The anisotropic structure of electro conductive leather studied by Van der Pauw method

Aulon SHABANI¹, Majlinda HYLLI², Ilda KAZANI², Pëllumb BERBERI³, Orion ZAVALANI¹, Genti GUXHO²

¹Department of Electrotechnics, Polytechnic University of Tirana, Tirana, Albania ²Department of Textile and Fashion, Polytechnic University of Tirana, Tirana, Albania ³Department of Engineering Physics, Faculty of Engineering Mathematics and Engineering Physics, Polytechnic University of Tirana, Tirana, Albania *aulonshabani@yahoo.com

Original scientific article UDC 675.017.57 DOI: 10.31881/TLR.2019.16 Received 29 December 2018; Accepted 25 March 2019; Published Online 10 May 2019

ABSTRACT

Determining the surface resistance of electro conductive refined natural leather materials is in the focus of this paper. Natural leather samples are initially transformed to conductive by applying chemical treatment process known as polymerization. Due to the existence of various techniques for measuring electrical resistance of conductive materials, we are focused on measuring surface resistance by arranging four electrodes in the edges of square leather samples, also known as Van der Pauw method. Improving the results accuracy, we use a multi-variant electrode placement over the sample edges. The result is the average of all results gained for different placements. Moreover, we use this electrode placement technique to analyse the anisotropy of conductive samples. The results of this research provide important knowledge about leather chemical treatment and its electrical proprieties.

KEYWORDS

Leather, conductivity, anisotropy, Van der Pauw method

INTRODUCTION

Textiles have a variety of uses, most commonly in the clothing industry. In recent years, smart textiles are used as they are able to respond to changes in the environment. These kinds of textiles are a mix of textile materials with electric, magnetic, chemical and thermal systems.

Smart textiles are used in different areas, for example, sportswear, where they monitor physical parameters, in clothing for elderly people where they monitor life signs, or in living spaces to help improve human thermal comfort and energy efficiency. Smart textiles are seen as the new trend in the last decades.

In this paper, we focus on electrical properties of conductive sheep leather obtained through polymerization. It is important to investigate electrical properties of leather materials in order to predict their possible applications in the future. Leather is used for clothes, accessories, on furniture, and car interiors.

Studies on electrical measurement of textile materials have been carried out since Hersh and Montgomery [1] used a novel apparatus to study the electrical resistance of textile fibres and fibre assemblies. They inves-

tigated electrostatic properties of natural fibres on different ambient conditions. They found that electrical properties of those fibres are highly dependent on material moisture. Another novel approach for evaluating electrical properties of textile assemblies was proposed by Berberi [2]. The author proposed a new multi-step method for evaluating electrical resistance. Furthermore, he developed a novel probe for resistance measurement using volume fraction properties of the material. Kacprzyk [3] described measurement of volume and surface resistance of textile materials as well. They compared different electrode systems for resistance measurement. Yang and Wang [4] provided an approach for measuring resistivity of thin film insulating material by developing a new circular probe.

The above mentioned methods focused on electrical properties of textile fibres, but a variety of methods can be found in literature that focus on measurement of textile's surface resistance by placing different number of electrodes over thin film surface material. The most commonly used measurement methods are the two- and the four-probe measurement methods. The two-probe methods evaluate electrical resistance of the material by using Ohm's law, but the accuracy is volatile in case of thin films. It is for this reason that four-probe methods are most commonly used. These methods are classified into two main groups: linear placement and peripheral placement. Wenner [5] proposed a surface resistance measurement by placing four equidistant electrodes in a line where two of them measure voltage drop and the remaining two measure the current flow. On the other hand, Van der Pauw [6] proposed a different four-probe system for measuring surface electrical resistance for any arbitrarily shaped thin material. In our work, we focus on Van der Pauw's technique for resistance measurement.

Many authors used this method for measuring electrical resistance. Authors [7] applied Van der Pauw's method for measuring electrical resistance on thin film materials; they also took into account the correction factor. The application of the method in textile material resistance measurement is published in a paper by Tokarska [8], where she investigated the contact diameter of electrodes and their arrangement. Kazani et. al [9] used van der Pauw's method to measure electrical resistance of anisotropic thin layers screen-printed on textile.

