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Investigations on Functioning of Conducting Fabrics for Application in Wearable Clothes

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Abstract: Different natural and synthetic fibers for instance cotton, silk and polyester in the form of the fabric was coated with conducting polymer nanoparticles via in situ oxidative polymerization from an aqueous solution of PANI with suitable oxidizing agent using hydrochloric acid as a dopant by means of an ultrasonic assistance. Each one of these coated fabrics were characterized by Thermal analysis (DSC, TGA), XRD, surface analysis (SEM), mechanical analysis (UTM). The encouraging results accounted in this study unlock new perceptions for potential future application of PANI-coated fabrics, from interactive and smart textiles to innovative conductive textiles for heating end-uses.

***Keywords*:** Conducting Fabric, Electrical Conduction and Heat Generation.

1. INTRODUCTION

Textile materials were introduced to the human kind a decade back just with an intention of producing a look good and feel good material. But beyond this limited envisage utility of the textile material scientists could foresee a platform for an innovative research thus making a route for a new kind of material namely the E- Fabric also known as the Electronic Fabric which deals with the assimilation of electronics in the everyday textiles or fabrics. So, E- Fabric is the convergence of two totally different field’s soft textile materials and much harder electronic field was a real challenge. With the development of this Touchy Feely Technology demand for the smart or more appropriately named intelligent or innovative clothing is on the rise. Until now metallic conductivity was impersonated by inserting either conducting filler in to insulating resin or by coating the plastic insulating substrate with conductive metal solution and electronic capability was built in to these textile fabrics by using several available conducting and semiconducting materials. The challenge of interconnection of two different fields was met with the development of organic conducting polymers that are compatible with the conventional textile materials or fabrics. Conductive polymers proved to be a promising material for producing conducting textiles. These intrinsically conducting polymers [Sudha *et al.* (2013), Sudha *et al*. (2013), Sudha *et al*. (2013)] possess an extended π-conjugation along their polymeric backbone i.e., alternative single and double bond which is an essential condition for charge carriers to move freely and conduct electricity along the chain when doping is carried out.

These synthetic metals offers wide range of remarkable applications as often stated- ‘from buckets to aircraft’ as their electrical conductivity can be tuned. However, the main disadvantage of these materials is that they possess poor mechanical properties so by coating conductive polymers onto textiles we produce materials, which own pleasing mechanical properties of textiles whilst holding the excellent electrical properties. Among conducting polymers, polyaniline (PANI) has received wide spread attention because of its environmental stability and moderate conductivity. The hetero atom –N– present in the polymer chain play an important role in the unique conduction mechanism in PANI. PANI exists in different oxidation states and each state has its own technological importance. In-situ oxidative polymerization of conducting polymers in the presence of textile material produces a long lasting coating of light weight and non-corrosive conducting polymer at the surface of fabric. It has been more recent that these conducting or electronic textiles have been put to some sophisticated application. Current will flow through these fabrics without inclusion of any wiring through them. The incessant conductive film also produces a more even flow of heat than that of fabrics containing wires and the heat production is not concerned with any slashes or tears in the fabric. Heat flow will just be redirected and the heat will still be produced through the conductive film as long as the power supply is sustained. This property would enable applications in the areas of wearable equipment for military, medical and outdoor purposes. Better results were attained when nano-particles were exfoliated as they have higher surface to volume ratio [Boschi *et al.* (2008)]. The impregnation of the conducting polymers in to the fabric matrix does not affect the essential fabric properties such as comfort, strength etc to large extent. This aspect of the conventional textile material or fabric can further be exploited and can be put in to various functional applications. There are several reports of such concepts in the literature. Polyester fabrics have been coated with polypyrrole (PPy) and used for obtaining heat generation textiles when a voltage was applied to the fabric [Wallace *et al.* (2007), Berberi (2014), Bhat *et al.* (2006)].

In the present article we shall be dealing with the heat generating capacity and the general properties of the PANI coated conducting fabrics. Three different fabrics namely cotton, silk & polyester were used and a comparison of their electrical conductivity, mechanical property and heat generating capacity have been made.

2. EXPERIMENTAL

2.1. *Materials*

Aniline, HCl and ammonium hydroxide (CDH chemicals, Mumbai, India), ammonium persulphate (Merck Ltd., Mumbai, India), and distilled before use. All of the textile materials were purchased from a local retail shop. Ammonium persulphate and hydrochloric acid were used as oxidant and dopant respectively. All the solutions were prepared in the deionized millipore water.

