ELECTRICAL AND ANTIBACTERIAL PROPERTIES OF POLYESTER NONWOVEN WITH CONDUCTIVE NANOMETALLIC SURFACE PREPARED USING TANNIC ACID

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Abstract

The surface of the polyester nonwoven fabric was covered with a layer of silver and copper-based nanoparticles obtained from their salts and reduced using tannic acid. Polyester nonwoven MILIFE® without surface modification was used as a carrier of the metallic layer. The repetitive technological steps of preparing the conductive layer led to an increase of color intensity of fabric with bronzing effect, which also manifested in their decreased electric resistance. Simultaneously, all the samples were tested for resistance to selected G+ and G- bacteria.

Keywords: Tannic acid, silver, copper oxide, nanoparticles, electric resistance, antibacterial

1.   INTRODUCTION

With the development and miniaturization of electronics, textiles are at the forefront of developers' interest due to their flexibility, breathability, comfort, low weight and considerable mechanical resistance. At the same time, the connection to electronics shifts the textiles to a qualitatively higher level. Therefore, in recent years, considerable attention has been paid to the electrical properties of textiles.

Most of the textiles act as very strong natural insulators. Electrically conductive fabrics can be made in several ways. Generally, conductive fabrics can be prepared by two methods. Firstly, conductive materials (e.g. metal nanoparticles, carbon nanotubes, graphene, conductive polymers) are added during the spinning process to obtain conductive fibers, and the fibers are then woven into conductive fabrics. [1,2] The disadvantage and limitation of this procedure are reduction of fiber spinnability, flexibility and many other mechanical properties. The second method of preparation of a conductive fabric is an additional covering of the fabric surface using above-mentioned conductive materials or their composites. [3] The disadvantages of this process are, for example, the unevenness of the conductive layer, the reduction of the breathability of the fabric, and the danger of exfoliation and delamination of the coating. Despite these risks, the second procedure is technologically simpler and cheaper.

One of the possible and sustainable paths of the development of new methods and technologies for eco-friendly advancements in preparation of conductive textiles is to use the green chemistry, particularly, its application in the deposition of metallic layers and reduction of metal nanoparticles on the surface of the fibers. Reduction of metal salts by plant derived compound like tannins fulfil the requirement of a chemical reductant. Hence, it renders the characteristics of green synthesis. Tannins as natural reductants (antioxidants) have potential to reduce some of their salts, which has been experimentally proven in the past research studies. Tannic acid has been used experimentally in the past for example to prepare nanoparticles of silver, gold, palladium and zinc. [4] Also, bimetallic nanoparticles such as Au-Pt were prepared using tannic acid. [5]

In this work, the bath method has been used for metal nanolayer coating of fibers surface when metal salts were reduced by natural reducing agent (tannic acid) in an alkaline environment. Thus, two aspects of polyester nonwoven with nanometallic layer were investigated, namely electrical resistivity and the ability to resist the action of selected G- and G+ bacteria (*Escherichia coli* and *Staphylococcus epidermidis).*

1.1. Mechanism of interaction of tannic acid with metal salts

Tannic acid is rich in electrons and embodies the capability of liberating freely reactive hydrogen atom. Presence of a hydrophobic "core," a hydrophilic "shell," and above all the polyphenolic nature of tannic acid make it an effective reducing agent. Numerous polyphenols bear antioxidant nature owing to the relative facileness of donating hydroxyl group to a free radical and the potency of the aromatic ring to carry an unpaired electron. Carboxylic acid groups (COOH) present in the tannic acid lose their hydrogen atom to become carboxylate ion (COO-) during the reduction process. The COO- so formed attaches to the surface of metal nanoparticles along with the remaining part of the polymer to act as surfactant and stabilize metal nanoparticles. [6]

