

Characterization of Conductive Polypyrrole Coated Wool Yarns

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Abstract: Wool yarns were coated with conducting polypyrrole by chemical synthesis methods. Polymerization of pyrrole was carried out in the presence of wool yarn at various concentrations of the monomer and dopant anion. The changes in tensile, moisture absorption, and electrical properties of the yarn upon coating with conductive polypyrrole are presented. Coating the wool yarns with conductive polypyrrole resulted in higher tenacity, higher breaking strain, and lower initial modulus. The changes in tensile properties are attributed to the changes in surface morphology due to the coating and reinforcing effect of conductive polypyrrole. The thickness of the coating increased with the concentration of p-toluene sulfonic acid, which in turn caused a reduction in the moisture regain of the wool yarn. Reducing the synthesis temperature and replacing p-toluenesulfonic acid by anthraquinone sulfonic acid resulted in a large reduction in the resistance of the yarn.

Keywords: Polypyrrole, Wool, Tensile, Electrical, Moisture, Morphology

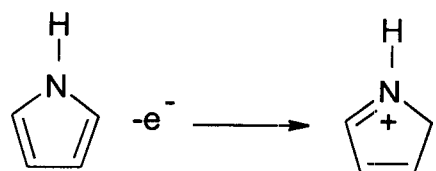
Introduction

Electrically conductive polymers have attracted a great deal of interest because of the variability of their electrical properties and the sensitivity of these properties to external effects such as radiation, temperature, and chemicals. Conducting polymers have the unique property of wide ranging modulation of their electrical conductivity. They can be synthesized with any conductivity value, from insulating to highly conductive, by incorporating specific concentrations of dopant counterions during polymerization. However, fabrication of conductive polymers into useful articles has proved difficult due to their unprocessability and poor mechanical properties. These drawbacks can be overcome by coating textile substrates with conductive polymers. Thus the desirable electrical properties of these materials can be combined with the strength and flexibility of the textile substrates to produce electrically conductive fabrics that can be used in a wide range of applications.

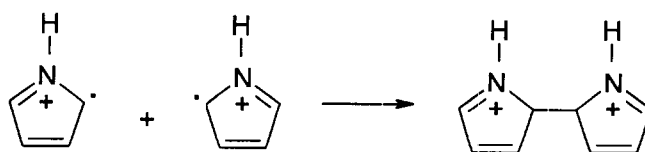
There have been a few publications on conductive polypyrrole coated fabrics[1-3]. However, there are no reported data on conductive polymer coated fibers and yarns. In most of the reports, coating was achieved by chemical polymerization in the presence of the substrate, which was exposed to an oxidizing agent, monomer and dopant simultaneously or sequentially following a particular recipe. The reaction is initiated by the oxidation of monomer into radical cations, which combine to form dimers. Continuation of the process leads to formation of insoluble oligomers in solution, which deposit on the surface and interstices of the textile fibers and fabrics. Due to low oxidation potential of pyrrole, a wide range of oxidizing agents can be used to initiate polymerization. Oxidant salts such as ferric chloride (FeCl_3) function as both the oxidant

and the dopant agent, and hence the polymer is obtained in the conducting form. Other transition metal salts can also be used as oxidizing agents for the polymerization of pyrrole. The transition metal ion is an electron acceptor. Therefore it oxidizes the π -electron system of the pyrrole ring at the initiation step. The intermediate steps of the polymerization of pyrrole initiated by FeCl_3 are as follows:

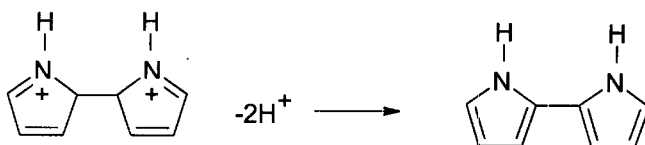
The pyrrole molecule is oxidized to yield a radical cation as follows[4]:



Radical cations recombine to form dication:



Deprotonation of dication to yield a dimer:



The above process continues by oxidation of the dimer to yield a radical cation of the dimer and the combination of radical cations to form trimers, tetramers, and polymers. The

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type of monomer and the dopant anion, concentrations, and synthesis variables such as time, temperature, agitation, and sequence of exposure to chemicals vary among different research groups and each of these parameters has an effect on the electrical, morphological and mechanical properties, and the stability of the resulting material[5-9].

