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Improvement of Adhesion of Conductive Polypyrrole Coating on Wool and Polyester Fabrics Using Atmospheric Plasma Treatment

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Abstract

In this paper wool and polyester fabrics were pretreated with atmospheric plasma glow discharge (APGD) to improve the ability of the substrate to bond with anthraquinone-2-sulfonic acid doped conducting polypyrrole coating. A range of APGD gas mixtures and treatment times were investigated. APGD treated fabrics were tested for surface contact angle, wettability and surface energy change. Effect of the plasma treatment on the binding strength was analyzed by studying abrasion resistance, surface resistivity and reflectance. Investigations showed that treated fabrics exhibited better hydrophilicity and increased surface energy. Surface treatment by an APGD gas mixture of 95% Helium/5% Nitrogen yielded the best results with respect to coating uniformity, abrasion resistance and conductivity.

Keywords: Polypyrrole; Textile; Plasma treatment; Abrasion

1. Introduction

Conducting polymer coated textiles can be made to possess a combination of desirable properties such as high conductivity, flexibility, strength and structural variations. Reversible response of these materials to external stimuli such as stress, temperature and exposure to electromagnetic radiation suggest potential applications in the fields of sensors [1, 2], actuators, electromagnetic shields and absorbers [3, 4] and heating[5]. In addition, recently developed techniques of printing conductive

patterns of soluble conductive alkyl polypyrroles (PPy) on textiles enable production of electronic textiles[6, 7].

The key impediments for commercial application of conductive polymer coated textiles have been degradation and poor adhesion of the coating to the fiber surface. Increasing the surface energy of the fiber could increase the polymer-fiber interaction and improve the binding strength. One way of modifying the surface energy of a textile is by treatment with atmospheric plasma, which is favorable over other methods for several reasons. It achieves surface modification whilst maintaining the bulk properties (penetration is only to a depth of $\approx$1000 Å [8]). It can produce different radicals and reactive groups on the surface by the use of different gas mixtures. The low treatment temperature avoids deterioration of delicate organic samples. The process is water free and avoids the need for costly effluent treatment. With an increasing ecological and economical concern, plasma treatment provide an environmental friendly and low energy alternative to improved surface wettability [9, 10], shrink resistance [11, 12] and dyeing properties [10, 13] of textiles.

Atmospheric plasma treatment generates different plasma constituents like electrons, ions, free radicals, meta-stables and UV photons. These either directly or indirectly participate in plasma-chemical reactions which introduce reactive groups and free radicals onto the surface, thus improving the adhesion of chemicals and polymers mostly by improved physical interaction. These interactions are normally seen in the form of hydrogen bonds, Van der Waals forces or dipolar interactions [14].

There are three types of atmospheric pressure plasmas: corona discharge, glow discharge, and dielectric barrier atmospheric pressure glow discharge (APGD). Of these APGD is preferred as it generates uniform and stable discharge with the ability to be made into a continuous process [15]. Experimental parameters including treatment time, discharge power, treatment gas and distance between electrodes can control the effectiveness of atmospheric plasma treatment. Mainly, oxygen [16], nitrogen [16, 17], air [17], water vapor [12], or mixtures of nitrogen and hydrogen [16] have been used in wool plasma treatment. There have been many investigations on atmospheric and low temperature plasma treatment on wool fabrics and their dyeing ability [13], but to the best of our knowledge no work has been published on polymerization of PPy on APGD treated wool and polyester (PET) fabric.

The main focus of this work is to examine the effect of gas mixtures in the APGD treatment on the binding strength of PPy coatings on PET and wool fabrics. Properties such as surface resistivity, abrasion resistance and change in colour were measured for the coated fabrics.

2. Experimental

2.1 Materials

Two fabrics were used for the experimental work. One was a scoured, unbleached and undyed 100% wool with a 2/1 broken twill weave. The wool fabric was 228 g/m^2 and had 38 ends/cm in the warp and 32 picks/cm in the weft direction. The second fabric was an undyed plain weave 100% polyester (PET) fabric that had been scoured and bleached. The PET fabric was 212 g/m^2 and had 48 ends/cm in the warp and 46 picks/cm in the weft direction. Each sample was cut to the dimension of 400 mm square for plasma treatment. Fabric specimens were conditioned in ambient laboratory conditions (65% RH and 21°C) before treatment.

