Studies on Electro-Conductive Yarns Prepared by *In Situ* Chemical and Electrochemical Polymerization of Pyrrole

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ABSTRACT: This work deals with preparation, characterization, and performance of electro-conductive yarns prepared by *in situ* chemical and electrochemical polymerization of pyrrole. Box-Behnken design in conjunction with response surface analysis has been used to study the electrochemical polymerization process. The effect of electrochemical process parameters on the electrical resistivity has been reported. Further, the electrical and electromechanical behaviour of the electro-conductive yarns thus produced has also been reported. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 455–462, 2012

Key words: electro-conductive yarn; *in situ* chemical polymerization; *in situ* electrochemical polymerization; electrical property; electro-mechanical property

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 π-conjugated links in these polymers has been the basis of the emergence of electro-conductive polymers. These electro-conductive polymers have shown remarkable electro-conductivity, however have shown limited successful applications mainly because of their lack of processability which is because of their inherent chemical structure. A high degree of conjugation along the polymer chain imparts some stiffness. In spite of these limitations, there have been some notable successes in converting these electro-conductive polymers into fibers, yarns, fabrics, and other flexible products. Kim et al.[2,3] reported a method to prepare electro-conductive fibers by melt blending and chemical coating of electro-conductive polyaniline and polypyrrole onto polyester and polypropylene fibers. Mirmohseni et al.[4] described a method to develop electro-conductive fibers by wet spinning of polyaniline and polyamide 6 solution. Xia and Lu[5] demonstrated a procedure to fabricate electro-conductive fibers by *in situ* chemical polymerization of polyaniline, poly-pyrrole, and poly3,4-ethylene-dioxythiophene onto silk fibers. Bhadani et al.[6–8] have also used a method to prepare electro-conductive fibers by *in situ* electrochemical polymerization of aniline and pyrrole onto cotton, silk, and wool fibers. Najar et al.[9] and Kaynak et al.[10] reported on the development of electro-conductive yarns by vapor phase polymerization of pyrrole. Kim et al.[11] prepared polyaniline coated polyester conductive yarn by *in situ* chemical polymerization. Bhat et al.[12] have used *in situ* chemical polymerization of aniline onto cotton fabrics to impart electro-conductivity. Babu et al.[13] also have reported a process to prepare electro-conductive fabrics by chemical and electrochemical polymerization of pyrrole onto cotton fabrics. Das et al.[14] in their study have reported a method for preparation of polyester electro-conductive fabric using *in situ* chemical polymerization of thiophene onto polyester fabric. Subianto et al.[15] have prepared electro-conductive cotton fabrics by *in situ* electrochemical polymerization of pyrrole. The other method of incorporation of electro-conductive polymers into textiles have been discussed by Anand et al.[16] The demand for the electro-conductive textile materials is growing rapidly not only in the areas such as sensing, electrostatic discharge, corrosion protection, electromagnetic shielding, heat generation, military applications but also as camouflage and stealth material.[17–21] In this work, an attempt has been made to study the electro-conductive yarns prepared by *in situ* chemical and electrochemical polymerization of pyrrole onto cotton, polyester, and cotton-polyester blended yarns with a view to investigate the effect of electrochemical process parameters on

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the electrical resistivity of the yarns. In addition it was intended to study the effect of tensile strain on electrical resistivity of thus prepared yarns.

EXPERIMENTAL

Materials and chemicals

In this work, a set of three different ring-spun yarns were used. The cotton yarn with its linear density as 75 tex, the polyester yarn with a linear density of 20 tex and the cotton-polyester blended yarn with a linear density of 50 tex were used. The chemicals used were sodium carbonate, sodium hydroxide, nonionic detergent lissapol N (HR Chemical, India), pyrrole (Spectrochem, India), ferric chloride, and p-toluene sulfonic acid (Lobal Chemie, India). All the chemicals used were of laboratory grade and they were used as received.

Preparation of electro-conductive yarns

The electro-conductive yarns were prepared by a combined *in situ* chemical and electrochemical polymerization of pyrrole onto cotton, polyester, and cotton-polyester blended yarns. The chemical polymerization was carried out prior to the electrochemical polymerization to impart some amount of electrical conductivity to the yarns, which was found to result in more uniform coating of polypyrrole on the surface of the yarns during electrochemical polymerization.

