

PLASMA PREPARED SILICON-BASED THIN LAYER AS THE ANTICORROSIVE PROTECTION OF CONDUCTIVE COPPER SURFACE ON POLYESTER NONWOVEN

Hana Křížová, Michal Krejčík and Stanislav Petřík

Technical University of Liberec, Institute for Nanomaterials, Advanced Technologies and Innovation,
Department of the Preparation and Analysis of Nanostructures, Bendlova 1409/7, Liberec, Czech Republic
hana.krizova@tul.cz

Abstract: Electrically conductive nonwoven polyester fabric MILIFE® with a chemically deposited copper layer was coated by the PECVD method using the mixture of HMDSO (hexamethyldisiloxane) as organosilicate precursor and oxygen. The metallized fabric with and without silica coating was subsequently tested under strongly corrosive conditions of acid and oxidizing environment. The degree of corrosion damage of the electrically conductive copper layer was determined by changes in electrical resistance measured on its surface. We have proven that silicon-based thin layer can protect the conductive metallic layers from corrosive environmental influences. The plasma-polymerized coating of silicon-based nanolayer significantly prolongs the life of metallized polyester nonwoven and extends its use to areas of long-term corrosive conditions.

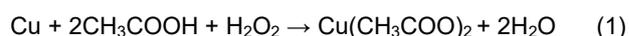
Keywords: metallized fabric, anticorrosive, conductive fabric, silicon, HMDSO, PECVD.

1 INTRODUCTION

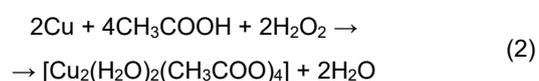
Electrically conductive fabrics have received increased attention for their high flexibility, low weight, porosity, airiness, and favorable price. A lot of ways to form conductive fabrics have been described in the literature, e.g., by adding various electrically conductive additives [1, 2], using conductive particles [3], carbon nanotubes [4], conductive polymers [5, 6], or chemically depositing metals on the fiber surface [7, 8]. New fabrics with metallic surfaces should have other properties such as physical, chemical or biological resistance, increased hydrophobicity or hydrophilicity of the surface, compatibility with the organism or environmental friendliness of their life cycles, to be widely used in industry, electrical engineering, optics or medicine and to compete with traditional materials. The corrosion resistance of materials is a typical requirement.

Copper is a metal with excellent electrical and thermal conductivity, but it decreases considerably with the content of impurities including oxygen and copper oxides respectively. Pure copper is subject to corrosion in long-term contact with the environment, where its surface is attacked e.g. by oxygen, carbon dioxide, acid rain, and other solid, gaseous or liquid substances present in the air. The changes are very slow and not entirely predictable. The composition of the verdigris that forms on the copper surface is essentially determined by the prevailing concentration of air pollution and environmental conditions. After several weeks in the air,

the reddish-orange copper obtains a brown shade (cuprous oxide, Cu_2O), which in turn darkens to black (cupric oxide, CuO). The greenish verdigris (copper carbonate, $(\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2)$) will be visible after about 20 years of the action of oxygen, air humidity and carbon dioxide. Conversely, the predominantly acidic environment is not aggressive for copper, but the oxygen plays an important role in the interaction of the copper metal with acids. In conjunction with oxygen or other oxidizing agents, the oxidative corrosion of the copper surface is rapid, even in the presence of so-called non-oxidizing acids such as HCl, where copper (II) chloride (CuCl_2) or basic copper chloride ($\text{Cu}_2(\text{OH})_3\text{Cl}$) are formed. The presence of acetic acid during copper weathering can lead to the formation of copper (II) acetate. The reaction of copper, acetic acid and hydrogen peroxide involves the formation of a free radical and an electrochemical corrosion process. The mechanism includes the creation of a strong oxidizer, peroxyacetic acid (CH_3COOOH), from dissolved oxygen [9]. The equation (1) shows simply the formation of copper (II) acetate:



In effect, according to reaction (2), tetraacetodiaquadicopper (II) complex is produced [10]:



All these corrosive reactions cause a loss of copper electrical conductivity, which degrades the conductive fabric and limits its life and use. Since the EU ban on the use of hexavalent chromium [11], which had previously been used in anti-corrosive coatings, came into force in 2007, environmentally friendly replacement materials and technologies are intensively sought.