2.2 Atmospheric plasma treatment

APGD treatment was conducted on a Sigma technologies International APC 2000 atmospheric glow plasma machine. Three different gas mixtures were used. These were: (i) Helium (He), 14 l$_{stp}$/min; (ii) Helium, 14 l$_{stp}$/min and Acetylene (A5%), 0.7 l$_{stp}$/min (5%); (iii) Helium, 14 l$_{stp}$/min and Nitrogen (N5%), 0.7 l$_{stp}$/min (5%). The fabric was attached to the treatment roller and rotated past the plasma source. Treatment was done for 5, 25 and 50 revolutions of the treatment roller. On each revolution of the treatment roller the fabric was exposed to the plasma source for 0.848 seconds. The power of the treatment plasma was 970 W and the frequency of the power supply was 90 KHz.

2.3 Contact angle and wettability

Contact angle and wettability measurements were conducted using KSV CAM100 contact angle and surface tension tester. The droplet used was distilled water and was 180 pixels in size. Five specimens of wool and PET for each of the APGD treatments were tested. For each measurement a 15 mm square sample was cut from the treated fabric and mounted onto a glass slide using double sided tape. Specimens were cut from random areas of the treated fabric. Wettability time was also calculated simultaneously using the KSV CAM100 software. The interval of the frames captured by camera was varied from 33 ms to 1 second depending upon the rate of absorption. For treated PET fabrics frame interval was set at 33 ms due to the fast rate of absorption. For treated wool fabrics the frame interval was set at 1 sec. All the readings were taken within 2 hours of plasma treatment.

2.4 Conductive coating

Polymerisation was carried out in an aqueous solution that contained 0.045 mol/l pyrrole (Sigma-Aldrich), 0.018 mol/l anthraquinone-2-sulfonic acid sodium salt (AQSA) monohydrate 97% (Sigma Aldrich), 0.1 mol/l ferric chloride hexahydrate and 0.25 g/l Albegal FFA (Ciba Specialty Chemicals) [18, 19], resulting in a black PPy coating on the fabric surface. Each coating was carried out on two 3.0 g fabric samples at a liquor ratio of 50:1. All stock solutions were made up to 10% strength of

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the original chemical strength apart from the pyrrole (5%) and AQSA (1%). The monomer, dopant and oxidant were stored at 2°C after being diluted. The fabric was coated in a 450 ml stainless steel dye pots. Coating was carried out for 2 hours at 10-15°C in a Rapid H240 rotary dyeing machine. Rinsing was conducted using cold tap water while the sample was opened out.

2.5 Surface Resistivity

Resistivity measurements were carried out on all conducting polymer coated fabrics before and after abrasion testing. Resistance was measured 10 times on each side of each sample and averaged. Two square copper electrodes measuring 6mm by 6mm, separated by 8mm, were pressed onto fabric by 0.856N of force. The resistance was measured with a Fluke 83 III Multimeter. Each measurement was multiplied by a factor of 1.33 to convert the measured resistance to surface resistivity (Sheet resistance, R_s). The formula for calculating the surface resistivity is given in equation 1.

$$R_S = R\left(\frac{L}{W}\right) \qquad (1)$$

Where, R_S is the sheet resistance in ohms/square, R is the resistance in ohms, L is the distance between electrodes and W is the width of the each electrode.

2.6 Abrasion resistance

Abrasion resistance measurements were performed using a Martindale abrasion tester. Each of the conductively coated fabrics was cut to produce a 38mm diameter sample. The sample was placed in the top holder of the Martindale under 9kPa of pressure. Each sample was abraded against SDC wool abradent fabric for 200 cycles. After abrasion each of the fabrics was measured for resistivity and UV/Visible reflectance.

