Development of Polypyrrole Coated Organic Textile Thermoelectric Materials

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Abstract

In this research, various spunlace non-woven fabrics (100% polyester, 100% viscose and 50/50 polyester-viscose blend) are coated with an electro-conductive polymer polypyrrole by in situ chemical polymerization with $FeCl_3$ as oxidant and thermo-electric effects of the coated fabrics are evaluated. In this approach, a flexible, wearable, and organic thermo-electric textile material is developed for conversion of heat energy to electrical energy. Electrical properties of the developed coated nonwoven textiles are evaluated and reported. The average electrical resistivity of a 60 GSM of 100% viscose fabric is obtained about 45.83 $k\Omega/cm^2$ with 11.11% of polypyrrole add-on. Thermo-electric performance of these polypyrrole coated fabrics is investigated for a wide range of temperatures. The Seebeck coefficient turns out to be comparable with that of metals and inorganic semiconductor-based thermocouples.

Keywords: *Electrical resistivity, In Situ polymerization, Non-woven fabric, Polypyrrole, Thermo-electric effect*

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1. Introduction

Clothing is worn by human being as its basic necessity. It has acted as an item of utility and adornment. Textiles have been worn next to the skin, making it a perfect medium for using body heat in order to generate power. It has unique features like comfort, flexibility, air permeability, etc. Now, these features are missing in semiconductor-based materials. Thus, textiles can be a perfect material as a thermoelectric generator to generate electricity utilizing body heat [1, 2]. In traditional method, conductive textiles are made by incorporating metallic fibers or metallic yarns in yarn or fabric structure. Though textile structures became conductive in nature by incorporation of metal fibers or yarns, their application areas became limited because of low flexibility, stiffness, low compatibility with other materials, increased weight, high cost involved in production [3]. Compared to the metal conductors, polymeric conductive textile has more advantages and thus make conductive textile unique in nature [4]. So conductive textile is one of the most promising and steadily growing fields in smart textile. If textiles are made as conductive without losing any of its natural characteristics like lightness, breathability, extensibility and flexibility, it can find more application areas [5, 7].

For this conducting polymer is taken in to account which can make conductive textile without compromising its natural properties. Conducting polymer field has come a long way since the Nobel Prize awarded discovery of the first member of this class- polyacetylene by A. J. Heeger, A. MacDiarmid and H. Shirakawa. Since then, more than 20 conductive polymers have been synthesized which have multiple applications [8, 9].

Polypyrrole is one of the most studied conducting polymers because of its fairly high conductivity, better environmental stability and ease of preparation [10]. Polypyrrole is one of the intrinsic conducting polymers very promising for wide thermoelectric applications because of its several attractive properties, such as easy preparation with low costs. Conductive textiles, with a modified polypyrrole coating have been commercially developed that are more conductive and thermally stable. While imparting electrical conductivity and a dark color to the substrates, the coating process barely affects the strength, drape, flexibility, and porosity of the starting substrates [11].

Synthesis of polypyrrole through in situ polymerization on textile substrates in the form of uniform coating was first reported by Kuhn et al 1995. Application of pyrrole on textile structure can be done in three different ways and they are chemical polymerization, electro-chemical polymerization and vapor polymerization [12,13]. Method adopted to polymerize pyrrole monomer in this study is two-step chemical polymerization. Formerly textile structure is impregnated in pyrrole enriched solution, latter put into oxidant solution for polymerization of pyrrole in second step.

Polypyrrole coated textile shows extremely low thermal diffusivity regardless of the electrical conductivity and their low thermal conductivity gives significant advantage to the thermoelectric figure of merit ZT, comparable with that of some traditional thermoelectric materials according to the study of Sparavigna et al, 2010[14]. So application of polypyrrole coated textiles as a heating and cooling garment is possible and there has been growing interest for applications of polypyrrole incorporated textiles in smart clothing, strain sensors, electrotherapy, resistive heating pads, stealth technology, electromagnetic interference (EMI) shielding, antistatic and electrostatic discharge (ESD) protection.