The plasma deposition of silicon-based thin films from a mixture of HMDSO and oxygen by low pressure was investigated and described as a method of anticorrosive treatment of steel. In the plasma-assisted deposition, smooth, continuous and dense films with good adhesion were produced which exhibited a polymer-like structure at low pressure. HMDSO is very often used as an organic precursor in CVD (Chemical Vapor Deposition) methods because it is relatively non-toxic and has high room temperature vapor pressure (64 mbar) [12]. The scientific literature examining the deposition of thin films on steel shows a correlation between the composition of the gas phase and the structure of the coating. The structure of the deposited layer is dependent on the percentage of HMDSO in the mixture of gases supplied to the plasma chamber. A high percentage of HMDSO produces a polymer film, while a low percentage of HMDSO forms a silica-like film with only a small amount of carbon content [13]. It seems that the deposition rate of the protective layer depends on the HMDSO content in the feed gas, with its higher content and the deposition rate increases. Also, the higher pressure and the associated higher process gas content in the plasma reactor (plasma chamber) usually results in a higher deposition rate of the layer. At the same time, the structure of the deposited layers and their adhesion change with increasing deposition rate [12, 13].

Plasma deposition of thin layers appears to be very promising, but conventional plasma techniques require a deposition temperature of 800 (silicon carbide) to 1100°C (silica). Logically, these high temperatures eliminate the use of most substrates for plasma deposition. For low-pressure PECVD (Plasma-Enhanced Chemical Vapor Deposition), which was used in this study, thin-film deposition takes place at a lower temperature than in the conventional arrangement. This is a major advantage of the PECVD method because low melting substrates, such as organic polymers, can also be used for deposition. Thus, besides a large number of scientific works that deal with silica coating layers on metal surfaces of steel [12-19], the studies have also emerged in which this carrier substrate is a polymeric material such as polypropylene [20], polystyrene [21] or PMMA [22]. The silica-based coating is known to have very good mechanical, tribological [23], chemical and electrochemical resistance [24].

2 MATERIALS

Polyester microfiber nonwoven fabric MILIFE® (JX Nippon ANCI Corporation, JP) with a chemically metallized surface (copper layer obtained by chemical reduction process, made by Večerník Ltd, CZ).

Properties of non-metallized MILIFE®:

- chemical composition: Poly(ethylene terephthalate/ethylene isophthalate) copolymer
- linear density: 0.6 dtex
- weight area: 10 g.m⁻²
- melting point: 220-260°C
- decomposition temperature: >300°C
- color: white

Properties of metallized MILIFE®:

- weight area: 14.5 g.m⁻²
- color: reddish-brown
- physical properties: electric conductivity, EM shielding and thermal insulation [25]

Hexamethyldisiloxane (HMDSO, C₆H₁₈OSi₂; boiling point 101°C; Sigma-Aldrich)

Acetic acid (2% solution)

Hydrogen peroxide (0.25% solution)

Paraffin oil

3 METHODS

3.1 Preparation of silicon-based thin layer

The polyester nonwoven MILIFE® with a chemically deposited layer of copper on the surface of the fibers was placed and fixed in the plasma chamber. Plasma excitation was obtained with use of an RF plasma generator Cesar (13.5 MHz) which provides the power in the range 0-2000 W. The deposition of thin silicon-based protecting layer was carried out by PECVD method under the following conditions: magnetron power 150 W, preload -500 V, plasma time 7 and 20 minutes, pressure in the plasma chamber 45 Pa, and 8 sccm (standard cubic centimeters or ml.min⁻¹ under standard conditions) of oxygen flow rate to the plasma chamber. The compound HMDSO was used as a silica precursor. The reactants were fed to the working chamber in a gaseous form. As mentioned in the introduction, HMDSO has a relatively high room temperature vapor pressure, so the temperature of the precursor was not increased, and its vapors were fed into the plasma chamber with nitrogen support. HMDSO vapors were fed with nitrogen at a flow rate of 3 sccm to the plasma chamber through a needle valve.