2.7 Reflectance

UV/Visible reflectance was measured for each of the abraded samples using a Datacolor Spectraflash 600. Each reflectance measurement was made at a 10° angle from the horizontal. The percentage reflectance for the wavelength of 430 nm was recorded for each sample.

2.8 Microscopy

Scanning electron microscope (SEM) observations were made with a Leica S440W scanning electron microscope. Images were taken at a magnification of 5000

times at a working distance 10 mm and an EHT of 10 kV. All samples were mounted and gold sputtered under vacuum prior to observation.

PPy coated yarn was mounted in Technovit 7100 resin (Kulzer) before being sectioned into 10 μm slivers using a Slee 5062 microtome. Optical microscopy was conducted using an Olympus BX51 optical microscope at a magnification of 1000 times using differential interference contrast (DIC).

3. Results and discussion

3.1 Contact angle and wettability

The results of the surface contact angle tests for the wool fabrics after plasma treatment are given in Table 1. Contact angles and wettability times are presented with the initial droplet image captured as part of the test. The images in Table 1 can be compared with the image in Figure 1 for a visual appreciation of the change in surface contact angle with plasma treatment. Plasma treatment reduces the contact angle for all of the treatment gases used over all of the treatment times when compared with the untreated sample. The rate of surface contact angle reduction and hence the improvement in wetting time is proportional to the number of treatment passes. Some of the treatment gasses have a better influence on the contact angle than others. A mixture of helium and acetylene is far less effective in improving fabric wettability than helium alone.

A mixture of helium and nitrogen is by far the best combination to use for improving wettability on wool fabrics. Various low pressure plasma treatments have shown that the use of nitrogen gas in the plasma treatment gas produces ($-NH_2$) groups on the surface of the fiber [16, 20]. These groups form on the outermost surface of the fiber (F-layer), which without the addition of the ($-NH_2$) groups is very hydrophobic in nature [20]. The addition of ($-NH_2$) groups on the F-layer improves the hydrophilicity of the fiber surface and provides bonding sites for subsequent polymer coatings.

The wettability results for the PET fabric were similar to those of the wool fabric. Each of the plasma gases had the effect of reducing surface contact angle however the degree of improvement was indistinguishable between the gases. After five passes of plasma treatment, the contact angle for the PET fabrics reduced from 98° to zero. This was the same for all of the treatment gas combinations. Figure 2 shows the first five images of the surface contact angle test for the 5 pass helium treated PET fabric. The time interval of each of the frames is 33 milliseconds. The images show that as the droplet is placed onto the fabric it is already starting to be adsorbed before the needle is detached.
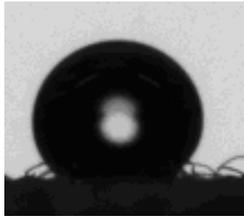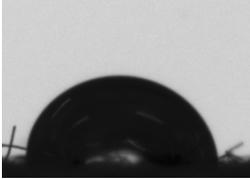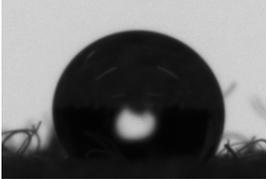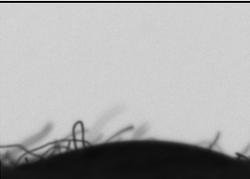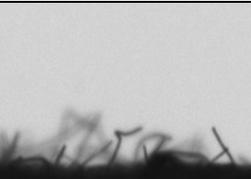
Fig. 1. Water droplet profile on untreated wool fabric

Table 1. Wettability and surface contact angle results for plasma treated wool fabric

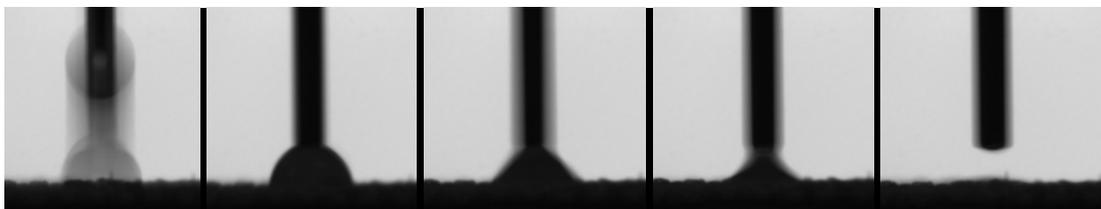| Parameter		Helium	Helium + A5%	Helium + N5%
5 passes		102.26°	127.66°	81.93°
Wettability	(sec)	14	300	16
25 passes		54.2°	81.14°	29.8°
Wettability	(sec)	1.18	7.0	0.495
50 passes		20°	70°	0°
Wettability	(sec)	0.21	1.4	0.099

