Development of conductive cotton fabric by \textit{in situ} chemical polymerization of pyrrole using ammonium peroxidisulphate as oxidant

Smita C Deogaonkar\textsuperscript{a} & Amol J Patil

The Bombay Textile Research Association, LBS Marg, Ghatkopar (W), Mumbai 400 086, India

Received 16 February 2013; revised received and accepted 6 August 2013

Cotton fabrics have been treated with polypyrrole by oxidative \textit{in situ} chemical polymerization to make them electrically conductive. Ammonium peroxidisulphate is used as an oxidizing agent to overcome corrosion problem caused by ferric chloride. The effect of polymerization duration, monomer concentration, and dopant addition has been studied with respect to conductivity and tensile strength of fabric. Coating of polypyrrole layer is evaluated in terms of electrical conductivity measurement. The conductive fabrics are characterized by HZATR- FTIR characterization and scanning electron microscopic analysis. Addition of dopant is found to improve conductivity of the fabric.

\textbf{Keywords:} Ammonium peroxidisulphate, Cotton, Conductive fabric, Chemical polymerization, Electrical conductivity, Polypyrrole

1 Introduction

Electrically conducting fabrics have been proposed for wide range of applications in electrostatic dissipation, EMI shielding, resistive heating, sensing mechanism and rechargeable batteries\textsuperscript{12}. In view of their numerous applications, the topic has attracted many researchers\textsuperscript{3,4}. At BTRA, electrically conductive fabrics have been developed by depositing intrinsically conducting polymer over the fabric. Conventionally conductive textiles rely on metal base technology, where metallic materials are introduced in the fibre, filament and by coating on textile substrate\textsuperscript{1}. However, these textiles have certain limitations, such as its complex and costly manufacturing process, inflexible property which reduces its handling and comfort properties\textsuperscript{2}. The best possible alternatives for imparting conductivity to textiles are intrinsically conductive polymers (ICP’s)\textsuperscript{3}, carbon nanotubes\textsuperscript{4} and quantum tunnelling composites\textsuperscript{5}. These materials add negligible weight to textiles and retain flexibility and aesthetic property\textsuperscript{6} among these; ICP’s have simple chemistry, lower cost of preparation and are easy for synthesis\textsuperscript{7}. These ICP’s posses alternate single and double bonds in their structure and become electrically conductive\textsuperscript{8,9}. A number of ICP’s are available, viz. polypyrrole, polyaniline and polythiopene for this purpose. Polypyrrole is the most favoured one for producing high electrical conductivity to fabrics due to its environmental stability, solubility, and ease of synthesis\textsuperscript{10}. The inclusion on textile substrate with special synthesis conditions and polymerization kinetics has been discussed in literatures\textsuperscript{7,8}.

In the present study, polypyrrole coated cotton substrate has been developed by oxidative \textit{in situ} chemical polymerization. The reaction involves addition of acidified solution of pyrrole as monomer and ammonium peroxidisulphate (APS) as oxidant in two single steps in same bath containing textile substrate. This process allows uniform deposition of polypyrrole (PPy) on textile substrate. This electrically conductive PPy coated cotton fabric is then characterized by Fourier transform infrared (FTIR) analysis and scanning electron microscopy (SEM). Electrical conductivity and mechanical property (tensile strength) results are compared with PPy coated fabric using FeCl\textsubscript{3} as oxidizing agent.

2 Materials and Methods

Pyrrole (99\%) used as monomer was obtained from Merck, India and used after distillation. Ammonium peroxidisulphate used as oxidant was obtained from Merck, India. Anthraquinone-
2-sulphonic acid sodium salt (AQSA) was procured from Sigma Aldrich and used as additional dopants. Plain weave cotton fabric was scoured before use.

2.1 Preparation of PPy Coated Cotton Fabrics

In situ chemical polymerization of pyrrole on cotton fabric was carried out in laboratory grade jigger machine. The cotton fabric was scoured and then cut along warp way (7cm x 110cm) direction to obtain 10 (+/- 0.1) g weight sample. The aqueous solution of pyrrole was prepared in hydrochloric acid. Dopant AQSA was also added to monomer solution with 1:0.2 molar ratio. The treatment time of fabric with monomer solution was set for 1h. Then pre-cooled, aqueous solution of ammonium peroxidisulphate was added drop-wise in same bath with varying duration. The monomer to oxidant ratio was varied. The complete reaction was carried out at a temperature of 4-5°C. Final fabric-to-liquor ratio was maintained at 1:40. After completion of treatment, fabric sample was removed, washed and rinsed with dilute HCl and dried over night.

