The color fastness properties of conductive leather improved by the use of mordants

M Hylli 1,4, A Shabani 2, I Kazani 1, S Drushku 3, G Guxho 1

1 Department of Textile and Fashion, Faculty of Mechanical Engineering, Polytechnic University of Tirana, Albania.
2 Department of Electrotechnics, Polytechnic University of Tirana, Tirana, Albania
3 Department of Industrial Chemistry, Faculty of Natural Science, University of Tirana,
4 Author to whom any correspondence should be addressed
mhylli@fim.edu.al

Abstract. Leather has limited uses in smart or advanced applications because it doesn’t conduct electricity. Applying double in situ–polymerization of pyrrole gives leather conductive properties. The treated leather changes its natural color into black color going through this double in-situ polymerization method and show very good conductivity. The problem we faced was the losing in color while using it in different applications. Therefore, in this research, we have concluded an increase of the color fastness resistance of the black leather, which was demonstrated by the electro conductive measurements and good resistance to rubbing.

Keywords: color fastness, conductivity, dyeing, leather, mordants, and polymerization.

1. Introduction

Leather is one of the most unique and fashionable material used in different products. It is so desirable and very useful, because it owns a wide range of positive qualities. Leather has good flexibility, tear strength, abrasion resistance and good insulating properties [1-2]. However leather has limited uses in smart or advanced applications because it doesn’t conduct electricity. There are some techniques that can be used to produce smart products such as printing, application of a conductive agent such as carbon black, embroidering a conductive thread or knitting a conductive complex [3].

Pyrrole is used a lot in research and applications because of its high conductivity, less toxicity and environmental friendly nature [3-4]. Polypyrrole coated fabrics have shown electrical conductivity, thermal properties and flexibility suitable for a number of applications. In addition, deposition of thin layers of conductive polymers on the fibre surface of fabrics or yarns does not noticeably change and sometimes even improves the mechanical properties of the original material [5-6].

In our previous research, the double in situ–polymerization of pyrrole was applied to give to the leather conductive properties [4]. After the treatment, the leather changes its white color into black color and shows very good conductivity, eliminating in this way the dyeing process with toxic dyes. Moreover, it was observed that these treated leathers lose color, while touching and operating with them. Consequently, the aim of this research is to increase the color fastness resistance of the black leather in order not to lose color, while using it in different smart applications.
2. Materials and Methods

2.1. Materials and chemical reagents
In this study was chosen white sheep crust leathers of Albanian origin, produced in a tannery in Berat (Albania).

The chemical used for the transformation of leather from nonconductive to conductive were pyrrole, ferric chloride and anthraquinone-2- sulfonic acid sodium salt monohydrate (AQSA). The selected mordants used to improve the color fastness resistance of the black leather samples were sodium sulphate, and iron sulphate.

All the chemical used were of laboratory grade and high purity (97-100%).

2.2. Methods, Chemical technology
The method used to produce conductive leather was double in-situ polymerization of pyrrole. At the beginning of the experiment the parameters (concentration of the solutions, time of the treatment and the number of rotations) were optimised to provide maximum conductivity [3].

The dimensions of the leather samples were 10 x 10 cm [7] and a thickness of 0.97 ± 0.2 mm [8]. Leather samples were treated at the beginning with a mixed solution of 0.15 M pyrrole and AQSA (10 wt % based on the weight of pyrrole) for 1 hour at room temperature rotating manually at 10 rpm. Then 0.4 M ferric chloride solution is added to the mixture as an oxidant to initiate the polymerization. The polymerization was carried out for 2 h at 5°C in 10 rpm. Treated leather was washed 4 times with distilled water and dried at 35 °C. Then the leather samples were treated again in a second bath containing half of concentrations of reactants following the same procedure to obtain double in situ PPy coated leather.

This polymerization method produces conductive and black coloured leather sample in one chemical treatment.

After this, the black leather samples are treated with selected mordants (sodium sulphate 2 % and iron sulphate 2 %) in order to improve the resistivity of the color. The selected mordant solution is added along the PPy treatment following three mordanting techniques: before, along and after treatment.