Fig. 2. Drop placement and adsorption onto plasma treated PET fabric at 33 millisecond intervals.

3.2 Surface energy

Surface energy can be calculated by using the Young-Dupré equation given in equation 2.

$$E = \gamma\left(1 + Cos\,\theta\right) \qquad\qquad (2)$$

Where, γ = Surface tension of water at 20°C, θ = Contact angle in degrees.

Figure 3 shows the calculated surface energy values for the wool fabric for each gas at 5 and 25 passes. An increase of over 7 times is seen for the wool fabric with 25 passes of plasma treatment. A similar increase was observed for the PET fabric, the surface energy of which changed from 62.69mJ to 145.2mJ with the treatment of the fabric. The pure helium and helium/nitrogen gas combinations showed similar surface energies after 25 passes. This correlates with the wettability information.
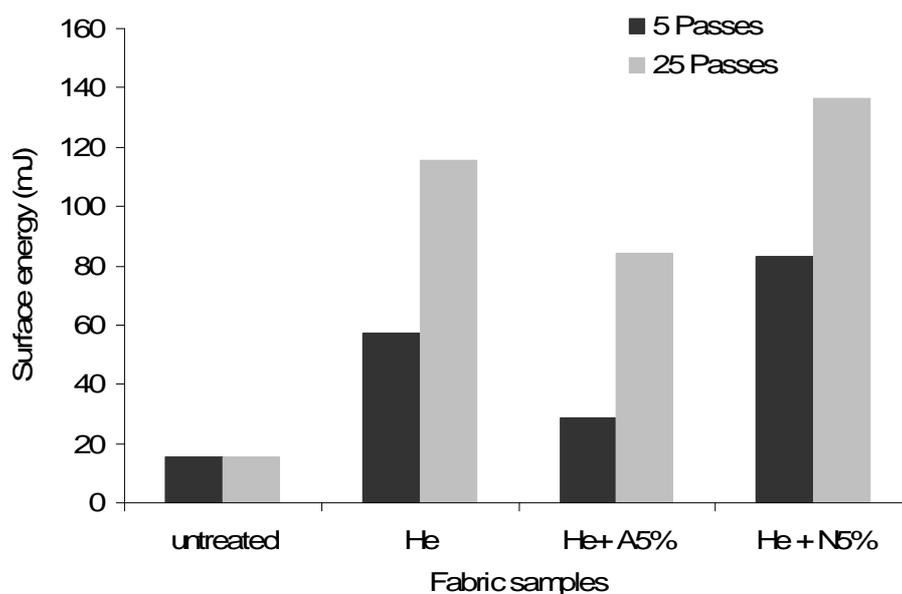

Fig. 3. Surface energy of wool fabric samples for each of the treatment gas combinations

3.3 Microscopy

All previous work investigating plasma treatment of wool fiber [13, 21] showed that the exocuticle layer of the fiber was significantly modified or partially removed by oxidation during plasma treatment. This break down of the exocuticle enables an easier passage of dye and chemical molecules into a wool fiber. Electron microscopy of the wool fiber treated in this work has shown that there has not been a significant

