

Polypyrrole-Silk Electro-Conductive Composite Fabric by *In Situ* Chemical Polymerization

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ABSTRACT: This article describes the preparation of polypyrrole-silk composite fabric by *in situ* chemical polymerization of pyrrole. *In situ* polymerization process has been optimized by employing Box-Behnken response surface design. The effect of process parameters on surface resistivity of the fabric has been statistically analyzed. Most significant process parameter and interaction effects have been identified. Thermal, electrical, and morphological properties of the composite fabric have been studied. Surface resistivity of the fabric obtained is 636.33 Ω . The fabric composite shows a linear *V-I* characteristic like an Ohmic conductor. An exponential rise of surface temperature of the fabric is observed by the application of DC voltage across it. Optical microscopic and SEM studies reveal uniform and even coating of polypyrrole on silk surface. FTIR studies indicate a possible chemical interaction between polypyrrole and silk. The polypyrrole-treated composite fabric exhibits enhanced thermal stability as is evidenced from DSC and TGA result. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41336.

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INTRODUCTION

The amazing discovery of electro-conductive polyacetylene by Alan MacDiarmid, Alan Heeger, and Hideki Shirakawa have resulted in the award of the Nobel Prize to them in chemistry in the year 2000 and encouraged a new field of research on conductive polymers. Since then many conductive polymers such as polyaniline, polypyrrole, polythiophene, etc. have been synthesized. These conductive polymers have conductivity in the range of 10–100 S/cm.¹ But, they have limited real-world applications due to their lack of processability to form fibres or filaments.^{2,3} The lack of processability is due to inherent structure of these polymers. A high degree of conjugation along the polymer chain imparts stiffness which, in turn, leads to intractability from the processing point of view. Among these conductive polymers, polypyrrole (PPy) has drawn considerable interest because of its low cost, good environmental stability and satisfactory electrical conductivity in doped condition.^{4–7} Textile materials are insulator in nature but strong, light-weight, and flexible. If conductive polymers are applied on the surface of textile material then an electro-conductive textile composite can be developed, which will be strong, flexible and light-weight unlike metals. Imparting electrical conductivity to the textile

materials by metal coating or incorporating metal wires into textile structure is a common practice.^{8–10} Also, now-a-days metal fibers are used during spinning of yarns to make it electro-conductive.^{11–13} These yarns are used in weaving or knitting to produce electro-conductive fabrics. But naturally the processing of these yarns and fabrics are difficult and also they lose the textile properties. Coating of textiles by electro-conductive polymers will be a useful alternative. Application of PPy on textile surface by hot molding process is found unsuitable due to lack of thermal stability of PPy whereas *in situ* polymerization methods are found very suitable.¹⁴ Electro-conductive textiles can be prepared by using *in situ* chemical, electro-chemical, and vapor phase polymerization processes.^{15–18} These electro-conductive textiles are proposed to be used in various applications such as heating pads,¹⁸ EMI shielding¹⁶, sensors,^{15,17} etc. Silk is a natural fibrous polymer produced by silk worm. It is one of the most extensively studied biomaterial because of its good biodegradability, biocompatibility, and oxygen permeability in the wet state.¹⁹ Also, recent studies have shown that conductive PPy has good biocompatibility.^{20,21} Polypyrrole coated silk as conductive material is proposed to be a promising alternative in many biomedical applications such as biodegradable conduits used for restoring the function of injured peripheral nerves and the regeneration of a nerve gap by

using electrical stimulation to support cell adhesion and facilitate the growth of cells,^{20–23} etc. Few studies have been reported on preparation of electro-conductive silk materials by the application of PPy. Smooth and continuous coating of PPy is achieved on various silk substrates by *in situ* oxidative polymerization from an aqueous solution of pyrrole (Py) at room temperature using FeCl₃ as catalyst.^{24–26} Continuous vapor phase polymerization of pyrrole on silk (116/2 tex) and cotton (20 tex) yarns enable production of uniformly coated yarns with electrical conductivity of 3.2×10^{-4} S/cm for silk and 6.4×10^{-4} S/cm for cellulose.²⁷ However, no attempt has been made on process optimization. In this study woven silk fabric is made electro-conductive by *in situ* chemical polymerization of pyrrole. The effects of process parameters of *in situ* chemical polymerization on electrical resistivity of the fabric are studied by employing Box-Behnken response surface design. Box-Behnken design is a class of rotatable or nearly rotatable second-order designs based on three-level incomplete factorial designs.²⁸ This design reduces number of experimental runs which saves time and money. It does not contain factor level combinations where the factors are all at their higher or lower levels, they may be useful in avoiding experiments under extreme conditions, for which unsatisfactory results may occur.^{28,29} So, in present work, Box-Behnken response surface design is employed to find optimum levels of the process parameters for obtaining minimum resistivity. Thermal, electrical, and morphological properties of prepared PPy-silk composite fabric are evaluated.

EXPERIMENTAL

Materials and Chemicals

Woven silk fabric of 80 g^{-2} made of warp of 4/22 denier (9.78 tex) reeled yarn and weft of 12.30 tex spun yarn having 41 ends per cm and 24 picks per cm procured from Himachal Silk Mills, HP, India, is used as substrate. Fabric is degummed before treatment. Pyrrole (Leonid Chemicals, Bangalore, India) is used as monomer, FeCl₃ (Qualigens Fine Chemicals, Mumbai, India) is used as oxidant, *p*-toluene sulphonic acid (PTSA) (S D fine-chem, Mumbai, India) is used as dopant. All these chemicals are laboratory grade and used as received.