2. Experimental

2.1 Materials and chemicals

Undyed spunlace non-woven fabrics made of 100% polyester, 100% viscose and 50/50 polyester-viscose blend each of 60 GSM are procured from Ginni Nonwovens, India. These spunlace nonwoven fabrics are used as substrate of coating of polypyrrole. The chemicals used are pyrrole (Leonid Chemicals, India) as monomer, $FeCl_3$ (Qualigens Fine Chemicals, India) and deionized water are solvent media. All the chemicals used are of laboratory grade and they are used as received.

2.2 Preparation of conductive fabric by coating through in situ polymerization method

100% Polyester, 100% viscose and 50/50 polyester-viscose blended fabric samples are taken and their weight are measured separately on a microbalance. Monomer and oxidant baths are prepared separately in separate beakers by dissolving required amount of pyrrole and ferric chloride in deionized water. The pyrrole and $Fecl_3$ concentrations in the bath are 0.1M and 0.2M respectively. Material to liquor (M: L) ratio is kept equal to 1:20 for both the bath. The fabric samples are first dipped into the monomer solution for 10 minutes at room temperature (22°C) with mild stirring so that pyrrole molecules get adsorbed onto fiber surface. After that, pyrrole enriched fabric samples are taken out from the monomer bath and dipped into oxidant bath for 60 min keeping inside a cryostat at 5°C. As a result, oxidative in-situ chemical polymerization takes place and adsorbed pyrrole molecules are converted into greenish back polypyrrole molecules. Then the polypyrrole coated fabrics were taken out of the oxidation bath and thoroughly rinsed and allowed to dry at room temperature (27°C and RH of 65%) for 3 days. All the fabric samples are converted in greenish black color which is the color of polypyrrole.

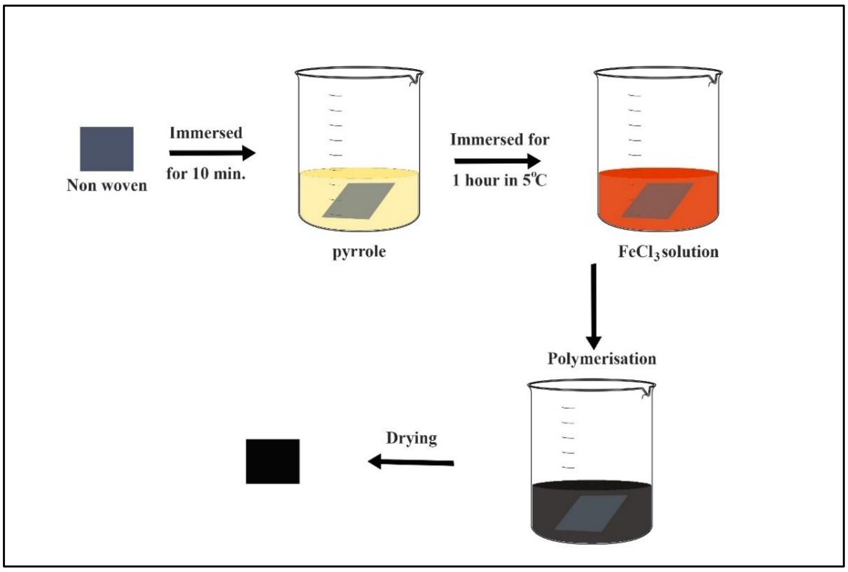

Figure 1- In situ Polymerisation process

2.3 Preparation of Textile-Thermocouple

Thermocouple is a combination of two joined dissimilar metals kept at different temperature. Depending on the temperature difference between two junctions, voltage generation in the thermocouple circuit will be observed. In place of metal, the Polypyrrole coated electro-conductive fabric is coupled with copper wire as shown in Figure 2. Here the dimensions of the fabric samples taken are 2 cm × 6 cm, and the copper plate dimensions are (2 × 4) cm. Then, fabric samples are triple layered for a considerable thickness and resistivity. Fabric samples are gripped between the copper plate (bended in the middle to cover both side of fabric) at both ends. Copper wires are connected at both ends for easy connection to the further instruments.