The electrical conductivity (Siemens/meter) of PPy coated cotton fabric was evaluated by reciprocating surface resistivity. This surface resistivity (ohm/square) was measured by two probe method according to AATCC-76:2005 standard. The electrically conductive PPy coated cotton fabric was characterized by Fourier transform infrared (FTIR) in ATR mode on Perkin-Elmer 2000. Its morphological and mechanical features were analysed by scanning electron microscopy (SEM) and the tensile strength (in warp direction) as per ASTM D 5035:06.

3 Results and Discussion

As polypyrrole structure contains alternate double and single bonds, it possesses π electrons. Electrical conductivity in PPy involves movement of positively charged carriers or electrons along polymer chains and hopping of these carriers between chains. During chemical polymerization, partial oxidation of chains leads to formation of positive charges on polymer backbone. The $S_2O_8^{2-}$ anions released by oxidants get settled near positive charges to maintain neutrality of PPy backbone. These anions play important role to create conductivity in PPy backbone as they are charge carriers. The large surface area of cotton fabric in reaction bath ensures diffusion of monomer and subsequent growth of polymer chain.

The electrical conductivity of untreated cotton fabric is about $10^{-12}$ S/m. With the application of 10% pyrrole in 0.25M HCl solution on weight of untreated cotton fabric and pyrrole to AQSA(dopant) with 1:0.2 ratio, electrical conductivity of PPy coated cotton fabric is increased by an order of 7 - 8 magnitude. Their electrical conductivity at 2 & 3 h durations of polymerization are $0.000105 \pm 0.00003$ and $0.00014 \pm 0.00004$ S/m respectively. It can be observed that as duration of polymerization increases from 2h to 3h, increase in conductivity is marginal. It implies that the rise in polymerization duration does not improve polymer growth over cotton substrate, in case of APS as oxidizing agent.

The addition of aromatic sulfonic acids makes significant rise in electrical conductivity and stability of PPy. Accordingly, AQSA is selected for doping during polymerization with monomer dopant ratio 1:0.2 for 3 h polymerization duration. It is observed that the inclusion of AQSA results in increase in electrical conductivity to the extent of 6 times $(0.00025 \pm 0.00007)$ to the corresponding value obtained in the absence of AQSA $(0.00003 \pm 0.00001)$. Peculiar positioning of AQSA dopant between PPy chains facilitates interchains charge, which contributes toward high conductivity.

The electrical conductivity of untreated cotton fabric $(10^{-12}$ S/m) is found to be increased to 0.00021 S/m with use of 10% pyrrole on wt. of fabric. This further increases to 0.00085 S/m as the concentration rises to 20% pyrrole on weight of fabric. No further significant increase is observed in electrical conductivity of PPy coated fabric with more than 20% pyrrole concentration.

It was observed that with using ferric chloride as oxidizing agent, conductivity of fabrics achieved corresponds to the presence of Cl dopant ions. The electrical conductivity of untreated cotton fabric $(10^{-12}$ S/m) increases substantially at 10% pyrrole concentration, which further increase up to 20% concentration and reaches a saturation level for 30% concentration. This rise in electrical conductivity is substantailly large when it is compared to present study. The electrical conductivity of PPy-FeCl$_3$ coated cotton fabrics for 10 % monomer concentration at 2, 3 and 4 h duration of polymerizations are $0.000368$, $0.000988$, $0.001058$ S/m (Siemens/meter). The electrical conductivity increases to 0.01163, 0.02272 and 0.03030 S/m for monomer concentration of 20% corresponding to 3 durations of polymerization. For
30% monomer concentration, the conductivity values are further increased to 0.03703, 0.05882 and 0.06667 S/m. It can be observed for all the three concentrations of monomer that as the duration of polymerization increases form 2 h to 3 h the increase in electrical conductivity is significant. With further increase in polymerization time to 4 h, the increase is marginal. This can be attributed to the gradual exhaustion of reactants as duration of polymerization increases. Hence, 3 h duration of polymerization is found to be optimum for polymerization in presence of FeCl$_3$, while for APS, 2 h polymerization is sufficient.