The sensitivity of electrical properties to exposure to gases has led to investigations of the gas sensing ability of conducting polymer-coated textiles. Reversible changes in conductivity of polypyrrole coated textiles upon sequential exposure to certain gases have been observed[10]. In another study on the gas sensing, polypyrrole and polyaniline coated PET fabrics[11] were used in detection of toxic vapours. Detection limits of parts per million were achieved for some pollutants and toxic gases. However, implementation of these fabrics as gas sensors was hindered due to background resistivity changes caused by fluctuating humidity levels. Thus, it is important to characterize the moisture regain and effect of moisture on the electrical properties of conductive polymer coated textiles.

Polypyrrole coated fabrics were tested in the frequency range of 2-80 GHz for microwave attenuation[4]. The fabrics were absorptive of microwaves over the frequency range tested. It was suggested that increasing the coating thickness resulted in higher attenuation of the microwaves. Similar results have been reported in an early study by Kaynak *et al.*[12] on electrochemically synthesized polypyrrole films, in which highly p-toluene sulfonate (PTS) doped films were highly reflective of microwaves whereas lightly doped films were highly absorbent of microwaves, suggesting potential in high frequency applications.

In this paper we report the effects of coating wool yarns by conductive polypyrrole films on the tensile, morphological, moisture absorption and, electrical properties of the yarns.

Experimental

Ring spun 100% wool yarn (88.4 Tex two fold, 396T/M single, 516 T/M folded) was used throughout this investigation. Each yarn sample, 4.5 ± 0.1 g dry weight, was loosely wound and then scoured with an Ahiba Nuance Top Speed dyeing machine. The amount and type of detergent used was 1.0 g/l Solpon 4488, pH control was with 0.75 g/l Sodium Carbonate (Na_2CO_3). Scouring was conducted at a liquor ratio of 11:1 (mls/g of fabric) for 20 minutes at 70°C. The scouring process was conducted to remove contaminates, dirt, and spinning lubricants from the surface of the fibers to help achieve a more uniform coating.

The oven drying method was used for drying yarns according to the American Standard ASTM D1576-84, Standard Test Method for Moisture in Wool by Oven-Drying. The drying temperature was set to 105°C.

Dilute solutions of pyrrole (1.4 g/l) p-toluene sulphonic acid (0.05-4.0 g/l) were prepared. The pyrrole monomer

solution was filtered through aluminium oxide before use. A liquor ratio of 11:1 was used in 50 ml bottles. The wool yarn samples were added at this point, and the bottles were lidded and placed into the 300 ml Ahiba Nuance dye pots. The pots were placed in a rapid rotary dyer and the polymerizations were carried out for 6 hours at 25°C. Agitation was supplied via rotation of the pots at 20 revolutions per minute. Rotation direction was changed every 2 minutes.

After polymerization the samples were rinsed twice at 50°C for 5 minutes at an 11:1 liquor ratio. The samples were hydro-extracted before preliminary drying with a Widdowson hot air dryer.

Electrochemical synthesis was performed galvanostatically in a single compartment cell using aqueous solutions of the monomer and dopant at a current density of 1.5 mA/cm². Pyrrole and p-toluene sulfonic acid concentrations of 0.2 mol/l and 0.01 mol/l were used respectively. The synthesis was carried out at room temperature for a period of one hour.

The coated yarns were oven dried for the coating weight gain measurement using equation (1):

$$\text{Weight gain (\%)} = \frac{W_{\text{Coated}} - W_{\text{Scoured}}}{W_{\text{Scoured}}} \quad (1)$$

where W_{Coated} and W_{Scoured} are the dry weights of coated yarn and scoured yarn respectively.

The coated yarns were then wound on bobbins and conditioned in a standard atmosphere of $20 \pm 2^\circ\text{C}$ and $65 \pm 3\%$ relative humidity.