Furthermore, the four-probe method is used by Schnabel [10] for evaluating anisotropy on parallel-plane crystals. Investigation of anisotropy of electrical properties of textile fabrics was the focus in Azoulay [11]. The author analysed the electrical properties in different weaving directions of the textile material. Tokarska, Frydrysiak, and Zięba [12] analysed the electrical properties of textile materials by exposing its anisotropy and homogeneity properties.

Other electrical properties are investigated by different authors as well. Asanovic et al. [13] analysed resistance and dielectric properties of different textile materials as function of air humidity. Banaszczyk et al. [14] modelled current distribution of electro-conductive fabrics. They modelled textile fabrics by using electrical circuit model and then mapping current distribution generated by the simulated circuit model.

The characteristics of textile materials are investigated after chemical treatment have been applied as well. For example, Yoon and Lee [15] assessed performance characteristics of developed breathable waterproof materials. The investigation of chemical treatments of textile fabrics is also reported in [16]. The authors focused on developing an electronic textile resistor by treating less conductive fabric with polypyrrole in order to increase conductivity. They developed a prototype for measuring electrical resistance on conductive fabric. Improving textile materials' conductivity using polypyrrole treatment is investigated by Kaynak and Beltran as well [17]. They analysed the relationship between surface resistivity and concentration of conductive elements used. Electrical conductivity of polypyrrole coated textiles was investigated by Varesano et al. [18]. Electrical surface resistivity of conductive polymers using statistical approach was investigated in [19]. Conductive transformation of textile materials is the focus of many authors. In recent publications, the investigation of leather conductivity and it possible applications to smart textiles has an important place. Conductive leather analysis for smart textile applications is the focus of Wegene and Thanikaivelan [20]. After using single in situ polymerization of pyrrole to produce conductive leather, they analysed polypyrrole coating by using Fourier transform infrared spectroscopy and electron microscopic analysis. In addition, the leather colour was investigated using reflectance measurements. Likewise, Yang et al. [21] produced artificial leather with high thermal conductivity by adding aluminium oxide (Al₂ O₃). Furthermore, they [22] developed high thermal conductive leather for smart electronic materials. Hong [23] processed leather in a conductive chemical treatment in order to develop conductive leather gloves.

Our study focuses on determining surface resistance of natural leather processed for conductivity by the four probe method known as the Van der Pauw method. Our previous works [24, 25] were focused on transforming nonconductive leather using chemical treatments. Attention was given not only to surface resistance, but to analysing anisotropy of conductive material after chemical processing as well.

VAN DER PAUW RESISTIVITY MEASUREMENT METHOD

This method, introduced by Van der Pauw, is intended for resistance measurement of any arbitrarily shaped flat sample of homogeneous thickness [6]. The method evaluates two-dimensional surface resistivity using a minimum of four measurements by placing four electrodes in different positions around the periphery of the sample as shown in Figure 1(a-h).

More specifically, according to the Van der Pauw's theory, surface resistance is calculated using the following equation:

$$e^{-\pi R_{vertical}/R_s} + e^{-\pi R_{horizontal}/R_s} = 1$$
(1)

where $R_{vertical}$ is the mean sample resistance of four configurations (Figure 1, b-d-f-h) defined by Ohm's law as the ratio between potential difference in two points with current flowing in the two other, opposite points. is calculated in a similar manner. Surface resistance is obtained by solving equation 1.



Figure 1. Electrode configurations for Van der Pauw's resistance measurement taking polarity into consideration