In situ chemical polymerization

The three yarns were 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. Then a two-step polymerization of pyrrole onto the yarns was followed. In the first step, the scoured yarns were immersed into pyrrole solution containing $1.0M$ pyrrole and $0.05M$ p-toluene sulfonic acid at 10°C for 20 min. In the second step, the pyrrole-enriched yarns were immersed into $0.25M$ ferric chloride solution of different concentrations so as to initiate polymerization onto the yarns at 10°C for 20 min. Afterwards, the yarns were washed thoroughly with deionized water and dried in an oven at 60°C for 40 min.

In situ electro-chemical polymerization

The *in situ* electro-chemical polymerization of pyrrole onto the three yarns was carried out in a potentiostat using a regulated DC power supply. The experimental set-up for electrochemical polymerization is shown in Figure 1. The electrodes used were made of stainless steel and they were kept vertically parallel to each other. The electrolyte solution was prepared in aqueous media with $0.05M$ p-toluene sulfonic acid. The chemically polymerized yarns were wrapped on the anode surface to produce electro-conductive yarns by electrochemical polymerization. Fifteen experiments were carried out on the cotton yarn with varying monomer concentration, polymerization time, and polymerization temperature according to the 3^3 Box-Behnken design of experiments as described in Table I. The lowest resistivity of the cotton yarn was observed at a monomer concentration of $0.6M$, polymerization time of 60 min, and polymerization temperature of 30°C. The same process conditions were used in the case of polyester and cotton-polyester blended yarns.

Box-Behnken design

The *in situ* electro-chemical polymerization process of pyrrole onto the cotton yarn was studied in detail by Box-Behnken design of experiments in conjunction with analysis of experimental results by response surface method using Design expert software. This was done to determine the process factors to obtain the minimum electrical resistivity of the electro-conductive cotton yarn and to examine the effect of different process factors on its electrical resistivity. The three process factors chosen for this study were monomer concentration, polymerization time, and polymerization temperature, and for each factor, three levels (low, medium, and high) were selected as shown in Table I. The scheme of experimental runs is presented in Table II. The mathematical relationship of the electrical resistivity to the process factors was described by the following model equation

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{12} x_1 x_2 + \beta_{23} x_2 x_3 + \beta_{31} x_3 x_1 + \varepsilon$$

where y denotes electrical resistivity of the yarn, x_1, x_2, x_3 indicate monomer concentration, polymerization time, and polymerization temperature, respectively, β_0 is a constant, β_1, β_2, β_3 are linear coefficients, β_{11}, β_{22}, β_{33} are pure quadratic coefficients, β_{12}, β_{23}, β_{31} are mixed quadratic coefficients, and ε is the error term of the model.

Measurement of electrical property of electro-conductive yarns

The electrical conductivity of the electro-conductive yarn is the inverse of electrical resistivity which is measured as resistance per unit length of the yarn. However, in this study, electrical resistance (kΩ) or resistivity (kΩ m^{-1}) has been used to measure resistance. The electrical resistance of the electro-conductive yarns was measured at four different lengths (0.1, 0.2, 0.3, 0.4 m) of the yarns using the two-probe test
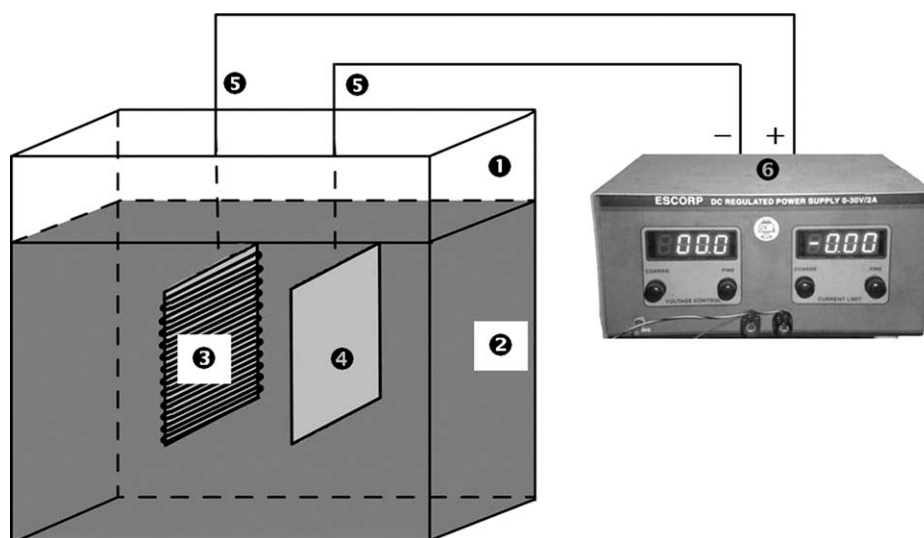
Figure 1 Schematic diagram of experimental set-up for electrochemical polymerization: ❶ 1polymerization bath, ❷ electrolyte solution, ❸ anode, ❹ cathode, ❺ electrical wire, ❻ power supply.