Electrical resistivity measurements were carried out on the yarns by using a multimeter connected to two gold-coated electrodes separated from each other at a fixed distance of 2 mm. To improve the contact of yarn with the electrodes, a kilogram weight was applied to the yarn. Two measurements were taken at each randomly selected location along the yarn with a pretension of 3.5 g applied to the yarn end before application of the pressure on the electrodes. At least 50 locations were measured for each yarn.

Tensile tests on the untreated and PPy coated wool yarns were performed on a Uster Tensorapid machine with a gauge length of 500 mm and a jaw separation speed of 200 mm/min (AS 2001.2.7, Determination of Breaking Force and Extension of Yarns, Australian Standard Methods of Test for Textiles). A total number of 50 tests were set for each yarn. All tests were conducted at standard atmosphere conditions of $20 \pm 2^\circ\text{C}$ and $65 \pm 3\%$ relative humidity and all samples were conditioned for more than 48 hours before the moisture regain, conductivity, and tensile testing. Tensile testing of electrochemically synthesised polypyrrole films was done by using a Lloyd LS 500 computer-controlled tensile testing machine. The experiments were performed at a crosshead speed of 2 mm/min, at a gauge length of 10 mm, using a 500 N load cell. Polypyrrole films were cut into dog-bone shapes by specially fabricated cutters.

Scanning electron microscopy analysis was performed by using a Leo 1530 Field Emission Gun Scanning Electron Microscope.

Results and Discussion

Tensile Properties of Electrochemically Synthesized Polypyrrole Films

Although polypyrrole films have excellent electrical properties, their main disadvantage is brittleness, which increases with aging. As seen in Figure 1, electrochemically synthesized polypyrrole films tested straight after synthesis exhibit high breaking stress and low breaking elongation. Figure 2 shows the reduction in breaking strain during short-term room-temperature aging of lightly p-toluene sulfonate doped (0.005 mol/l) galvanostatically synthesized polypyrrole films. These films lost around 35% of the breaking strain after ten days of synthesis. This rapid embrittlement is

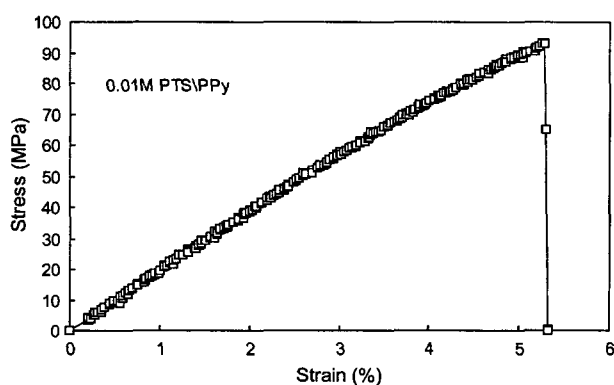


Figure 1. Stress strain curve of electrochemically synthesized polypyrrole film (pyrrole: 0.2 mol/l, p-toluene sulfonate: 0.005 mol/l).

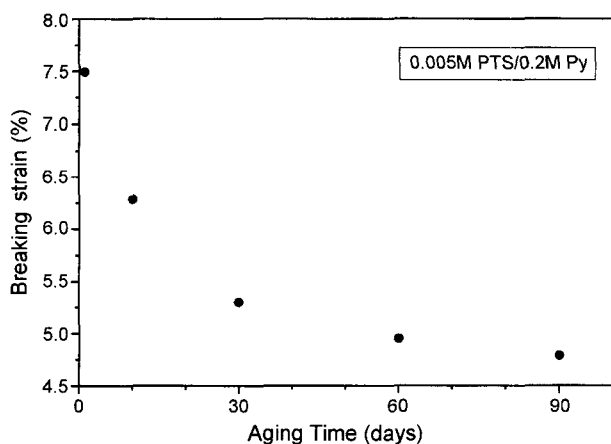


Figure 2. Change in percent breaking elongation with time of lightly p-toluene sulfonate doped polypyrrole film (pyrrole: 0.2 mol/l, p-toluene sulfonate: 0.005 mol/l).

attributed to the loss of the solvent, which has a plasticising effect on the polymer[9]. The disadvantages of brittleness and lack of processibility of these polymers were overcome by choosing wool yarns as a substrate on which the conductive polymer was deposited by chemical polymerization as reported in the following section.