1.2. Antibacterial properties of metal nanoparticles

Silver nanoparticles and nanoparticles of copper or copper oxides have been examined many times as biocides. The mechanism how nanoparticles can penetrate bacteria is not understood completely but studies have suggested that when bacteria are treated with copper nanoparticles, changes take place in its cell membrane morphology. Copper ions have the capacity to kill bacteria by destroying their cell walls and membranes because they have a strong reduction ability, which can extract electrons from the bacteria, causing their cytoplasm to escape and oxidizing the cell nucleus. [7] The opposite charges of bacteria and copper ions released from nanoparticles are thought to cause adhesion and bioactivity due to electrostatic forces. Copper ions can combine with the plasma membrane by electrostatic attraction and then penetrate the cell membrane through opening or closing of membrane channels. This alters the permeability of cellular membranes, which causes leakage of intracellular ions and low molecular weight metabolites. At the same time, copper ions entering cells combine strongly with intracellular amino acids and proteases, resulting in degeneration that leads ultimately to denaturation of proteins. The overall charge of bacterial cells at biological pH-values is negative due to the excess of carboxylic groups present in the lipoproteins at the bacterial surface, which, upon dissociation, makes the cell surface negative. [8] Also, the actual bactericide mechanism of silver nanoparticles is not well known. Some researchers support the idea that silver species release Ag+ ions and they interact with the thiol groups in bacteria proteins, affecting the replication of DNA. It has also been reported that Ag+ ions uncouple the respiratory chain from oxidative phosphorylation or collapse the proton-motive force across the cytoplasmic membrane. [9]

2. EXPERIMENTAL PART

2.1. Material and chemicals

Silver nitrate, copper sulfate pentahydrate, sodium hydroxide and sodium carbonate (all chemicals in analytical grade, Lach-Ner, Czech Rep.), tannic acid (Sigma Aldrich), thermally bonded polyester nonwoven MILIFE® of area weight 10 g/m^2 and fiber diameter 20 µm (JX Nippon, Japan), TSA (tryptone-soya agar) in Petri dishes (Oxoid, Czech Rep.), *Escherichia coli* and *Staphylococcus epidermidis* in suspensions.

2.2. Devices

Digital insulation tester (Chauvin Arnoux CA 6543 1 kV Megohmmeter) was used to determine the electrical conductivity or electrical resistance of textile samples with metallic layers, and the values were compared with the value of MILIFE® without the nanometallic layer. The measurement was carried out 3 times in different areas of the samples, each fabric in 1, 2 and 4 layers lying on each other. The basic statistical analysis was carried out again. Scanning electron microscope (UHR SEM Ultra Plus, Carl Zeiss, Germany) was used to display and measure the metallic nanolayer on the fibre surface.

2.3. Antibacterial tests

The ability to resist G- and G+ bacteria was based on standard [10] and tested using suspension of *Escherichia coli* and *Staphylococcus epidermidis*, each at a concentration of 10^6 CFU/ml. The test samples were placed on agar inoculated with the bacterial strain. Cultivation took 24 hours at 37 °C. Subsequently, the growth of the bacteria under the sample and the size of the inhibition zone around the sample were evaluated.

Second antibacterial test was based on modified standard [11]. This dynamic shake flask test is designed to evaluate the antimicrobial activity of non-leaching, antimicrobial-treated specimens under dynamic contact conditions. Its first phase is the dynamic contact of the antimicrobial treated surface with a bacterial suspension. The contact of samples with bacterial suspension took 1 hour. In the subsequent phase, shaking of the textile samples in water is carried out, shake ratio of 1:50 (weight of the fabric in grams: volume of water in ml). These extracts were further diluted 100x and 1 ml of this eluate was plated on agar. After 24 hours at 37 °C, colonies of bacteria were counted. This second test was provided with *E. coli* only.

