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EXTENSION OF THE RANGE OF TEXTILES MODIFIED AT NANO-LEVEL

Summary of the Doctoral Thesis

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Doctoral thesis to obtain the doctor's degree in engineering sciences is publicly defended at 12:00 o'clock on June 30 of 2014 at Riga Technical University Institute of Design Technologies in 18 Azenes street, in auditorium No. 117.

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APPROVAL

I confirm that I have elaborated current promotion thesis, submitted to Riga Technical University for the Doctoral degree in engineering sciences. The promotion thesis is not submitted for a scientific degree to any other university.

Svetlana Vihodceva …………………………… Date: ………………………

The promotion thesis was written in Latvian and consists o fan introduction, 4 chapters, conclusions and bibliography, containing 125 figures and 22 tables, 207 pages in total. The bibliography includes 217 sources.

ABBREVATIONS

UV – ultraviolet light

UPF – ultraviolet protection factor

SEM – scanning electron microscopy

EDX – energy dispersive x-ray spectroscopy

AFM – atomic force microscopy

Pa – pressure in air permeability measurments

TEOS – tetraethylorthosilicate

ZSH – zinc sulphate heptahydrate

ZAD – zinc acetate dihydrate

CFU – colony-forming unit

P. aeruginosa – *Pseudomonas aeruginosa*

S. epidermidis – *Staphylococcus epidermidis*

S. aureus – *Staphylococcus aureus*

E. coli – *Escherichia coli*

C. albicans – *Candida albicans*

P. fluorescens – *Pseudomonas fluorescens*

S. cerevisiae – *Saccharomyces cerevisiae*

T. viride – *Trichoderma viride*

CONTENTS

1. GENERAL DESCRIPTION OF THESIS

1.1. Introduction

Incorporation of the additional functionality into traditional textiles allows adding new valuable functional properties, finding new application areas, solving ecological problems and enhancing the quality of the consumer life, as a result of that the added value and marketability of the product shall increase. Deposition of nano-level coatings onto the surface of traditional textiles in addition to textile existing properties such as flexibility, lightness, softness etc., shall allow obtaining versatile textile products with new valuable functional properties. Future trends in textile industry include multifunctional materials from natural fibers with integrated functional properties such as UV protection, antimicrobial activity, water-repellence, photocatalytic qualities etc. and the combination of these functions into a single textile material.

Natural fiber textiles have been modified by depositing copper (Cu) coatings because Cu over the centuries considered to be a chemical element with strong antimicrobial properties and Cu are classified as non-harmful to human organism. By sol-gel technology obtained amorphs Zn and Si containing coatings alow to add to modified textiles new properties: antimicrobial activity, UV protection and water-repellency. Textiles with incorporating antimicrobial functional compounds can be used in dressings, patches, bed linen and interior textiles, patient and personal clothing in hospitals, nursing homes, rehabilitation centers and as clothing or textile products for special uses etc. Antimicrobial coatings on the surface of textile allows to avoid cross infections by pathogenic micro-organisms, to control the infestation by micro-organisms, to arrest metabolism in micro-organisms in order to reduce the formation odour, to safeguard the textile products from staining, discolouration and quality deterioration.

Considering that, the amorphs Si and Zn containing coatings greatly enhance the textile UV protection properties, which offer wide range of applications for modified textiles in both everyday and special use clothing, as well as in diverse outdoor textile products. Due to the depletion of the ozone layer, the UV intensity of solar radiation has increased, for this reason increase necessity in the UV protective clothing and accessories. Most of the everyday summer clothing and hats do not provide sufficient UV protection. Textile hats and textile clothing with incorporated UV filters shall allow protecting humans from the harmful effects of UV, as well as the protective coating shall extend the life cycle of natural fiber textile products. Textiles, hats, clothing from textile materilas with UV filters will protect people from harmful UV exposure, as well as the will make it possible to extend the natural fiber textile life.

Technical and special use textiles often need a finishing coat ensuring water-repellence i.e. hydrophobic features. Natural - cellulose fibers have the highest content of active hydroxyl groups (-OH) thus providing most effective moisture binding properties. The ability to repel water provides important additional functions in clothing as well as these features be well in demand across different textile products for outdoor use.