technique at a constant load of 75 g-force on the yarns (Fig. 2). The resistance was measured by a digital multimeter and the resistivity was calculated. The test was carried out at $27 \pm 2°C$ temperature and $65 \pm 2\%$ relative humidity. The resistance versus length data of the electro-conductive yarns were fitted to the equation of a straight line passing through the origin by standard regression technique (Fig. 10) and the slope of the line thus obtained was taken as the electrical resistivity of the yarn.

Measurement of electro-mechanical property of electro-conductive yarns

The electro-mechanical property of the electro-conductive yarns was evaluated by using the Instron tensile tester model 4301, at a gauge length of 250 mm and the traverse speed of 50 mm s^{-1}. The two ends of the yarn near to the jaws were connected respectively, to the two probes of a digital multimeter for recording the electrical resistance. The effect of strain on electrical resistance was studied by moving the upper jaw at the traverse speed mention above. A schematic diagram of this test set-up is shown in Figure 3. This test was carried out at $27 \pm 2°C$ temperature and $65 \pm 2\%$ relative humidity.

Scanning electron microscopy

The scanning electron microscopic images of the electro-conductive and control yarns were taken at a magnification of 1500X to study the deposition of polymer onto the surface of yarns.

FTIR spectroscopic studies

The Fourier transform infra-red (FTIR) spectroscopy of electro-conductive as well as control yarns was carried out on yarn samples, which were powdered and mixed with KBr to make pellets before testing.

Measurement of crystallinity

The crystallinity of the electro-conductive as well as control yarns was calculated using wide angle X-ray diffractogram on Philips Analytical Instrument from

TABLE I
Factors and Levels

	Levels		
	Low	Medium	High
Factors	−1	0	+1
Monomer concentration $(x_{1[M]})$	0.3	0.6	0.9
Polymerization time $(x_{2[min]})$	20	40	60
Polymerization temperature $(x_{3[°C]})$	10	20	30

TABLE II
Scheme of Experimental Run

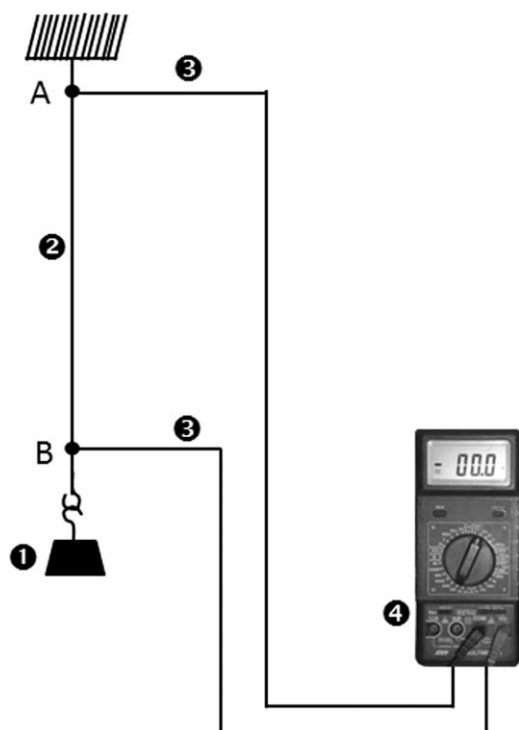| Run	$(x_{1[M]})$	$(x_{2[min]})$	$(x_{3[°C]})$
1	0.3	40	10
2	0.9	40	10
3	0.3	40	30
4	0.9	40	30
5	0.3	20	20
6	0.9	20	20
7	0.3	60	20
8	0.9	60	20
9	0.6	20	10
10	0.6	20	30
11	0.6	60	10
12	0.6	60	30
13	0.6	40	20
14	0.6	40	20
15	0.6	40	20