Preparation of Electro-Conductive Fabric by *In Situ* Chemical Polymerization

A two stage single bath process, as described below, is adopted for *in situ* chemical polymerization. In the first stage, control fabric is soaked with oxidant solution and in the second stage; monomer solution is added to oxidant solution containing fabric for *in situ* polymerization. Oxidant solution is prepared by dissolving FeCl₃ and PTSA in deionized water. Material to liquor ratio is taken 1 : 300. Monomer solution is prepared by dissolving pyrrole in de-ionized water. Material to liquor ratio of monomer solution is 1 : 100. Polymerization is conducted in cryostat water bath at 5°C. Molar ratios of all the reactants are given in Table I. After polymerization samples are taken out, thoroughly rinsed with cold water and are allowed to dry at room temperature ($25 \pm 2^\circ\text{C}$ temperature and $65 \pm 2\%$ relative humidity) for 48 h before measurement.

Box-Behnken Design

Box-Behnken response surface design is employed for optimization of process parameters of *in situ* chemical polymerization.

Table I. Process Parameters and Their Levels

Factors	Labels	Levels		
		Low	Medium	High
Oxidant concentration [M]	A	1.5	2.5	3.5
Dopant concentration [M]	B	0.05	0.125	0.20
Polymerization time [Min]	C	30	90	150

Effect of different process parameters on electrical resistivity is examined statistically. The three process parameters which are considered in this study for optimization are molar concentration of oxidant, molar concentration of dopant, and polymerization time. The monomer concentration is kept 1M and polymerization temperature is maintained constant at 5°C for all experiments. For each process parameter, three levels (low, medium, and high) are chosen as shown in Table I. The levels of process parameter are chosen based on literature survey and experimental observations. The scheme of experimental runs in accordance with 3³ Box-Behnken experimental design is presented in Table II. The mathematical relationship of the electrical resistivity to the process factors is described by the following model equation:

$$R = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{12} AB + \beta_{23} BC + \beta_{31} CA + \varepsilon$$

where, R denotes surface resistivity of the fabric; A , B , and C indicate oxidant concentration, dopant concentration, and polymerization time, respectively; β_0 is a constant; β_1 , β_2 , β_3 are

Table II. Scheme of Experimental Runs

Run	A _[M]	B _[M]	C _[min]
1	-1	-1	0
2	1	-1	0
3	-1	1	0
4	1	1	0
5	-1	0	-1
6	1	0	-1
7	-1	0	1
8	1	0	1
9	0	-1	-1
10	0	1	-1
11	0	-1	1
12	0	1	1
13	0	0	0
14	0	0	0
15	0	0	0
16	0	0	0
17	0	0	0

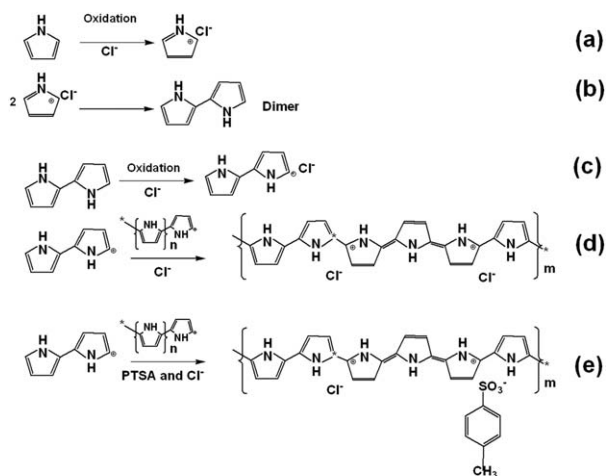


Figure 1. Schematic representation of PPy formation with FeCl_3 and PTSA.

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 Methods

Surface resistivity of fabrics is measured at $25 \pm 2^\circ\text{C}$ temperature and $65 \pm 2\%$ relative humidity by concentric ring electrode probe method as per AATCC Test Standard 76-2005. All the measurements are done with the help of a digital multimeter (MASTEC[®] MAS830L). AATCC Test Method 76-2000 is followed for the measurement of Voltage-Current ($V-I$) characteristics using two rectangular flat copper electrodes ($80 \text{ mm} \times 20 \text{ mm}$) separated by a gap of 40 mm. A regulated DC power supply of (Aplab L3202) of 0–32 V is used as DC voltage source. A digital ammeter is connected in series for the measurement of current for different applied DC voltage. Dimensions of the specimen are $80 \text{ mm} \times 80 \text{ mm}$ to cover the entire area of the electrodes. The current values are recorded for the corresponding applied voltage. Surface temperature of the fabric due to application of voltage is measured by a noncontact type infrared thermometer (KUSAM-MECO-IRL 300).

Fourier Transform Infra-Red Spectroscopy Analysis

Fourier Transform Infra-Red (FTIR) analysis of untreated and PPy coated silk fabric are done by using Bruker 10074570 spectrometer. Spectrum is recorded in the range of $4000\text{--}600 \text{ cm}^{-1}$ by accumulating 24 scans at a resolution of 4 cm^{-1} .

Optical Microscope and Scanning Electron Microscope Analysis

Morphological analysis of polypyrrole-silk composite fabric is done by optical microscope (Nikon Eclipse E200) at the magnification of $20\times$ and as well as by Scanning Electron Microscope (JEOL JSM-6610LV) at magnification of $500\times$ and $1500\times$.