2.2. *Preparation of PANI nanofiber coated fabric*

Fig. 1 shows an illustration of in-situ polymerization to form PANI coated conducting fabric. Fabrics were cut in to rectangles of 2.5×3.5 cm. PANI deposition was carried out via in-situ chemical oxidative polymerization in an aqueous solution [4]. Prior to the coating all the fabrics were subjected to thorough cleaning by first rinsing it in ethyl alcohol solution for half an hour on an ultrasonic bath to remove any manufacturing oil or dust adhered to the fabric and thus to improve Polyaniline coating , further washing it with water and then drying it in an oven at 45^{o}C. All three types of the fabrics (cotton, silk, polyester) were immersed at the same time in 0.2 M aniline in 1M aqueous solution of hydrochloric acid and kept on an ultrasonicating bath and stoichiometric amount of 0.2 M aqueous solution of ammonium peroxodisulphate was added slowly to the reaction mixture. Polymerization starts and a PANI layer uniformly coat the fabrics. The sonication was continued for another one hour so as to have the even coating of the fabric and also to augment the diffusion of the PANI in to the fiber structure of the textile or the fabric. Fabrics were left overnight in the reaction mixture and then rinsed thoroughly in millipore water and dried in an oven at 50^{o}C.

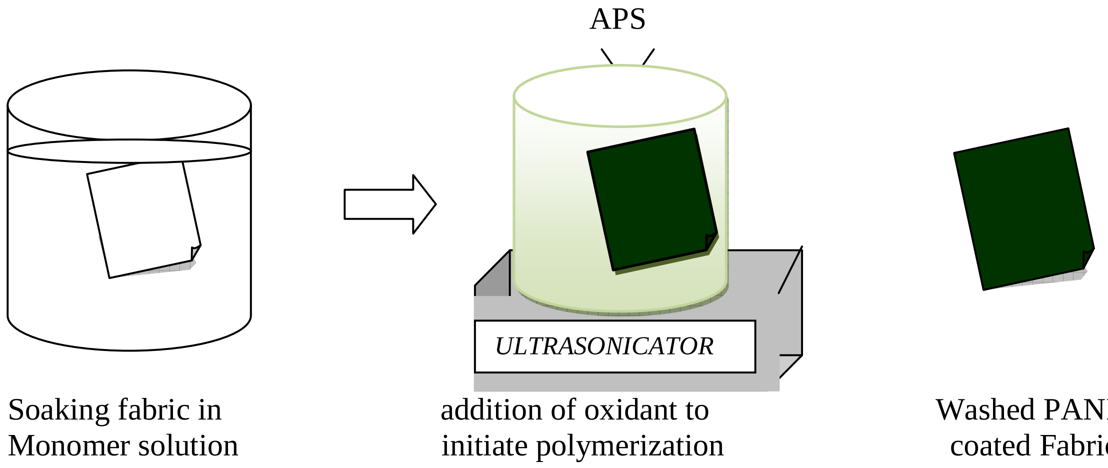

Fig. 1. Illustration of in-situ polymerization to form PANI coated conducting fabric.

2.3. *Weight increment after coating*

The amount of polyaniline (PANI) deposited on to the different fabrics were determined by weighing the fabric before and after the polymerization reaction at room temperature. The percentage increase in weight was calculated as given in equation (1);

$$\% \text{ weight} = [(w_f - w_i)/w_i] \times 100 \quad (1)$$

Where w_i & w_f are the initial and the final weight of the fabric respectively.

2.4. *Durability of fabric*

To assess the durability of conductive fabric to continuous use and maintenance treatment, the samples of PANI coated fabrics were subjected to water washing and soap washing cycles. Drop of conductivity after the domestic washing of these samples were studied.

2.5. *Thermal properties*

Important information regarding thermal stability of these fabrics are obtained from thermogravimetric measurements. TGA of all fabrics were carried out with TGA Q50 instrument (TA instruments), by scanning sample from room temperature to 650^{0}c, at a heating rate of 10^{o}C/min in a cell swept using N_2 during the analysis.

2.6. *Tensile properties*

To evaluate whether coating of PANI on the fabric has any effect on the mechanical properties of the fabrics, tensile properties of the three fabrics were measured by an Electronic Universal Testing Machine (UTM), Instron 3369 at a % sensitivity of 30mm/sec before and after coating.