Figure 2 Schematic diagram of test set-up for measuring effect of length ❶ load, ❷ yarn length AB under test, ❸ connecting wire and probe, ❹ multimeter.

10° to 80° two theta range using an X-ray generator with 40 kV voltage and 30 mA current. The yarn samples were powdered before taking diffraction spectrum.

RESULTS AND DISCUSSION

Study of electrochemical polymerization process

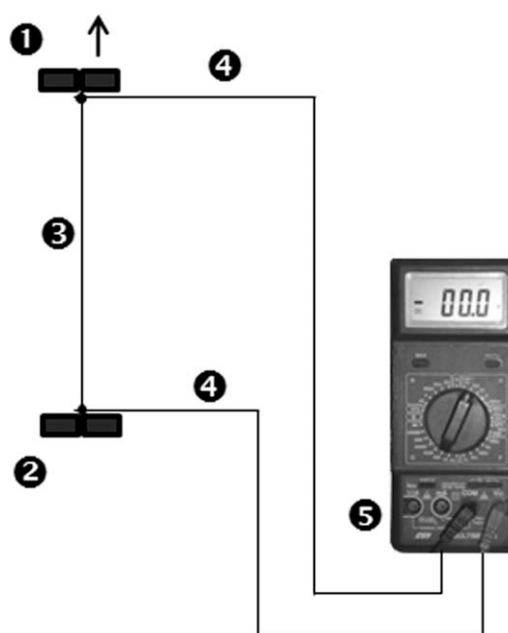A set of 15 experiments were run on the cotton yarn according to a 3^3 Box-Behnken design. The results of

Figure 3 Schematic diagram of test set-up for measuring effect of strain ❶ moving jaw, ❷ fixed jaw, ❸ yarn segment under test, ❹ connecting wire and probe, ❺ multimeter.

experiments are shown in Table III. The experimental results were analyzed by response surface methodology and the following response surface equation was obtained

$$\hat{y}_{[K\Omega \cdot m^{-1}]} = 36.1573 - 2.7264x_{1[M]} - 0.1729x_{2[min]}$$
$$- 1.6757x_{3[°C]} - 13.4932x_{1[M]}^2$$
$$+ 0.0045x_{2[min]}^2 + 0.0342x_{3[°C]}^2 + 0.0284x_{1[M]}x_{2[min]}$$
$$- 0.0128x_{2[min]}x_{3[°C]} + 0.6646x_{3[°C]}x_{1[M]}$$

TABLE III
Results of Resistivity of Cotton Yarn: Experimental, Prediction, and Error

| Run | Process factors | | | Results | | |
	$(x_{1[M]})$	$(x_{2[min]})$	$(x_{3[°C]})$	Resistivity, $K\Omega m^{-1}$ (experimental)	Resistivity, $K\Omega m^{-1}$ (prediction)	Error in resistivity, $K\Omega m^{-1}$
1	0.3	40	10	19.4875	18.2866	1.2009
2	0.9	40	10	8.7000	11.6048	−2.9048
3	0.3	40	30	8.8375	5.8802	2.9573
4	0.9	40	30	6.0250	7.1736	−1.1486
5	0.3	20	20	10.2875	11.6710	−1.3835
6	0.9	20	20	11.3500	8.6360	2.714
7	0.3	60	20	6.6250	9.2558	−2.6308
8	0.9	60	20	8.3750	6.9024	1.4726
9	0.6	20	10	16.6750	16.4373	0.2377
10	0.6	20	30	11.5625	13.1385	−1.576
11	0.6	60	10	21.1500	19.4829	1.6671
12	0.6	60	30	5.7750	5.9441	−0.1691
13	0.6	40	20	8.2750	8.5307	−0.2557
14	0.6	40	20	6.8375	8.5307	−1.6932
15	0.6	40	20	9.0250	8.5307	0.4943

