

# Development of Conductive Cotton Fabrics for Heating Devices

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**ABSTRACT:** Recent developments in the area of textiles to make fabrics more functional have led to synthesizing "intelligent fabrics." This can be achieved by making the fabrics electrically conducting. In the present study it is reported that the cotton fabrics, when impregnated with polypyrrole, achieve enhanced level of conduction. The method of diffusion of pyrrole, followed by polymerization using iron chloride as oxidant, was used. The different levels of conduction were achieved by varying the contents of monomer in the bath from 0.01 to 0.1M during the synthesis. The conductivity could be enhanced from the initial value of  $10^{-12}$  to  $10^1$  S/cm. It is shown that when a fixed voltage is applied to such a modified piece of cloth, the heat generated is up to  $1000 \text{ W/m}^2$  depending on the per-

centage of pyrrole present. Such fabrics can be used as heating pads and integrated into the apparel to keep the wearer warm enough using a portable 9.0-V battery. Being flexible and breathable, such fabrics have better comfort properties (compared with conventional heating pads). It can find applications in dresses for army personnel and old-age patients. Such conductive fabrics can also find applications in many areas such as electromagnetic interference shielding, gas sensors, and temperature indicators. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4690–4695, 2006

**Key words:** cotton fabrics; polypyrrole; electrical conduction; heating pads

## INTRODUCTION

The demand for newer types of textile fabrics has been on the rise not only because of fashionable clothing but for it to be more functional.<sup>1</sup> Fibers can be modified to be smart or intelligent by imparting various properties to it such as crease resistant, hygienic, antflammable, antibacterial, etc.<sup>2</sup> However, truly intelligent fabric should be able to sense the surrounding, respond to it, and act accordingly. This is possible by making the fibers electrically conducting, i.e., departing from its traditional use as electrically insulating material. Various devices can be made from such modified fabrics and integrated with the apparel to make the dress smart. The idea of "wearable motherboard" has been advanced by Georgia-tech.<sup>3</sup>

Making the fibers conducting and eventually replace the household wiring (of copper) has been the dream of scientists for the last few decades. Use of various materials such as carbon black, aluminum fibers, etc., as fillers in polymeric composites has made it possible to raise the conductivities of fibers from  $10^{-12}$  to  $10^{-6}$  S/cm or so. However, with discovery of conducting polymers (CPs) such as polyacetylene,

polypyrrole, polyaniline, etc., it appears that the level of conductivity can now be raised to  $10^{-1}$  S/cm or even higher.<sup>4</sup> The electrical conductivities of CPs can be varied over a wide range of values right from insulating to highly conducting and also found to be sensitive to heat, surrounding gas, and pressure. Therefore CPs find wide applications in the field of sensors, actuators, electromagnetic interference shielding (EMI), etc. Unfortunately, the main disadvantage of these materials is that the mechanical properties and stability are poor. Therefore composites of these materials have been made using another host polymer having good mechanical properties. There have been some papers published on the synthesis and electrical properties of conductive textile fibers.<sup>5–7</sup> A few papers have also appeared regarding heat generation by using CPs and textiles.<sup>8</sup>

Our research investigations in the area of textiles have shown that the textile fibers/fabrics can be impregnated with polypyrrole (PPy) and polyaniline (PANi).<sup>9</sup> Depending on the experimental conditions, the CPs either diffuse, get grafted, or just get coated on the surface of the fibers. The effect of oxidizing agents, time, temperature, and polymerizing process on the conductivity of fabrics has been reported. It is anticipated that the formation of film or impregnation within the fibers will allow the flow of current in the fabrics. Since the weavings in the fabric allow interfiber connectivity, the flow of current will be unobstructed.

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We have already reported<sup>10</sup> that one of the main applications of such modified fabrics will be for making wearable heating pads. Such pads will be very useful to defense personnel where only low power energy sources will be available. Other possible uses of conductive fabrics are for EMI shielding, antflammable, and antibacterial apparel.