LEATHER CONDUCTIVE TRANSFORMATION

Leather is a natural material created by tanning raw hides to make it durable, resistant, flexible, etc. White sheep crust leather is treated chemically in order to make it conductive. Different methods can be used to prepare conductive leather. We decided to use the single in-situ polymerization of pyrrole method which produces conductive and coloured leather samples in one chemical treatment and is environmentally friendly. The leather samples are taken in accordance with ISO 2418 : 2017 (Leather – Chemical, physical and mechanical and fastness tests. – Sampling location). The samples (8 x 8 cm) were first treated with a pyrrole/AQSA mixed solution for 1 hour at room temperature rotating manually at 10 rpm in order for the solution to penetrate in a homogenous way. Next, ferric chloride solution, which plays the role of an oxidant, was added to initiate the polymerization. The concentrations of monomer (pyrrole), AQSA as a dopant, and FeCl₃ as oxidant, were varied and optimized in order to provide the maximum conductivity of leather. Polymerization was carried out for 2 h at 5°C rotating manually at 10 rpm. Finally, the polypyrrole coated leather samples were washed with distilled water and dried at 35 °C. The treated leather samples were conditioned according to ISO 2419:2012 method (Leather – Physical and mechanical tests – Sample preparation and conditioning) before the electrical measurements.

MEASUREMENTS OF SURFACE RESISTANCE OF LEATHER SAMPLE

The purpose of this study was to determine surface resistance of conductive leather samples and compare how chemical substrate was distributed during the process. Surface resistance was determined using fourprobe method which indicates the ratio of voltage drop between one pair of electrodes with current flow between the other pair of electrodes placed opposite each other in case of square shaped samples. The anisotropy of leather samples was observed using four-electrode technique, by adding different probe placement scenarios. Each of the results is the observation of five repetitions and the error of measurement is estimated using the standard deviation formula.

I. Surface resistance measurements

Leather samples resistances were calculated based on electrode placement as shown in Figure 1(a-h). First, the ratio between voltage drop and current flow was calculated and then a script file was used to solve Van der Pauw's equation for determining square-shaped surface resistance. In order to conduct this experiment, a Tektronix DMM4050 Multimeter, a DC Power supply PS23023 and four measurement probes were used as shown in Figure 2. The surface resistances obtained for four different leather samples are shown in Table 1 and Table 2.



Figure 2. Leather sample measurement schematics for multi-scenario electrode placement

		Sam	ple 1		Sample 2				
Variant	Fig.2.a	Fig.2.b	Fig.2.c	Fig.2.d	Fig.2.a	Fig.2.b	Fig.2.c	Fig.2.d	
Voltage (V)	1.74	2.09	0.76	0.84	0.8	0.98	2.6	2.2	
Current (A)	0.08	0.1	0.1	0.11	0.09	0.09	0.09	0.07	
Resistance (Ω)± estimated std ^a	21.75 ±1.41	20.9 ±1.128	7.6 ±0.53	7.63 ±0.61	8.889 ±0.578	10.889 ±0.59	28.88 ±2.02	31.42 ±1.89	
Surface resistance (Ω/m^2)) ± estimated std		60.15	± 4.04		78.53 ± 4.89				

Table 1. Electrical properties of leather samples 1-2

Table 2: Electrical	properties of leather samples	3-4

		Sam	ple 3		Sample 4				
Variant	Fig.2.a	Fig.2.b	Fig.2.c	Fig.2.d	Fig.2.a	Fig.2.b	Fig.2.c	Fig.2.d	
Voltage (V)	1.14	1.35	1.8	1.67	1.22	1.52	1	1.25	
Current (A)	0.08	0.09	0.09	0.08	0.05	0.06	0.05	0.07	
Resistance (Ω) ± estimated std	14.25 ±0.92	15 ±1.2	20 ±1.24	20.87 ±1.48	24.4 ±1.78	25.33 ±1.65	20 ±1.139	17.85 ±1.17	
Surface resistance (Ω/m^2)) ± estimated std		78.69	± 4.81		98.61 ± 6.14				

II. Anisotropy observation

In our study, anisotropy indicates how the chemical treatment of leather samples was applied from the electrical point of view. We observed it using different electrode placements as shown in Figure 3. 12 different variants were used in order to observe electrical properties each of them based on the opposites principle. In the first variant, AB points were used as voltage measurements and the two remaining points were used as the path for current flow. In the second variant, AB points were used as current flow and the voltage drop was measured on the CD points.