modification of the exocuticle of the wool fiber (Fig. 4). The lack of surface modification of the exocuticle layer defends the proposition that the improved adhesion of the polymer layer could be caused by the increase of amino groups (-NH$_2$), other reactive groups and radicals on the fiber surface.
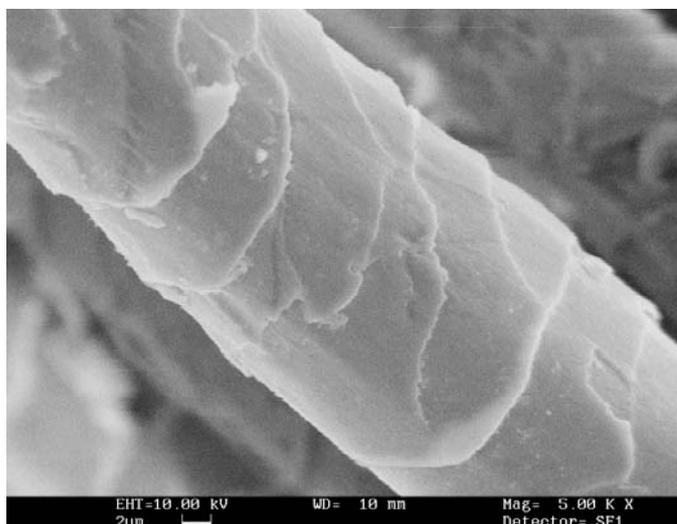

Fig. 4. SEM image of a helium plasma treated wool fiber (50 passes)

Optical microscopy of the sectioned wool fibers showed significant differences between the untreated and plasma treated coated fiber. The plasma treated coated fiber (Fig. 5a) shows a thin layer of conductive polymer bonded to the exocuticle which is not present in the untreated fiber (Fig. 5b). Both the untreated and treated fibers show a significant amount of PPy coating that is not attached to the fiber. The PPy coating is not attached to the fiber because as the fiber is prepared for aqueous coating it undergoes expansion due to the absorption of water from the coating liquor. The coating is subsequently deposited on a highly expanded fiber. During drying the fiber undergoes significant contraction and this causes the coating to delaminate from the fiber surface for a significant part of the surface. Plasma treatment does not stop the delamination of the PPy coating entirely however, the mechanism is changed from a fiber/PPy delamination to a PPy/PPy delamination. This leaves a thin layer of coating still attached to the whole surface area of the fiber after contraction which provides an explanation for the observed improvement in conductivity and abrasion resistance of plasma treated wool fibers.

PET fibers do not show the same delamination of the coating from the fiber surface that is seen in the wool. This can be explained by the level of hygral expansion of the PET fibers within the coating parameters. The cross sectional area of the PET does not significantly change when added to water at low temperatures so drying after coating does not cause a delamination of the coating from the fiber surface. There was little difference in the coating appearance of the PET with or

without plasma treatment and due to this only the plasma treated image has been shown in Fig. 6.
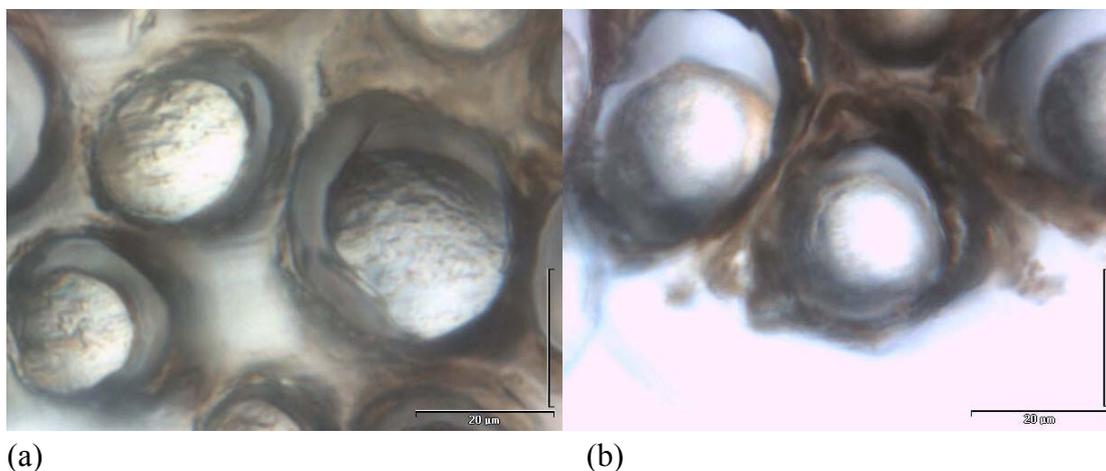
(a)   (b)

Fig. 5. Cross sectional microscopy of the PPy coated plasma treated (a) and untreated (b) wool fibers.