Sources of variation	Sum of squares	Degree of freedom	Mean square	F-value	P-value
Model	269.17	9	29.91	3.40	0.0958
Residual	43.98	5	8.80		
Total	313.15	14			

where $\hat{y}$ is the predicted resistivity of the yarn. The predicted value of resistivity obtained by this equation for the 15 runs is listed in Table III. The difference in experimental value of resistivity and predicted value of resistivity is also listed as error in resistivity. The sum of squares due to error was observed as 46.8392 KΩ m^{-1} and the coefficient of determination (R^2) was found as 0.8596. The summary of the analysis of variance for the aforesaid response surface model is presented in Table IV.

Effect of monomer concentration and time of electrochemical polymerization

The response surface and contour plots representing the minimum resistivity of the cotton yarn for the monomer concentration ranging from $0.3M$ to $0.9M$ and the polymerization time ranging from 20 min to 60 min against the polymerization temperature at 20°C are shown in Figure 4. It can be seen that as the monomer concentration increases the resistivity decreases. This is mainly due to more polymer formation at higher monomer concentration. It can be also seen that as the polymerization time increases, the resistivity initially decreases and then increases. The decrease in resistivity may be attributed to more polymer formation and uniform polymer deposition due to more time available while the increase in resistivity at high polymerization time may be ascribed to the over oxidation of the polymer lead-
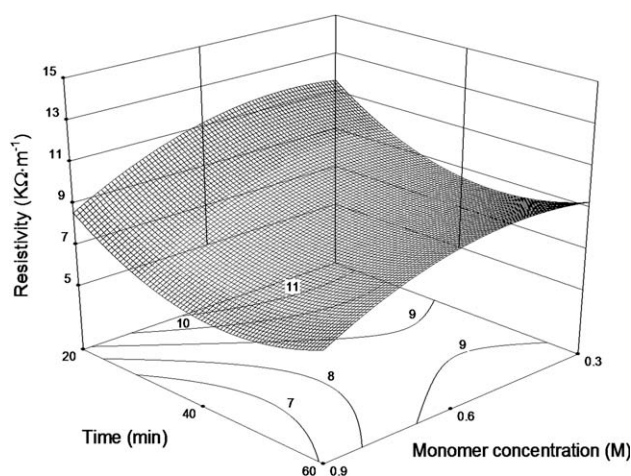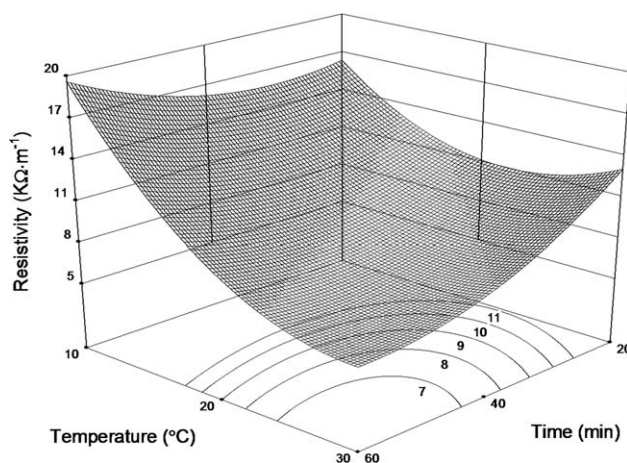

Figure 5 Plots of polymerization time and polymerization temperature on electrical resistivity.

ing to deterioration of the electrical properties. This observation is in line with the findings of Christensen et al.[22]

