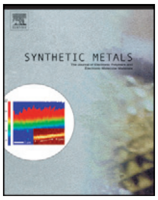
Synthetic Metals 159 (2009) 1353–1358

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Polypyrrole microstructure deposited by chemical and electrochemical methods on cotton fabrics

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ARTICLE INFO

Article history:
Received 1 January 2009
Received in revised form 4 March 2009
Accepted 6 March 2009
Available online 21 April 2009

Keywords:
Conducting textiles
Polypyrrole
Electrochemical oxidation
Constant current electrolysis
Cotton
Electrical conductivity

ABSTRACT

Electrochemically and chemically coated cotton fabrics with polypyrrole are comparatively evaluated and characterized in order to produce the conducting fabrics/textiles. The polypyrrole coated fabric is obtained electrochemically by constant current electrolysis (2 mA cm^{-2}) at room temperature for 4 h. The stability, electrical conductivity and electrochemical behaviour of such composite coating are evaluated by means of SEM, FTIR, TGA, DSC, four-probe conductivity, impedance spectroscopy and cyclic voltammetry. When compared to chemical method thicker films of polypyrrole with globular microstructure could be obtained by electrochemical technique and the conductivity of the polypyrrole film was also high (1.9×10^{-2} to 3.3×10^{-1} S cm^{-1}). The weight uptake and the electrical conductivity of the coated fabric increase with concentration of pyrrole and time of electrolysis. Many other physico-chemical properties of the polypyrrole films obtained by the two methods were found to be qualitatively similar.

1. Introduction

Modification of electrical properties on cotton fibres and fabric employing conducting polymers to achieve specialized functional properties is an active current research area. Conducting polyaniline [1] and polypyrrole (Ppy) [2] were chemically coated on cotton fabric using persulphate and ferric chloride respectively as oxidizing agents. The polyaniline coated cotton fabric exhibits some antimicrobial activity [3]. The Ppy is an important conducting polymer with high electrical conductivity and appreciable environmental stability [4,5]. The Ppy coated fabrics also exhibit electrical heating behaviour [6]. A detailed report on the performance of the Ppy coated cellulose fabric is available in literature [7]. Electromagnetic interference (EMI) shielding properties of the Ppy coated nylon fabrics prepared via direct chemical polymerization techniques have been evaluated [8]. The novel vapour phase two-stage polymerization methods are introduced recently [9]. Methods for improvement of the dielectric characterization techniques for the measurement of such a conducting polymer coated fabrics are also been developed [10]. Further functionalization of conducting polymer coated fabrics using triethoxysilane is also possible [11].

A few reports on formation of conducting polymer coated textile fibres are noticed in recent literatures. The Ppy composites have been chemically coated on cellulose as well as protein fibres and their electrical properties were evaluated [12,13]. The continuous vapour phase polymerization technique can also be employed for coating cotton, nylon and wool yarns [14]. The conductivity of polypyrrole coated fabric did not decrease significantly after subjecting the fabric to the laundering test [15] as prescribed by textile processing industry in Australia (AS 2001.4.15-1994).

Electrochemical polymerization of aniline as well as pyrrole on cotton fibres was achieved by winding the fibre around the platinum foil anode [16,17]. Modification of the Ppy covered nylon and polyester fabrics through electrochemical method with the Ppy/hybrid materials have been developed recently [18,19]. In the present work, the electrochemical method is used to prepare the Ppy coated cotton fabric by tightly fixing it on the graphite, which serves as the anode material. The physico-chemical properties of these conducting fabrics are evaluated and also compared with the Ppy coated fabric prepared by chemical method.

2. Experimental

Cotton fabrics were scoured and bleached before coating with the Ppy. Pyrrole (98%), ferric chloride ($FeCl_3$, AR Grade) and sodium chloride (NaCl, AR grade) were purchased from SRL, India. Deionised water was used for all the experiments. Pyrrole was distilled before use.

Chemical polymerization of pyrrole was carried out by keeping the molar ratio 1:2:2 for monomer, NaCl and $FeCl_3$ respectively in all the experiments. The control cotton fabric sample (4 cm × 4 cm) was impregnated in 0.1 mol L^{-1} pyrrole monomer solution con-

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doi:10.1016/j.synthmet.2009.03.005

taining 0.2 mol L^{-1} NaCl and was mechanically stirred for 30 min. Temperature was maintained at 4–6 °C throughout the experiments. After 30 min, 0.2 mol L^{-1} $FeCl_3$ was added into the reaction mixture and stirring continued for another 2 h. A black precipitate was deposited on the cotton cloth. The excess polymer was removed from the fabric by washing with water at 60 °C for 15 min and air dried. While studying the concentration effect of monomer the molar concentrations of NaCl and $FeCl_3$ were also increased to keep their overall molar ratio of 1:2:2.

The electrochemical polymerization was performed under galvanostatic condition. In a single compartment cell, cotton fabric wounded on graphite electrode (all the edges and backside of the electrode were completely masked using insulating tape and the exposed area was 7 cm × 7 cm) and stainless steel were used as anode and cathode respectively. A constant current of 100 mA (2 mA cm^{-2}) was subjected to the electrolyte containing 0.1 mol L^{-1} pyrrole and 0.2 mol L^{-1} NaCl. The pyrrole and NaCl ratio was kept constant at 1:2 in all the experiments. The initial polymerization of pyrrole occurred on the electrode surface (below the cotton fabric) and after approximately 1 h, a black deposit was found on the cotton surface. Observation of a uniform conducting polymer on the cotton surface within 1 h was considered as the proper fixing of the fabric on the electrode surface. The electrolysis was continued for 4 h to complete the polymerization (charge passed was 5760 C). After electrolysis, the fabric was taken out, washed with water at 60 °C for 15 min and air dried.