1.2. Goal of the thesis

Development/adjustment and optimisation of technologies for modification of natural fiber textiles at a nano-level to enable products with additional functionality.

1.3. Tasks of the thesis

1. Review of published sources, systematisation and formation of an analytical review on the possibilities to acquire additional functionality via modification of textile surfaces.
2. Comparative analysis of technologies suitable for the modification of natural fiber textile surfaces.
3. Selection of functional elements/groups thereof for modification of textile surfaces in order to ensure the effect set out in the goal of the paper.
4. Selection of processing stages, technological process and parameters as well as optimization thereof.
5. Production of modified cotton fabric samples and perfection of technologies.
6. Formation of methodology for analysis of metal treated textile surface coatings.
7. Testing of binding, functional and operational properties in line with standards and/or methodology developed in the course of the paper.
8. Analysis of modified cotton textile functional properties and sustainability, definition of possible ways of use.

1.4. Scientific novelty of the thesis

1. Explored the effects of cotton fiber textile pre-treatment in the media of low-pressure air plasma depending on the duration of the processing and the effect thereof on the binding properties of textile with metal coatings during thermal vacuum evaporation process.

2. The comparative study of the effects of thermal vacuum evaporation and magnetron sputtering technologies on the antimicrobial properties of copper coating at various microorganism levels of concentration and types provided a sufficient basis for a determined selection of modification method as well as it gave an insight into the selectivity of the inhibition to be expected.
3. A "Non-contact method for surface changes examination of the metal coatings and metal coated textiles" was developed based on measurements of reflected and transmitted light intensities. It provides a detailed insight into the changes of textile surfaces after depositing of metal layers, as well as it allows studying the technologies and the relative effect of technological parameters on the uniformity of the coating and assessing the damage caused to the coating as a result of use.
4. The sol-gel method adapted for the treatment of cotton textile materials, the appropriate content of sol and optimised method for synthesis of sol as well as combination of processing and post-processing modes. That allow received textile products providing antimicrobial, water-repellent properties and protection against both UVB and UVA spectrums exposure with a single processing session. In the meantime, preserving the air permeability and hygroscopicity required to ensure the necessary level of comfort.
5. The performed multifunctional property tests and follow-up of properties in sequential cycles of hydrothermal processing as well as the assessment of mechanic influences allows determining the gradual changes of the added properties the effect thereof on the intrinsic qualities of textile. Thus substantially increasing the volume of knowledge on the adaptability of sol-gel technology for the modification of materials with low heat resistance

1.5. Thesis to be defended

1. It was proven that copper coating can be deposited on the natural textile surface by thermal vacuum evaporation and magnetron sputtering technology with adjusting technological parameters to natural fibers; copper coating depositing technology influenced the antimicrobial properties of the copper layer.
2. By thermal vacuum evaporation and magnetron sputtering technologies, modified textile materials with antimicrobial copper layers from the point of view of the developed technology are applicable to production of single-use medical products that will be not subjected to hydrothermal treatment.

3. With synthesized sol composition, with appropriate CAD concentrations and technological parameters, by the sol-gel technology, modified textiles ensure very good/good adhesion between the coating and textile fiber that proven by the preservation of properties after multiple hydrothermal processing cycles of the textiles.
4. By the proposed sol-gel process modified cotton textiles can be successfully integrated into the variety of applications, where is needed protection against pathogenic microorganisms, UV, water-repellency (hydrophobicity).

1.6. Practical value of the thesis

The practical value of the paper is reflected by the volume of information yielded during the development of the paper as well as the acquired Latvian patent titled "Biocide infection dressing". The content of sol obtained as the result of the research along with technology and technological parameters provides functionality required for diverse areas of use maintaining the properties during use as supported by the analysis conducted in the framework of the paper. Offered elaborations are a result of a series of diverse research, ready for use and may be used as prototypes for development of manufacturing technologies that may be easily integrated as additions to the existing textile processing technologies or developed as independent technological processes.

