Quantification of the silver content of a silver-plated nylon electrode according to the nature of the laundering detergent

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Abstract. In this study, the loss of the silver content was determined accurately when silver plated nylon electrodes dedicated to a measurement of human physiological parameters are washed with detergents containing bleaching agents. Thermogravimetric analysis and morphological observations based on SEM images have been conducted to determine the quantity of remaining silver on the electrodes. This loss of the conductive silver content is critical for the electrodes as it reduces their electrical conductivity and therefore their capacity to be used to measure either low voltages from the skin generated by ECG (electrocardiograph), EMG (electromyograph) or even EEG (electroencephalograph) or to determine the bioimpedance of human body or specific organs. The reduced surface conductivity leads also to a very complex contact impedance between the electrodes and the skin and therefore to their high sensitivity to any movement. This also results in noisy signals that are not useful to monitoring of physiological parameters and the concept of predictive medicine.

1. Introduction

Although the market of smart textile has been predicted to grow exponentially in the last few years, no connected garment has been a commercial success yet. However, since 2000s many e-textile prototypes have been designed and fabricated by researchers [1] but only a few of them were put on the market yet [2]. The poor reliability and washability of smart garment prototypes can account for that [3] even though the withstanding to washes has been identified as a critical element to focus on, when designing a wearable textronic [4]. Whatever the conductive material used (intrinsically conductive polymers like PEDOT [5], metal plated yarns [6] or fabric printed with conductive ink [7]), the washing process tend to impact the conductivity, more specifically to reduce it. Indeed, this phenomenon has been mostly explained by the rubbing of the conductive material due to the mechanical constraint of the washing drum. However, chemical impact of the washing process has not been much studied although electronic parts are mostly made with metal, which have a great tendency to oxidize into water. This oxidization was reported by Kellomäki et al. [8] who studied the color change of an antenna made with silver which has darkened with the washes. Very few similar studies can be found in the literature as most of them used bleach free detergents. One study by Slade et al. [6] concluded that the performance of their
developed metal-coated fabrics were poor after washing them with a detergent containing bleaching agents. Nonetheless their specific roles were not studied. 

In a previous study [9], the impact, on the electrical conductivity, of oxidizing bleaching agents on a silver-plated-nylon fabric used as a sensing skin electrode in a smart garment was investigated. It has been found that using detergents containing these agents reduces dramatically the overall electrical conductivity of the electrode. The oxidation of the silver layer, evidenced by the darkening of the electrode, can account for the loss of conductivity as silver oxides tend to be less conductive. However, a morphological study, using a scanning electron microscope (SEM), shows also that the silver coating has been damaged. As a result, the silver content tends to diminish with the washings, according to the detergents used. In this study, the loss in silver is precisely quantified. To this purpose silver plated nylon yarns were washed with detergents with and without bleaching agents, then their silver content was determined by thermogravimetric analysis (TGA).

2. Materials and Methods

2.1. Design and manufacturing of textile electrodes

Three silver-plated-nylon yarns were bought from three different suppliers. In the following study they will be referred to as yarn A, B, and C. Double jersey fabrics (reverse side in cotton with a polyester bonding, see Figure 1.) were knitted with yarn A, B and C respectively. An industrial circular knitting machine (CMO4A, Orizio) was used.

2.2. Washing Conditions

Domestic washing conditions were tried to be reproduced as this study was funded by a clothing manufacturer. That is why a domestic washing machine (ENF 1486 EHW, Electrolux) was used using the cycle delicate which consists in a one-hour-washing at 30°C with a maximum spinning speed of 400 rpm). Different detergents were used: A powder detergent which contains bleaching agents (Omo Concentrated Professional, Diversey S.A) was used for lot n°1 whereas a liquid one (Eco bulle Bio from Bulle Verte), without any bleaching agents was used for lot n°2. which does not contain any bleaching agents. A large sample (60x50 cm²) was divided into smaller sampler of 10x10 cm² and placed inside the washing with 1.8kg of random everyday clothes to simulate a real household washing, in compliance with the AATCC135 standard for laundry. Every cycle one sample was withdrawn and line dried, until 30 cycles. As a result, 90 (3*30) samples were collected in each washing condition (lot n°1 and lot n°2) but fewer samples (samples washed 10, 15, 20, 30) were deeply analyzed in this study.

2.3. Scanning Electron Microscope (SEM) Observation

A scanning electron microscope (Phenom ProX, ThermoFischer Scientific, US) was employed to look closer at the silver layer of the metal-plated-yarn and observe the potential damages.

The different chemical elements present at the surface of the fabric were identified by the Element Identification (EID) software package which included an Energy Dispersive Spectrometer (EDS). It was used to determine the percentage of silver which remains on the washed samples. But also, to investigate the potential formation of a silver oxide. The sample that has not been washed (reference sample) and samples washed respectively 10, 20 and 30 times have been observed and compared.