Thermal Analysis

Differential Scanning Calorimetry (DSC) is performed with a Mettler Toledo DSC 823[°] instrument. Samples of treated and untreated silk are heated from 40°C to 600°C at scanning rate of $10^\circ\text{C}/\text{min}$ in nitrogen atmosphere. The thermogravimetric

analysis (TGA) is carried out with a TG/DTA 6300, SII EXSTAR 6000 thermogravimetric analyzer from 40°C to 700°C at scanning rate of $10^\circ\text{C}/\text{min}$ in nitrogen atmosphere.

Dry Cleaning and Washing Fastness

Dry cleaning fastness is assessed as per ISO D01 with trichloroethylene solvent. PPy-coated control fabric sample is treated with trichloroethylene at $30 \pm 2^\circ\text{C}$ for 30 min with a liquor ratio of 1 : 50 and then the sample is placed in between absorbent fabric to remove surplus solvent. Washing fastness is evaluated by ISO CO1-Test 1 in launderometer. The sample is washed with 5 g l^{-1} soap solution at $40 \pm 2^\circ\text{C}$ for 30 min with a liquor ratio of 1 : 50. Then the sample is rinsed with cold water. After drying, surface resistivity of control sample, dry cleaned sample, and washed samples are measured and compared.

RESULTS AND DISCUSSIONS

In Situ Polymerization of Pyrrole

In presence of FeCl_3 , the *in situ* polymerization reaction is initiated by the oxidation of pyrrole monomer into radical cations (Figure 1(a)), which combine to form bipyrrole [Figure 1(b)]. Continuation of the process leads to formation of polypyrrole (PPy) which is insoluble in water. As a result, PPy precipitates from the solution and in the process part of them are deposited on the surface of the silk fabric by adsorption. Cl^- is a counterion necessary to balance the charge on the polymer backbone. The counterion is intercalated between the planar polymer chains. When PTSA is used as dopant during synthesis, the p-toluenesulfonate ions replace some Cl^- ions in the polymer backbone as shown in Figure 1(d). This intercalation of anion of PTSA has significant effect on the surface resistivity and environmental stability of PPy coated composite textiles.³⁰ Incorporation of p-toluenesulfonate anion enhances environmental stability of PPy because it is difficult to remove from PPy backbone due to its larger size in comparison to Cl^- anion. Incorporation of p-toluenesulfonate anion in PPy structure beyond an optimum level may reduce in intermolecular hopping of charge carriers due to increased gap between the polymer chains by bulky side groups of the anions and thereby adversely affecting surface resistivity.³¹

Optimization of In Situ Chemical Polymerization Process

To investigate the effects of process parameters on surface resistivity of fabric a set of 17 experiments are conducted according to a 3^3 Box-Behnken design. The results of experiments are shown in Table III. The experimental results are analyzed by response surface methodology and the following response surface equation for surface resistivity (R) is obtained in coded unit.

$$R = 4.75 - 27.96A - 29.24B - 76.78C - 11.45A^2 + 36.37B^2 + 65.75C^2 + 12.17AB + 36.33AC + 38.05BC$$

The coefficient of determination (R^2) and adjusted- R^2 values are found as 0.9371 and 0.8562, respectively. The summary of the analysis of variance for the aforesaid response surface model is presented in Table IV. The Model F -value of 11.59 implies that the model is significant. There is only 0.20% chance that a “Model F -Value” this large could occur due to noise. P -values indicate that most significant process parameter is

Table III. Experimental and Predicted Result of Surface Resistivity of Electro-Conductive Silk Fabric

Run	$A_{[M]}$	$B_{[M]}$	$C_{[min]}$	Experimental mean resistivity (k Ω)	Predicted resistivity (k Ω)	Error in resistivity (k Ω)
1	-1	-1	0	78.8	99.0425	-20.2425
2	1	-1	0	22.07	18.79	3.28
3	-1	1	0	12.94	16.22	-3.28
4	1	1	0	4.88	-15.3625	20.2425
5	-1	0	-1	187.33	200.1213	-12.7913
6	1	0	-1	35.23	71.54375	-36.3138
7	-1	0	1	10.21	-26.1038	36.31375
8	1	0	1	3.43	-9.36125	12.79125
9	0	-1	-1	283.98	250.9463	33.03375
10	0	1	-1	132.44	116.3688	16.07125
11	0	-1	1	5.22	21.29125	-16.0713
12	0	1	1	5.86	38.89375	-33.0338
13	0	0	0	3.92	4.748	-0.078
14	0	0	0	6.08	4.748	-0.878
15	0	0	0	4.67	4.748	-0.828
16	0	0	0	3.87	4.748	1.332
17	0	0	0	5.2	4.748	0.452

polymerization time (C) and most significant interaction effects is dopant concentration–polymerization time (BC) interaction. So, for obtaining lowest surface resistivity time of polymerization reaction has immense importance. Significant BC interaction implies that dopant can control the rate of polymerization effectively.

