Effect of weight reduction pre-treatment on the electrical and thermal properties of polypyrrole coated woven polyester fabrics

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Abstract

Weight reduction increased the amount of deposited polypyrrole (PPy) on the polyester (PET) fiber surface, leading to a considerable decrease in electrical resistance and improved heat generation capacity for the PPy coated PET fabrics. Application of DC voltages to an insulated roll of PPy-coated fabric increased the temperature to about 90 ^{o}C. This showed the suitability of these fabrics for heating applications. The optimum PPy deposition of about 2.8% was obtained in samples weight reduced by aqueous sodium hydroxide treatment. AFM images revealed a smooth surface morphology of the untreated fiber whereas the treated fiber had a high surface roughness.

Keywords: Weight reduction, PET woven fabric, polypyrrole coating, electrical properties, thermal properties.

1. Introduction

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In contrast to conventional materials conducting polymers can have conductivity values ranging from 10^{-5} S/cm to 10^{3} S/cm. Polymerization of these materials on textiles enables the production of flexible conductive materials with a wide range of conductivity, structure, mechanical and electromagnetic properties [1-7]. Printing these materials in intricate patterns facilitates the production of intelligent textiles and wearable sensors [8-10]. Specially designed layers of conducting polymer coated fabrics are able to achieve high insertion loss in microwave frequencies and they may be candidate materials for electromagnetic radiation absorbers in wireless applications [3,4].

Conducting polymer coating on fabrics is usually carried out by chemical polymerization techniques via oxidation of the monomer [11]. The oxidant, dopant and monomer solutions can be mixed to form a reactant bath, in which the fabric sample is immersed. The reactants can also be applied to the fabric sequentially. In the latter method the monomer is applied to a preoxidized fabric in either vapor or solution phase. Previous research from our laboratories specifies the optimized conditions for the coating of fabrics and fibers by both solution and vapor polymerization methods [12,13]. Vapor phase polymerization results in conductive coatings with smoother surface morphology. We have also reported direct methods of application of soluble conducting poly(3-alkylpyrroles) on fabrics by hand brushing, dipping, spray painting and printing techniques. Direct application of the polymer on textile surface avoids use of corrosive oxidizing agents. All the conductive fabrics made with the above mentioned methods were compared with respect to surface resistivity, surface morphology, stability and abrasion resistance. These properties were dependent on the coating technique, reactant concentrations, time and temperature of the reaction and on the surface properties of the precursor fabric [14,15]. Effect of atmospheric plasma glow discharge surface pretreatment on the coating fastness was reported in a previous publication [16], emphasizing the importance of the surface morphology and pretreatment of the surface of the substrate fabric on the abrasion resistance of the conducting polymer coating. These investigations showed that treated fabrics exhibited improved hydrophilicity, surface resistivity and abrasion resistance.

In this work, weight reduction of polyethyleneterephthalate (PET) fabric [17] was explored as a new method of improving the electrical and thermal properties of PPy coated PET fabrics. Weight reduction of PET is a well established finishing process that modifies surface properties to improve the handle and drape characteristics of the fabric,

leading to a silky touch and handle. These modifications are the result of the hydrolysis reaction of aqueous sodium hydroxide on PET fibers. Hydrolysis attacks starts at the outer layers of the fibers, working through the center as time, temperature and alkali concentration increase [18]. Hydrolysis leads to dissolution of the outer layer of fibers in a way that a more complex or irregular surface topology forms on the fiber surface. Obviously, the diameter of the fiber decreases accordingly, as the macromolecules on the outer layer are broken by the hydrolysis and the resulting PET oligomers dissolve away in the alkali solution. The study of topological and micro-structural changes as a result of weight reduction of PET fabrics is the subject of another study. The aim of this research was to investigate the effect of the weight reduction process for the precursor PET fibers on the thermal and electrical properties of polypyrrole coated PET fabrics.