Tensile Properties of Polypyrrole Coated Wool Yarns

Wool is a moderately strong and highly extensible fiber. The elongation of the control yarn was around 28%. Surprisingly, when the brittle conductive polypyrrole was deposited on the wool yarns, elongation at break of the yarns increased by around 17-21% compared to that of the uncoated control sample (Figure 3). This is attributed to the modification of the surface morphology of the wool fibers by the deposition of polypyrrole (Figure 4). The rough nodular morphology of electrochemically synthesized polypyrrole films seems to be absent on the surfaces of wool fibers coated by polypyrrole. The significant effect of the concentration of the dopant anion, p-toluene sulfonate on the

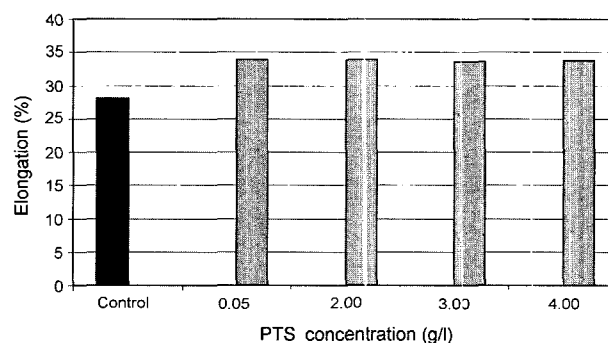


Figure 3. Change of yarn extensibility after coating (pyrrole: 1.4 g/l, ferric chloride: 11.5 g/l).

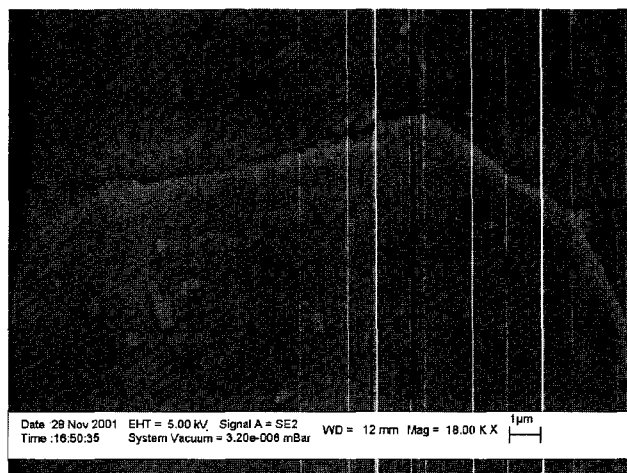


Figure 4. Scanning electron micrograph of polypyrrole coated wool fiber (magnification: 18000X).

surface morphology in electrochemically synthesized polypyrrole films has been reported in a previous publication[13]. The SEM micrographs at magnifications of 1000X showed surface protrusions reaching several microns in the case of highly doped films (0.05-0.1 mol/l)[13]. The lightly doped films (0.001-0.005 mol/l) had a nodular morphology as well, but the film surfaces were smoother[13] compared to that of highly PTS doped films. In the case of polypyrrole coated wool yarns, even at magnifications as high as 18000X there was no apparent nodular growth. The coating did not give rise to bonding between fibers, but a thin layer of conductive polymer was formed on individual fibers, which affected the frictional properties of the fibers particularly by smoothing the sharp edges of the scales (Figure 4). The tactile properties of the yarn were not significantly affected as there was no bonding between fibers. A significant increase in yarn tenacity was obtained upon coating wool yarns with polypyrrole (Figure 5). The increase in the tenacity of polypyrrole coated wool yarns is attributed to the reinforcing effect of the high strength and modulus conductive polymer coating on the fiber, as the free

standing films have high tensile strength. For example, electrochemically synthesized polypyrrole films showed high tensile strength, exceeding 90 MPa, and Young's modulus around 0.5 GPa (Figure 1). The reduction in the initial modulus of the yarns upon PPy coating (Figure 6) may also be attributed to the change of frictional properties of wool fibers due to coating.