It can be deduced by comparing the above data that the electrical conductivity of PPy-coated fabric with FeCl$_3$ as oxidizing agent is higher compared to that with APS as oxidizing agent. In such way, for a chemical reaction, the oxidizing agent decides the rate of reaction. But as this FeCl$_3$ creates the problem of corrosion in the bath to achieve certain extent of conductivity to fabric (10$^{-3}$ Siemens/m), we can replace FeCl$_3$ oxidant by APS.

3.1 FTIR-ATR Characterizations

FTIR studies of untreated cotton and PPy coated cotton fabrics are studied. Most intense peak of cotton is observed at 1027 cm$^{-1}$ corresponding to C-O stretch. Broad C-H stretching band appears at 2840 cm$^{-1}$. The asymmetric bridge of C-O-C peak is observed at 1154.97 cm$^{-1}$. CH wagging and O-H stretching are observed at 1314.74 cm$^{-1}$ and 3252 cm$^{-1}$ respectively. Peak at 895 cm$^{-1}$ corresponds to asymmetric out of phase ring stretch.

After deposition of PPy over cotton substrate, additional bands are observed along with the peculiar bands of cotton. The characteristic fundamental vibration of PPy ring is observed at 1544 cm$^{-1}$. The bands at 778.9 and 1284 cm$^{-1}$ are associated with C-N bond and C-H deformation respectively. The C=C stretch is observed at 1640 cm$^{-1}$. Over oxidation of PPy represents the band at 1170 cm$^{-1}$. This confirms the deposition of PPy over cotton substrate.

3.2 Effect on Tensile Strength

Figure 1 shows that there is no significant reduction in tensile strength as the concentration of pyrrole rises from 10% to 30%, and introduction of dopant takes place in polymerization. There is slight drop in tensile strength to the tune of 10% for AQSA doped 10%PPy coated fabric. But as this concentration of pyrrole rises it increases to its initial strength. Hence, polymerization of PPy on cotton substrate can be carried out in presence of AQSA dopant, without any significant deterioration in strength.

In case FeCl$_3$ used as oxidizing agent, it is found that at higher concentrations of pyrrole (20% and 30%), there is decrease in strength in the range of 17-24% (Fig. 2). This loss can be attributed to the fact that oxidative degradation of cotton could also have played a role, as ferric chloride is a strong oxidizing agent.

3.3 Surface Morphology of PPy Coated Cotton Fabric

SEM images of untreated cotton fabric and polypyrrole coated cotton fabrics with 10% pyrrole concentration with and without dopant addition are shown in Fig. 3.

Control cotton fibres are smooth and cylindrical. With in situ chemical polymerization the amount of polypyrrole diffused on to fibre structure increases. Figures 3 (d) and (e) shows that the polymerization of pyrrole on cotton fabric takes place through diffusion of polymer inside fibre bulk as well as deposition on the fibre surface and in to the interstices.

Fig. 1—Effect of polymerization on warp-way tensile strength of PPy coated fabric using APS-oxidizing agent at different concentrations of pyrrole

Fig. 2—Effect of polymerization on warp-way tensile strength of PPy coated fabric using FeCl$_3$-oxidizing agent at different concentrations of pyrrole
of fabric. SEM images reveal that due to the addition of dopant-AQSA there is more uniform deposition of PPy on cotton substrate as compared to absence of dopant.

4 Conclusion

Electrically conductive PPy coated cotton fabric can be prepared by in situ chemical polymerization with using ammonium peroxidisulphate as oxidant. The electrical conductivity of untreated cotton substrate can be decreased to $10^{-3}$ Siemens/m from initial value $10^{-11}$ - $10^{-12}$. Hence, it is suitable for application area of static protection. The FTIR and SEM studies prove deposition of PPy on cotton substrate. Under the studied reactant concentration, it can be concluded that, as concentration of monomer rises conductivity increases up to certain extent (20% PPy on weight of fabric), beyond which there is no considerable increase in conductivity. Experimental study confirms that the addition of dopant improves conductivity of PPy coated cotton. The effect of polymerization reaction on tensile strength of fabric is found negligible, reflecting innocuous nature of the treatment. Ammonium peroxidisulphate can be used as oxidant to carry out the in situ chemical polymerization of pyrrole. However, it gives poor adhering of PPy on cotton substrate.

References
11. Hyperphysicsphyastrgsuedu/hbase/electric/resis.html (assessed on March 2012).