2.3. Methods used to measure electrical properties
Shabani et. al. [9] mentioned that to measure the electrical properties of the conductive transformed leather throughout a polymerization chemical process, there are a variety of methods which are used before on conductive textiles. One of them is measuring the surface resistance by placing a different number of electrodes over the surface of thin film material [9-10]. The most used measurement methods are two and four probe measurement method. ‘Van Der Pauw’ proposed a different four probe system for measuring surface electrical resistance for any arbitrary shape thin material. In our study, we used Van Der Pauw technique for resistance measurement. In order to measure the square resistance with this method, four contacts are required on the boundaries of the conductive simple [9-12].

The electrical resistance was measured three times on the grain side of the coated leather and an average resistance of the sample was calculated.

This method has proved to be very useful for measuring the sheet resistance of conductive coated and printed fabrics.
Furthermore, the samples treated and not treated with mordants were subject of the rubbing test, where their color fastness were assessed with grey scale [13-14].

3. Results and discussion

After the leather samples were treated with double in situ polymerization method and the selected mordants, the electric properties were measured. From the results was found that the selected mordants and the technique of mordanting has an influence to stabilise and increase the color fastness. As it can be seen from the figure 2 where the mordant used is FeSO$_4$ the leather samples with very good conductivity were from the simultaneous – mordanting where the value of resistance is 142.95 $\Omega/\square$ and for the post-mordanting the value of resistance is 89.67 $\Omega/\square$. Leather samples treated with pre-mordanting technique has given the higher value of resistance 719.17 $\Omega/\square$.

![Figure 2](image_url)

**Figure 2.** Resistance of coated grain side leather samples treated with double in situ polymerization and FeSO$_4$ as a mordant.

In the figure 3 are shown the values of resistance where the second selected mordant used is Na$_2$SO$_4$ X 10 H$_2$O. The leather samples with very good conductivity were from the simultaneous – mordanting where the value of resistance is 136.55 $\Omega/\square$ and for the post-mordanting the value of resistance is 107.15 $\Omega/\square$. Leather samples treated with pre-mordanting technique has given the higher value of resistance 557.5 $\Omega/\square$. 

![Figure 1](image_url)

**Figure 1.** Scheme of Van Der Pauw measurements of the coated leather.
Figure 3. Resistance of coated grain side leather samples treated with double in situ polymerization and Na$_2$SO$_4$ x 10 H$_2$O as a mordant.

The use of pre-mordanting technique, compared to the other two techniques of mordanting has given lower conductivity of the treated leather samples, which may be due to the less absorption of the pyrrole. From the figure 2 and 3 we can conclude that mordant Na$_2$SO$_4$ show to have higher conductivity for the pre-mordanting and simultaneous-mordanting methods. When it comes to the post-mordanting method, it is the mordant Fe SO$_4$ which has the best conductivity, not only for this method but also compared to all methods used.

In order to observe the color fastness resistance of the treated leather, the analyses are done according the dry rubbing method, and the evaluation is done with the gray scale. The results are shown in table 1 and 2 for both selected mordants.

From the color fastness resistance tests (dry rubbing), in comparison with samples not treated with mordants, table 1 and 2 was found that the color fastness to rubbing has shown better results for the leather samples treated with mordants.

### Table 1. The color fastness resistance to dry rubbing for leather samples treated with FeSO$_4$ as a mordant.

| Samples | Methods of mordanting (FeSO$_4$) | Grade of Color fastness to dry rubbing |
|---------|----------------------------------|--------------------------------------|
| 1       | Pre-mordanting                   | 4                                    |
| 2       | Simultaneous -mordanting         | 4                                    |
| 3       | Post- Mordanting                 | 3                                    |
| 4       | No mordants                      | 2-3                                  |

### Table 2. The color fastness resistance to dry rubbing for leather samples treated with (Na$_2$SO$_4$ x 10 H$_2$O) as a mordant.

| Samples | Methods of mordanting (Na$_2$SO$_4$ x 10 H$_2$O) | Grade of Color fastness to dry rubbing |
|---------|-----------------------------------------------|--------------------------------------|
| 1       | Pre-mordanting                               | 4                                    |
| 2       | Simultaneous -mordanting                     | 4                                    |
| 3       | Post- Mordanting                             | 3                                    |
| 4       | No mordants                                  | 2-3                                  |

Moreover the samples treated in the pre and simultaneous mordanting technique have shown the grade 4, compared to post- mordanting technique which has shown a lower grade of 3. The reason may be that when we use post- mordanting technique the mordant is added after the polymerization process, and in this way the conductive coating that is formed cannot allow the penetration of the mordant.