The present article reports general characterization of conductive cotton fabrics and their use for heat generation. Cotton fabrics were impregnated with PPy using  $\text{FeCl}_3$  as oxidizing agent. Seven different concentrations of pyrrole were used to determine the optimum conditions. A comparison is made of their electrical conductivity, heat generation capability, and stability. Analysis is also made of the degradation process with the passage of current and ways to regenerate the conductivity.

## EXPERIMENTAL

### Materials

Textile fabrics of cotton were obtained from Century Mills, Mumbai, India. The fabrics were scoured and conditioned in ambient laboratory conditions before use. This fabric will be referred to as the control cotton.

Pyrrole monomer (99% pure) was obtained from Aldrich, USA, and was distilled before use. Ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) (96%) was obtained from S.D. Fine Chemicals (Boisar, India) and was used as oxidizing agent.

### Preparation of polypyrrole-impregnated cotton fabrics

Cotton fabric samples were mounted on rectangular frames and soaked in a solution of pyrrole in water with concentrations varying from 0.01 to 0.1M for 2 h. The bath containing the fabric was then cooled to 5°C. The solution of  $\text{FeCl}_3$  was added to the reaction vessel so as to polymerize the monomer keeping the oxidant to monomer molar ratio of 2 : 4. The polymerization time was 2 h and was carried out at 5°C with occasional stirring. The weight of each dry cotton fabric was  $5.0 \pm 0.1$  g, and the total amount of solution in the bath was 1000 mL, which gave the material to liquor ratio of 1 : 200. After polymerization, the fabric was rinsed thoroughly with sufficient amount of water in different beakers. The samples were allowed to dry under ambient conditions for 24 h and then preserved in the desiccators. Considerable precipitation was noticed on the fabric, which could be easily washed off. However the reacted/diffused polypyrrole (PPy) could not be easily removed and that made the fabric black in color (in contrast to white color for the original control fabric).

### Weight uptake and dimensions

The weight of the fabric was obtained after drying for 24 h. There was considerable gain in the weight. The thickness of the fabric after the reaction was measured using micrometer screw gauge. The diameters of the fibers, for both the control and the impregnated, were measured by optical as well as scanning electron microscope (SEM). An average of 10 measurements were obtained (with an error of  $\pm 0.1 \mu\text{m}$ ).

### Surface morphology by SEM

SEM was carried out using JEOL Model JSM 5400 microscope at various magnifications (at 10 kV). The samples were mounted on the holder using double sided adhesive tape. The samples were further coated with gold to get good electrical contact and avoid charging. Occasionally the samples were not coated with gold since they already had sufficient conductivity.

### Structural analysis using X-ray diffraction and IR spectroscopy

X-ray diffraction was carried out using Philips X-ray generator PW1720 and goniometer 1710. X-rays were obtained from the sealed tube having copper anode and the emission line  $\text{Cu K}\alpha$  with wavelength of 1.542 Å was used. The samples were cut and grounded in the form of fine powder and were made in the form of pellet using a press on an aluminum holder. The holder was mounted on the rotating stage of the goniometer. The diffraction scanning was done in the range of 10°–40°.

IR spectra were obtained using PerkinElmer model 2000. ATR technique was used, as the samples were thick and dark in color. The spectra were recorded in the region of 400–4000  $\text{cm}^{-1}$ .

### Heat generation studies

A DC power supply obtained from M/s. Equiptronics, Mumbai, was used. The voltage could be varied between 0 and 24 V. A voltage of 9 V was used throughout the experiments because commercial batteries of this voltage are available as standards. A fabric of dimension 9 cm in length and 5 cm in width was held between two specially prepared jaws to get a good electrical contact. The temperature of the fabric was measured during the heating using a thermocouple or a sensitive thermometer. The temperature was monitored at the center of the sample.

The variation in the current was recorded with time, initially every half a minute and thereafter for 1 min each. The temperature was also noted continuously every 1 min as the heating proceeds.

The power dissipated during heating can be found as

$$P = IV = V/RV = V^2/R,$$

where  $P$  is the power dissipated,  $R$  is the resistance of the fabric, and  $V$  is the voltage applied.