2.7. *Heat generation*

Schematic set up shown in Fig. 2 was used to measure the heat generating capacity of the prepared conducting fabric [8, 9]. A 9 V battery source was used which was connected to the fabric. Multimeter was used to study the current voltage relationship across the fabrics.

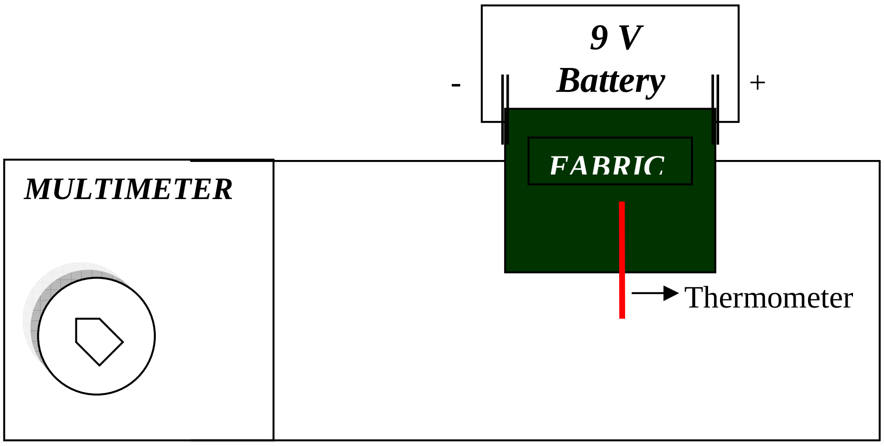

Fig. 2. Diagram of the experimental set up for measuring heat generating capacity of the PANI coated fabric.

3. RESULTS AND DISCUSSION

3.1. *Weight increment after coating*

The generation of conductivity within the matrix fabric is because of diffusion of PANI inside the fibers as well as the coating of a conducting polymer layer on its surface. During the polymerization aforementioned fabrics were 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. 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 it came out to be 9.98% for Polyester, 34.74% for Silk and 4.33% for cotton. The change in weight percentage revealed effective coating of fabric. Since the polymerization is carried out in the acidic medium and this acid may prove to be a deteriorating factor in case of cotton. Since acid can catalyze de-polymerization and cross linking of cellulose molecule in cotton and hence leading to its irreversible degradation. Similarly, in case of synthetic fabric like polyester which contains ester linkage can also be hydrolyzed in an irreversible manner in the presence of strong acidic medium. While silk being composed of amino acids and the fibroin protein of silk is being encased by the outer seracin layer remains protected even after the acid treatment. So, the extent of structural deformation of polymer system of silk is less and the % weight gain after coating is more in silk than other remaining fabrics.

3.2. *Tensile properties*

To reckon whether the coating of PANI on the fabric affects its mechanical and tensile properties, comparison of its ultimate tensile strength (UTS) and % elongation were made. The results were reported in Table-1. Coating of the conducting polymer does not affect the tensile properties to a very large extent. But coating of PANI on cotton fabric lead to loss in tensile strength this may be attributed to the attack of the cellulosic structure in cotton by the acid used during the polymerization. In some cases such as within silk fabric coating can even enhance the mechanical properties. The change in the tensile properties of the fabrics after soap washing was not significantly different. As stated earlier that the polymerization condition deteriorate the cellulosic polymer chain in cotton. So, the reduction in UTS is observed. While no such deformation is observed in case of silk and polyester. A comparison of another very important property Young's modulus also called the modulus of elasticity characterized as the "stiffness" or ability of a material to resist deformation within the linear range has also been made. Young's modulus values are also indicative of the loss of resistance to deformation of fabric on coating with polymer. Major loss in resistance to deformation was observed in case of cotton fabric which is consistent with the visual observance and from other analysis.