2.4. Preparation of samples

The following stock solutions were prepared: tannic acid (3g/l), $AgNO_3$ (2 g/l), $CuSO_4·5H_2O$ (2 g/l), Na_2CO_3 (2 g/l), NaOH (4 g/l). The $CuSO_4$ solution was converted to $Cu(OH)_2$ by addition of NaOH. The solutions of both metals were heated to 75 °C. A sample of the clean fabric MILIFE® was placed in an $AgNO_3$ solution for 5 minutes. Subsequently, it was gently dried and immersed into tannic acid solution for 1 minute and further alkalized by brief immersion in Na_2CO_3 solution. Since 2-3 repetitions were not sufficient to create a conductive layer on the surface of the fabric, this procedure was repeated 8 times until the visual effect of the so-called „bronzing" (change in the color of the surface giving the appearance of aged bronze). This is a condition where multiple metallic layers with a typical optical effect are formed on the fabric surface. Preparation of the copper nanolayer on the fabric was carried out similarly but without additional alkalization of Na_2CO_3. The procedure was repeated 8 times, too.

3. RESULTS AND DISCUSSION

3.1. SEM images

Figure 1 and **Figure 2** show the structure of the metallic layers formed on the surface of the PES fibers by the process of repeated application of metal ions from the solution and reduction by tannic acid.
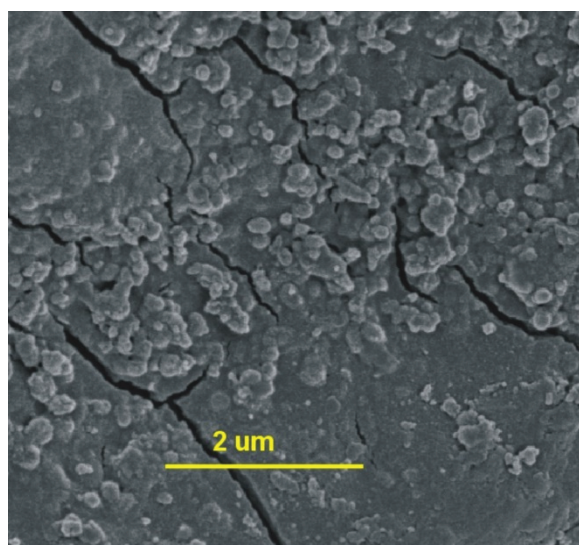

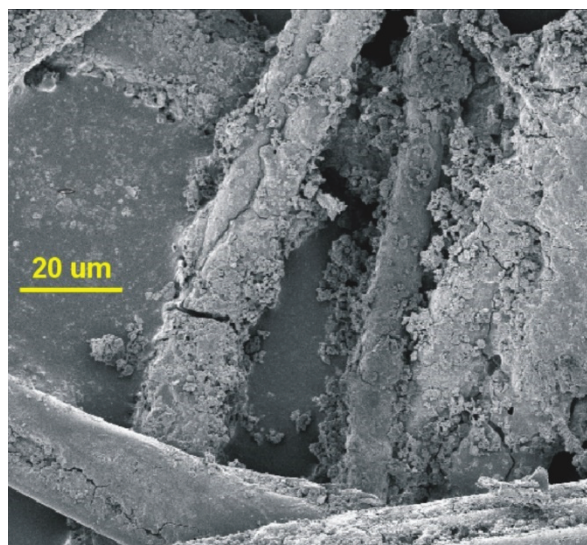**Figure 1** Copper-based nanolayer (10 000x)

Figure 2 Bronzing silver (multi) nanolayer (500x)

In **Figure 1**, the amorphous particles are visible, but it can hardly be recognized whether they are copper particles, copper oxide or copper tannates. The orange color indicates that it could be copper (I) oxide, but at the same time, it is impossible to recognize the cubic structure typical for spontaneous crystallization of Cu_2O, even at high magnification. It is very likely that a mixture of oxides and copper tannates is present. **Figure 2** confirms that the cause of the optical bronzing effect was actually the presence of multiple metallic layers of reduced silver. This layer was not homogeneous, and its disadvantage would therefore be that it would be delaminated and exfoliated under mechanical abrasion.