Effect of Oxidant and Dopant Concentration on Surface Resistivity

The response surface plot for surface resistivity of PPY-coated silk fabric for $FeCl_3$ concentration ranging from 1.5 to 3.5M and the

dopant concentration ranging from 0.05 to 0.20M against polymerization time of 90 min is shown in Figure 2. It can be seen that as the $FeCl_3$ concentration increases the resistivity decreases. The decrease in resistivity may be attributed to more polymer formation due to enhanced rate of reaction in presence of more oxidant. Also, at higher $FeCl_3$ concentration more Cl^- anion is incorporated in PPY structure as charge carrier which enhances conductivity. It can also be seen that as the dopant concentration increases, the resistivity initially decreases and then again increases at higher concentration. The minima of surface resistivity is at about 0.16 molar concentration of dopant. Initially,

Table IV. Analysis of Variance of Response Surface Quadratic Model

Source	Sum of squares	Degree of freedom	Mean square	F Value	P-value	Significance at 99% confidence level
Model	96965.89	9	10773.99	11.58829	0.0020	Significant
A	6253.534	1	6253.534	6.72618	0.0358	
B	6841.575	1	6841.575	7.358667	0.0301	
C	47164.42	1	47164.42	50.72914	0.0002	Significant
A^2	552.0346	1	552.0346	0.593758	0.4662	
B^2	5571.042	1	5571.042	5.992105	0.0442	
C^2	18203.61	1	18203.61	19.57946	0.0031	Significant
AB	592.1922	1	592.1922	0.636951	0.4510	
AC	5279.476	1	5279.476	5.678502	0.0487	
BC	5789.688	1	5789.688	6.227277	0.0413	
Residual	6508.112	7	929.7303			
Lack of Fit	6504.671	3	2168.224	2520.399	<0.0001	significant
Pure Error	3.44108	4	0.86027			

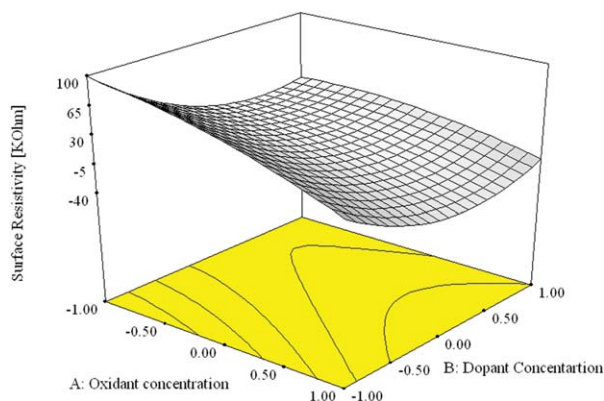


Figure 2. Response surface plot of surface resistivity vs. oxidant concentration and dopant concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

incorporation of dopant anions in the PPy chain creates charge carriers and enhanced the electrical conduction. With further increase in dopant there may be reduction in intermolecular hopping of charge carriers due to increased gap between the polymer chains by bulky side groups of the anions and thereby adversely affecting surface resistivity.³¹

Effect of Dopant Concentration and Polymerization Time on Surface Resistivity

The response surface plot of surface resistivity of PPy-coated silk fabric for dopant concentration ranging from 0.05 to 0.20M and polymerization time ranging from 30 to 150 min against oxidant concentration of 2.5M is shown in Figure 3. The surface resistivity initially decreases and then increases with the further increase in dopant concentration. As polymerization time increases, the surface resistivity initially decreases and then increases. The minima of surface resistivity is found at about 120 min. The decrease in surface resistivity may be attributed to more polymer formation and uniform polymer deposition due to enough available time. The increase in surface resistivity at higher polymerization time may be due to over oxidation of the

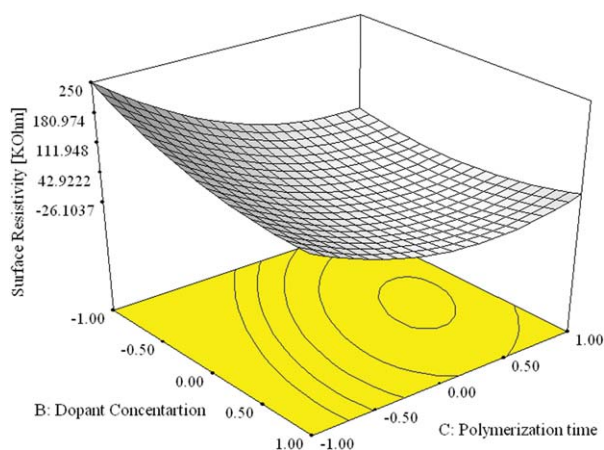


Figure 3. Response Surface plot of surface resistivity vs. dopant concentration and polymerization time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

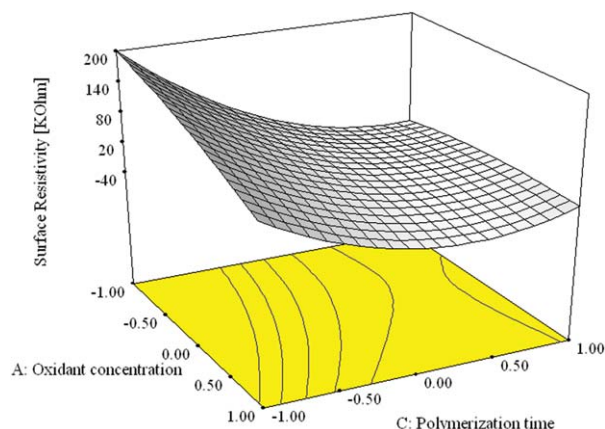


Figure 4. Response surface plot of surface resistivity vs. oxidant concentration and polymerization time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymer leading to deterioration of the electrical properties. Similar observation is also reported by Maiti et al.¹⁵

Effect of Oxidant Concentration and Polymerization Time on Surface Resistivity

The response surface plot of surface resistivity of PPy-coated silk fabric for oxidant concentration ranging from 1.5 to 3.5M and polymerization time ranging from 30 to 150 min against dopant concentration of 0.125M is shown in Figure 4. As expected, similar trend of oxidant concentration and polymerization time are observed here. The surface resistivity decreases and then increases with the increase in polymerization time. But the surface resistivity continuously decreases with increase in oxidant concentration.