Fig. 6. Cross sectional microscopy of the PPy coated plasma treated PET fibers.

3.4 Surface resistivity

One of the problems with coating wool with conductive PPy is the unevenness of the coating. The epicuticle, which surrounds each cuticle cell of the wool fiber, consists of an outermost fatty acid monolayer and a protein matrix. Fatty acid chains are oriented away from the fiber to produce a "polyethylene-like" layer at the fiber surface, thus making the epicuticle hydrophobic and resistant to the bonding of polymer coatings [22, 23].

The wool fabrics that had undergone plasma treatment had a more uniform coating on their surface. The plasma treated PPy coated fabrics were deeper black in

color. Optical microscopy of a sectioned group of coated/plasma treated fibers showed that this was due to a thin even coating of the whole fiber surface (Fig.6). This improvement in coating coverage led to improved conductivity, which is shown in Fig 7. Surface resistivity of all samples subjected to plasma treatment decreased and the decrease was proportional to the number of passes of plasma treatment. The treatment gas mixture of helium and nitrogen resulted in the lowest resistivity.
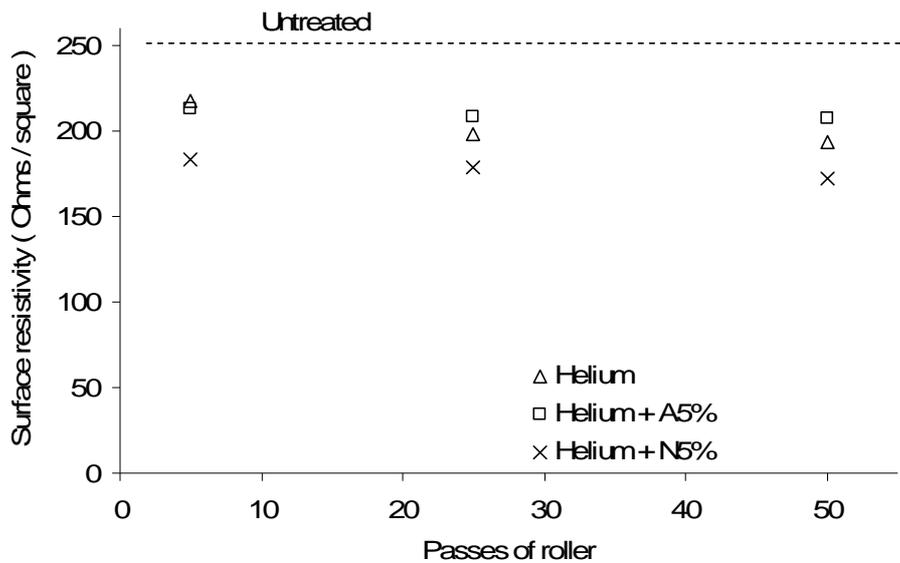

Fig. 7. Surface resistivity changes in wool fabric due to plasma treatment

Abrasion resistance and coating uniformity are correlated since the improvement of abrasion resistance manifests as more uniform coating. The coating system used was a dynamic process where the fabric sample was tumbled through the coating solution to facilitate PPy to surface interaction. During this process poorly fixed polymer can be abraded from the surface of the fabric as it contacts with the surface of the coating vessel. After the dynamic coating process, untreated wool fabrics had small patches of white on their surface where the PPy coating had been abraded away. Such uneven patches were not visible in plasma treated fabrics due to improved abrasion resistance of the coating. The improved fastness of the coating may be attributed to formation of bonding sites on the epicuticle surface by the plasma treatment.