2. Experimental

A 100% PET woven fabric (170 g/m^2) with an equal warp and weft density of 20 threads per centimeter was used. Warp and weft were of the same type set textured yarn. The weight reduction was carried out in aqueous solution of sodium hydroxide (350g/l) with L:R 20:1 at a temperature of 60 – 65 ºC. Treatment times for 4 samples were 10, 20, 30 and 40 minutes. After weight reduction, coating with polypyrrole was carried out by chemical polymerization of pyrrole on the surface of the substrate. Samples (13 x 17 cm) were first soaked in a solution of 250 ml/l of pyrrole 98% (Sigma Aldrich) in analytical ethanol from Univar containing 0, 4, 8 and 10 g/l para toluene sulphonic acid 98% (pTSA), (Sigma Aldrich) as dopant for 3 minutes. The soaked samples were then rapidly transferred into another bath containing a solution of 250 g/l of ferric chloride hexahydrate (Merck) in ethanol and removed after 3 minutes. The samples were then hung in the fume cupboard until completely dry. During this period, polymerization of pyrrole that already started in the ferric chloride solution bath completed and the color of the fabric turned to a deep black. Four groups of samples were prepared, each containing 4 treated and one untreated sample, adding up to 20 samples in total. The concentrations reported here were optimized after testing with different concentrations of pyrrole and ferric chloride. After overnight drying, the samples were rinsed in copious amount of water until the rinsing bath was clear. The samples were dried in the standard conditioning room at 65% RH and 21 °C. Resistance measurements were

carried out for a period of 10–15 days by positioning two square copper electrodes (6 x 6 mm) separated by 8mm, on the fabrics. The copper plates were fastened to the base of an iron block (total weight = 0.856N). The copper plates were connected to a Fluke 883 III multimeter, from which the average resistance of the fabric (15 readings) was measured.

Atomic force microscope (AFM) images of the fibers extracted from the fabrics were obtained by using a DS 4540 (Danish Micro Engineering) microscope. Rubbing fastness of the samples was tested according to ISO 105 A03:1993 (under D65). The electrical and thermal properties of the samples were investigated by using a DC power supply (Goodwill). Datacolor spectrophotometer was used for measuring the depth of the black color of the coated samples.

3. Results and Discussion

Fig. 1 shows the variation of polypyrrole deposited on the coated PET fabrics versus the weight reduction time. It is seen that weight percent of polypyrrole relative to the fabric weight increases with the hydrolysis time. This is due to the fact that the hydrolysis of PET by sodium hydroxide solution creates an uneven surface topology on the fiber surface [10]. This enables an additional capacity for the deposition of polypyrrole. The amount of pTSA does not seem to influence a trend in the weight percent of PPy deposited.

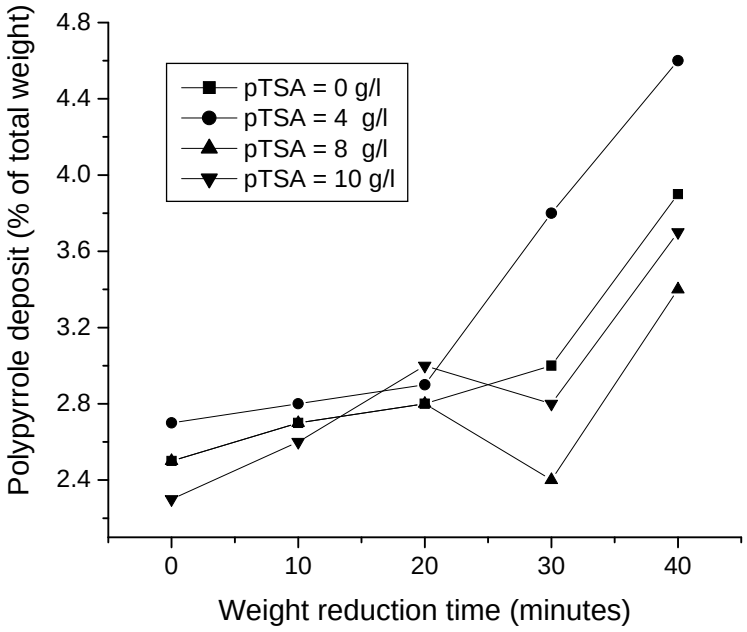

Fig.1 Variation of polypyrrole take-up versus weight reduction time of PET fabric