Table 1. Tensile properties of coated and uncoated fabrics

S. No.	Sample	UTS (N/mm^2)	% Elongation	Young's modulus (N/m^2)
1	Cotton	11.3	10.7	105.6
2	Coated Cotton	0.4	3.7	10.6
3	Water Washed Cotton	1.3	6.2	21.7
4	Soap Washed Cotton	0.5	2.9	19.3
5	Silk	2.8	14.7	18.9
6	Coated Silk	3.9	53.7	7.2
7	Water Washed Silk	2.4	51.5	4.6
8	Soap Washed Silk	1.6	56.7	2.9
9	Polyester	6.8	20.5	33.1
10	Coated Polyester	4.4	16.5	26.6
11	Water Washed Polyester	3.0	13.2	23.0
12	Soap Washed Polyester	6.4	21.5	7.2

3.3. *Thermal properties*

TGA graphs show that initial weight loss upto 200 ^oC that is due to loss of moisture and dopant. Onset of polymer degradation for silk starts at 360 ^oC, for cotton starts at 265 ^oC and for polyester 340 ^oC and the degradation continuous upto 480 ^oC for silk, 385 ^oC for cotton and 485 ^oC for polyester (shown in fig. 3 to fig. 5). PANI coated fabrics show decreased stability than that of the uncoated fabric which may be due to the breakdown of the PANI backbone but it is possible that PANI coated fiber maintaining the fibrous form exposed to degradation a greater surface as compare with the pure uncoated fabric whichforms a drop when it melts.

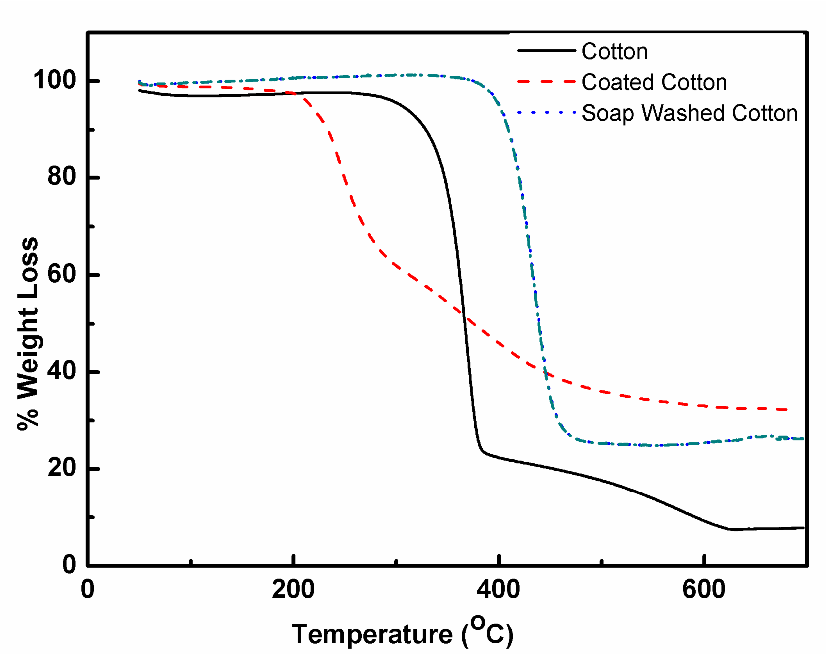

Fig. 3. TGA spectra for cotton fabric before and after PANI coating with soap washing.

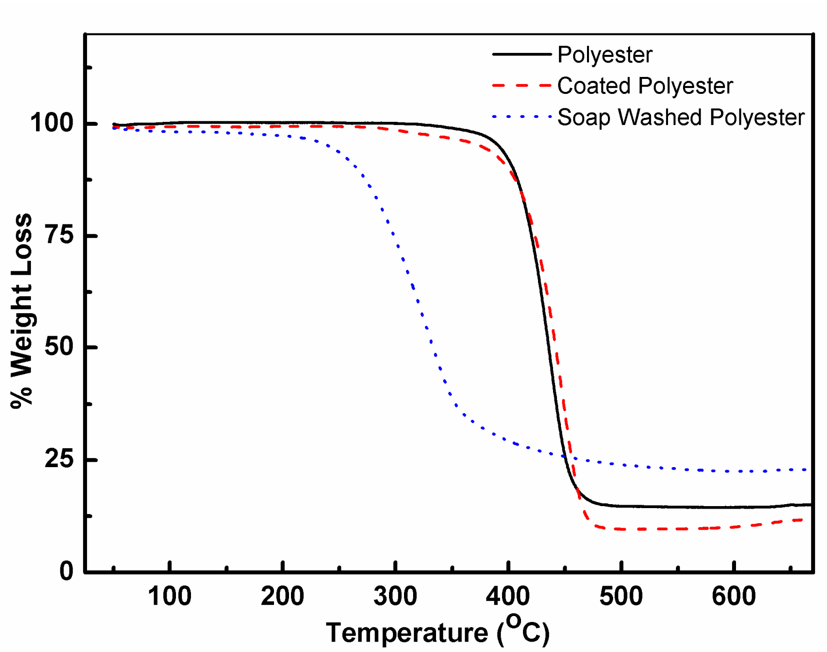

Fig. 4. TGA spectra for polyester fabric before and after PANI coating with soap washing.