3.2. Electrical resistance

Table 1 contains an overview of measuring the electrical resistivity of the samples in a simple, double and quadruple-layer fabric to each other. The measurement was performed at a set value of 500 V. It is obvious that the resistivity decreased with the number of multiple layers because of increased conductivity due to a growing number of contacts fibers with metallic layers. Silver layer values show much better conductivity compared to copper-based coating. This result supports the assumption that, in the case of copper, a layer of Cu_2O was formed on the surface of PES fibers. In general, the oxides are non-conductive as they have a full valence band. Copper (I) oxide does not complete the valence rings and this is a metal deficient semi-conductor. Cu_2O is known to have a high electrical resistivity which varies with the method of preparation. [12] Whereas the resistivity of the carrier fabric was in the hundreds of GΩ, the fabric with copper-based layer had an electric resistivity of 1-2 orders of magnitude lower and the fabric with silver surface of 4 orders of magnitude lower compared to the non-metallic fabric.

Table 1 Mean values and 95 % confidence intervals of means for electric resistivity of samples

	MILIFE® (blank)	MILIFE® (copper)	MILIFE® (silver)
1 layer	450 ± 25.1 GΩ	28.5 ± 8.6 GΩ	117 ± 14.1 MΩ
2 layers	470 ± 32.2 GΩ	14.2 ± 4.8 GΩ	36 ± 5.6 MΩ
4 layers	550 ± 37.4 GΩ	7.7 ± 1.9 GΩ	25 ± 0.9 MΩ

3.3. Antibacterial properties

Figures 3a and b show the resulting interaction of samples with bacteria after 24 hours of cultivation. The samples are placed from left to right in the order of: MILIFE® (blank), MILIFE® with copper and MILIFE® with silver. Samples without surface treatment are completely covered by bacteria in both cases, the copper sample having about 1 mm zone of resistance. The best antibacterial effect shows the silver sample. Bacteria have not grown under it and, in the case of *E. coli*, a significant halo zone of 2.5 mm is visible.
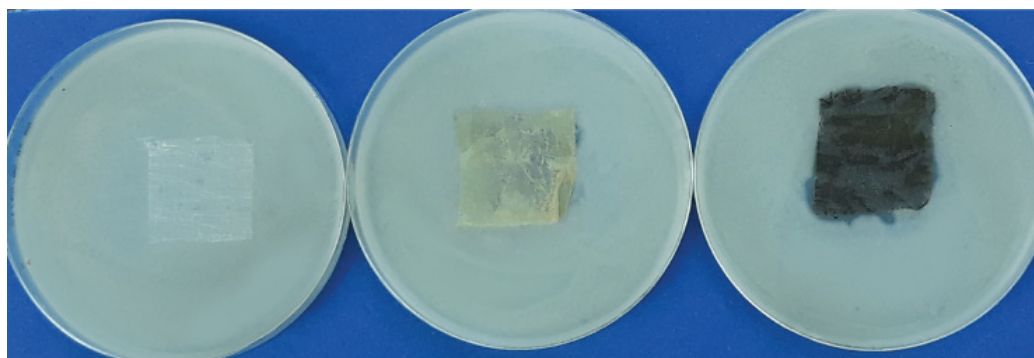

Figure 3a Samples on agar plates with *Staphylococcus epidermidis,* bacteria 10^6 CFU/ml
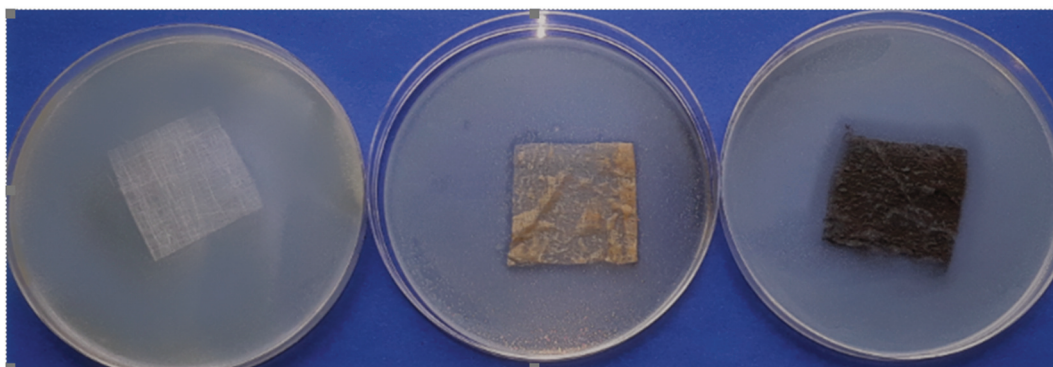
Figure 3b Samples on agar plates with *Escherichia coli*, both bacteria 10^6 CFU/ml