3.2 Evaluation of silicon-based thin layer

The surface of the plasma protective layer on metallized polyester fibers was evaluated by electron microscope images (UHR FE-SEM Carl Zeiss Ultra Plus). The thickness of the plasma prepared silicon-based layers was measured

on a flat glass surface using the mechanical profilometer Bruker Dektak XT (US). Samples coated in the range of 5-30 minutes were used to measure the thickness of layers. The roughness profile of fabrics was observed by laser scanning confocal microscopy (Olympus OLS 3100) and evaluated according to the ISO 4287:1997 standard. The chemical composition of the layer was analyzed by EDS (Energy-dispersive X-ray spectroscopy) and IR (Infrared spectroscopy). EDS (which is part of electron microscope) allows the elemental composition of the samples to be measured. Four samples coated in the range of 2-20 minutes were used for IR analysis. Infrared spectroscopy gives a more specific picture of the chemical structure of the sample, particularly as regards the typical chemical groups present in the sample using ATR technique on Ge crystal (Nicolet™ iS10 FTIR Spectrometer Thermo Scientific™).

3.3 Testing under corrosive conditions and measurement of electrical surface properties (electrical resistance)

Conditions that are highly corrosive to copper (acidic pH in the presence of oxygen) were simulated using a mixture of acetic acid (2%) and hydrogen peroxide (0.25%), pH 3. Three samples were tested: metallized MILIFE® without protective thin layer (sample called "blank"), metallized MILIFE® with a thin layer plasma-treated for 7 minutes (sample called "MF/Cu/SiO_x/7"), and metallized MILIFE® with a thin layer plasma-treated for 20 minutes (sample called "MF/Cu/SiO_x/20"). The surface electrical resistance of all samples was measured using a digital multimeter DT9205A. Device parameters: maximum measuring range 0-200 MΩ (+/-0.8%), alkaline battery 9 V as a voltage source. Twenty measurements of each sample total were performed, i.e., 5 measurements in 2 mutually perpendicular directions on both sides of each fabric (vertical and horizontal directions were selected according to the visually prevailing direction of the fibers on each side of the nonwoven fabric); spot measurements were chosen randomly across the fabric, keeping the contact electrode distance of 1.5 cm at each measurement.

The acetic acid solution was boiled briefly before the test to displace a larger part of the oxygen from the solution. Metallized MILIFE® samples were left for 48 hours in a 2% acetic acid solution at room temperature. The surface level in the test tubes was covered with a 0.5 cm thick layer of paraffin oil which prevents oxygen in the air from dissolving into the acid solution. Subsequently, the fabrics were rinsed in water, dried at 50°C and their surface electrical resistance was measured again. After that the samples were placed in a (separate) bath with acetic acid/hydrogen peroxide mixture for 2 minutes, followed by thorough rinsing in water and drying for 2 minutes at 50°C. The dried samples were

re-measured, and this cycle was repeated until the final total time of 10 minutes in the acidic oxidizing bath. Each set of 20 electrical resistance measurements was evaluated statistically; the average surface electrical resistance of the fabric and the 95% confidence interval were calculated.

4 RESULTS AND DISCUSSION

Figures 1-3 show the surface of the MILIFE® microfiber without coatings, with a copper-metallized coating and with plasma-polymerized silicon-based layer on the metallized surface. All three surfaces have approximately the same magnification (10 000x). The nano-roughness of the fiber surface at 10 000x magnification was investigated. It is evident that the nano-roughness of metallized fibers with silicon-based coating (Figure 3) is higher than before the plasma treatment (Figure 2).