In contrast to wool fabrics, PPy coated PET fabrics showed only a slight improvement in appearance after plasma treatment. There was also only a negligible improvement in surface resistivity with the values ranging between 140-160 Ω/square for all the samples. The surface energy of the untreated PET fabric was higher than that of the untreated wool fabric. The higher untreated surface energy of the PET fabric produced a highly uniform coating. Plasma treatment did not significantly

improve coating uniformity and hence the difference in resistivity between untreated and plasma treated PPy coated PET fabrics was not significant.

3.5 Martindale abrasion

Martindale abrasion testing has confirmed that plasma treatment has resulted in improved binding of PPy coating to both the wool and PET fabrics. Fig. 8 shows the surface resistivity for the wool fabric samples after 200 cycles of abrasion on a Martindale abrasion tester. Without plasma treatment the surface resistivity for the wool fabric increased to 6000 Ω/square and a large amount of the coating had been abraded from the fabric surface. With plasma treatment the surface resistivity of the wool fabric after abrasion was as low as 200 Ω/square. Each of the plasma treatment gases had a different effect on the resistance to abrasion. The helium and nitrogen mixture was far more effective than either of the other gas combinations. Surface energy results were in agreement with these observations.
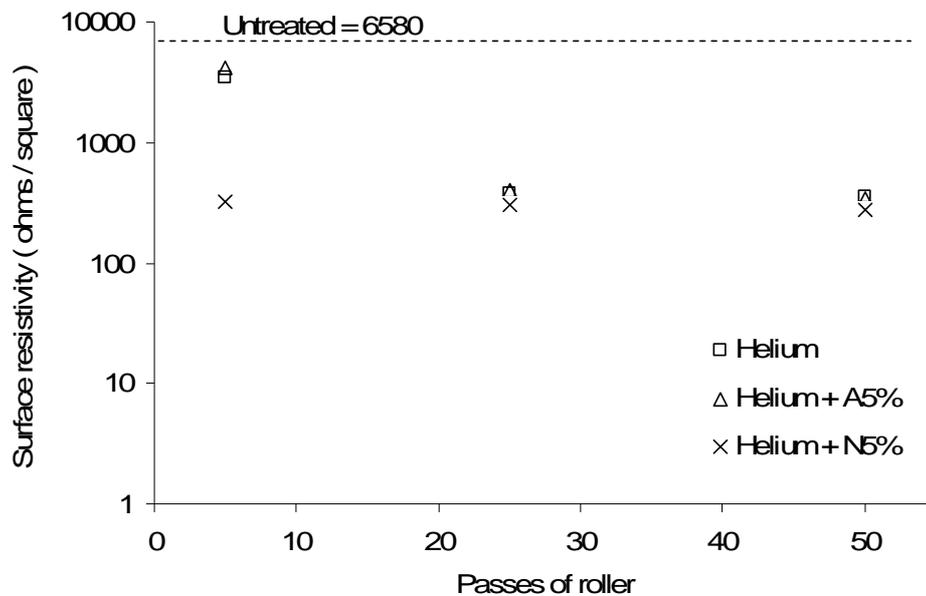

Fig. 8. Surface resistivity of the wool samples after 200 cycles of abrasion
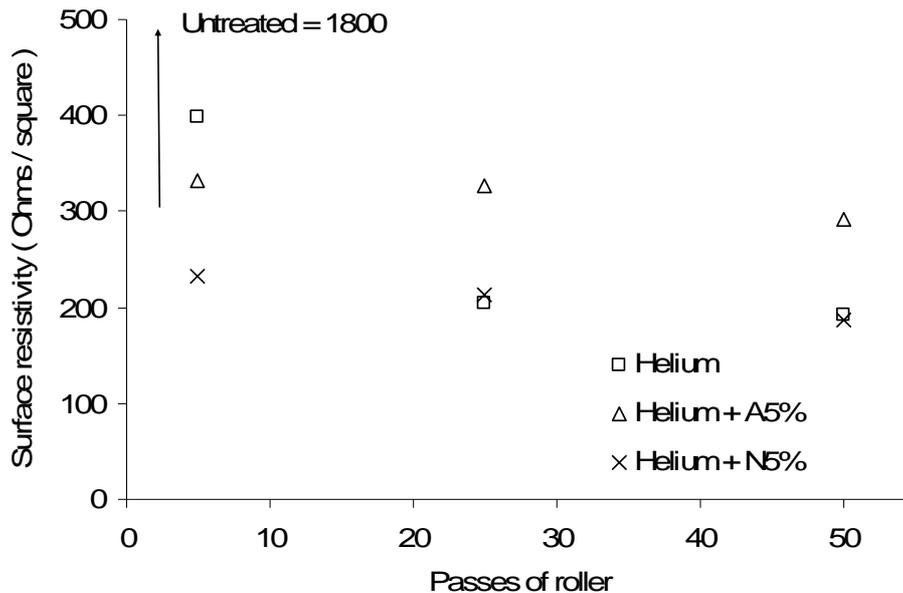
Fig. 9. Surface resistivity of the PET samples after 200 cycles of abrasion