2.4. Thermogravimetric Analysis (TGA)
To quantify the impact of the laundering on the silver content of the different fabrics, thermogravimetric analyses were carried out by a thermogravimeter (TGA 4000, Perkin Elmer). To improve the readability of the TGA curves and to obtain more accurate silver contents, silver plated nylon yarns were unknitted from the fabric which also contains cotton and polyester yarns (Figure 1). For each measurement, approximately 20 mg of silver yarn were put in the crucible and heated from 30° to 900°C in an oxygen atmosphere, then cooled down to 30°C. As the degradation of nylon starts at around 330 °C and silver is not degraded till 900 °C, the weighed residue is only composed of pure silver at such temperature. It turned out that measurements have a high standard deviation. It can be explained because on the one hand the plating of silver is not strictly identical from one bobbin to another and on the other hand mechanical constraints from the washing drum are not equally applied on the fabric during the washing cycles. That’s why a deeper analysis was done on yarn A for investigating the impact of the bleaching agents on the silver content. Seven successive measurements were done for each of the searched silver content (before washing and after being washed 30 times with and without bleaching agents). A comparison between yarns was also done. For each yarn (A, B and C), five measurements were done: before washing (reference), washed 15 and 30 times with and without bleaching agents.

3. Results and Discussion
At first glance, it can be noted that the 30-time-washed sample from lot n°1 has darkened visually compared to sample from lot n°2 which looks like the reference sample. This darkening of the samples washed with bleaching agents has been further characterized in a previous study [9]. At the yarn level, SEM observations (Figure 2) reveal that the silver layer on the filaments is significantly damaged after 30 washing cycles with bleaching agents but much less when washed without.

As both samples underwent the same mechanical stress, this difference can only be explained by the presence of bleaching agents during the washing process. They have probably oxidized the silver layer which made it more vulnerable to the rubbing from the machine drum.

Regarding the EDS analysis (Figure 2), it seems that half the silver (19.11 compared to 38.77) has been removed by 30 washing cycles without bleaching agents, which is quite high value. However, it is relatively low when compared with the same number of washings with bleaching agents where only an eighth (5.09 compared to 38.77) of the silver layer seems to remain. However, such comparisons can’t be drawn directly between yarns as the observed material can’t be strictly the same. Indeed, due to the surface inhomogeneity of yarn, it is impossible to observe strictly the same number of filaments in the same spatial configuration, although the magnification is the same. As a result, the analyzed silver

| Element | Atomic Weight | Element | Atomic Weight | Element | Atomic Weight |
|---------|---------------|---------|---------------|---------|---------------|
| C       | 0.33          | C       | 0.33          | C       | 0.33          |
| Ag      | 0.67          | Ag      | 0.67          | Ag      | 0.67          |
| O       | 0.12          | N       | 0.01          | O       | 0.01          |
| N       | 0.01          | N       | 0.01          | N       | 0.01          |
surface varies from one observation to another. Furthermore, the observed zone is only 0.16 mm² which is not significant for determining the average silver content of a sensor electrode which is 8 cm².

That’s why a more precise quantification of the silver content was done by thermogravimetric analysis. In the first place, the silver content of the reference sample was measured. As the silver coating is not strictly homogenous, due to the metallization process, seven measurements were done to obtain an average reference content of silver of 18.88% ± 0.23% for the yarn A.

Then seven measurements were done for each 30-time-washed sample from the two lots. Results show that the average silver content of a yarn washed with bleaching agents is 15.44% ± 0.34% compared to 17.12% ± 0.26% when washed without. To put this figure into perspective, a comparison of the effective silver weight on a silver-yarn sensor has been drawn. Indeed, as silver is the conductive material, every single microgram is involved in the final conductivity of a sensor. For this comparison, a 0.2 g silver-plated-nylon electrode (which corresponds approximately to an 8 cm² ECG sensor) was considered. As a result, this electrode would lose almost two times more silver if it is washed with a detergent with bleaching agents compared to without (Table 1).

Table 1. Comparison of the remaining silver content regarding the presence of bleaching agents in the detergent.

| Electrode weight (mg) | Silver weight (mg) | Silver Loss in weight (%) | Loss Ratio |
|-----------------------|-------------------|---------------------------|------------|
| With Bleaching agents | 200               | 37.76                     | 18.21      | 1.95       |
| Without Bleaching agents | 30 washes         | 30.88                     | 34.24      | 5.33       |
|                       | 30 washes         | 18.21                     |            |            |

The fact of losing silver leads inevitably to a loss in conductivity at the yarn level and so a loss of information at the sensor level. Indeed, the silver removed from the conductive layer will decrease its thickness, so increase its resistance, in the first washing cycles. As the conductive layer is thin, this small removal will rapidly create discontinuities (cf. Figure 2) in that layer that hinder the electrons’ move. As a result, a complete loss of conductivity can be observed after less than 30 washing cycles. More details can be found in our previous study [9].