If  $R_s$  is the surface resistance, then the total resistance  $R$  can be expressed as  $R = \frac{R_s l}{w}$  where  $l$  is the length and  $w$  is the width of the fabric.

$$\text{Thus } I = \frac{V}{R} = \frac{V}{R_s} \times \frac{w}{l}.$$

Therefore the power density per unit area ( $P'$ ) is

$$P' = IV = \frac{V^2}{R_s} \times \frac{w}{l}$$

Or after substituting for  $R_s$ , we get

$$P' = IV/lw.$$

### Surface resistivity

The surface resistivity was calculated from the resistance value and probe dimensions. AATCC test method 76-1995 was used to measure the surface resistivity of the samples. Two rectangular copper electrodes ( $25 \times 25 \text{ mm}^2$ ) separated by a distance of 50 mm were placed on the sample and pressed by a force to give good contact. The resistance was recorded by Keithly electrometer model 617. The measured resistance could be converted to surface resistance  $R_s$  using the relation

$$R = R_s l/w,$$

Here  $R_s$  is the surface or sheet resistance expressed in ohms per square.

## RESULTS AND DISCUSSION

### Weight uptake

The fabric substrates get conductivity because of diffusion of CP (PPy) phase inside the fibers as well as because of the coating of a layer on the surface. The fab-

ric is exposed to monomer, dopant, and oxidizing agent in the solution. The reaction is initiated by the oxidation of monomer (forming radical cations) which combines to form dimer, trimer, etc., leading to full polymerization. The monomer diffuses into the fiber and polymerization can occur inside the fiber. In addition, the radicals bonded to the surface can bring about surface polymerization, leading to the formation of a thin film on the fabric. The insoluble polymer is formed in the solution as well as on the surface of the fabric. The bulk polymerized material in the solution can deposit on the fabric and particularly cling over the crossovers of the weaves. Because of such combined effect it was noted that the weight of the fabric after the reaction increases. The weight uptake during different reactions was therefore determined and is given in Table I. The concentrations of monomers used are also listed in Table I. It was noted that the thickness of the fabric increased, indicating that the individual fibers swell. The percentage increase in thickness was calculated and is given in Table I. The increase in the diameter of a single fiber was determined microscopically and the values agree with thickness changes.