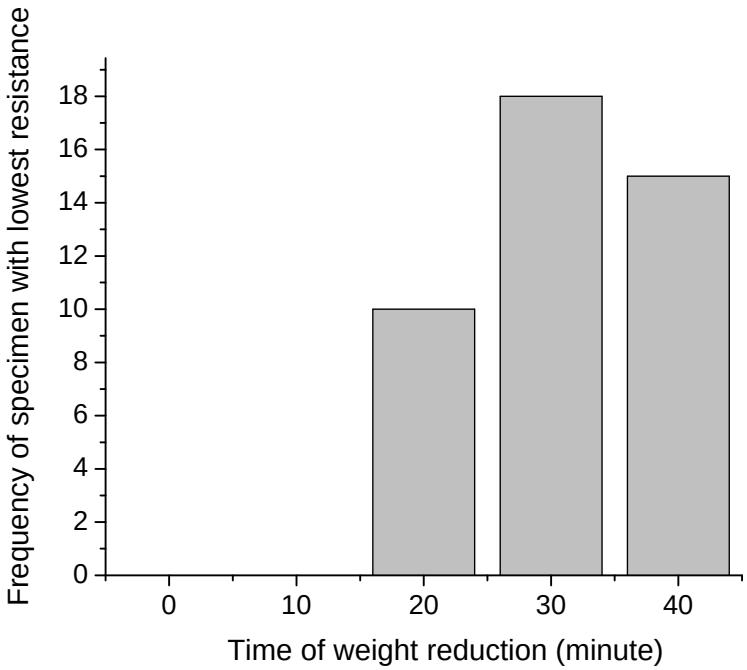

Fig.2 Histogram of the frequency of weight reduced PET fabric specimen with lowest resistance versus weight reduction time

Histogram of the frequency of weight reduced PET fabric samples with lowest resistance versus weight reduction time is shown in Fig. 2. As already mentioned, for all the samples the pyrrole and ferric chloride concentrations were fixed at 250 ml/l and 250 g/l but each group had different dopant (pTSA) concentrations of 0, 4, 8 and 10 g/l. As the resistance of each sample was measured 10 times over a period of about two weeks, 200 data were collected from the fabrics. In other words, for each group, 5 data was available for each day and the minimum was chosen. The total number of minimums in Fig. 2 is over 40 because, in a few cases 2 out of the 5 data for each group per day were equal minimums. The electrical resistance of the samples proved to be very sensitive to small changes in the atmospheric conditions of the conditioning room. As the relative humidity of the conditioning room varied by up to ± 5%, the results fluctuated on a daily basis, but an overall increase in resistance was observed in the course of 15 days. The lowest average resistance value recorded was 352 ohms. In Fig. 3 the histogram of the frequency of the samples with lowest resistance versus percentage of deposited polypyrrole relative to fabric weight is shown. It is seen that the lowest resistance occurs at about 3-4% polypyrrole deposit. The optimum PPy deposition of 2.8% corresponds to a weight reduction time of 30 minutes, in perfect agreement with the results of Fig. 2.

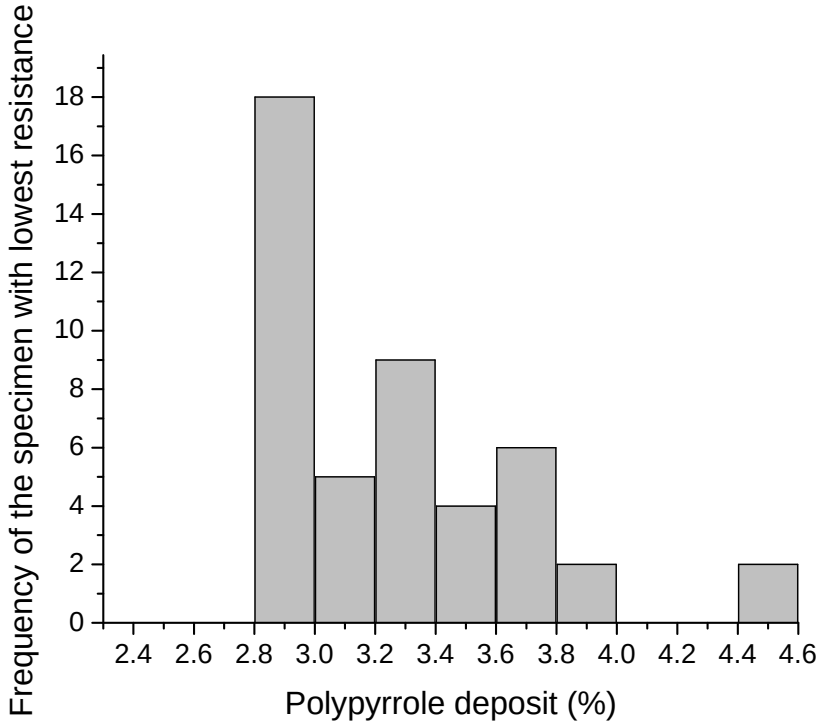

Fig.3 Histogram of the frequency of the weight reduced PET fabric specimen with lowest resistance versus polypyrrole take-up