Thermogravimetry (TG) and corresponding derivative thermogravimetry (DTG) curves from the unwashed (reference) yarn A are given in Figure 3. The plots show that yarn A undergoes thermal degradation between 392°C and 764°C with a DTG peak at 493,50°C which almost corresponds to the nylon 6,6 T_{max} [10]. Nevertheless, the degradation of silver-plated nylon is not as sharp as pure nylon which loses more than 90% of its mass between 480 and 520°C. Silver plated nylon tends also to lose sharply 75% of its weight between these temperatures but the remaining 25% decrease slowly and steadily from 520 to 800°C.

Figure 3. TG and DTG curves of the silver-plated nylon yarn (sample A) before washing cycles.
A very slight decrease in weight can be noticed at the early beginning of the heating process. It corresponds to the small amount of ambient moisture absorbed by the nylon polymer. Figure 4 shows TGA curves of the three silver plated yarns. Not surprisingly their shapes are quite similar, even nearly identical for yarn A and C. However, it should be noted that their silver contents are significantly different. Indeed, yarn C contains only 13.88% whereas yarn B contains 23.42% and yarn A 18.8% as seen before. This difference in the silver content can account for the difference in prices of those yarns, which varies accordingly to their silver content.

![Figure 4. TG curves of the three yarns.](image)

Furthermore, regarding their washing resistance, it is interesting to note that the more expensive yarn, presenting the higher silver content, is also the most resistant one to washing cycles (Table 2). It suggests that the thicker the silver layer, the more resistant it is. Indeed, yarn C is highly degraded by the washing cycles. Curiously the silver loss is even more significant when washed without bleaching agents.

![Table 2. Comparison between yarns of their silver loss, according to the number of washings.](image)

### 4. Conclusion

The silver layer appears to be more damaged when the textile is washed with a detergent containing bleaching agents (powder detergents). In fact, on one hand, the sensor tends to be visually darker. On the other hand, at a microscopic level, the silver layer appears rubbed and scratched. Indeed, it turns out that silver layer has been rubbed nearly twice (in weight) in such washing conditions compared to when washed without bleaching agents. Bleaching agents have probably oxidized the silver layer making it more amorphous and so more easily removable under mechanical stress. This loss in silver, which makes the yarn conductive, results in a decrease of conductivity during the first washing cycles (<15 cycles) but drives to a total loss of conductivity after 30 washing cycles. It means that sensors are no longer able to neither record bio-signals nor transmit them. As a result, “smart garment” will no longer be “smart” under those oxidizing laundering conditions unless sensors are replaced. However, in order to have better acceptability, sensors should be preferably integrated seamlessly in the garment which makes them unreplaceable. Moreover, sensors are mostly responsible for the high retail prices of such garments, as conductive materials and their integration are expensive, so replacing them every 15 washing cycles won’t be accepted by customers. That’s why the focus should be put on making sensors...
more resistant to washings and finding washing processes that are less aggressive for them. According to this study liquid detergents (without bleaching agents) are highly recommended for the laundering of textiles incorporating silver plated nylon sensors for the sake of their durability. Otherwise, the pure silver content of the sensors will decrease more quickly (it will be oxidized and then torn off more easily), resulting in reducing the overall conductivity of the electrodes so its long-term reliability.

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References
[1] Fernández-Caramés T and Fraga-Lamas P 2018 Towards The Internet-of-Smart-Clothing: A Review on IoT Wearables and Garments for Creating Intelligent Connected E-Textiles Electronics 7(12) p. 405.
[2] Vagott J and Parachuru R 2018 An overview of recent developments in the field of wearable smart textiles J. Text. Sci. Eng. 8 p.364.
[3] Tao X, Koncar V, Huang T H, Shen C L, Ko Y C and Jou G T 2017 How to Make Reliable, Washable, and Wearable Textronic Devices Sensors 17(4) p. 673.
[4] Gniotek K and Krucińska I 2004 The Basic Problems of Textronics Fibres Text. East. Eur. 45(1) pp. 13-16.
[5] Ankhili A, Tao X, Cochrane C, Coulon D and Koncar V 2018 Washable and Reliable Textile Electrodes Embedded into Underwear Fabric for Electrocardiography (ECG) Monitoring Materials 11(2) p. 256.
[6] Slade J et al. Washing of electrotextiles 2002 MRS Proc.736.
[7] Karaguzel Bet al. 2009 Flexible, durable printed electrical circuits’, J. Text. Inst. 100(1), pp.1-9.
[8] Kellomäki T, Virkki J, Merilampi S and Ukkonen L 2012 Towards Washable Wearable Antennas: A Comparison of Coating Materials for Screen-Printed Textile-Based UHF RFID Tags Int. J. Antennas Propag. 2012 pp. 1–11.
[9] Gaubert V, Gidik H, Bodart N and Koncar V 2019 2A3_0644_ towards washable smart textiles: investigating the impact of oxidizing bleaching agents on silver-plated textile electrodes Proc. 19th World Text. Conf. - Autex 2019, pp. 6–6.
[10] Pashaei S, Siddaramaiah S, Avval M and Syed A 2011 Thermal degradation kinetics of nylon6/GF/crysnano nanoclay nanocomposites by TGA Chem. Ind. Chem. Eng. Q. 17(2) pp. 141–151.