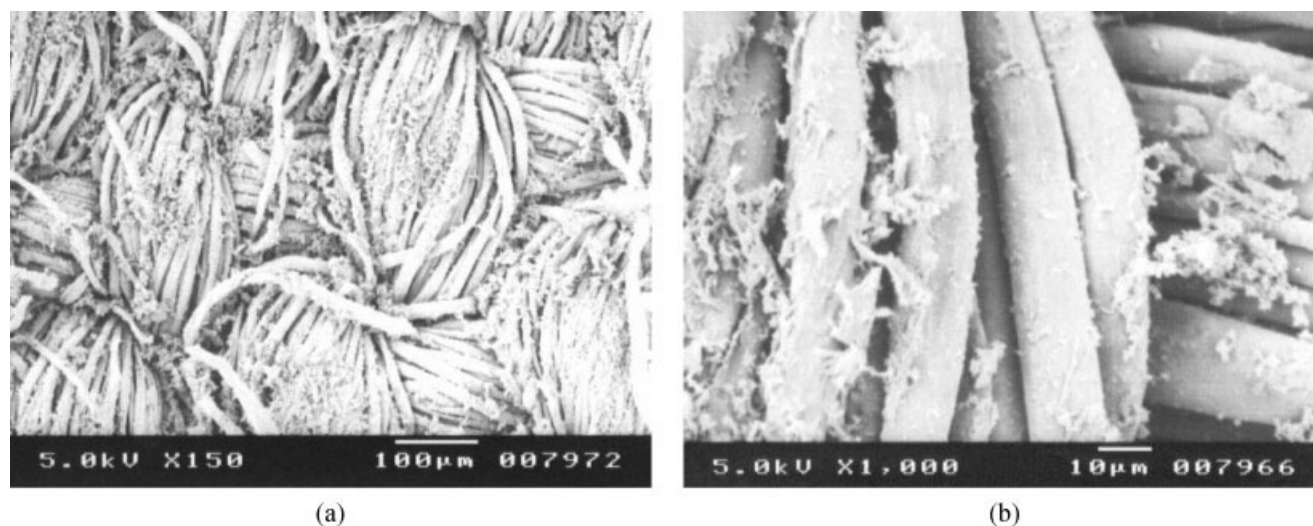
### Morphology using SEM

The surface structure was investigated using SEM. It can be seen from Figure 1 that the surface is coated with granular structures formed from PPy. A good amount of coating with particle sizes varying from 1.0 to 3.0  $\mu\text{m}$  could be seen. At low magnifications one could see heavy depositions within the weaves. The cross sections of the yarns were seen by optical microscopy as well as by SEM and the diameters of the fibers were measured before and after the PPy treatment. It was found that on average the diameter increased by 1.5  $\mu\text{m}$  or about 10% in the case of fabrics treated with 40% pyrrole. The thickness of the fabric increased from 274.0  $\mu\text{m}$  for control to 302 and 380.0  $\mu\text{m}$  for the samples treated with 40 and 80% pyrrole respectively.

The feel of the fabrics was noted to be getting harsh/rough and becoming less pliable with increasing percentage of PPy content. Good fabric properties were still retained up to 60% of Ppy.

TABLE I  
Weight Uptake and Increase in Thickness of Cotton Fabrics Treated with Polypyrrole Using Ferric Chloride as Oxidant

Ratio of fabric/ monomer	Code name of sample	Time for soak + add + polym. (hr)	Weight uptake (%)	Increase in thickness (%)
100 : 10	C10PPY	2 + 2 + 2	4.52	4.5
100 : 25	C25PPY	2 + 2 + 2	11.65	9.5
100 : 40	C40PPY	2 + 2 + 2	24.76	16.0
100 : 50	C50PPY	2 + 2 + 2	-	19.0
100 : 60	C60PPY	2 + 2 + 2	34.64	23.0
100 : 80	C80PPY	2 + 2 + 2	43.28	31.0
100 : 100	C100PPY	2 + 2 + 2	45.88	-



**Figure 1** SEM image of cotton fabrics coated with PPy. Synthesis time, 2 h, temperature, 5°C. (a) Low magnification—note a large number of granular deposits within the weaves; (b) high magnification—note the uniform coating with some granules.

### Structural properties by XRD and IR spectroscopy

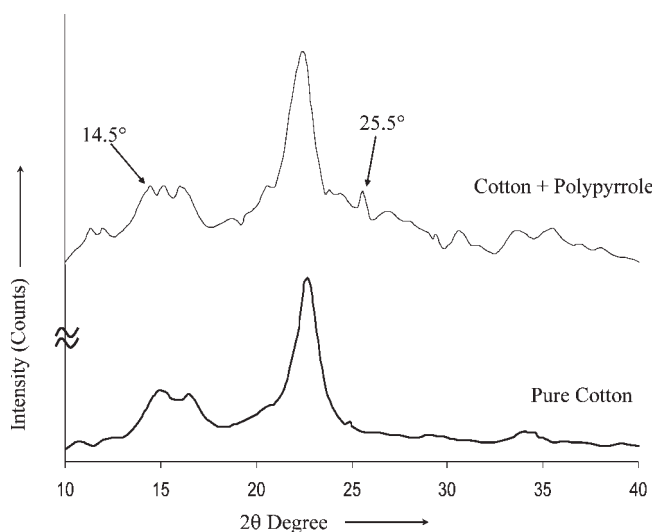
X-ray diffraction studies were carried out to see the effect of diffusion of pyrrole monomer on the crystalline and amorphous regions of the cotton cellulose. The control cotton sample has three diffraction peaks, corresponding to  $2\theta$  values of  $15^\circ$ ,  $16.4^\circ$ , and  $22.6^\circ$  and the corresponding indices of planes are 101,  $10\bar{1}$ , and 200 respectively, (Fig. 2). The area under amorphous scattering is considerable, and the percent crystallinity was calculated by the method of area measurement by the formula

$$\% \text{ Crystallinity} = \frac{\text{Area under crystalline peaks}}{\text{Area under both the peaks}}$$