Effect of temperature and time of electrochemical polymerization

The response surface and contour plots representing the minimum resistivity of the cotton yarn for the polymerization time ranging from 20 min to 60 min and the polymerization temperature ranging from 10° to 30°C against the monomer concentration at $0.6M$ are shown in Figure 5. As expected, the resistivity is initially decreasing and then increasing with the increase in polymerization time. But, with the increase in polymerization temperature, the resistivity is decreasing. The decrease in resistivity may be attributed to higher kinetic energy which helps in monomer movement towards anode leading to more and uniform polymer formation. Interestingly, at
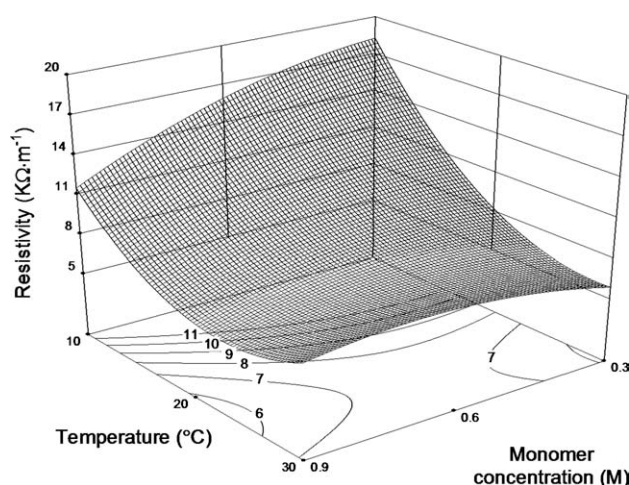

Figure 4 Plots of effect of monomer concentration and polymerization time on electrical resistivity.

Figure 6 Plots of monomer concentration and polymerization temperature on electrical resistivity.

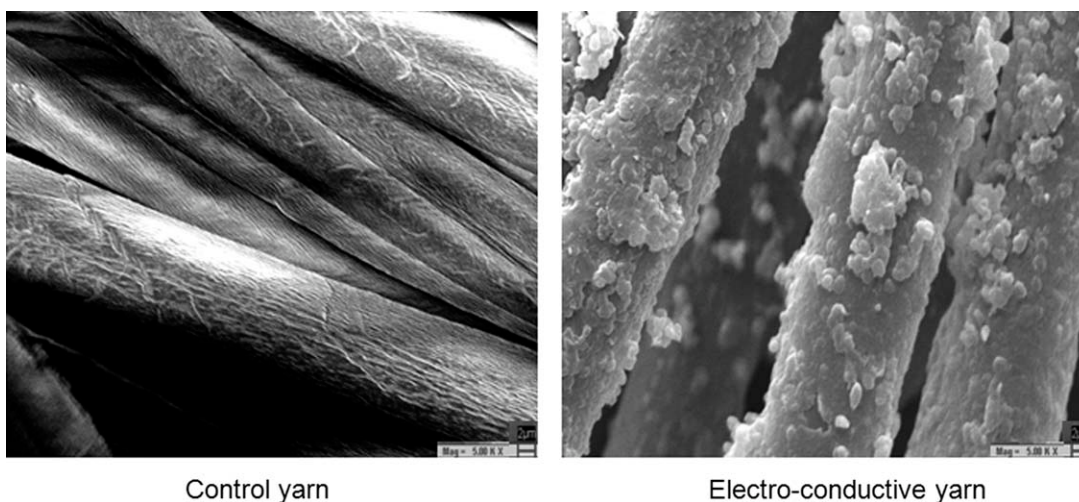Control yarn   Electro-conductive yarn

Figure 7   Scanning electron microscopic images of cotton yarns.

low time and high temperature of polymerization, the resistivity goes through a minimum which may be due to increased entropy hindering the monomer movement. But when sufficient time is given even at higher temperature the monomer gets pulled toward anode due to the applied potential.

Effect of monomer concentration and temperature of electrochemical polymerization

The response surface and contour plots representing the minimum resistivity of the cotton yarn for the monomer concentration ranging from $0.3M$ to $0.9M$ and the polymerization temperature ranging from 10 to 30°C against the polymerization time at 40 min are shown in Figure 6. As expected, the resistivity is decreased with the increase in monomer concentration as also with the increase in polymerization temperature. Interestingly, the effect of monomer concentration is more at lower temperature compared to higher temperature. At higher temperature,

the kinetic factors seem to play a major role in electrochemical polymerization.