A highly visible difference between the untreated and weight reduced coated fabrics was the depth of the black color of the deposited polypyrrole. Fig. 4 shows this variation as the lightness versus weight reduction time for the samples treated in solutions of 250 ml/l of pyrrole 8 g/l of pTSA and 250 g /l of ferric chloride. A lower value of lightness shows a darker color or higher depth. As it is seen the depth of black of samples increases with the weight reduction time up to 30 minutes. This is in agreement with Figs. 2 and 3, confirming that 30 minutes was the optimum time for weight reduction for sodium hydroxide concentration used.

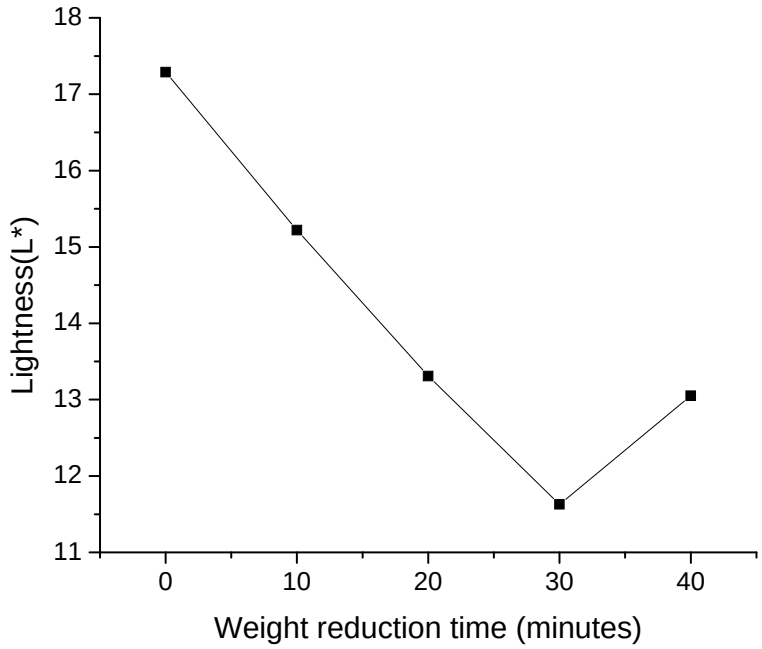

Fig.4 Variation of the lightness of the polypyrrole coated fabrics versus weight reduction time

The effects of weight reduction process on the thermal and electrical properties of the polypyrrole coated fabrics were compared using direct currents. Fig. 5 shows the variation of the temperature of samples versus percent polypyrrole deposited at DC voltages of 15, 20 and 25 V for durations of 5, 3 and 2 minutes respectively for a PPy coated PET fabric. The experiment was conducted on the same fabric by consecutive applications of the potentials mentioned above.