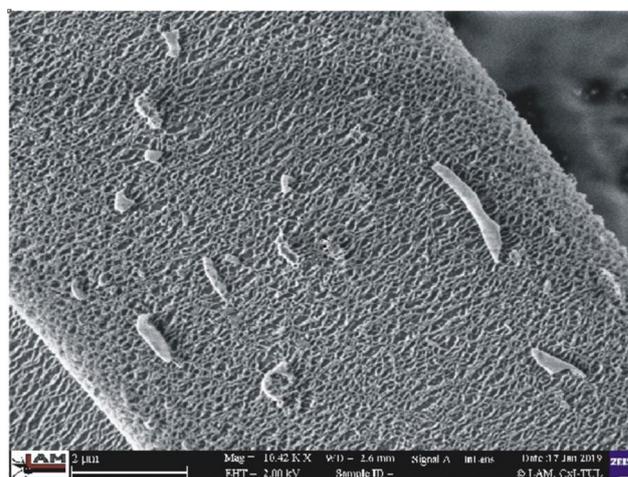


Figure 1 SEM image of MILIFE® microfiber with impurities on the surface (10 420x)

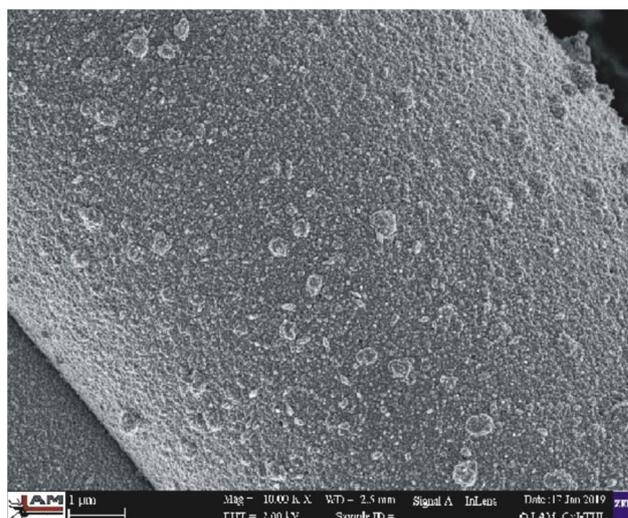


Figure 2 SEM image of copper-metallized MILIFE® microfiber with copper clusters on the surface (10 000x)

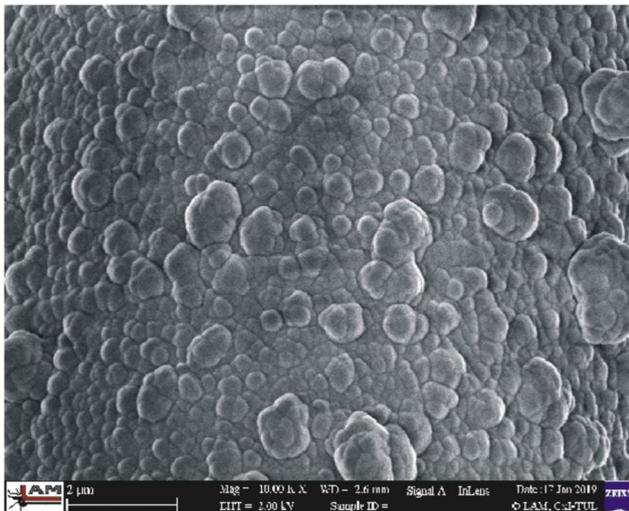


Figure 3 SEM image of copper-metallized MILIFE® microfiber with plasma-prepared silica-based coating (10 000 x)

The copper clusters appear to have functioned as nucleation centers for the growth of the polymeric silicon-based layer, and thus the surface roughness of the fiber surface has increased at the nanoscale. In addition, the tendency for higher roughness of silicon-based plasma coated layers using higher radio frequency power in the presence of oxygen has already been demonstrated. The study [26] showed RF-input power determines the crosslink density and the hydrocarbon content in the layers and plays a key role in the occurrence of higher roughness. The presence of oxygen at higher RF power also significantly increased the roughness of the resulting surface.