It has been observed that higher oxidant concentration results a decreasing trend of surface resistivity. So, it is assumed that further increase in the oxidant concentration from 3.5M may further lower the surface resistivity. The other two parameters i.e., dopant concentration and polymerization time are kept at the level where minima values of surface resistivity is obtained, i.e. at 0.16M and 120 min respectively. Pyrrole concentration is taken 1M and polymerization temperature is kept 5°C. The result is shown in Figure 5. A continuous fall in surface resistivity is observed with increase in FeCl₃ concentration from 3.5 to 5.0M. But less difference of surface resistivity is noted between molar concentration ratio of 4.5 and 5.0. So considering the consumption of chemical and chances of over oxidation due to ketone formation,³² the concentration of 4.5M is considered as optimum. Now, with this level of oxidant concentration when monomer concentration is increased from 1 to 3M then surface resistivity of the fabric is found decreasing, as shown in Figure 6. At monomer concentration of 2M, the resistivity is measured 636.33 Ω and further increment of monomer concentration does not show significant decrement of resistivity. To avoid wastage of costly pyrrole, this concentration of 2M is chosen as optimum. So, optimum process parameters for obtaining this lowest value of surface resistivity are 2M pyrrole concentration, 4.5M oxidant concentration, 0.16M PTSA concentration,

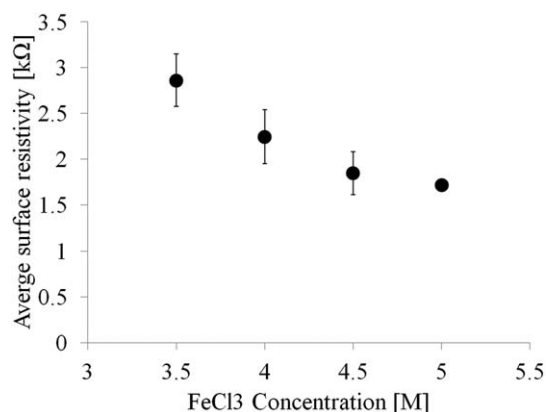


Figure 5. Effects of FeCl₃ concentration on surface resistivity of electro-conductive silk fabric.

120 min of polymerization time and 5°C of polymerization temperature.

Morphological Properties of PPy-Coated Silk

Optical Microscopy and SEM images of the untreated silk fibers and polypyrrole-treated silk fibers (optimized sample) are shown in Figures 7 and 8, respectively. The untreated silk shows a smooth clean surface, whereas treated silk becomes black in color due to deposition of PPy on its surface. The deposition is quite uniform. Granular morphology of PPy on the silk surface is observed in SEM images. These findings confirm that the polymerization proceeded smoothly, resulting in the formation of a uniform layer of polymer around the individual fibers, which is in good agreement with the results previously reported by Boschi et al.²⁴

FTIR Spectroscopy Analysis

FTIR spectra of untreated and polypyrrole treated silk fabric are shown in Figure 9. The spectra of untreated silk is characterized by strong vibrations of the peptide group falling in three well-defined ranges, namely Amide I at 1630 cm⁻¹ which are almost entirely due to the (C=O) stretch vibrations of the peptide linkages, Amide II at 1520 cm⁻¹ which is due to in-plane (N-H) bending and from the (C-N) stretching vibration and the Amide III with peaks at 1227 cm⁻¹. Their position and inten-

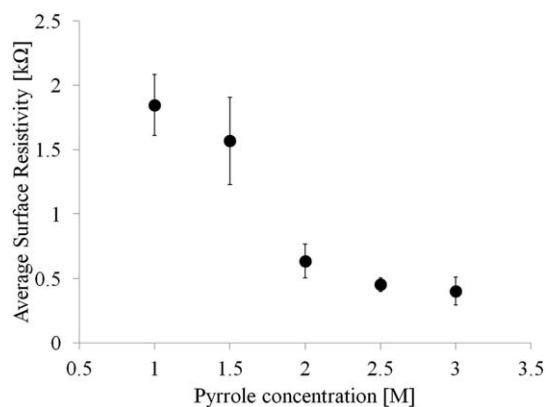


Figure 6. Effect of monomer concentration on surface resistivity.

sity are consistent with the prevailing β -sheet molecular conformation of the silk fibers.^{25,26} The FTIR spectra of PPy treated silk show a mixed spectral pattern with bands typical of silk and PPy overlapping over the entire wave numbers range. It shows a red shift of Amides I and II bands at 1600, and 1513 cm⁻¹, respectively. Also, Amide III band disappears. This may be attributed to the interaction of PPy with peptide linkage of silk.^{24,26}