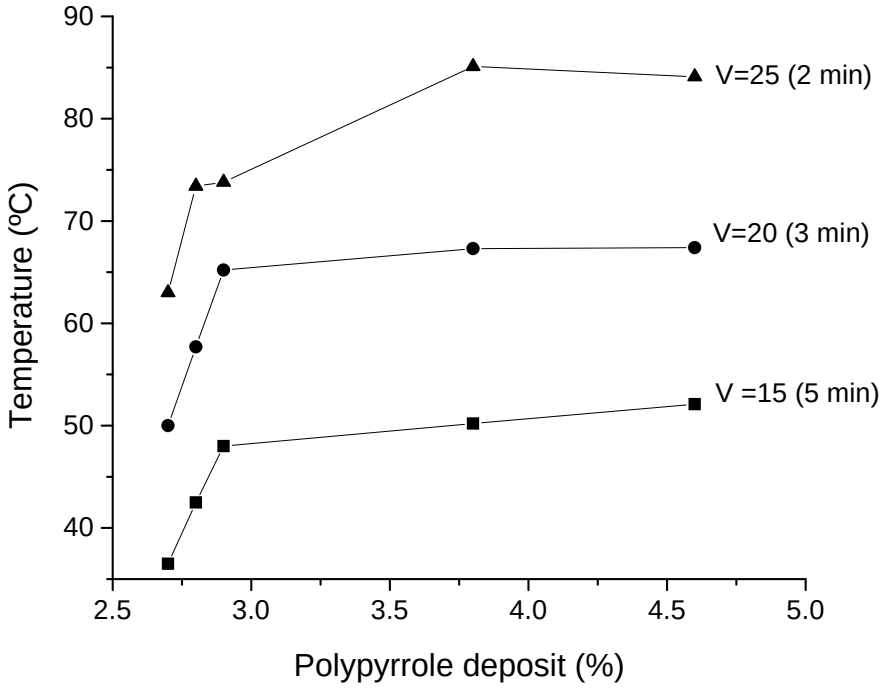

Fig.5 Variation of the temperature (heat generation) of PET fabric versus polypyrrole take-up

The temperature was recorded by rolling each fabric sample around a thermometer, so that thermometer was positioned half way; then the top and bottom of the fabric roll was connected to the terminals of the power supply. The whole roll was insulated by wrapping a wool fabric around it. The current was read from the meter positioned in the circuit and then the resistance calculated. Fig. 5 shows that for 15 volts and 20 volts the temperature rises with the weight percent PPy up to a maxima of 48 °C and 65 ºC respectively at about 3% PPy, followed by a plateau, but with 25 volts, the rise in temperature continues up to 4% PPy, reaching a considerably high temperature of 85 ºC . Fig. 5 demonstrates the capability of polypyrrole coated PET fabrics for heat generation and at the same time the role of weight reduction in increasing the heat generating capacity. Moreover, the much better handle and drape of the weight reduced fabric is an additional advantage. One could design a light garment from polypyrrole coated fabric, which could be heated by connecting it to a light DC battery. Light weight electric blankets could also be made out of polypyrrole coated fabrics.

Fig. 6 shows the variation of temperature of polypyrrole coated weight reduced PET fabric (Weight reduction = 16.4%, Polypyrrole take up = 3%) with time. The

temperature increases with the applied voltage and exponentially with time, reaching a plateau at longer times. Fig. 6 shows the ease with which heat could be generated by employing a reasonable DC voltage.

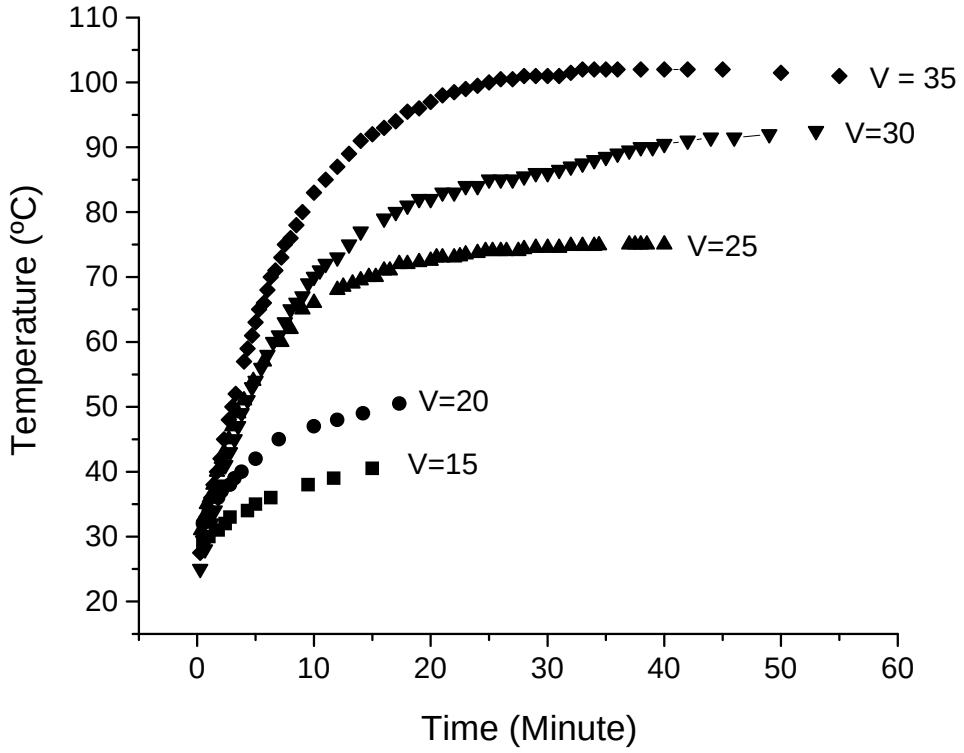

Fig.6 Variation of the temperature of polypyrrole coated weight reduced PET fabric with time (Weight reduction = 16.4%, Polypyrrole deposit = 3%)