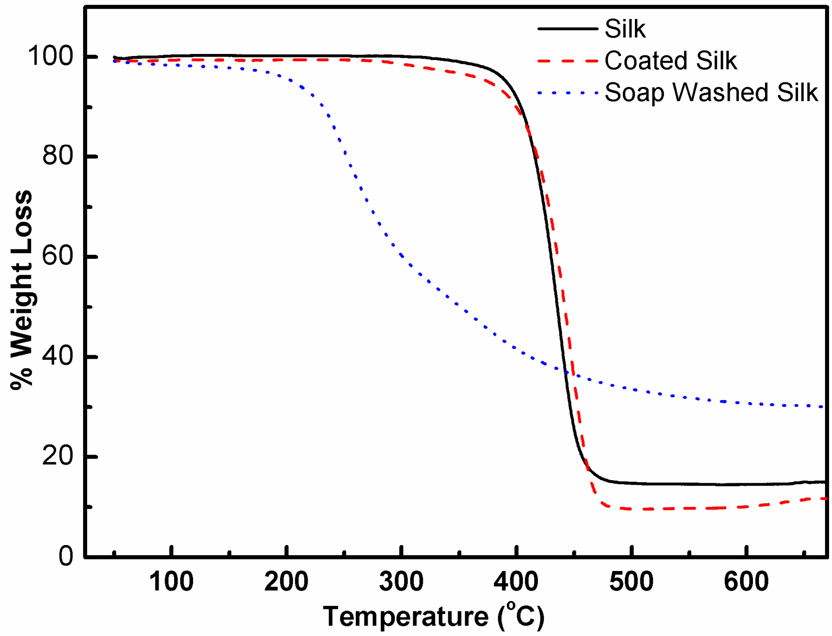

Fig. 5. TGA spectra for silk fabric before and after PANI coating with soap washing**.**

It is observed that water and soap washing increases the stability of the fabric as the unreacted acid and oligomers adhering to the surface of fabric are washed away or neutralized by this treatment simulating better lifetime and stability of the as formed fabric. From the residual char, we can conclude the greater percentage of un-degradable fraction of the sample is observed in case of the soap washed coated fabric. This indicates the greater stability of the soap washed coated samples among all the samples as the alkali present in soap will neutralize the extra acids. Degradation of the soap washed fabrics start at lower temperature than the other samples since soap solution being alkaline causes the fiber filament to swell. This is due to the partial separation of the fiber polymer by the molecule of alkali. Salt linkages, hydrogen bond and Vander-waal forces holding the polymer system of fiber together are being hydrolysed by the alkali leading to the dissolution of the fiber in the alkaline solutions.

3.4. ***XRD***

X-ray diffraction studies were carried out to study the structural effect of diffusion of PANI on the crystalline and amorphous regions of the fabric. The area under amorphous scattering is considerable, and the percent crystallinity was calculated by the method of area measurement by the formula [Sudha and Kumar (2013)] (equation 2);

% Crystallinity = (Area under crystalline peak/ Area under both the peaks) ------------- (2)

When the fabrics were treated with PANI, it was found that there was a change in the diffraction pattern (Fig. 6 to Fig. 8). The percentage crystallinity was found to have decreased from 64 to 34% in cotton, 39 to 24% in silk and 41 to 7% in polyester when fabric was treated with PANI. This shows that diffusion of PANI in the fabric structure takes place and the crystalline region is affected marginally. It is likely that most of the diffusion of PANI is in the amorphous region. This data of amorphous percentage (100 – Crystallinity percentage) in the fibre is also in agreement with the % weight uptake by corresponding fibres. Like cotton fibre with the least % of amorphous regions or high molecular weight and highly crystalline cellulose prevent the forming of PANI oligomer & from penetrating in to the fibre bulk [Sparavigna *et al.* (2010)]. While the silk with maximum % of amorphous region shows maximum uptake of polymer. In Cotton fabric, the peaks in the region of 2θ =14-17 degree have been affected. There is an appearance of additional peak at 17 after coating with PANI.