Thermal Analysis

The thermal analysis of untreated silk and PPy coated silk is carried out by DSC and TGA. The results are shown in Figures 10 and 11, respectively. The DSC thermograph of untreated silk shows a broad exothermic peak at 320°C. This is attributed to intrinsically high thermal stability of silk fibroin with oriented β sheet crystalline stable structure. These secondary structures are stabilized by inter-chain hydrogen bonding in which every amino acid are laterally bonded twice to its nearest neighbor chain segments. The thermal stability of silk is further enhanced by PPy treatment. The degradation peak shifted to a higher temperature of about 5°C at 325°C with a narrower one. This narrower peak with a shift at higher temperature signifies more thermal stability of silk by PPy coating. Similar observation is reported by Cucchi et al.²⁵



Figure 7. Optical microscopic images of (a) untreated silk and (b) PPy-coated silk [$\times 20$ magnification]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

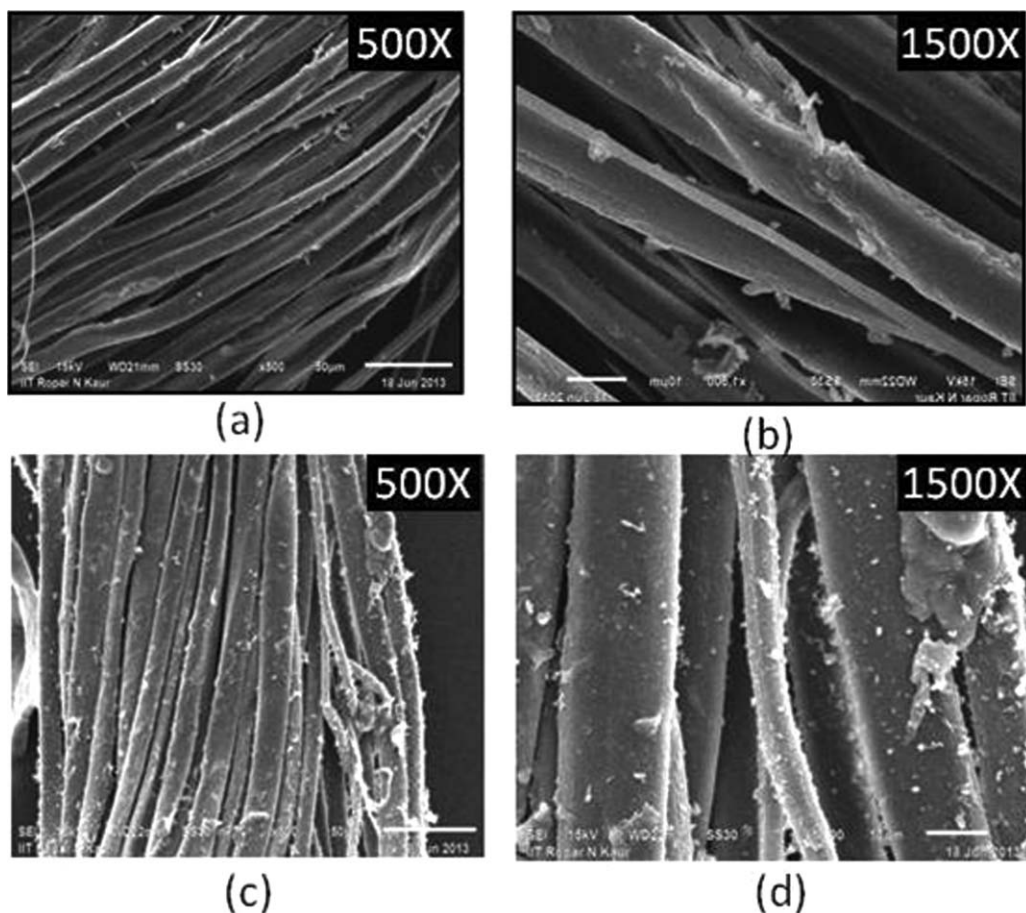


Figure 8. SEM images of (a) untreated silk ($\times 500$), (b) untreated silk ($\times 1500$), (c) PPy-treated silk ($\times 500$), and (d) PPy-coated silk ($\times 1500$) magnification.

Figure 11(a) shows the weight loss versus temperature curve of untreated silk. The loss in weight from 48°C to 52°C is due to loss of moisture. Major weight loss due to decomposition starts from 265°C . In case of PPy-treated silk, the decomposition starts from 320°C onwards as shown in Figure 10(b). The % weight loss vs. temperature curves as obtained from the TGA curves are shown in Figure 12. From the Figure 12 it can be seen that $\sim 4\%$ weight loss occurred for untreated silk at 300°C ,

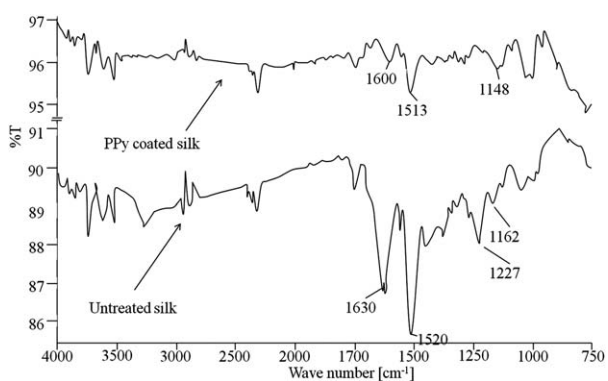


Figure 9. FTIR spectra of untreated and PPy-treated silk fabric.

whereas for PPy-treated silk fabric 500°C temperature is necessary to bring about similar 4% weight loss. This confirms that the PPy layer acts as protective skin, which protects the silk from thermal degradation. The PPy treated silk acts as a composite structure with an outer layer of PPy and a fiber core.