The graph in Figure 4 shows the thickness of the plasma-polymerized silica layer as a function of the plasma time obtained from the analysis of layers deposited on glass. Each value was calculated from 5 values measured at the flat glass plasma-coated surface using the mechanical profilometer. These samples were prepared in a plasma chamber under the same conditions as plasma-coated textile samples, but different plasma times (5, 10 and 20 minutes) were used. The reason for using the glass to apply this layer was to determine more precisely the thickness of the coated layer: a flat solid object with a partial covering allows a more accurate measurement of the thickness of the thin layer than flexible textile fibers.

The graph in Figure 4 shows that the thickness of the plasma-polymerized layer coated the copper layer on fibers was approximately 120 nm (sample MF/Cu/SiO_x/7) and 388 nm (sample MF/Cu/SiO_x/20). Some unevenness was caused mainly by power fluctuations, which could not be kept completely constant during plasma times. Essentially, however, the thickness of the plasma-coated layer is linearly dependent on the plasma time while maintaining a stable flow rate of process gases, power of matching network, and plasma chamber pressure. The plasma deposition rate under the set conditions was approximately 0.3 nm.s⁻¹.

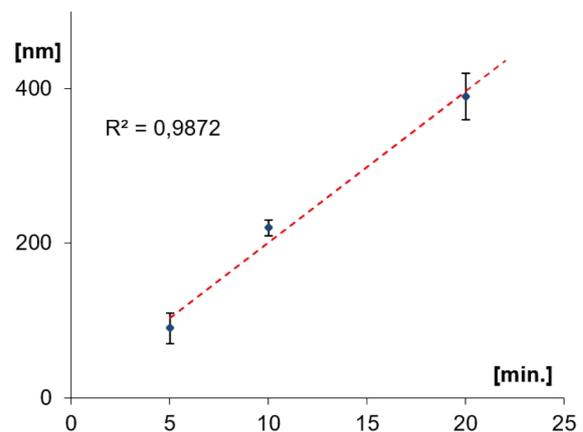


Figure 4 Thickness of silica-based coating depending on the time of plasma-treatment

As for the chemical composition of the plasma-polymerized layer, the EDS analysis of the surface of plasma-prepared layer (Figure 5) shows the presence of silicon and oxygen as the main elements. This is a sample of polyester non-woven MILIFE® (non-metallized) with a thin silicon-based layer after 20 minutes of plasma treatment, i.e., a layer about 388 nm thick. The similar weight ratio of silicon to oxygen (silica 34.9 wt.%, oxygen 34.1 wt.%) represents an Si:O atomic ratio of about 1:1.7. This suggests that the formed layer contains mainly silica (SiO₂). However, considering the weight fraction of carbon (29.8 wt.%), the total atom content in the deposited layer was SiO_{1.70}C_{1.98}. However, the EDS analysis penetrates to a depth of 1-2 microns, so the oxygen and carbon contained in the polyester of the carrier fabric could be included in this analysis as well.