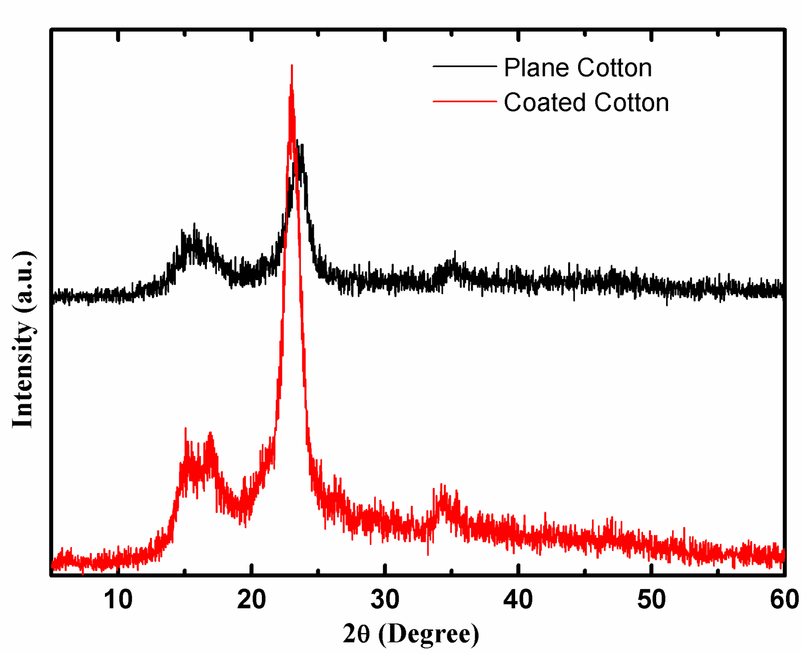

Fig. 6. X-ray diffraction pattern of pure cotton and PANI coated cotton fabric.

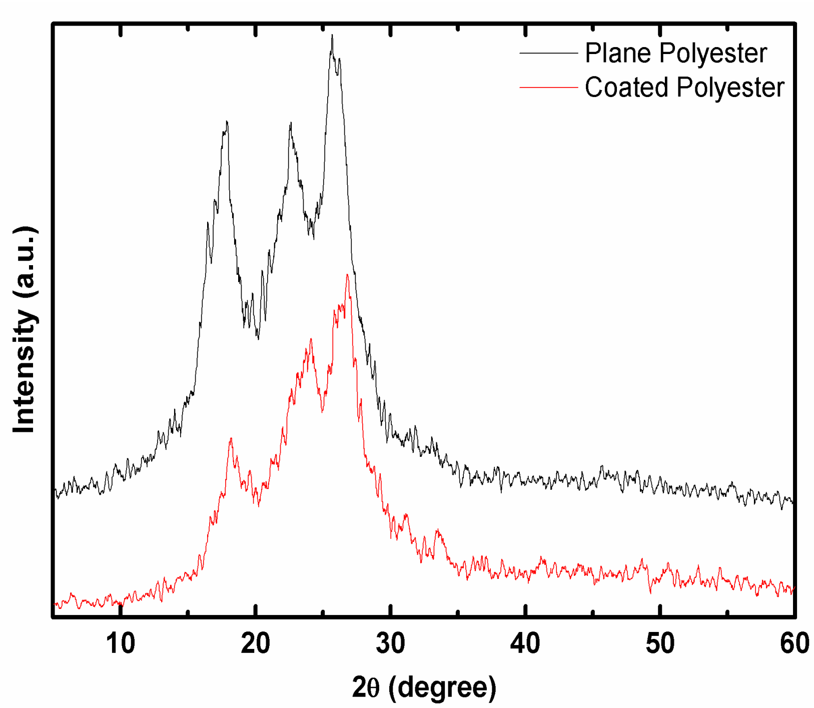

Fig. 7. X-ray diffraction pattern of pure polyester and PANI coated polyester fabric.