Scanning electron microscopic images of yarns

Figure 7 displays the scanning electron microscopic images of the control and the electro-conductive cotton yarns. It can be observed that the polypyrrole was deposited quite uniformly onto the surface of the cotton yarn. A similar observation was made from the scanning electron microscopic images of the other yarns used in this work. The relatively low value of electrical resistivity of the electro-conductive yarns is evidently due to enough deposition of electro-conductive polymers onto the surface of the yarns.

FTIR analysis

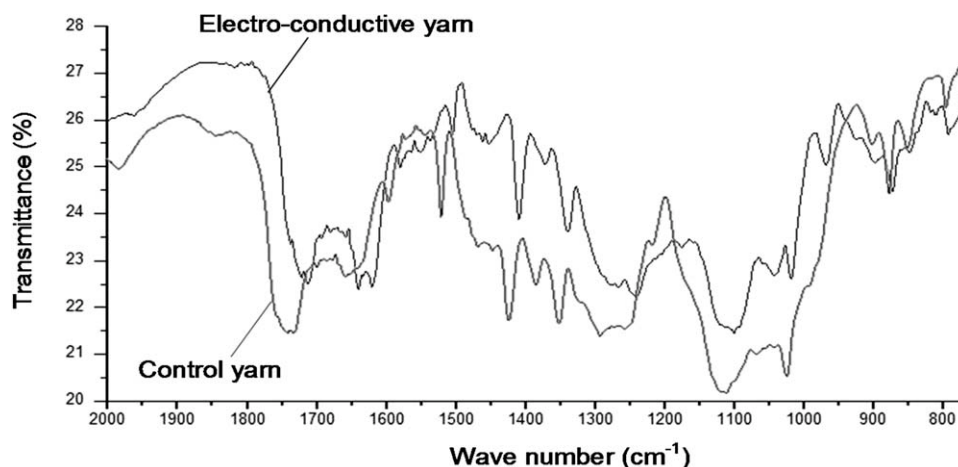The FTIR spectrum of the electro-conductive and control cotton yarn is shown in Figure 8. Two new

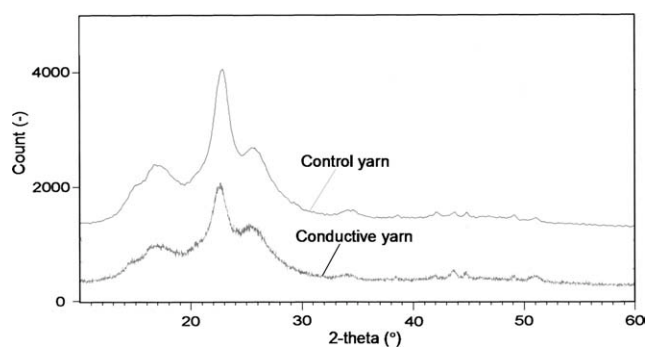**Figure 8**   FTIR spectra of control and conductive cotton yarns.

Figure 9 XRD diffractograms of control and conductive yarns.

Figure 10 Plot of electrical resistance versus length of yarns.

peaks may be observed at about 1170 cm^{-1} and 965 cm^{-1} wave numbers in electro-conductive yarn as compared to the control yarn. The peak at 1170 cm^{-1} wave number is generally assigned to N—C stretching band and the peak at 965 cm^{-1} wave number is ascribed due to pyrrole as reported by Vishnuvardhan et al.[23] These peaks indicate that the polypyrrole was *in situ* polymerized onto cotton.

Wide angle x-ray analysis

The X-ray diffraction spectrum of the electro-conductive and control cotton yarn is shown in Figure 9. There is no significant change in the spectra. It can be therefore stated that the polymerization process did not result in any remarkable change in the crystal structure of the fibers.