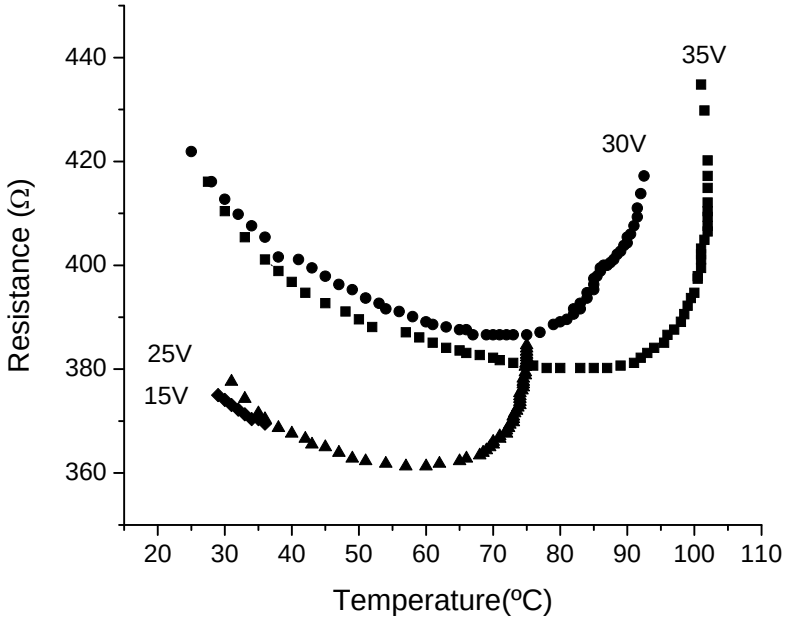

Fig.7 Variation of the resistance of a PPy coated weight reduced PET fabric with temperature (Weight reduction = 16.4%, Polypyrrole deposit = 3%)

Fig.7 shows the variation of the resistance of a weight reduced PPy-PET fabric (Weight reduction = 16.4%, Polypyrrole take up = 3%) with temperature. It must be pointed out that the data for the graphs of Fig.7 were obtained on the same fabric sample, starting from 15 volts and increasing the voltage by steps to 35 volts. It is seen that resistance decreases to a minimum followed by a sharp increase. It is important to note that the minimum starts at a temperature corresponding to the deflection point on the temperature-time curve of Fig.6. The trend in the first part of the graph of resistance-temperature is a decrease in resistance similar to the behaviour of amorphous semiconductors. Further increase in the temperature causes polymer degradation, which is manifested by the increase in resistance. When the same sample is cooled to room temperature to repeat the experiment at a higher voltage level, the starting resistance was observed to be higher than the initial resistance. This cyclic loss of ambient conductivity is attributed to the electrical degradation of the conductive composite. However, the small conductivity loss due to occurrence of short term degradation as a result of heat generated in PPy during the experiments did not have any perceptible effect on the heat generating capacity of the fabrics. Although experiments were

conducted in the environmental laboratory with controlled humidity and temperature, the resistance measurements were highly sensitive to temperature and humidity fluctuations, and this may have caused some overlap in the resistance data.