Dynamic shake flask test (**Figure 4**) provided some surprising results. The number of colonies in the resulting diluted eluates was 310 (blank), 470 (copper), 24 (silver) CFU/ml. A similar result, when the number of colonies from the copper sample exceeded the number of colonies from the blank, was reached even with repeated tests. One explanation for the cause could be that the layer did not contain copper or copper oxide, but rather a complex copper tannate whose antibacterial effects were not sufficient. The rugged surface of copper-based nanolayer was the reason that they caught larger number of bacteria than untreated samples.
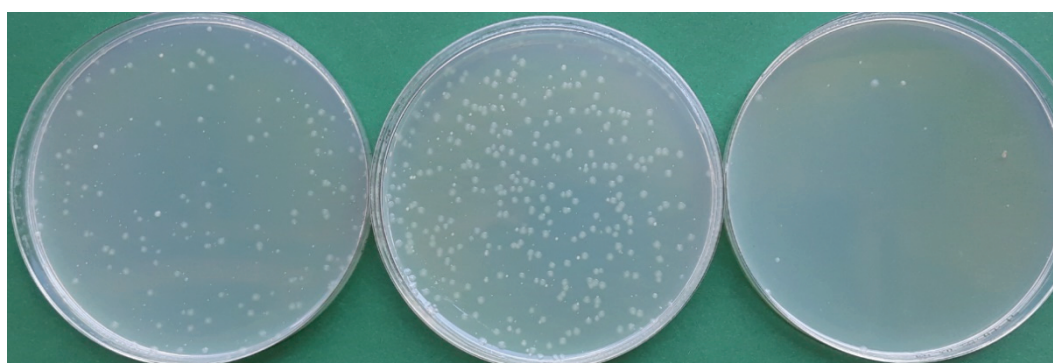

Figure 4 Cultivation of 100 times diluted eluates following dynamic contact with *Escherichia coli*
(10^6 CFU/ml). From left to right: leach samples of MILIFE® (blank), MILIFE® (copper) and MILIFE® (silver)

In any case, even in this test, excellent antibacterial properties of silver nanoparticles were confirmed again, as the eluate from the silver surface sample was almost sterile.

4. CONCLUSION

In this work, we studied the preparation of metallic nanolayers on the surface of polyester nonwoven MILIFE® via green chemistry and the verification of the antibacterial and electrical properties of these samples. Thanks to the silver layer, MILIFE® obtained up to 10,000 times lower electrical resistivity than the original untreated fabric. Resistivity has decreased in the electrical measurement of multiple layers of fabric by creating a plurality of conductive joints. However, to achieve significant conductivity, it was necessary to repeat the application process and reduction of silver on the surface of the fibers up to eight times, but this resulted in non-homogeneous coating and formation of multiple metallic layers and plates, which optically manifested itself in the so-called bronzing. On the other hand, the simple layer of silver fabric also exhibited good antibacterial properties, especially against G- bacteria *Escherichia coli*. To prepare a copper-based conductive layer, a different procedure must be chosen because the layer resulting from the tannic acid reduction appears to have a high resistivity due to content of copper (I) oxide. The process of preparing the silver layer by means of green

chemistry is promising. However, it is necessary to develop a process for production a homogeneous silver layer on the surface of the fibers.

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