The yarn samples were also separately treated with solutions of ferric chloride (oxidant), and p-toluene sulfonic (dopant) acid (PTSA) respectively. The tensile properties of the treated yarns were compared with those of the control yarn. There was no significant change in the yarn tenacity upon treatment with the solutions of the abovementioned chemicals. The average tenacity of the control wool sample and samples treated with solutions of FeCl₃ only and PTSA only were 8.27 cN/tex, 8.20 cN/tex and 8.30 cN/tex respectively. On the other hand, there was a significant increase in the elongation of the yarns individually treated

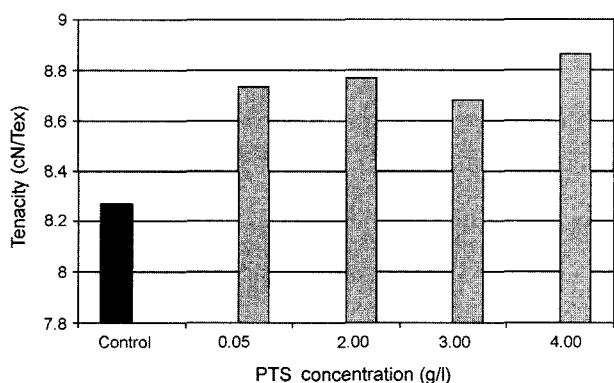


Figure 5. Effect of dopant concentration (p-toluene sulfonate) on the strength of wool yarns.

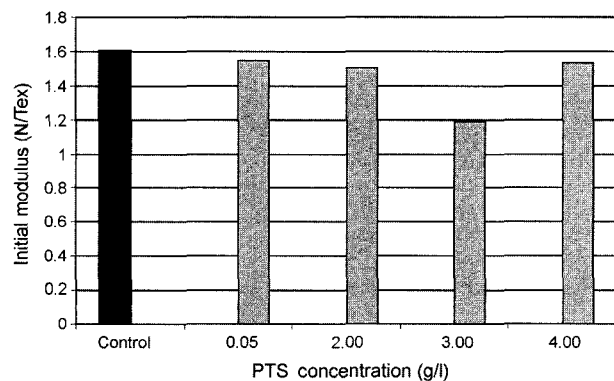


Figure 6. Change of yarn initial modulus after coating (pyrrole: 1.4 g/l, ferric chloride: 11.5 g/l).

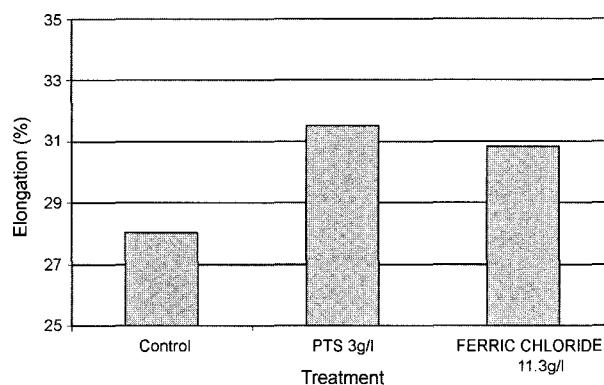


Figure 7. Yarn elongation change under individual chemical treatment.

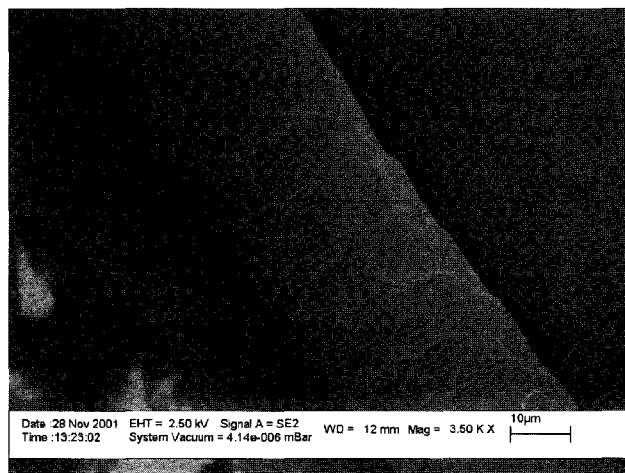


Figure 8. SEM micrograph of the control sample (magnification: 3500X).