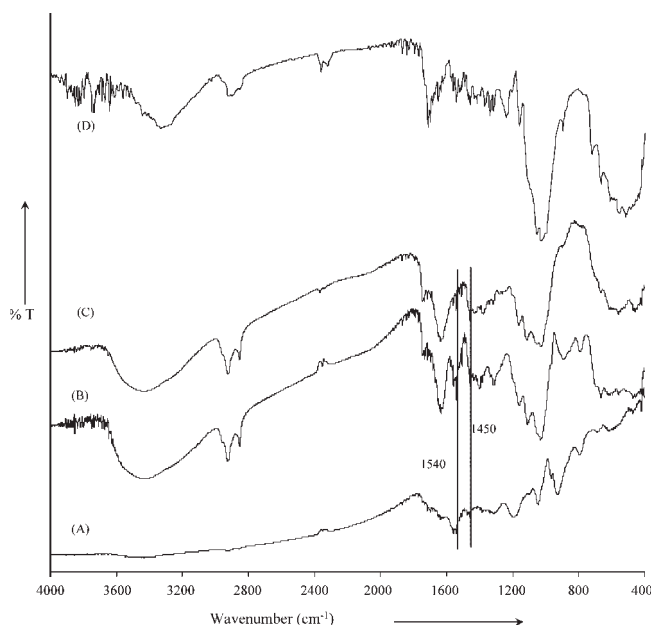
When the cotton fabric was treated with PPy, it was found that there was a change in the diffraction pattern. The percentage crystallinity was found to have decreased from 70 to 64% when the fabric was treated with pyrrole (100%). This shows that diffusion of PPy in the cellulose structure takes place and the crystalline region is affected marginally. It is likely that most of the diffusion of pyrrole is in the amorphous region with some in the para-crystalline region. In addition, the peaks in the region of  $14^\circ$ – $16^\circ$  have been affected. There is an appearance of additional peak at  $14.5^\circ$ . This is either due to structural change or due to addition of PPy in the cellulose structure (Fig. 2). It was also seen that there is an appearance of one extra peak at  $25.5^\circ$ . Comparison of diffraction data for pure PPy reveals that it has two broad peaks in the region of  $14^\circ$  and  $26^\circ$ .<sup>11</sup> Therefore interaction and diffusion of PPy is evident.

IR spectra of pure PPy show characteristic absorption bands at 3400 (N—H), 2940 (C—H), 1540 (ring

vibrations), 1480 (C=C), 1430 (C—N), 1080, 1020 (C—H in plane) and  $900 \text{ cm}^{-1}$ .<sup>12</sup> We have also recorded FTIR spectra of pure PPy synthesized chemically during the present investigation, which is shown as curve A in Figure 3. Most of the reported absorption bands are present in our spectrum except that some peaks are shifted by a few  $\text{cm}^{-1}$ . IR spectra of cotton fabrics impregnated with PPy show (Fig. 3) all the absorption bands corresponding to pure PPy, out of which one can note appreciable intensity and good resolution for bands at 1540 and  $1450 \text{ cm}^{-1}$ . It can be seen from Figure 3 that intensity of bands at 1540 and  $1450 \text{ cm}^{-1}$  increases with the concentration of PPy in the composite (refer curve C for 10% Ppy and curve B for 60% Ppy in Fig. 3). In Figure 3 curve D has been