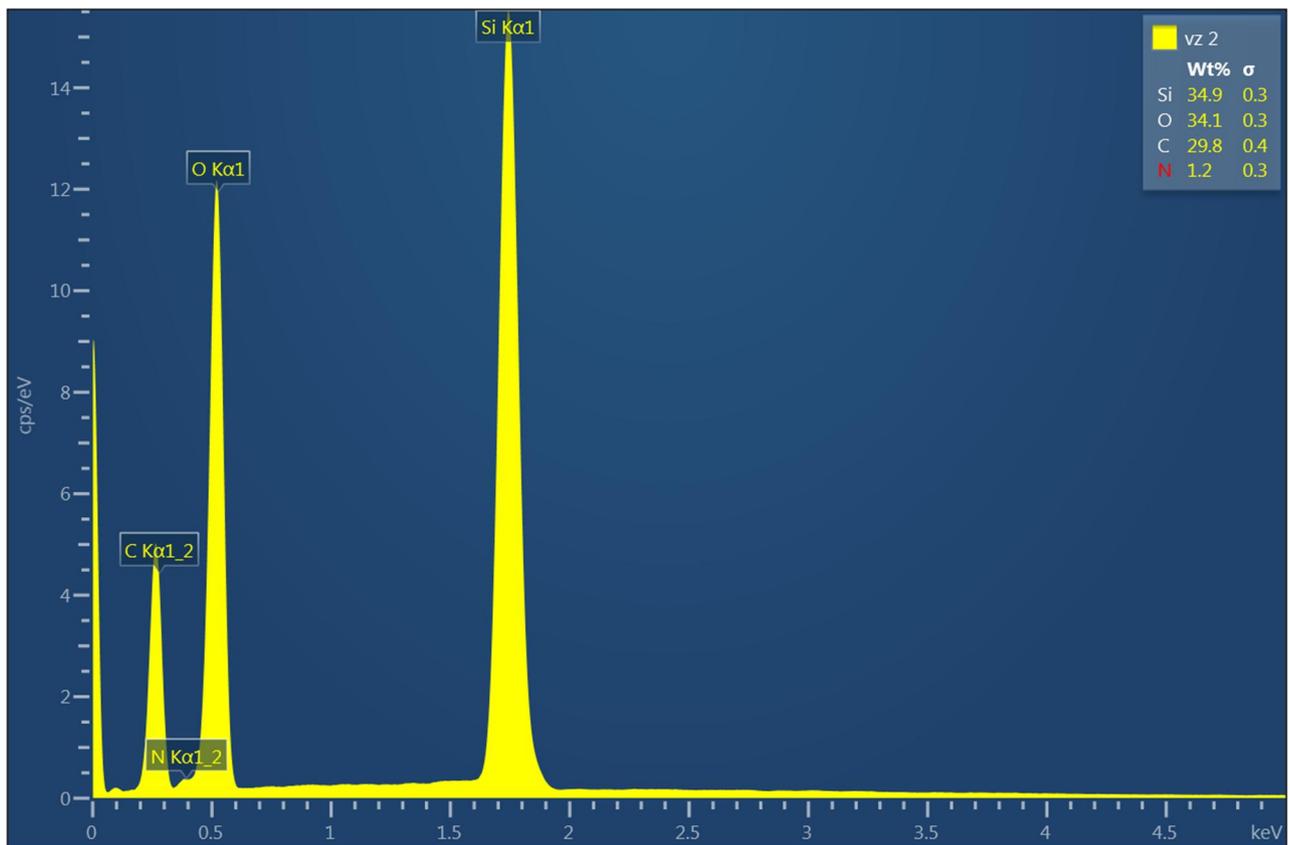


Figure 5 EDS analysis of MILIFE® fabric with plasma-prepared coating from HMDSO/O₂