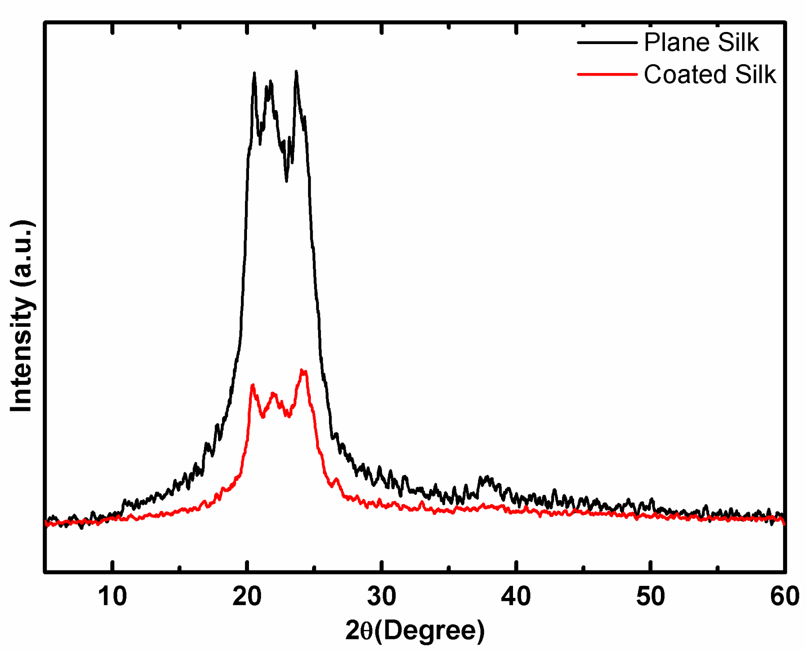

Fig. 8. X-ray diffraction pattern of pure silk and PANI coated silk fabric.

This may be either due to some structural changes induced or due to accumulation of PANI in the cellulose structure. In case of coated polyester fabric, an additional peak at 34 degree is induced due to PANI polymerisation and rest of the spectra resembles as for pure polyester. In coated silk additional peak at 26 and 37 is indicative of coating of PANI on to the fabric.

3.5. *SEM*

The surface structure was investigated by means of SEM studies. It can be seen from Fig. 9, that the surface is coated with PANI.

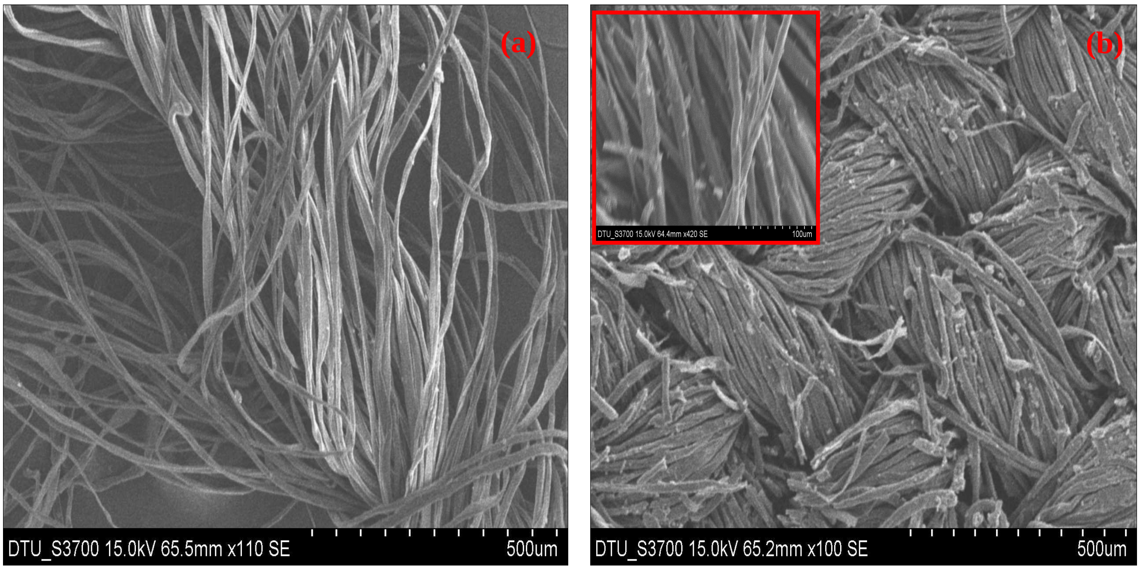

Fig. 9. SEM image of (a) Plane silk fabric; (b) PANI coated silk fabrics.