### 4. Conclusion

In this research the polypyrrole treated leather became black in color after polymerization process. In this way we not only obtain conductive black leather but also along this treatment we proposed to avoid using toxic dyes. Double in-situ polymerization method of pyrrole with optimized parameters has given
the conductive colored leather with a resistivity ranged from 89.67 up to 719.17 Ω/□. All the treated samples could operate successfully, even with different resistivity, on smart devices and in addition, the method used is environmentally friendly. The use of the mordants increases the color fastness of the dyed leather, reaching the aim of this research by not losing color, while using it.

References
[1] Hylli M, Guxho G and Drushku S 2014 The influence of environmental conditions on the mechanical properties in finished leather 6th Int. Conf of Textile 2014 Tirana, ALBANIA.
[2] Covington T 2009 The Science of leather The Royal Society of Chemistry pp 2-27
[3] Wegene J D and Thanikaivelan P 2014 Conducting leathers for smart product applications Industrial & Engineering Chemistry Research 53(4), pp. 18209-15
[4] Hylli M, Shabani A, Kazani I, Beqiraj E, Drushku S and Guxho G 2018 Application of double in-situ polymerization for changing the leather properties 8th Intn Conf of Textile 2018 Tirana, Albania pp. 42-47
[5] Varesano A, Dall’Acqua L and Tonin C 2005 A study on the electrical conductivity decay of the polypyrrole coated wool textile Polymer degradation and stability 89 , pp. 125-132
[6] Gasana E, Westbroke P, Hakuzimana J, Clerck K, Prinitakis G, Kiekens P and Tseles D 2006 Electroconductive textile structures through electroless deposition of polypyrrole and copper at polypyrrole surface Surface and coatings Technology 201, pp 3547–3551
[7] ISO 2418:2017Leather- Chemical, Physical and Mechanical and Fastness Tests, Sampling Location
[8] ISO 2589:2016 Leather- Physical and Mechanical Tests, Determination of thickness
[9] Shabani A, Hylli M, Kazani I and Berberi P 2019 Resistivity behaviour of leather after electroconductive-treatment Textile and Leather Review Vol 2, Issue 1, pp. 15-22
[10] Shabani A, Hylli M, Kazani I, Berberi P, Zavalani O and Guxho G 2019 The anisotropic structure of electroconductive leather studied by Van Der Pauw method Textile and Leather Review 2(3), pp. 136-144
[11] Banaszczyk J, Mey G D, Schwarz A and Langenhoove L V 2010 The Van Der Pauw method for sheet resistance measurements of polypyrrole coated woven fabrics Journal of Applied Polymer Science 117, pp. 2553-8
[12] Kazani I, Mey G D, Hetler C, Banaszczzyk J. Schwarz A, Guxho G and Langenhoove L V 2011 Van Der Pauw method for measuring resistivities of anisotropic layers printed on textile substrates Textile Research Journal 81(20), pp. 2117-2124
[13] ISO 20433:2012 Leather- Tests for colour fastness -Colour fastness to crocking
[14] ISO 105-A03:1993 Textiles- Tests for colour fastness-Part A03 Grey scale for assessing staining
[15] Hylli M, Kazani I, Shabani A, Komici D, Guxho G and Drushku S 2017 Transforming leather properties from nonconductive to conductive Ist Intern. Conf. Eng. and Entrepreneurship 2017 Tirana Albania . pp 214-219
[16] Zhang H, Zou X, Liang J, Ma X, Tang Zh and Sun J 2011 Development of Electroless Silver Plating on Para-Aramid Fibers and Growth Morphology of Silver Deposits Journal of Applied Polymer Science 124, pp. 3363–3371
[17] Lacerda S N, Gonçalves L. M and Carvalho H 2013 Deposition of conductive materials on textile and polymeric flexible substrates 2 Journal of Materials Science: Materials in Electronics 24, pp. 635–643
[18] Cetiner S 2014 Dielectric and morphological studies of nanostructured polypyrrole-coated cotton fabrics Textile Research Journal 84, pp. 1463–1475
[19] Petersen P, Helmer R, Pate M and Eichhoff J 2011 Electronic textile resistor design and fabric resistivity characterization Textile Research Journal 81(13) pp. 1395–1404