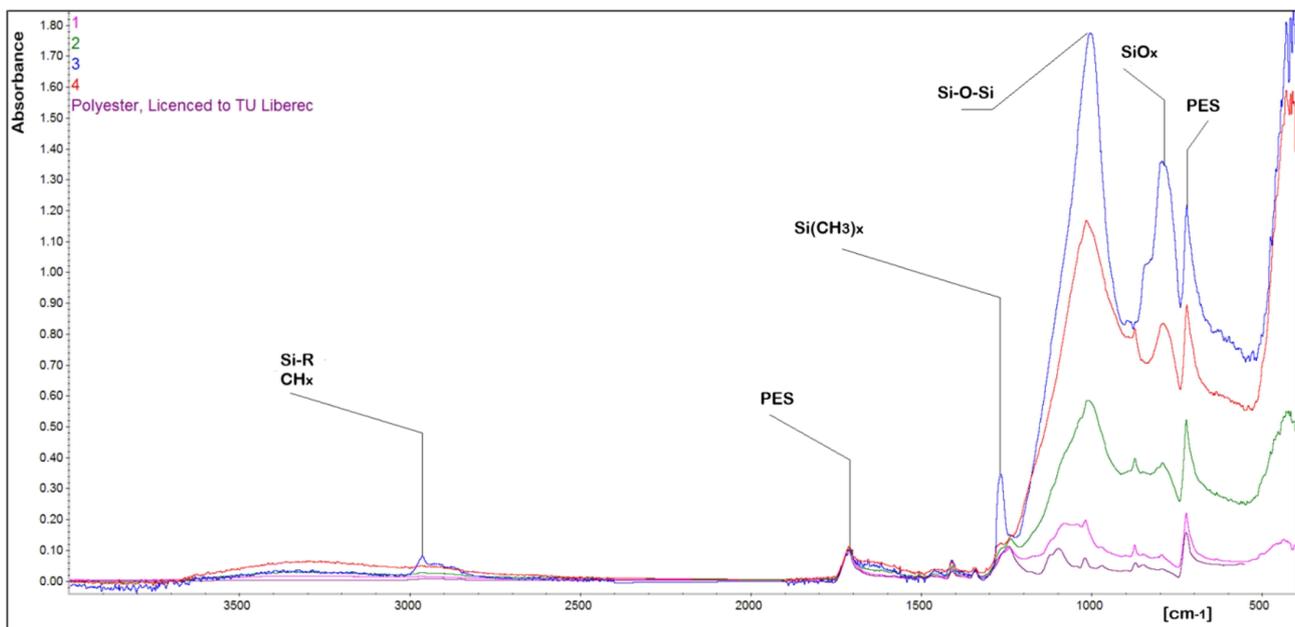


Figure 6 FTIR spectra of four samples (1-4) of metallized MILIFE® fabric with different thickness of plasma-prepared coating from HMDSO/O₂. The purple line at the bottom of the graph ("Polyester Licensed to TU Liberec") corresponds to the material of pure MILIFE® (without copper and silicon) and is a part of the FTIR spectrum library

Figure 6 shows the IR spectrum analysis of the four samples with layers of different thicknesses prepared in a plasma chamber within 2-20 minutes by the process described above. We can observe an increasing signal response depending on the plasma time and the thickness of the formed silicon-based layer. However, for all curves, it is clear that silica (silicon oxide) is only one component of the plasma-prepared thin film. There are other peaks in the spectrogram representing organosilicon compounds, for example siloxanes. The term "silicone-based thin layer" therefore appears to be appropriate and quite apt for this hybrid thin layer, which has been prepared by the PECVD method. It has been shown that a chemically diverse mixture of silicon oxides and silicon-based organic compounds was formed. The resistivity of excellent insulators is higher than $10^{16} \Omega \cdot m$ at $20^\circ C$ (e.g. $10^{21} \Omega \cdot m$ for polyethylene terephthalate), but copper as an excellent electrical conductor has a very low electrical resistivity (approximately $1.7 \times 10^{-8} \Omega \cdot m$) [27]. Our measurements confirmed the pure non-metallized MILIFE® has electrical insulator properties. The electrical resistance measured on the surface was outside the measuring range of the instrument used, i.e. it was higher than 200 M Ω , and this means at least 10^8 times higher than on the copper metallized fabric. The electrical resistance values measured on the surface of the metallized samples (Table 1) confirmed that the acidic environment of acetic acid did not have a major effect on copper and that the corrosive conditions only occurred in the presence of hydrogen peroxide. Surface resistance values were not changed for 48 hours in a 2% acetic acid solution (pH 3) in a closed tube without oxygen. However, after the addition of hydrogen peroxide, the surface resistance of the sample without the plasma-polymerized protective coating increased significantly over for 10 minutes, due to the oxidation of copper, practically up to the values non-measurable by use of the digital multimeter. Even a thinner coating of MF/Cu/SiO_x/7 sample was not sufficiently resistant to the corrosion and an increase in surface electrical resistance was apparent, although a little

slower than on the sample without the protective layer ("blank").

The surface of the metallized MILIFE® without the silicon-based layer (MF/Cu blank) and the MF/Cu/SiO_x/7 sample with a thinner coating visually changed the color from the original red-orange to brown-red and brown-black during the acetic acid and hydrogen peroxide treatment, while the solution was colored to light blue. This confirms the corrosion process involved both oxidative changes in the copper surface (the production of copper oxides responsible for the tarnish on the copper metal surface) and at the same time the dissolving of copper (the production of copper (II) ion accounts for the light blue color in test solution).