**Figure 2** X-ray diffraction pattern of pure cotton fabrics and composite of cotton fabric with PPy.

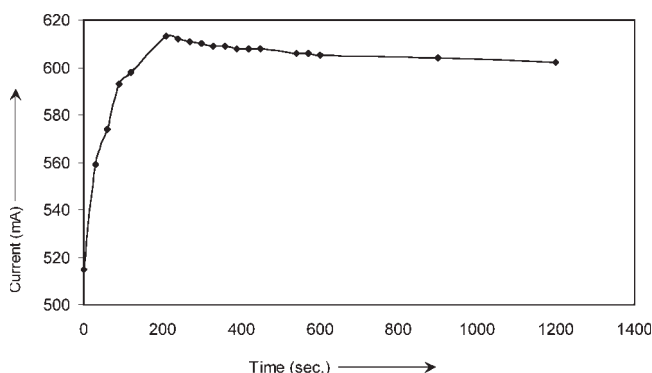


**Figure 3** FTIR spectra of (A) pure PPy, cotton fabric impregnated with (B) 60% PPy, (C) 10% PPy, and (D) pure cotton fabric.

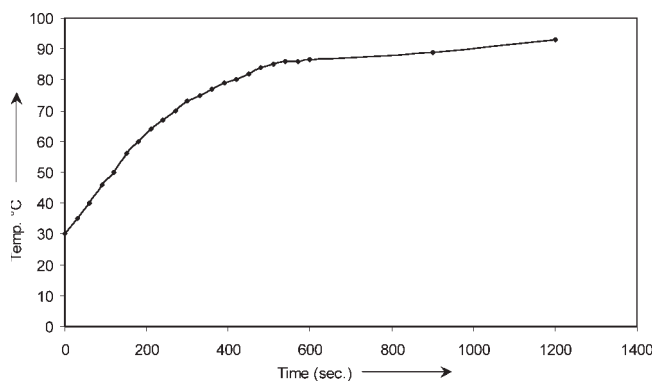
introduced to represent the FTIR spectrum of pure cotton for the sake of comparison and to see why resolution of some bands are not clear.

### Heating effects

Variation of current with time is depicted in Figure 4, which shows that the current increased initially very rapidly and then decreased very slowly with time. The reduction in the current is about 5% over a period of 20 min. It could be further seen from the plot of temperature versus time (Fig. 5) that the maximum temperature could be attained in about 20 min for different samples. The temperatures attained are given in Table II, the maximum value being 95°C for 100% treated sample. As the voltage was kept constant during the



**Figure 4** Variation of current with time for the Cotton + PPy fabric during the heating period of 20 min. Polymerization time, 2 h at 5°C; applied voltage, 9 V.



**Figure 5** Variation of temperature with time for the Cotton + PPy fabric during the heating period of 20 min. Polymerization time, 2 h at 5°C; applied voltage, 9 V.

heating experiment, the steady decrease in current (Fig. 4) can be attributed to the oxidative degradation of the CP which causes the loss of conjugation of the polymer backbone. In spite of that it was observed that the stability of heat generated and the temperature attained was quite stable. The temperature varied at the most within about  $\pm 3^\circ\text{C}$  after the steady state was reached. However, the samples showed some effect of aging in terms of reduced heat generation after a period of 8 months because of  $\sim 30\%$  reduction in the current flowing in the sample.

The percentage contents of pyrrole used for making different fabrics was varied from 10 to 100% (Py : cotton). Plots for all these samples (Fig. 6) show that as the PPy content increased the current also increased. The sample with 100% Py had a maximum current of 500 mA. The values of surface conductivities for the samples are given in Table II.

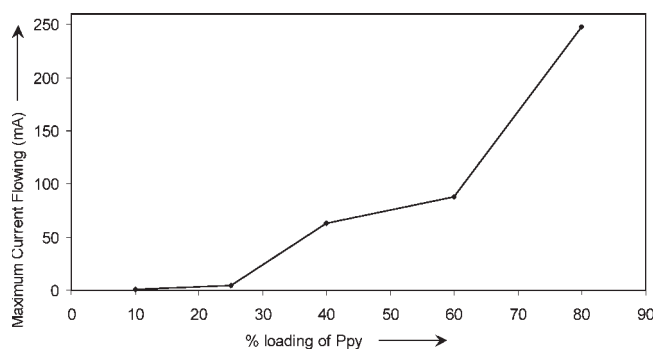
The power density per unit area for various samples were calculated using the equation.

$$P = \frac{IV}{Lw} (W/m^2)$$
, where  $L$  and  $w$  are the length and width of the fabrics.