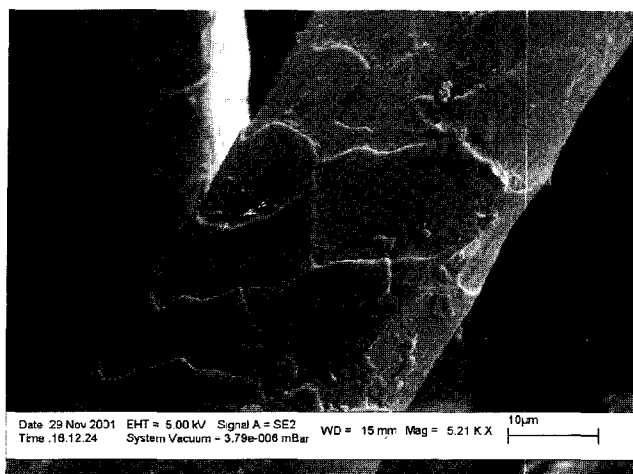


Figure 9. SEM micrograph of the wool fiber treated with FeCl_3 (magnification: 5210X).

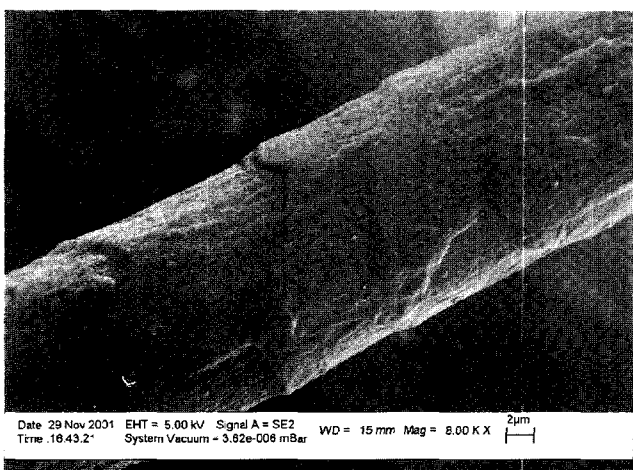


Figure 10. SEM micrograph of wool fiber treated with p-toluene sulfonic acid (PTSA) only. (magnification: 8000X).

with PTSA and FeCl_3 respectively (Figure 7).

SEM micrographs of the control sample, and ferric chloride and p-toluene sulfonic acid treated wool fibers can be seen in Figures 8-10, respectively. The control sample appears smooth (Figure 8), whereas the FeCl_3 (Figure 9) and PTSA treated (Figure 10) fiber surfaces seem to be modified. The sheet-like effect of coating can be seen in the case of PTSA only treated fibers (Figure 10), where the coating seems to have filled in the tips of the scales of the wool fibers, whereas FeCl_3 only treated fibers revealed significant surface damage (Figure 9) with broken scales and fragments of broken scales on the fiber. When wool is treated by p-toluene sulfonic acid solution, the p-toluene sulfonate anions attach themselves to the positively charged amino groups in wool molecules. The weight gain when the wool fiber is exposed just to p-toluene sulfonic acid solution may be