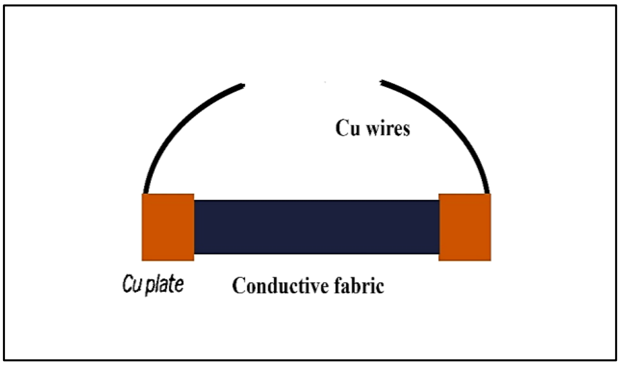

Figure 2 - Preparation of textile thermocouple

2.4 Measurements Polypyrrole Add-on percentage on fabric

Samples are weighed before and after the in situ chemical polymerization. In order to measure the add-on % of the coated fabrics accurately, fabric samples are dried properly at room temperature before coating to reduce the influence of moisture on add-on%. And then the weight of the fabrics is measured, also the same procedure was carried out to measure the weight of fabrics after the polymerization process. The percentage weight increases or weight add-on% (W %) is calculated by using Equation (1).

$$W\% = \frac{W_f - W_i}{W_i} \quad (1)$$

Where, *Wi* - Initial weight and W_f - Final weight

2.5 Surface resistivity of Polypyrrole coated Spunlace fabric

The surface resistivity was measured as per AATCC 76-2005 standard and using a concentric ring electrodes setup where, R_1 is the outer radius of the center electrode, R_2 is the inner radius of the outer ring electrode, as it is shown in Figure 3. It is important to remember that when testing the surface resistivity (or resistance) of any material, it is assumed that all the currents flow between electrodes along the surface and do not penetrate into the bulk of the material. In order to ensure that the surface currents are measured properly, some more advanced techniques for surface resistivity measurements have been developed.

The value of surface resistance is given by $R_S = \frac{\rho_S}{2\pi} \ln(\frac{R_2}{R_1})$, Where, R_S is the surface resistance, ρ_S is the surface resistivity (obtained from literature part) or $\rho_S = R_S \cdot K$, Where K is constant value. So, the unit of surface

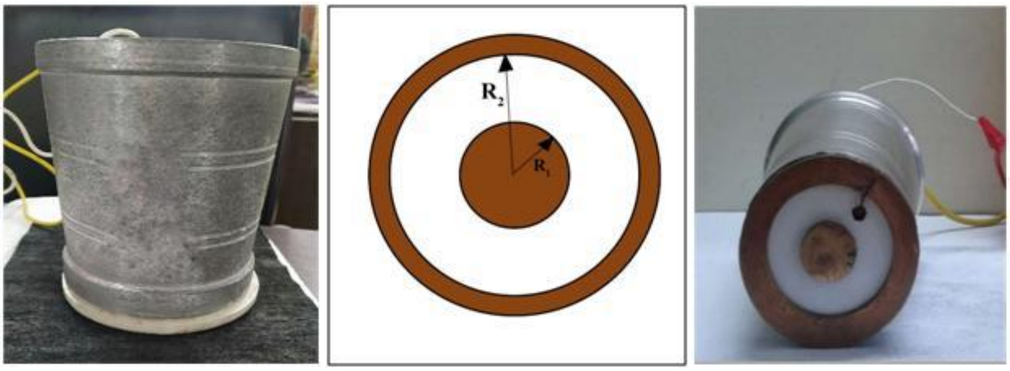

Figure 3 - Surface resistivity measurement setup

2.6 V- I characteristics

The prepared sample shows the electrical conductivity, so the fabric prepared is connected to a D.C. voltage supplier. The voltage is supplied up to 30 V across the coated fabrics and corresponding current flows across the fabrics are measured.

2.7 Thermoelectric effect measurement

For measuring the thermoelectric effect of conductive fabric samples, one end of the textile thermoelectric was kept at room temperature and other end was kept at variable temperature with the help of heating element. Thermal image camera is used to measure the temperature difference between the junctions. A microvoltmeter is being used for measuring the generated e.m.f.

Here the setup for the measurement of thermoelectric effect is given in Figure 4. And the left side junction is at low temperature (cold junction) and rightside junction is heated (hot junction).