The trends seen in the wool fabric samples were also seen in the PET samples (Fig. 9). The difference between the wool and the PET was that the untreated PET fabric had a better surface resistivity before abrasion (1800 Ω/square). This can be attributed to the higher surface energy of the untreated PET fabric and the lack of delamination of the coating. As seen with the wool fabric the helium and nitrogen treatment gas mixture produced the best coating adhesion for the PET fabric.

Figures 8 and 9 show that for the helium/5%nitrogen plasma treatment gas a shorter plasma treatment time (5 passes) can produce good resistivity values after abrasion, which is comparable to higher treatment times (25 and 50 passes) of the same gas mixture. This is a significant economic advantage as only a short plasma treatment time is sufficient to provide substantial improvement in the surface resistivity after abrasion.

The samples in Figures 10 and 11 show visually the effect of abrasion on the samples. The samples that had no plasma treatment had a large amount of the coating abraded from their surface. The helium/nitrogen treatment gas has given the best abrasion resistance for both the wool and PET fabrics. The visual results reinforce the resistivity results as a reduction in the conductive attached to the fiber is proportional to a reduction in resistivity.
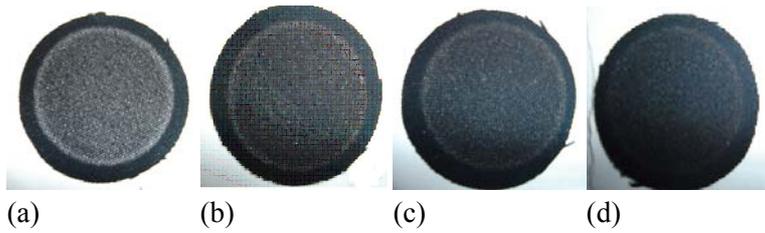
(a)   (b)   (c)   (d)

Fig. 10. PET samples after 200 cycles of abrasion (a) untreated, (b) helium 50 passes, (c) helium/5%acetylene 50 passes and (d) helium/5%nitrogen 50 passes

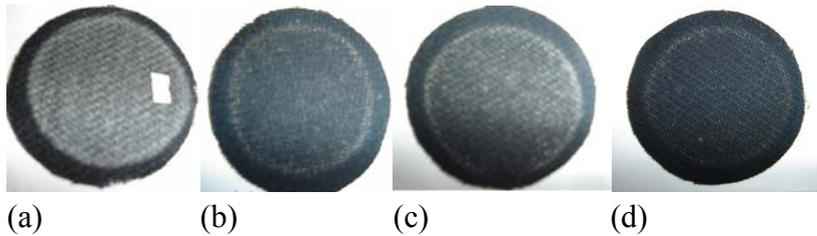(a)   (b)   (c)   (d)

Fig. 11. Wool samples after 200 cycles of abrasion (a) untreated, (b) helium 50 passes, (c) helium/5%acetylene 50 passes and (d) helium/5%nitrogen 50 passes

3.6 Reflectance

Reflectance measurements of the fabric before and after abrasion testing showed a similar trend to the resistivity results. As the black coating was abraded from the surface of the sample the fabric reflectance increased. As the reflectance measurements followed the same trend as the resistivity measurements it was not necessary to report the individual reflectance data.

Acknowledgements

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