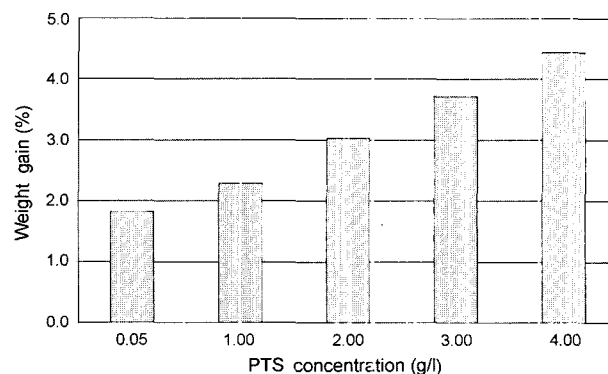
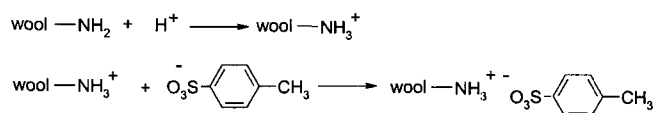
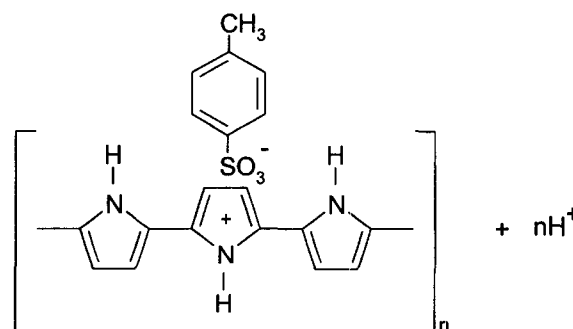


Figure 11. Percent weight gain of wool yarn with the increase in p-toluene sulfonate concentration.

attributed to the molecular attraction between positively and negatively charged groups. First, the amino groups in wool become positively charged by the acid ion. Then an ionic link is formed between the positively charged amino group on wool and the p-toluene sulfonate anion as follows:



Sulfonate anion also attaches itself to pyrrole molecule during chemical polymerization. Oxidation of polypyrrole results in a partial positive charge on the pyrrole ring, which attracts anionic species such as p-toluene sulfonate in order to achieve charge neutrality as follows:



The affinity of sulfonate anions to oxidized polypyrrole can be seen in the chart of percent weight gain of polypyrrole coated wool yarns with respect to p-toluene sulfonate concentration (Figure 11). Similar results were obtained in galvanostatic electrochemical synthesis of polypyrrole films where low PTS concentrations (0.001 mol/l) resulted in thin films (20-30 microns) whereas high dopant concentrations (0.1 mol/l) yielded thicker films (80-90 microns) (synthesis time of 30-40 minutes) with high

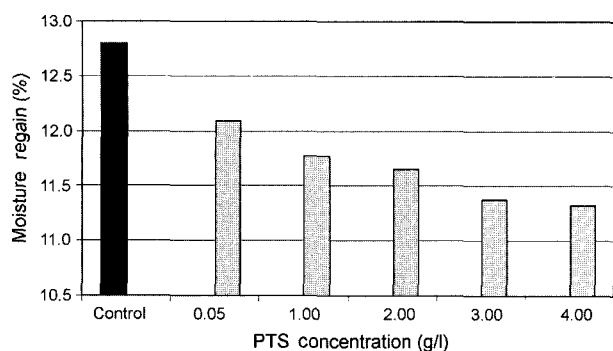


Figure 12. Change of yarn moisture absorbance after coating (pyrrole: 1.4 g/l, ferric chloride: 11.5 g/l).

average surface roughness[9].

Since FeCl_3 is an oxidizing agent it modified the surface of the wool fibers by damaging the epithelial cells (Figure 9). Although PTS and FeCl_3 treatments affect the surface morphology in different ways, the former by coating and the latter by damaging epithelial cells, the overall effect on the breaking strain of both chemical treatments seems to be similar (Figure 7).

Moisture Regain

Wool is a very absorbent fiber due to the abundance of hydrogen-bonding sites on the molecules and relatively lower crystallinity of the wool permits accessibility of the water molecules to these sites. Since polypyrrole is not a hydrophilic polymer, the PPy coating reduces the moisture regain in wool yarns (Figure 12) by forming a barrier to the absorption of moisture by the fiber. As the percent weight gain increased, the moisture regain of the wool yarn decreased. In other words, increasing the coating thickness decreased the moisture regain. Increasing the p-toluene sulfonate concentration not only increased the conductivity of the polymer but also increased the polymer film thickness as the bulky anion attached itself to the partial positive charge on the oxidized pyrrole ring. The treatment of the yarns with ferric chloride resulted in about 10% increase in the moisture uptake. This is attributed to the oxidative damage of the ferric chloride on the epithelial cells.