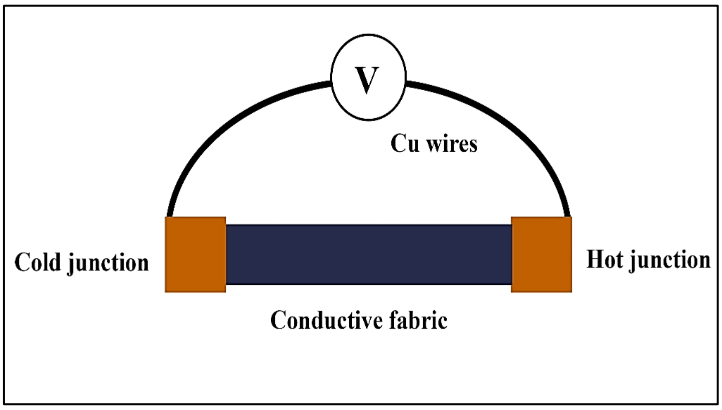

Figure 4 - Thermoelectric effect measurement setup

3. Result and discussion

3.1 Add-on percentage of Polypyrrole on fabric

100% polyester, 100% viscose and 50/50 polyester-viscose are coated with polypyrrole and the weights before and after the polymerization are recorded, add-on values are calculated and the results are shown in Figure 5. 100% viscose fabric shows the highest add-on percentage of 11.11%. This is due to the high absorbency viscose fiber, with high amorphous area and irregular cross-section of the fibers.

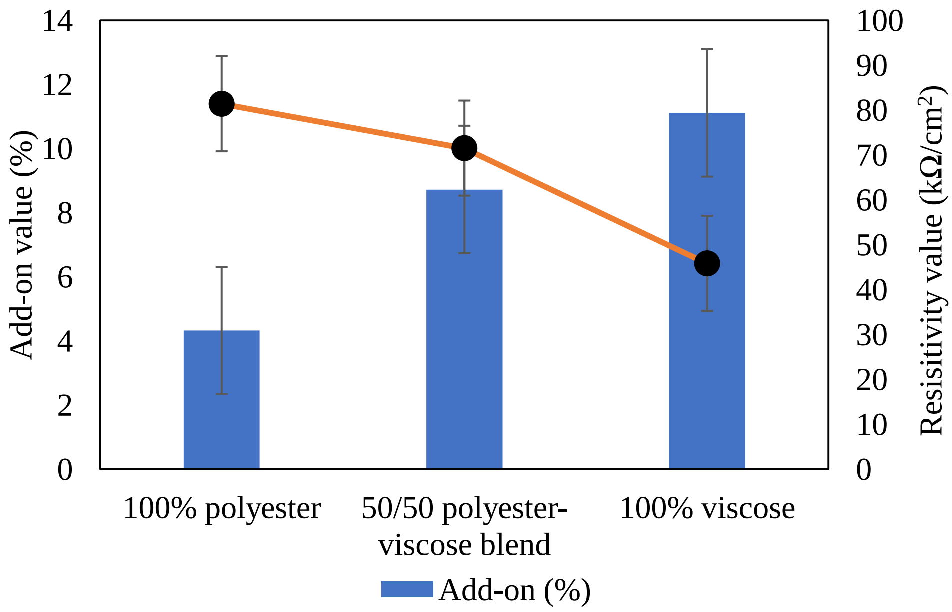

Figure 5 - Add-on percentage and surface resistivity of PPy coated spunlace nonwoven fabrics

3.2 Surface resistivity of PPy coated Spun lace fabric

The surface resistivity of all fabric sample is measured using concentric ring electrodes and the results are shown in Figure 5. The value of surface electrical resistivity for 100% viscose fabric is found to be 45.83 kΩ/cm^2, which is lowest among all these three fabrics. Least resistivity of viscose nonwoven is due to highest polypyrrole add-on.

3.3 V – I Characteristic

The prepared sample shows the electrical conductivity, so the fabric prepared is connected to a D.C. voltage supplier and current flows across it is measured. The voltage is supplied up to 30 V and the variation in current flows across the 100% viscose sample is plotted in the graph (Figure 6). Here the voltage – current (V-I) characteristics of 100% viscose fabric is only shown as its performance is best among 100% polyester and polyester/viscose blended (50/50) fabrics. From figure 6, it is clear that the V-I characteristic is non-linear unlike Ohmic conductor. So, the fabric has non-ohmic electrical properties like inorganic thermo-electric materials.

