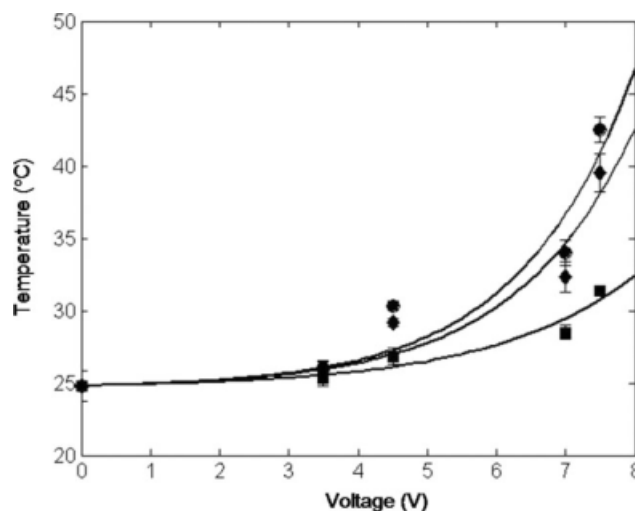


Figure 8 Voltage-temperature profile of electro-conductive fabric (■, 1 min; ◆, 3 min; ●, 5 min).

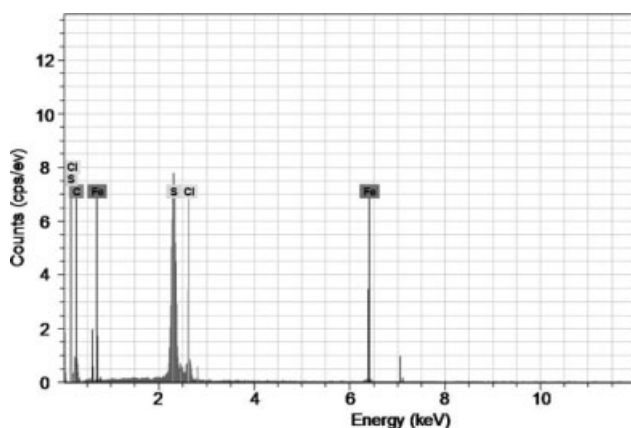


Figure 9 EDX spectra of polythiophene powder.

respectively, V indicates the voltage applied across the fabric, and c_0 and c_1 refer to the exponential coefficient and exponent, respectively. These curves are shown by solid lines in Figure 8. We observed that the value of the coefficient remained almost unchanged with the duration of voltage applied across the fabric, however, the value of the exponent increases with longer duration of the voltage applied across the fabric.

Analyses of polythiophene powder

The result of elemental analysis of polythiophene powder is displayed in Figure 9. This confirms the presence of carbon, sulfur, iron, and chlorine in polythiophene powder. The presence of carbon and sulfur is an indicative of formation of polythiophene, and the appearance of iron and chlorine reveals that a small amount of ferric chloride was still left in the powder. Figure 10 illustrates the thermo-gravimetric behavior of polythiophene powder. One can observe

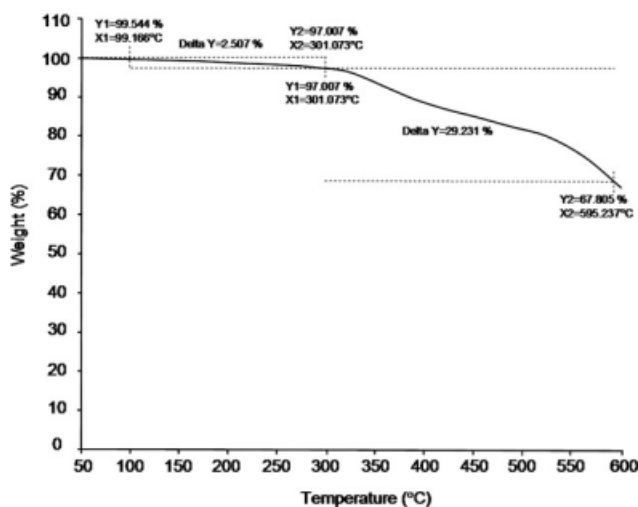


Figure 10 Thermo-gravimetric profile of polythiophene powder.

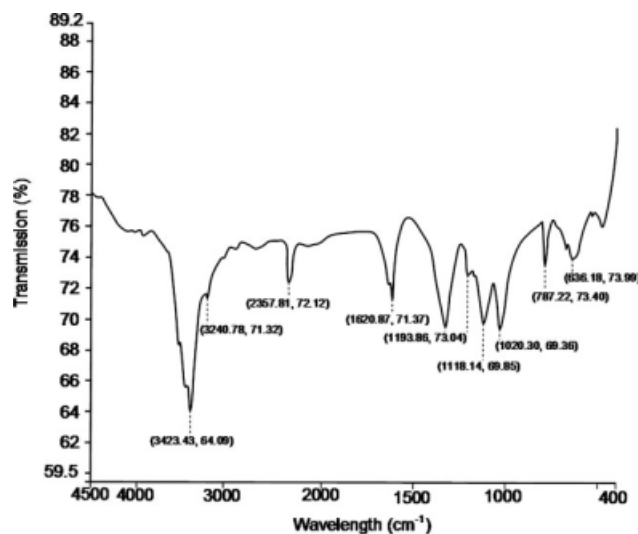


Figure 11 FTIR spectra of polythiophene powder.

that even at a high temperature of 600°C , only 33% degradation of the powder was taken place. This describes high thermal stability of the polythiophene powder. The FTIR spectrum of polythiophene powder is shown in Figure 11. This shows peaks at around 3423 cm^{-1} wavelength due to stretching of O—H bonds, 3240 cm^{-1} wavelength due to stretching of C—H bonds, and 1620 cm^{-1} wavelength due to stretching of C=O bonds. The vibrations of C—S—C bonds and C—S bonds are seen at about 1118 cm^{-1} and 1030 cm^{-1} wavelength, respectively. The vibrations seen at 1118 cm^{-1} and 636 cm^{-1} wavelength confirm that the powder formed was polythiophene as it is known as finger-print region of polythiophene. The X-ray analysis of polythiophene powder demonstrated that it was highly amorphous.

CONCLUSIONS

The *in situ* chemical polymerization of electro-conductive thiophene is a suitable process for developing electro-conductive fabrics. The process, studied for polyester, although generally applicable, consists of two steps: (1) Immersion of a scoured and hydrolyzed fabric into a solution of thiophene (monomer) and acetonitrile (solvent), and (2) immersion of the thiophene-enriched fabric into a solution of ferric chloride (oxidant) and APS (dopant) to initiate polymerization. This process need to be carried out at cold temperature in order to get enhanced electro-conductivity of the fabric. Thus, produced electro-conductive thiophene treated polyester fabric showed surface resistivity as low as $16.74\text{ K}\Omega$. This fabric showed excellent electromagnetic shielding performance as high as 94% shielding effectiveness at a frequency of 8 GHz. The voltage-current

behavior of fabric was found to be nonlinear, and a remarkable rise in surface temperature of this electro-conductive fabric was observed as a result of higher amount of the voltage applied across the fabric for longer duration.

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