A good amount of coating with particle sizes varying from 1.0 to 5.0 μ could be seen. Untreated degummed silk fibres are characterized by a very smooth surface. Only a slight longitudinal striation, denoting the fibril structure of fibres, can be observed. After PANI polymerisation, fibres appeared homogeneously coated with a film of PANI seen clearly from the micrographs. At low magnifications one could see heavy depositions within the weaves. When polymerisation began, the deposition of the first layer of polymer onto the fibre surface most likely hindered any further prospect for the monomer to penetrate within. Accordingly, the thickness of the PANI layer increased progressively and resulted in the formation of a PANI-silk composite with a crust-core structure where the protein fibre forms the core and the conjugated polymer as peripheral cover. The behaviour of silk closely resembles that of synthetic fibre like polyester which also demonstrates the formation of a superficial layer of conductive polymer. The feel of the fabrics was noted to be getting harsh/ rough and becoming less supple with increasing percentage of PANI content. The roughness at the surface of fabric after PANI coating is more in cotton than polyester and silk.

3.6. *Durability and heating effect of conducting fabrics*

The evidence of wash fastness of the conducting fabrics was elucidated from conductivity measurement before and after washing. They still exhibit conductivity suitable for static charge dissipation application.

It could be further seen from plot of temperature versus time (fig. 10) that the maximum temperature could be attained in polyester. As the voltage was kept constant during the heating experiment, the steady decrease in current can be attributed to the oxidative degradation of the conducting polymer 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 variation of temperature and current in PANI coated fabrics is like polyester > cotton > silk at constant voltage and room temperature. The variation is dependent upon the % of PANI coating. As the PANI content increased the current also increased. Based upon it, developing heating pads with polyester 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 the persons comfort. It is noted that for such applications the power required is about $50 W/m^2$.

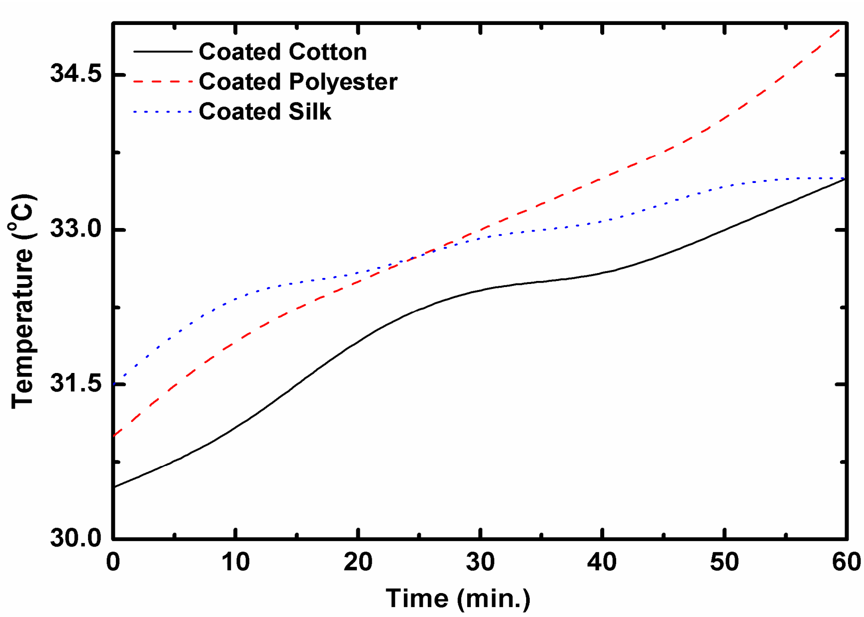

Fig. 10. Variation of temperature with time for the PANI coated during the heating period of 60 min at applied voltage, 9 V.

The results of these examination pointed out that this level of power can be easily generated using a conventional 9-V battery. Further, since the current drawn is very low, the lifespan of battery can be higher. The switch for on/off can be incorporated within the person's attire so that he can utilize the power carefully as per needs. On the basis of good flexibility and sufficient heat generation it was found that polyester coated samples are the best and give optimum performance even after repeated heating/cooling cycles.

4. CONCLUSION

On the basis of these studies it is concluded that Polyester fabrics can be used for higher heat generation out of cotton, silk and polyester with better electrical conductivity. The structural changes accompanied were investigated by SEM, TGA and XRD. 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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