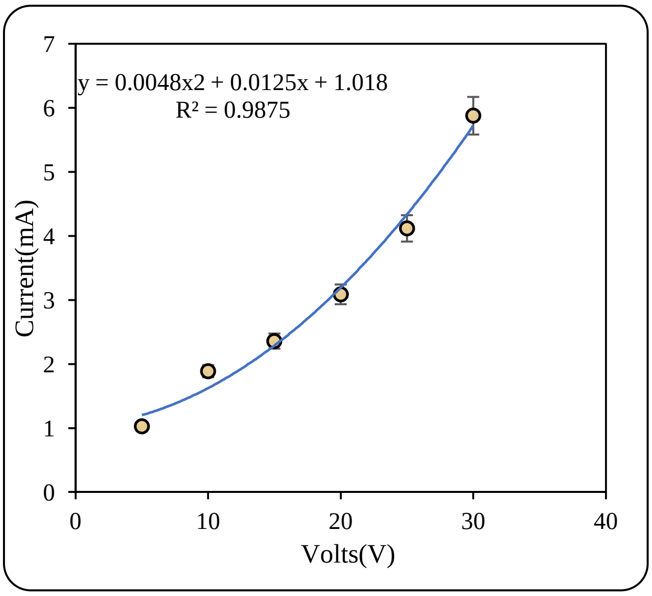

Figure 6 - Voltage - current behaviour of PPy coated spunlace viscose fabric

3.4 Thermoelectric effect measurement

The emf obtained from PPy coated 100% viscose fabric shows the maximum emf of 0.27 mV/°C. And if the cold and the hot sides are reversed, thermoelectricity will be negative. It is much better result from the previously obtained values from different fabric types which is given in the range of 0.15 mV/°C (E Hu, A kaynak, Y Li, at-el 2005) [13].

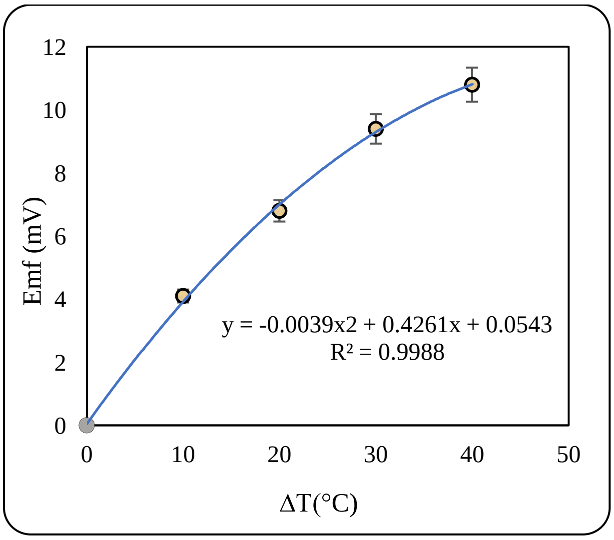

Figure 7 - Thermo-electric effect of PPy coated 100% viscose fabric thermocouple

4. Conclusions

The three different spunlace nonwoven fabrics viz. 100% polyester, 100% viscose and polyester–viscose blend (50/50) are coated with polypyrrole by in-situ chemical polymerization for the evaluation of their thermoelectric performance. Among these three spunlace fabrics, the performance of 100% viscose fabric is found to be best in terms of highest PPy add-on (11.11%), lowest electrical resistivity (45.83 kΩ/cm^2) and highest thermoelectric effect (0.27 mV/°C). The voltage-current (V-I) behavior clearly shows non-Ohmic characteristic of the PPy coated conductor. Unlike inorganic semiconductors such kind of PPy coated textile thermoelectric materials is organic, non-toxic, environment friendly, as well as flexible, wearable, strong and durable. Therefore, such types of textile thermoelectric materials are excellent alternative materials to conventional inorganic materials and can play a big role for conversion of waste heat energy to electrical energy in near future.

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