Electrical properties for both chemical treatment samples were measured under ambient conditions (19 °C and 47%). The values of the measurements were taken 60 seconds after the current started flowing through the leather sample. Five measurements were done for each sample and the mean value was calculated. As can be seen in Table 3, the resistance values obtained using two variants of swapping electrode placement were R_a =21.75 Ω and R_b =20.9 Ω , meaning that anisotropy of conductive material distribution occurred. For the results in Table 3, there was an obvious conclusion that the conductive substrate was not spread homogeneously leading to anisotropy in electrical properties of the leather.

^a Estimated standard deviation measures the dispersion of five different measurements



Figure 3. Electrode placement for anisotropy identification

	Sample 1											
Variant Attribute	Fig.4.a	Fig.4.b	Fig.4.c	Fig.4.d	Fig.4.e	Fig.4.f	Fig.4.g	Fig.4.h	Fig.4.i	Fig.4.j	Fig.4.k	Fig.4.l
Voltage (V)	1.74	2.09	0.76	0.84	0.7	0.54	3.6	3.85	1.12	1.27	1.99	2.01
Current (A)	0.08	0.1	0.1	0.11	0.11	0.1	0.16	0.16	0.1	0.12	0.12	0.11
Resistance (Ω) ± estimated std	21.75 ±1.41	20.9 ±1.12	7.6 ±0.53	7.63 ±0.61	6.36 ±0.41	5.4 ±0.38	22.5 ±1.68	24.06 ±1.32	11.2 ±0.89	10.58 ±0.74	16.58 ±1.12	18.27 ±0.92
						Sam	ple 2					
Variant Attribute	Fig.4.a	Fig.4.b	Fig.4.c	Fig.4.d	Fig.4.e	Fig.4.f	Fig.4.g	Fig.4.h	Fig.4.i	Fig.4.j	Fig.4.k	Fig.4.I
Voltage (V)	0.80	0.98	2.6	2.2	0.74	0.69	1.09	3.37	3.14	1.82	1.4	1.79
Current (A)	0.09	0.09	0.09	0.07	0.09	0.09	0.09	0.16	0.15	0.09	0.11	0.09
Resistance (Ω) ± estimated std	8.889 ±0.58	10.89 ±0.59	28.88 ±2.02	31.42 ±1.89	8.22 ±0.51	7.67 ±0.53	12.11 ±0.78	21.06 ±1.19	20.93 ±1.46	20.22 ±1.62	12.73 ±0.83	19.89 ±1.57

Table 3. Electrical characteristics of four samples using different electrode placement

	Sample 3											
Variant Attribute	Fig.4.a	Fig.4.b	Fig.4.c	Fig.4.d	Fig.4.e	Fig.4.f	Fig.4.g	Fig.4.h	Fig.4.i	Fig.4.j	Fig.4.k	Fig.4.l
Voltage (V)	1.14	1.35	1.8	1.67	0.47	0.26	3.23	3.15	0.55	0.62	2.24	2.04
Current (A)	0.08	0.09	0.09	0.08	0.09	0.08	0.14	0.13	0.09	0.08	0.09	0.09
Resistance (Ω) ± estimated std	14.25 ±0.92	15 ±1.2	20 ±1.24	20.87 ±1.48	5.22 ±0.33	3.25 ±0.23	23.07 ±1.49	24.23 ±1.35	6.11 ±0.42	7.7 ±0.61	24.9 ±1.61	22.67 ±1.78
						Sam	ple 4					
Variant Attribute	Fig.4.a	Fig.4.b	Fig.4.c	Fig.4.d	Fig.4.e	Fig.4.f	Fig.4.g	Fig.4.h	Fig.4.i	Fig.4.j	Fig.4.k	Fig.4.I
Voltage (V)	1.22	1.52	1	1.25	0.39	0.38	3.16	3.03	0.78	0.67	1.55	1.93
Current (A)	0.05	0.06	0.05	0.07	0.09	0.08	0.12	0.12	0.09	0.08	0.07	0.08
Resistance (Ω) ± estimated std	24.4 ±1.78	25.33 ±1.65	20 ±1.14	17.85 ±1.17	4.33 ±0.31	4.75 ±0.41	26.33 ±1.71	25.25 ±2.16	9.75 ±0.68	8.37 ±0.66	22.14 ±1.43	24.13 ±1.90

CONCLUSION

Conclusion results from the conducted analysis on conductive transformed leather resistance measurements. The results of this research can provide important knowledge about electrical proprieties of conductive leather.