There was no significant increase in electrical resistance during testing of MF/Cu/SiO_x/20 sample and its about 388 nm thick silicon-based thin layer was already able to effectively protect the polyester nonwoven MILIFE® with copper surface against oxidation and loss of electrical conductivity.

The porosity density of metallized and non-metallized MILIFE® is about 80% [25]. The high porosity of the textile carrier was most likely the reason why the thinner silicon-based layer was not able to sufficiently protect the copper surface of the fabric from corrosion. Changes in porosity after plasma deposition have not been investigated in this study, but based on previous research, it is clear that the porosity decrease is directly dependent on the plasma deposition time of the HMDSO film [28]. Although the deposition of the film gradually covers the pores and reduces the porosity, the subsurface pores retain their original, open structure. The structure of the film is weakened at the pores of the fabric, and in fact there may be a film thinner than shown by measuring the thickness of the deposition layer on a flat solid surface. This caused cracks in the thinner layer of the sample MF/Cu/SiO_x/7. The corrosive medium easily penetrated the copper layer through the defects, while the thicker layer of the sample MF/Cu/SiO_x/20 already acted as a reliable anti-corrosion barrier.

Table 1 The superficial electrical resistance of the samples

		MF/Cu (blank) [Ω]	MF/Cu/SiO _x /7 [Ω]	MF/Cu/SiO _x /20 [Ω]
Initial electrical resistance		1.2 (+/-0.1)	2.1 (+/-0.1)	1.5 (+/-0.1)
Time	Medium			
48 hours	2% acetic acid	1.2 (+/-0.1)	2.2 (+/-0.1)	1.5 (+/-0.1)
2 min.	2% acetic acid 0.25% H ₂ O ₂	1.3 (+/-0.1)	4.3 (+/-0.1)	1.5 (+/-0.1)
4 min.		1.5 (+/-0.1)	10.6 (+/-0.2)	1.6 (+/-0.0)
6 min.		5.4 (+/-1.8)	13.3 (+/-1.4)	1.8 (+/-0.1)
8 min.		75.2 (+/-12.5)	17.5 (+/-2.2)	2.2 (+/-0.1)
10 min.		1616.2 (+/-45.6)	50.1 (+/-4.4)	2.4 (+/-0.4)

5 CONCLUSION

We tested the metallized polyester nonwoven MILIFE®, which has excellent electrically conductive properties due to chemically copper coated fibers. The copper coating results in a very low value of electrical resistance (1.2 Ω) measured on the fabric surface by contact electrodes at 1.5 cm. We have shown that, while in the acidic environment of 2% acetic acid without air access, the conductivity (the resistance) on the fabric surface did not change even after 48 hours, this product is highly sensitive to corrosive changes in the acid environment with the presence of an oxidant. In a solution containing 2% acetic acid and 0.25% H₂O₂, the metallized surface of the fabric already chemically changed within 4 minutes, which resulted in the increasing of electrical resistance and gradual color changes of the copper surface of the fabric and of the corrosive solution itself. The silica-based plasma-polymerized layer with the thickness of 388 nm was able to reliably protect the copper surface on polyester fibers from corrosive changes even after 10 minutes in the acidic and oxidizing medium at room temperature. This protective layer was prepared from a mixture of HMDSO precursor and oxygen. Low pressure in the working chamber (45 Pa) allowed plasma-polymerized deposition already at the RF generator power of 150W. The 20-minutes treatment did not damage the nonwoven polyester carrier MILIFE®, the heat resistance of which is stated by the manufacturer up to a maximum of 300°C. We have shown that the method of deposition of a protective silica-based layer using PECVD low-pressure plasma could be a promising way to protect the metallized polyester fabric surface from the corrosive effects of the acidic and oxidizing environment with minimal consumption of the organosilicate precursor. This would extend the field of applications and the life of this product.

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