Electrical property of electro-conductive yarns

The electrical resistance of the electro-conductive yarns was measured at different lengths along the yarn. The experimental results are presented in Figure 10 along with the results of two more yarns i.e., polyester and cotton-polyester which were *in situ* electrochemically polymerized at the same process conditions as that of cotton yarn. It may be seen that the resistance increases almost linearly with the length of the yarn. The experimental results were fitted to the equation of a straight line passing through the origin and the slope of the lines thus obtained was taken as the electrical resistivity of the respective yarns. The resistivity of the cotton, polyester, and cotton-polyester blended yarns was obtained as 5.7750 KΩ m^{-1}, 11.4900 KΩ m^{-1}, and 6.0870 KΩ m^{-1}, respectively. The reason for higher electrical resistivity of the polyester yarn as compared to the cotton yarn may attributed to higher electrical resistance of the polyester fiber,[24,25] which in turn may be ascribed to hydrophobic nature of polyester. Punyatoya also observed that the hydrophilic cotton fiber surface adds to conductivity of the fabric.[26]
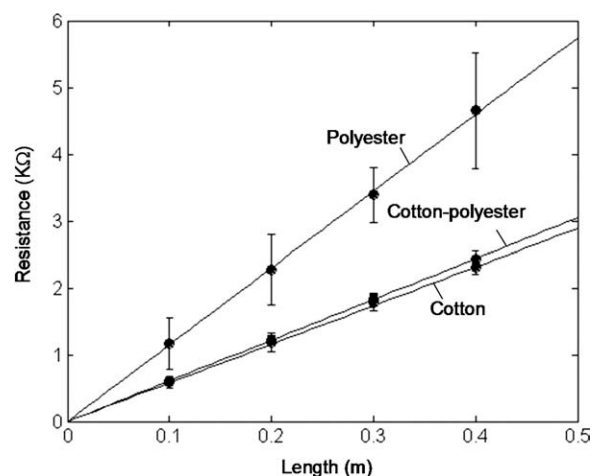
Effect of tensile strain on resistivity

The electro-mechanical behaviors of the three electro-conductive yarns are depicted in Figure 11. It may be seen that the electrical resistivity of all the yarns is initially decreasing and then increasing with the increase in strain percentage. The initial decrease in resistivity is possible because of compaction, being twisted yarns, and to better alignment of the fibers along the axis of the yarns, thus creating better compactness and less electrical resistance. On the other hand, at higher strain level, the increase in electrical resistivity can be attributed to the disruption of continuity due to breakage of polymer coatings or due to breakage of fiber, as was observed in case of cotton of fibers. At low strain level, this yarn may be used as strain sensor.
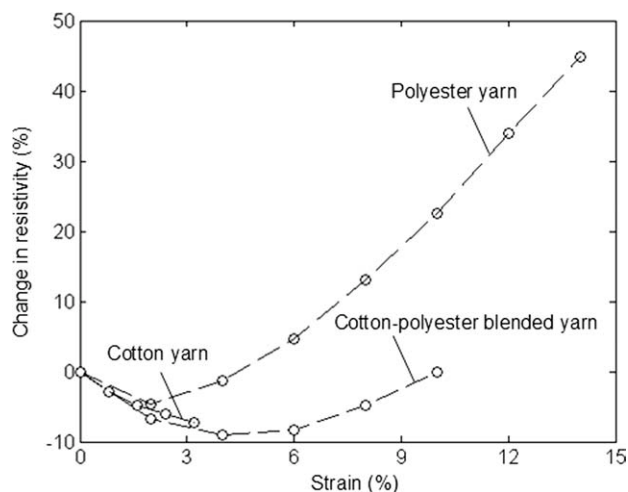

Figure 11 Plot of electro-mechanical behavior of electro-conductive yarns.

CONCLUSIONS

This work describes a novel method for preparing electro-conductive yarns by *in situ* electrochemical polymerization of pyrrole. The electrochemical polymerization process in the case of cotton yarn was studied by using Box-Behnken design of experiments in conjunction with response surface methodology of analysis. The concentration of monomer, time and temperature of electrochemical polymerization process were found to play important roles in determining the electrical resistivity of the yarn. In general, the electrical resistivity of the yarn was decreased with higher monomer concentration and higher polymerization temperature; however, with an increase in polymerization time, the resistivity was decreased initially and then increased. It was found that the electrical resistivity was directly proportional to the length and significantly dependent on strain. At lower strain level these yarns may be used as strain sensor.

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