The following conclusions result from analysis of transformed nonconductive to conductive by applying chemical treatment. Understanding the transformed samples, electrical proprieties are surveyed, taking into consideration surface resistance for conductivity analysation and linear resistances in case of anisotropy. Both of these methods rely on four probe measurement techniques.

Obtained surface resistance values indicate significant outcomes, where we have samples with high conductivity values. Analysing leather conductivity values will be subject to upcoming research, since the research interests are in the application of them in the real life scenarios.

The other measurement technique also applies different electrode placement, where linear resistance values indicate anisotropic characteristics of leather samples. These results show that chemical treatment of conductive leather is not uniformly distributed.

We aimed to provide important knowledge about the electrical properties of conductive leather materials, a problem not so treated in literature.

As a future improvement of this research, we aim to try the effectiveness of conductivity transformation on real applications.

REFERENCES

- [1] Yoon B and Lee S. Designing waterproof breathable materials based on electrospun nanofibers and assessing the performance characteristics. Fibers and Polymers. 2011 12(1):57-64. Available from: https://link.springer.com/article/10.1007/s12221-011-0057-9
- [2] Yang Z, Wang Q. A simple approach to measure the surface resistivity of insulating materials. In: IECON 2011 - 37th Annual Conference of the IEEE Industrial Electronics Society [Internet]; 7-10 Nov. 2011; Melbourne, VIC, Australia. Available from: https://ieeexplore.ieee.org/document/6119630 doi: 10.1109/IECON.2011.6119630

- [3] Tokarska M, Frydrysiak M, Zięba J. Electrical properties of flat textile material as inhomegeneous and anisotropic structure. Journal of Materials Science: Materials in Electronic. 2013 24(12):5061-5068. Available from: https://link.springer.com/article/10.1007/s10854-013-1524-4
- [4] Ramadan AA, Gould RD, Ashour A. On the Van der Pauw method of resistivity measurements. Thin Solid Films. 1994 239(2):272-275. Available from: https://www.sciencedirect.com/science/article/ pii/004060909490863X doi: 10.1016/0040-6090(94)90863-X
- [5] Wenner F. A Method of Measuring Earth Resistivity. Bulletin of the Bureau of Standards. 1916 12:469-478.
- [6] Banaszczyk J, De Mey G, Schwarz A, Van Langenhove L. Current Distribution Modelling in Electroconductive Fabrics. In: 2007 14th International Conference on Mixed Design of Integrated Circuits and Systems [Internet]; 21-23 June 2007; Ciechocinek, Poland. Available from: https://ieeexplore.ieee. org/document/4286196 doi: 10.1109/MIXDES.2007.4286196
- [7] Van der Pauw L. A method of measuring the resistivity and Hall coefficient on lamellae of arbitrary shape. Philips Technical Review. 1958 59(8):220-224.
- [8] Yang C, Wang J, Li L. Innovative artificial leather with high thermal conductivity as a new leather product. Textile Research Journal. 2017 87(20):2487–2504. Available from: https://journals.sagepub.com/doi/ full/10.1177/0040517516673328 doi: 10.1177/0040517516673328
- Hong KH. Preparation of Conductive Leather Gloves for Operating Capacitive Touch Screen Displays.
 Fashion & Textile Research Journal. 2012 14(6)1018-1023. Available from: http://koreascience.or.kr/ article/JAKO201205759628105.page doi: 10.5805/KSCI.2012.14.6.1018
- [10] Varesano A, Dall'Acqua L, Tonin C. A study on the electrical conductivity decay of polypyrrole coated wool textiles. Polymer Degradation and Stability. 2005 89(1):125-132. Available from: https://www. sciencedirect.com/science/article/pii/S0141391005000418doi:10.1016/j.polymdegradstab.2005.01.008
- [11] Chenxiao Y, Wang J, Li L. A novel approach for developing high thermal conductive artificial leather by utilizing smart electronic materials. Textile Research Journal. 2017 87(7):816-828. Available from: https://journals.sagepub.com/doi/10.1177/0040517516641356 doi: 10.1177/0040517516641356
- [12] Kaynak A, Beltran R. Effect of synthesis parameters on the electrical conductivity of polypyrrole-coated poly (ethylene terephthalate) fabrics. Polymer international. 2003 52(6):1021-1026. Available from: https://onlinelibrary.wiley.com/doi/10.1002/pi.1195 doi: 10.1002/pi.1195
- [13] Hersh PS, Montgomery DJ. Electrical resistance measurements on fibers and fiber assemblies. Textile Research Journal. 1952 22(12):805-818. Available from: https://journals.sagepub.com/ doi/10.1177/004051755202201207 doi: 10.1177/004051755202201207
- [14] Gomes de Souza Jr F, Soares BG, Pinto JC. Electrical surface resistivity of conductive polymers A non-Gaussian approach for determination of confidence intervals. European Polymer Journal. 2008 44(11):3908-3914. Available from: https://www.sciencedirect.com/science/article/pii/ S0014305708003510 doi: 10.1016/j.eurpolymj.2008.07.022
- [15] Asanovic KA, Mihajlidi TA, Milosavljevic SV, Cerovic DD, Dojcilovic JR. Investigation of the electrical behavior of some textile materials. Journal of Electrostatics. 2007 65(3):162-167. Available from: https:// www.sciencedirect.com/science/article/abs/pii/S030438860600074X doi: 10.1016/j.elstat.2006.07.008
- [16] Tokarska M. Measuring resistance of textile materials based on Van der Pauw method. Indian Journal of Fibre & Textile Research. 2013 38(2):198-201. Available from: http://nopr.niscair.res.in/ handle/123456789/19252
- [17] Azoulay J. Anisotropy in electric properties of fabrics containing new conductive fibers. IEEE Transactions on Electrical Insulation. 1988 23(3):383-386.