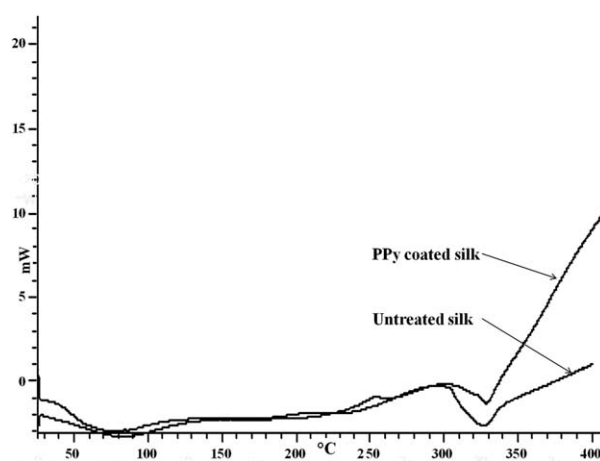


Figure 10. DSC thermograph of (a) untreated silk and (b) PPy-treated silk.

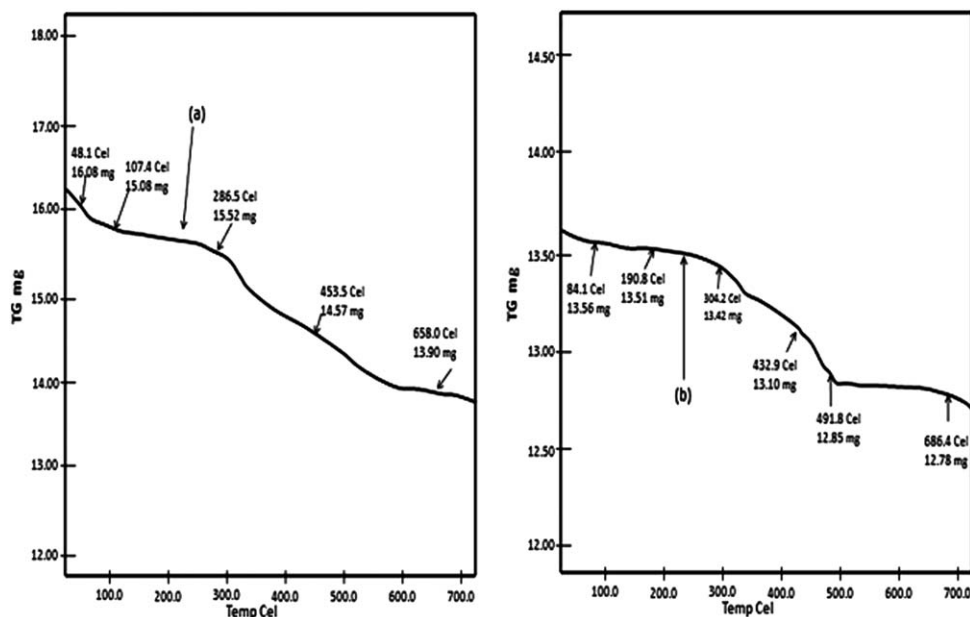


Figure 11. TGA curves of (a) untreated silk and (b) PPy-treated silk.

Voltage–Current (V–I) Characteristics of Electro-Conductive Silk Fabrics

A progressively increased DC voltage from 0 to 30 V is applied to the electro-conductive silk fabric and the corresponding current across the fabric is measured by a digital ammeter. This measurement is done in two orthogonal directions (parallel to warp and weft) of the fabric. The data plotted as V – I characteristics is shown in Figure 13. It can be seen from Figure 13 that in this applied voltage range, fabric exhibits a linear V – I characteristics, like Ohmic conductor, in both orthogonal directions. Similar linear trend is observed by Dall'Acqua et al.³³ and by Maity et al.¹⁸ The slope of the V – I curve for weft direction is found to be higher than that of the warp direction. Warp threads of the fabrics are reeled yarns, whereas wefts threads are coarser spun yarns. Coarser spun yarns are more porous than that of the finer reeled yarn and as a result a significant amount

of PPy entered and trapped in fiber interstices. Due to this, in weft direction, more current is observed. This observation is in good agreement with the results reported by Maity and Chatterjee.¹⁷

Voltage–Temperature (V–T) Characteristics of Electro-Conductive Fabric

The electro-conductive fabrics are tested for their voltage–temperature characteristics by applying a range of DC voltages. Temperature measurement is done after an interval of 1 min of voltage application. The results are shown in Figure 14. It can be seen that as voltage is increasing, temperature is also increasing exponentially. Similar observations are reported earlier by different researchers for other substrates.^{17,18,34} As expected, the rate of heat generation is found higher in weft way direction than that of the warp way direction due to better conductivity of the fabric in weft way direction.

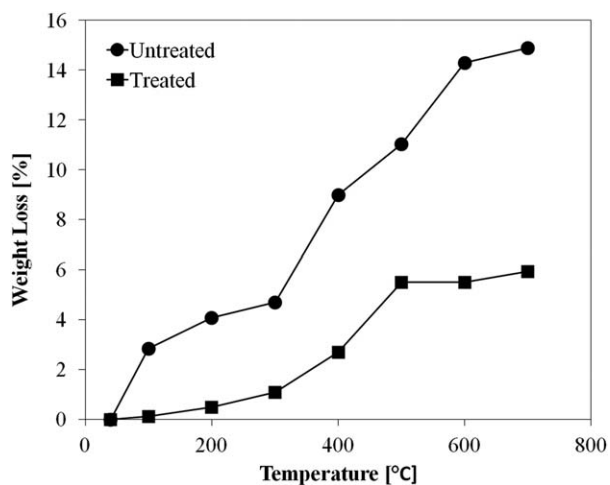


Figure 12. Weight loss vs. temperature plot of untreated and PPy-treated silk fabric.