Scanning Electron Microscopy images were obtained using HITACHI Model S-3000H at various magnifications to study the surface morphology of the control cotton and the Ppy coated cotton fabrics. The control cotton was gold sputtered to get electrical contact. The conductivity of the materials was measured using a four-probe technique connected to a digital multimeter (Keithley Model-2010) having a capacity of 2400 source meter and 2187 nano voltmeter. The thickness of the coated fabric before and after coating with conducting polymer was determined using PosiTector 6000 thickness meter. The difference between these two measurements gave the thickness of the conducting polymer. The control cotton fabric shows the thickness of 260 μm. X-ray diffraction data sets were collected at room temperature on a PANalytical X'PERT PRO system in Bragg–Brentano geometry using Cu $K\alpha_1$ (1.540 Å) radiation. The powder diffraction covered the $10° < 2\theta > 40°$ range with 0.0170° steps. FT-IR spectra were recorded using PerkinElmer FTIR spectrophotometer, Model Paragon 500. Gel permeation chromatograph was performed using the instrument JASCO, Japan. Thermal stability of the Ppy coated fabrics was determined by Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) using TA Instruments Model SDT Q600 (Software: Thermal Advantage) from 10 to 500 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

The cyclic voltammetry and impedance measurements were performed using BAS IM6 Electrochemical Analyser, USA with Thales 3.18-USB software. In a conventional three electrode system, a graphite and the Ppy coated cotton covered graphite (0.5 cm × 0.5 cm) were used the working electrode for cyclic voltammetry. A platinum foil and saturated calomel electrode were the counter and reference electrodes respectively. The test solutions were deaerated at least 15 min with N_2 to eliminate interfering oxygen. All the experiments were performed at 300 ± 2 K. Impedance measurements were made in the frequency range of 10 mHz to 100 KHz and the amplitude was 10 mV, by sandwiching the Ppy coated cotton fabric (1 cm diameter) between two stainless steel (SS304) blocking electrodes contacts, without any electrolyte.

3. Results and discussion

Cotton fabric is a non-conducting material. Providing electrical contact to such fabric to enable electrochemical polymerization is indeed a difficult task. In the present work, it is possible to tightly fix the cotton fabric on graphite substrate and form a uniform polymer film on the cotton surface under galvanostatic condition at a current

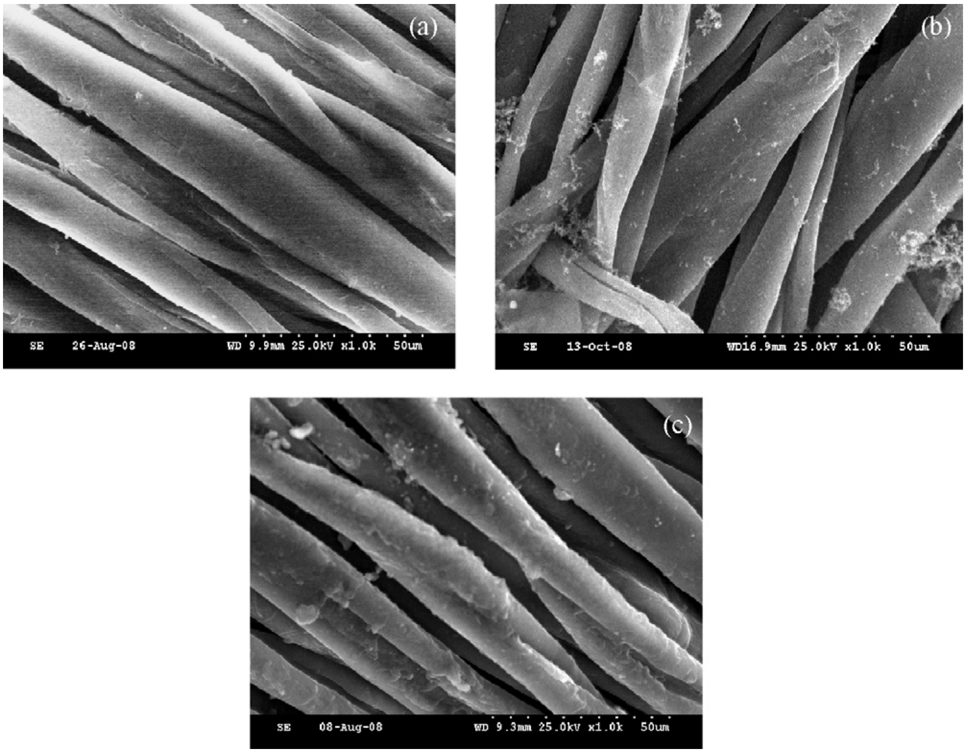

Fig. 1. SEM images of the surface of (a) pure cotton fabric; Ppy coated cotton obtained using 0.1 mol L^{-1} pyrrole concentration by (b) chemical method and (c) electrochemical method at a magnification of 1.0k.