- [18] Wegene JD, Thanikaivelan P. Conducting Leathers for Smart Product Applications. Industrial and Engineering Chemistry Research. 2014 53(47):18209-18215. Available from: https://pubs.acs.org/doi/ abs/10.1021/ie503956p doi: 10.1021/ie503956p
- [19] Berberi PG. A New Method for Evaluating Electrical Resistivity of Textile Assemblies. Textile Research Journal. 1998 68(6):407-412. Available from: https://journals.sagepub.com/doi/ abs/10.1177/004051759806800604 doi: 10.1177/004051759806800604
- [20] Kacprzyk R. Measurements of the volume and surface resistance of textile materials. Fibres & Textiles in Eastern Europe. 2011 19(1):47-49. Available from: http://www.fibtex.lodz.pl/article461.html
- [21] Hylli M, Shabani A, Kazani I, Beqiraj E, Drushku S, Guxho G. Application of Double In-Situ Polimerization for Changing the Leather Properties. In: 8th International Conference of Textile Proceedings; 2018; Tirana, Albania.
- [22] Hylli M, Kazani I, Shabani A, Komici D, Guxho G, Drushku S. Transforming leather properties from nonconductive to conductive. In: 1st International Conference: Engineering and Entrepreneurship; 2007; Tirana, Albania.
- [23] Petersen P, Helmer R, Pate M, Eichhoff J. Electronic textile resistor design and fabric resistivity characterization. Textile Research Journal. 2011 81(13):1395-1404. Available from: https://journals. sagepub.com/doi/10.1177/0040517511404591 doi: 10.1177/0040517511404591
- [24] Schnabel P. Four-Point Method for Measuring the Anisotropy of Resistivity. Philips Research Reports. 1964 19:43-52.
- [25] Kazani I, De Mey G, Hertleer C, Banaszczyk J, Schwarz A, Guxho G, Van Langenhove L. Van der Pauw method for measuring resistivities of anisotropic layers printed on textile substrates. Textile Research Journal. 2011 81(20):2117-2124. Available from: https://journals.sagepub.com/doi/10.1177/0040517511416280 doi: 10.1177/0040517511416280