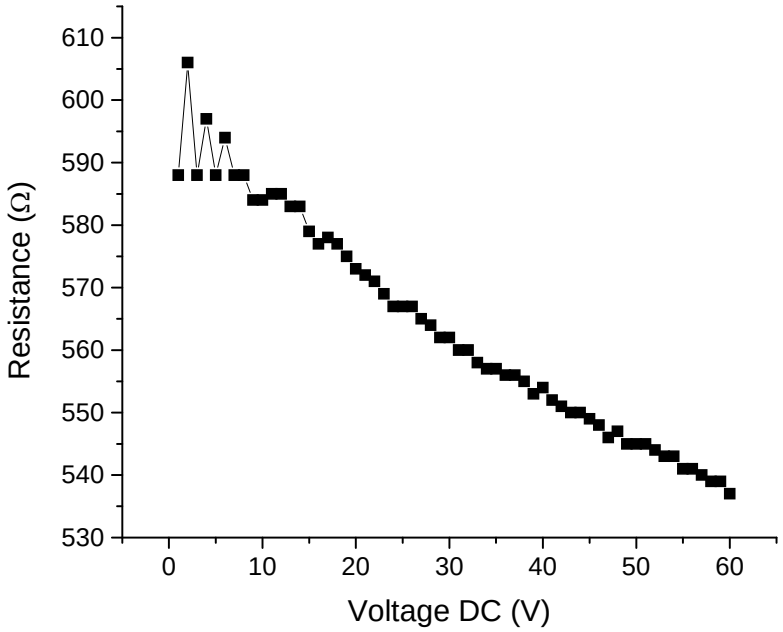

Fig.8 Variation of the resistance of polypyrrole coated weight reduced PET fabric versus voltage (Isotherm - Direct current) (Weight reduction = 16.4%, Polypyrrole deposit = 3%)

Fig. 8 shows the variation of the resistance of polypyrrole coated weight reduced PET fabric (Weight reduction = 16.4%, Polypyrrole take up = 3%) versus direct current voltage in isothermal conditions. To carry out this experiment, two ends of the sample were connected to the terminals of the power supply and the heat generated was blown away by a fan. Again the reduction of resistance with voltage after the initial fluctuations in resistance is unlike that of metals whose resistance remains almost constant with increasing voltage. Increasing the applied voltage increases the temperature of the PPy and hence causes a reduction in resistance. The temperature dependence of DC conductivity is in agreement with the trends in literature [19,20].

Table 2 Rubbing fastness of polypyrrole coated fabrics

Weight reduction time (min)	Thickness (mm)	PPy deposit (%)	Rubbing fastness
0	0.57	2.5	3
10	0.57	2.7	2-3
20	0.56	2.8	2
30	0.55	3	2
40	0.55	3.9	2

The effect of weight reduction on the rubbing fastness was also investigated. The rubbing fastness scale ranges from 1 to 5, where the value of 5 corresponds to the maximum rubbing fastness. Table 2 shows that due to the weight reduction process there is a slight decrease in the coating fastness which may be attributed to the rough surface topology of the weight reduced fabrics with higher coefficient of friction

AFM images of Figs. 10, 11 and 12 show that the topology of the coated fibers varies quite noticeably with weight reduction. The surface of the untreated fiber appeared to be smooth but the surface roughness increased substantially with the weight reduction treatment time (Figs. 10-12). Etching the fibre surface by sodium hydroxide treatment gave rise to a reduced fabric weight and a rough surface morphology, which enabled increased polymer take up by the fabric, reduced fabric/polymer weight ratio, improved heat generating capacity, drape and handle of the conductive fabric.

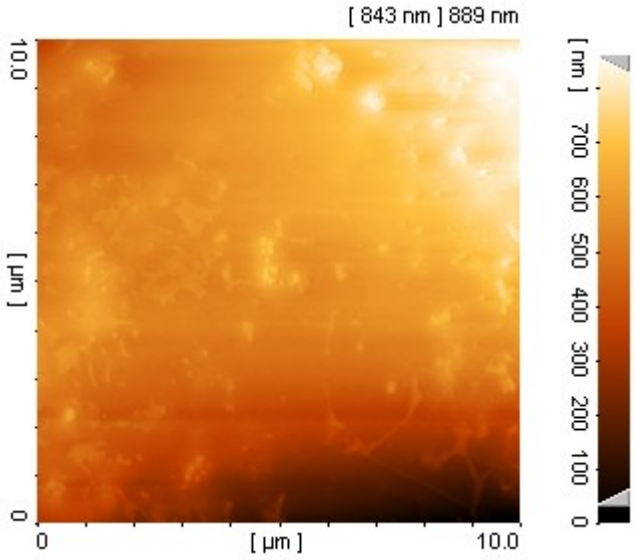

Fig.10 AFM image of polypyrrole coated PET fabric (untreated)