When this is calculated as a function of content it was noted that the 80% PPy sample has more than 200

**TABLE II**  
The Maximum Current Flowing, the Maximum Temperature Reached, and the Surface Conductivity of Cotton Fabrics Treated with Polypyrrole

Sample code	Maximum current flowing (mA)	Maximum temperature reached after 20 min ( $^\circ\text{C}$ )	Surface Conductivity ( $10^{-3}$ S/square)
C10 PPy	1.00	—	—
C25 PPy	3.70	30.0	0.79
C40 PPy	62.60	36.0	1.80
C50 PPy	—	—	—
C60 PPy	88.50	38.5	14.0
C80 PPy	248.00	62.0	66.0
C100 PPy	500.00	95.0	—



**Figure 6** The maximum current flowing through the fabric with different percentages of doping levels of PPy.

times the power density of the 10% Ppy coated sample. The maximum value of power density found for 80% Ppy treated sample was  $500 \text{ W/m}^2$  while that for 100% Ppy treated sample is  $1000 \text{ W/m}^2$ .

We tried to develop the heating pads with cotton fabrics as this is highly flexible and can be made wearable. Further, the fabric is breathable and soft so that it will not be uncomfortable. It can be sewn into the dress at those points where warming of the body part is essential. For example, during winter, the fingers toes can be warmed up slightly to make the person comfortable. It is noted that for such applications the power required is about  $50 \text{ W/m}^2$ . The results of these investigations show that this level of power can be easily generated using a conventional 9-V battery. Further, since the current drawn is very low, the life of battery can be higher. The switch for on/off can be integrated within the person's jacket so that he can economize the power as per the needs.

On the basis of good flexibility and sufficient heat generation it was found that 60% Ppy (C60PPY) samples are the best and give optimum performance even after repeated heating/cooling cycles.

## CONCLUSIONS

On the basis of these studies it is concluded that cotton fabrics could be impregnated with different levels of PPy to achieve enhanced level of electrical conduction. The structural changes accompanied were investigated by SEM, XRD, and FTIR. The modified cloth could be used for heat generation by applying 9 V D.C. supply. Being flexible and breathable, such fabrics can be used for making heating pads and can be integrated into apparel.

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## References

- Gupta, S., Ed. *Smart Textiles—Their Production and Marketing Strategies*; NIFT: New Delhi, 2000.
- Bajaj, P. *Indian J Fiber Text Res* 2001, 26, 162.
- Park, S.; Jayaraman, S. *Smart Fibres, Fabrics and Clothing*; Woodhead Publishing: Cambridge, UK, 2001; p 226.
- Nalwa, H. S., Ed. *Handbook of Organic and Conductive Molecules and Polymers*, Vols. 1–4; John Wiley: New York, 1997.
- Gregory, R. V.; Kimbrell, W. C.; Kuhn, H. *Synth Met* 1989, 28, 823.
- Kuhn, H. H.; Child, A. D.; Kimbrell, W. *Synth Met* 1995, 71, 2139.
- Hakansson, E.; Kaynak, A.; Lin, T.; Nahavandi, S.; Jones, T.; Hu, E. *Synth Met* 2004, 21, 144.
- Bhat, N. V.; Seshadri, D. T.; Radhakrishnan, S. *Text Res J* 2004, 74, 155.
- Desai, A. N.; Bhat, N. V.; Seshadri, D. T.; Bambole, V. A. In *Proceedings of the International Conference on High Performance Textiles and Apparels*, Kumarguru College of Technology, Coimbatore, India, July 2004; p 475.
- Bhat, N. V.; Seshadri, D. T.; Nate, M. M.; Gore, A. V. In *Proceedings of the Joint Technological Conference of ATIRA, SITRA, NITRA, and BTRA*, Mumbai, India, Feb. 2004; p 172.
- Bhat, N. V.; Gadre, A. P.; Bambole, V. A. *J Appl Polym Sci* 2001, 80, 2511.
- Street, G. B. In *Handbook of Conducting Polymers*, Vol. 1; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; p 280.