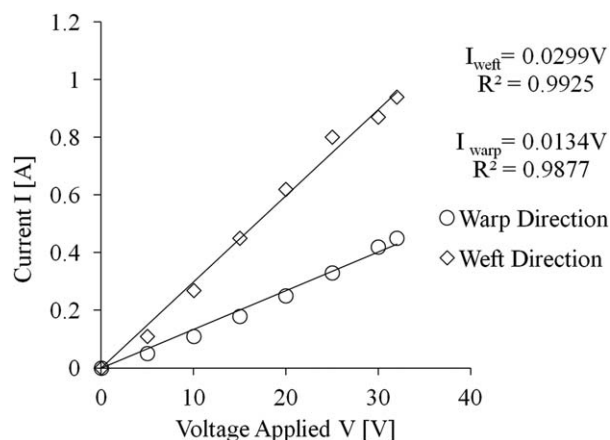


Figure 13. Voltage-current characteristics of PPy-treated silk fabric.

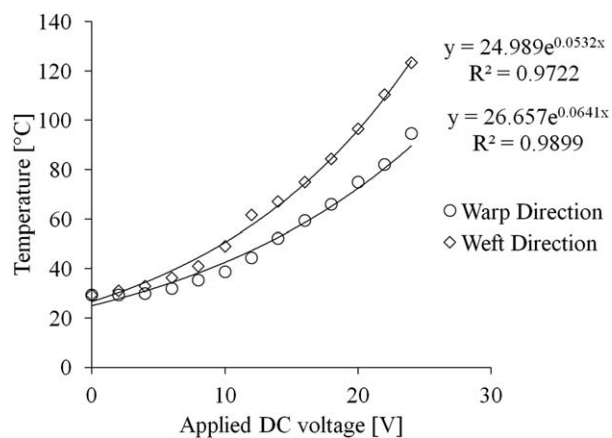


Figure 14. Voltage–temperature characteristics of PPy-treated silk fabric.

Durability Properties

It has been seen by tensile testing of untreated silk fabric and PPy-coated silk fabric that there is little or no change in breaking load and breaking extension due PPy coating. Dry cleaning and washing fastness of the fabric are also evaluated. After *in situ* polymerization of pyrrole fabric samples are taken out from the polymerization bath and rinsed thoroughly by cold water. Then they are dried and measured for surface resistivity. Then these control samples are subjected to dry cleaning and domestic washing separately according to ISO standards. After dry cleaning and domestic washing surface resistivity again measured and results have been shown in Figure 15. It can be observed from Figure 15 that the surface resistivity of PPy-coated sample is increased when subjected to both dry cleaning and domestic washing. But the durability of samples when subjected to dry cleaning is found better than that of the domestic washing. The domestic washing was carried out using soap as washing agent at alkaline pH. The polypyrrole may undergo dedoping in the presence of alkali environment due to solvation of chlorine ions. Hence, it leads to drastic increase in surface resistivity.

CONCLUSIONS

Woven silk fabrics can be made electrically conductive by *in situ* chemical polymerization of pyrrole. Analysis of the effects of process parameters of *in situ* polymerization on surface resistivity reveals that higher oxidant concentration shows a decreasing trend of surface resistivity. As polymerization time and dopant concentration increase the surface resistivity initially decreases and then increases. Among these process parameters the polymerization time is the most significant factor influencing the surface resistivity. A minimum surface resistivity of 636.33 Ω can be obtained by optimizing process parameters at 2M pyrrole concentration, 4.5M oxidant concentration, 0.16M PTSA concentration, 120 min of polymerization time, and 5°C of polymerization temperature. Morphological analysis shows that PPy coating on the silk surface is quite uniform. The FTIR spectra of PPy-coated silk show a mixed spectral pattern with bands typical of silk and PPy overlapping over the entire wave numbers range and as well as red shifts of amide bands which reveal the chemical interactions between silk and PPy. PPy-silk composite fabric exhibits enhanced thermal stability. *V–I* character-

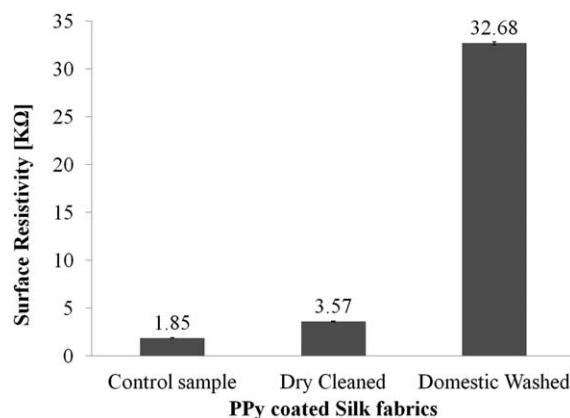


Figure 15. Effect of dry cleaning and washing on surface resistivity of PPy-coated fabric.

istics shows a linear trend like an Ohmic conductor and *V–T* characteristics shows an exponential trend.

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