

**STUDIES ON PREPARATION AND  
CHARACTERIZATION OF ELECTRO-CONDUCTIVE  
TEXTILES BY *IN SITU* ELECTROCHEMICAL  
POLYMERIZATION OF PYRROLE**

by

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Submitted

in fulfilment of the requirements of the degree of  
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to the



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**DEDICATED TO MY PARENTS AND SISTERS**

## **CERTIFICATE**

This is to certify that the thesis entitled “**Studies on preparation and characterization of electro-conductive textiles by *in situ* electrochemical polymerization of pyrrole**” being submitted by **Mr. Syamal Maiti**, to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in the department of Textile Technology, is a record of bonafide research work carried out by him. Mr. Maiti has worked under our guidance and supervision and fulfilled all the requirements for the submission of the thesis, which has attained the standard required for a Ph.D degree of this institute.

The results contained in this thesis have not been submitted, in part or full, to any other university or Institute for the award of any degree or diploma.

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## ABSTRACT

In this study, an attempt has been made to develop fundamental understanding of *in situ* electrochemical polymerization of pyrrole. The effects of process parameters namely monomer and dopant concentrations, polymerization time and temperature, and applied voltage on the polymer yield and the monomer-to-polymer conversion have been reported. The system current was found to play a very important role in determining the yield, while the normalized system current correlated well with the conversion. Using the experimental results, a simple and easy-to-use expression for predicting the system current was also developed. Further, the influence of the distance between electrodes on the yield and conversion were examined and reported. The distance was found to follow a power law relationship with the yield and system current. Furthermore, the effect of size of electrodes on the polymer yield was investigated. It was observed that the yield was more or less constant irrespective of the electrode size at a lower level of system current, but, at a higher level of system current, the yield increased as the electrode size was increased before finally leveled off. Thermochemistry of electrochemical polymerization was also studied. The electrochemical polymerization of pyrrole was found to be an exothermic process. The enthalpy of polypyrrole formation was calculated from the data obtained from the calorimetric studies. The enthalpy was found to increase with the increase in temperature. The pyrrole film was characterized by using EDX, XRD, TGA, and SEM techniques. The surface roughness of the film was also quantitatively determined. The surface with higher roughness exhibited higher electrical resistivity and vice-versa.

The preparation and characterization of electro-conductive fabrics and yarns prepared by *in situ* electrochemical polymerization of pyrrole have been studied in detail. Optimization of electrochemical polymerization process was done to minimize the surface resistivity of the electro-conductive textiles. The electro-conductive fabrics were prepared by a two-stage process that involved *in situ* chemical polymerization prior to *in situ* electrochemical polymerization. This was done to obtain uniform deposition of polypyrrole onto the fabrics. The effects of electrochemical polymerization process parameters on the surface resistivity of electro-conductive fabrics have been analyzed and reported. The process parameters of interest were monomer concentration, dopant concentration, polymerization time, polymerization temperature, and applied voltage. A set of electro-conductive fabrics were prepared in accordance with a Taguchi design of experiments and the surface resistivity of the fabrics was measured. The key influencing parameters were found to be the applied voltage, polymerization time and polymerization temperature. Taking these three process factors into consideration, a set of experiments was carried out according to a  $3^3$  Box-Behnken design of experiments. The results of the experiments were analyzed by using response surface methodology. Here too, the applied voltage was found to be the most significant parameter as far as the surface resistivity of the electro-conductive fabrics was concerned. The process parameters were optimized in order to achieve the least possible surface resistivity of the electro-conductive fabrics. Similar set of results were obtained on yarns. The effect of deposition of polymer on the surface resistivity of the electro-conductive fabric was examined. As the surface roughness was increased the surface resistivity also increased. The voltage-current, voltage-temperature, and electromagnetic shielding behaviors of the electro-conductive fabrics were studied and reported. The voltage-current and voltage-

temperature characteristics were found to be exponential in nature. The electro-conductive fabric exhibited very high electromagnetic shielding efficiency with and without grounding. The electro-conductive yarn showed high sensitivity with respect to resistivity against small mechanical strain.

It was understood that the preparation of electro-conductive textiles by means of combined chemical and electrochemical polymerization was too time-consuming, mainly because of slower *in situ* chemical polymerization process. It was, therefore, of interest to develop a novel process for rapid and uniform deposition of polymer onto textiles. The principle was evolved and the efficacy of the suggested process was experimentally substantiated. It was established that the *in situ* chemical polymerization process could be totally replaced by treating the fabric with suitable metal salts that could also act as oxidizing agents. The selection of such compounds was based on the free energy of conversion to the desired state. In this way, a uniform electro-conductive fabric was produced without pre-chemical polymerization. It was also established further that the system current could be controlled by a suitable adjustment of the voltage and the distance between the electrodes to develop a rapid polymerization process. This may pave the way for a continuous process for *in situ* electro chemical polymerization of pyrrole on to textiles.

An attempt was also made to develop automated equipment for measurement of the electrical properties of electro-conductive textiles. The design, fabrication, testing, and standardization of such equipment have been reported. The fabricated instrument is multifunctional and fully computerized. It was able to record automatically the surface resistivity of the textile sample with increasing time, temperature and relative humidity. It could also measure the volume resistivity of the electro-conductive fabrics. With this instrument it was possible to measure the voltage-current and

voltage-temperature characteristics of electro-conductive textiles as well. In addition, the equipment could be operated by remote triggering. The repeatability and reproducibility study was conducted on this equipment and the variability in the gage was found to be small relative to the variability in the product. This indicated that the gage was capable of distinguishing among different grades of product.