Electrical Conductivity

Room temperature synthesis with ferric chloride and dilute solutions of p-toluene sulphonic acid and pyrrole resulted in low conductivity yarns with resistance in the mega ohm region. Yarn resistance decreased with the concentration of the p-toluene sulfonate (Figure 13). When the dopant anion p-toluene sulfonate was replaced by anthraquinone sulfonic acid (AQSA), a large reduction in the resistance from $\text{M}\Omega$ region to 10-50 Ω was achieved. During the chemical polymerization, both bulk polymerization

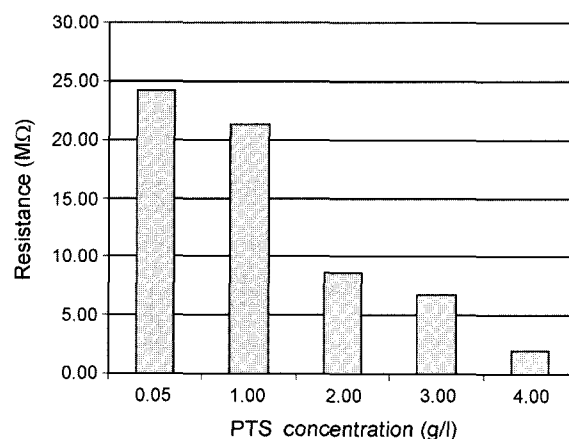


Figure 13. Effect of p-toluene sulfonate concentration on the yarn electrical resistance.

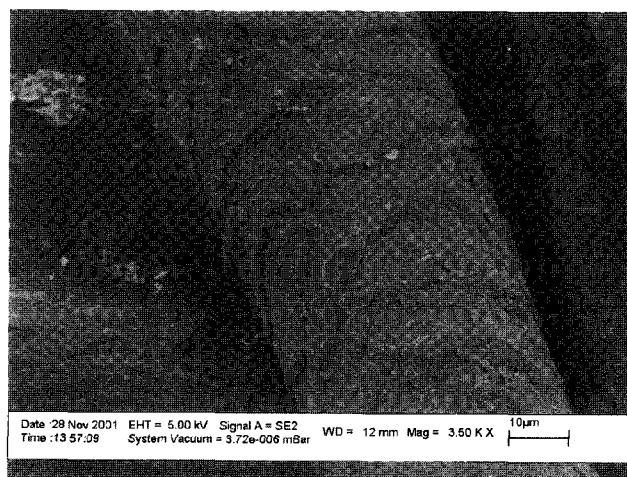


Figure 14. Wool fiber coated with polypyrrole doped with anthraquinone sulfonic acid (AQSA) at 3°C.

(polymers form insoluble precipitations) and polymer deposition on the surface of the substrates occurred. In the case of anthraquinone sulfonic acid, a better yield of surface-deposited conductive polymer was achieved (Figure 14).

Conclusions

Coating the wool yarns with conductive polypyrrole resulted in higher tenacity, higher breaking strain, and lower initial modulus. The tensile properties of electrochemically synthesized polypyrrole films were referred to in order to explain the changes in the tensile behaviour of wool yarns upon coating. Electrochemically synthesized polypyrrole films exhibited high tensile strength and low breaking strain. The changes in tensile properties of the wool yarns upon coating are attributed to the changes in surface morphology

and reinforcing effect of conductive polypyrrole. As a result of chemical polymerization, a thin layer of conductive polymer was deposited on individual fibers, which affected the frictional properties of the fiber particularly by smoothing the sharp edges of scales. The thickness of the coating increased with the concentration of p-toluene sulfonic acid, which in turn caused a reduction in the moisture regain of the wool yarn. Reducing the synthesis temperature and replacing p-toluenesulfonic acid by anthraquinone sulfonic acid resulted in a large reduction in the yarn resistance and improved coating. Wool has proved to be a good choice as a substrate for conductive polymer coating due to the abundance of molecular groups to which the polymer-dopant system can attach themselves through ionic and hydrogen bonds. Moreover, the scalar surface morphology and twisted shape of wool fibers offer sites for adsorption of the conductive polymer.

Acknowledgements

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