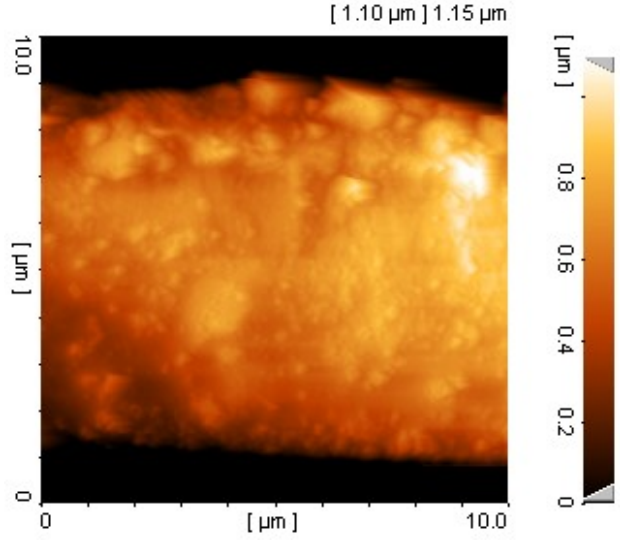

Fig.11 AFM image of polypyrrole coated PET fabric (weight reduction time10 min.)

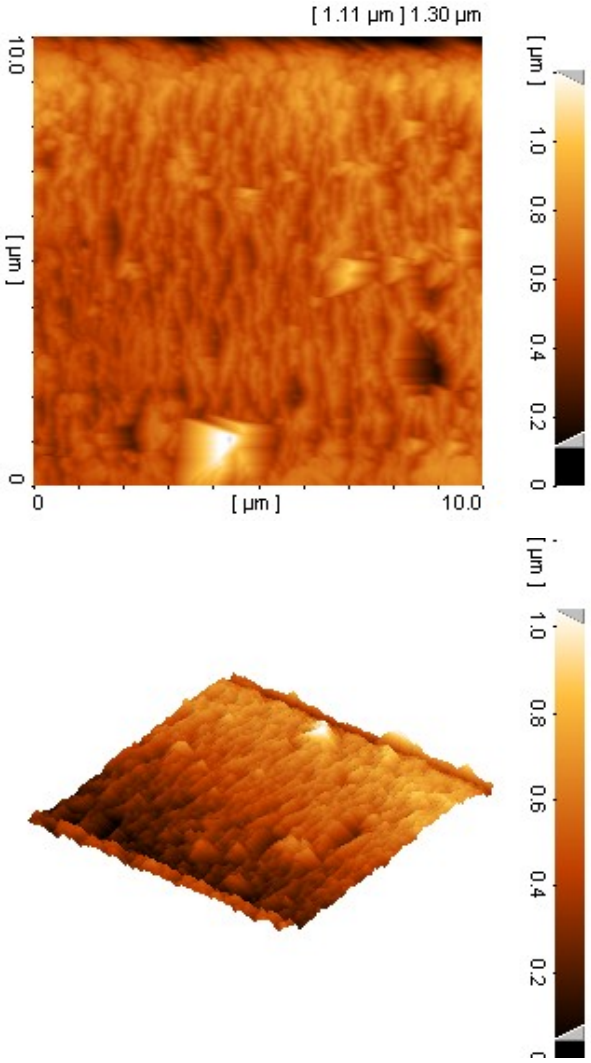

Fig.12 AFM image of polypyrrole coated PET fabric (weight reduction time 40 min.)

3. Conclusion

This research showed that weight reduction of PET fabrics affected the electrical and thermal properties of polypyrrole coated PET fabrics markedly. The amount of deposited polypyrrole on the fiber surface increased as a result of the rough surface topology brought about by alkaline weight reduction. The minimum electrical resistance of the polypyrrole coated fabric occurred when PET fabrics were weight reduced for 30 to 40 minutes. The optimum PPy deposition of about 2.8% corresponded to a weight reduction time of 30 minutes. Weight reduction also led to a deeper black tone of the coated fabrics. The heat generating capability of PET fabrics was also enhanced through

higher polypyrrole deposition, which was caused by the weight reduction process. Temperatures of up to 100 ºC were obtained for an insulated roll of polypyrrole coated fabrics (13 x17 cm). Electrical resistance of the coated fabrics decreased with increasing DC voltage. The rubbing fastness of coated fabrics suffered by half to one grade of grey scale as a result of weight reduction. This was attributed to the increased surface roughness of the fibers.

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