1.7. Approbation of the thesis

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1. Kukle S., Vihodceva S., Zommere G. Traditional fibrous products from basic to functionality// Proceedings of 7^{th} International Conference on Manegment of Technological Changes. – 2011. – pp. 641-644. ISBN 978-960-99486-2-3. **
2. Kukle S., Barloti J., Blums J., Vihodceva S. Functionalization of cotton textiles with metals// Proceedings of 5^{th} International textile, Clothing & Design Conference, Magic World of Textiles. – 2010. – pp. 335-339. ISSN 1847-7275.
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15. Vihodceva S., Kukle S. „Improving of UV blocking properties of natural fabric via sol-gel method” 4th Conference on Natural Fibre Composited, Rome, Italy. 17.10.2013. – 18.10.2013.
16. Vihodceva S., Kukle S., Muter O. „Evaluation of antibacterial and fungicide activity of cotton textile treated via sol-gel method” 18th International Scientific Conference „Ecobalt 2013”, Vilnius, Lithuania. 25.10. – 27.10.2013.

2. SITUATION ANALYSIS

Cotton as a natural cellulosic fiber is generally more susceptible to micro-organisms activity than synthetic fibers – the growth of bacteria, yeast and fungi on the textile surface can lead to functional, hygienic an esthetic difficulties as discoloration, coloured stains, fibre damages and unpleasant odours [1-3]. Textiles of all varieties are considered to be very proficient at carrying micro-organisms and serving as a reservoir for the transmission of infections [4, 5]. Hereby, textiles with antimicrobial finishing can be of great assitance in the recovery process of transplantant patients, people with immunodeficiency diseases, low immunity patients and staff protective clothing.

For the imparting an antimicrobial properties on textile materials nowadays use different metals or metal oxides (Ag, ZnO, TiO_2 etc.). The most widely for textiles, modification used silver (Ag). Nowadays textiles modified with Ag commercialized and widely available in the market, textile materials modified with other metals or metal oxides are mostly in the researching process and they have represented slightly or not in the market.

Another material appropriate for medical textile applications is copper, which is broad-spectrum antimicrobial agent; the fungicidal properties of copper were demonstrated in controlled laboratory studies starting in the early 1950s and since then copper and copper compounds have been shown to effectively kill a wide range of yeast and fungi. Thus, copper fungicides have become indispensable and many thousands of tons are used annually all over the world in agriculture [6]. Above that, copper is an essential trace element involved in numerous human physiological and metabolic processes, including wound repair, therefore many over-the-counter treatments for wound healing contain copper. The recognition that copper has potent antibacterial properties followed and was well established based on the vast amount of antimicrobial efficacy testing, in March 2008 US Environmental Protection Agency approved the registration of copper alloys as materials with antimicrobial properties [6-8]. In spite of the fact that some of copper applications are already being amply used, novel possible applications of copper may have a major effect on our lives. One area is the reduction of transmission of health associated (nosocomial) pathogens in hospitals, clinics and elderly homes by making hospital softs surfaces, like sheets, patient robes and pajamas, and nurse clothing, from copper-impregnated textiles. Due to its potent virucidal properties is its use in filtration devices that can deactivate viruses in contaminated solutions, such as contaminated blood products and breast milk [6].

One more antimicrobial materials that is found in a wide range of medical and healthcare products is zinc (Zn). Hereby, it’s compounds used in production of a wide range of cosmetics and personal care products including makeup and nail products, baby lotions, bath soap etc., it provides anti-irritant, antimicrobial, anti-inflammatory, smoothening properties and diaper rashes treatment.

A number of studies carried out in the last decades and the reported statistical data indicate of the increase in the incidence of malignant skin growths particularly in the risk groups with light and thin skin [10]. The primary reason for the increased incidence of malignant skin growths is attributed to stratospheric ozone depletion as a result of increasing of the UV, as well as sunscreen creams insufficient protection, because part of the sunscreen creams protect only from UVB as a result exposing organism to uncontrolled high doses of UVA. Epidemiology study and experimental data shows that UV can facilitate development of various malignant skin growths - it may serve as a complete carcinogen as an initiating agent as well as a promoter of carcinogenesis; the rate of malignant skin growths has increased rapidly over the last decade [11]. Exposure to beams of UVA/UVB spectrum not only facilitates the development of malignant formation, but it also contributes to photoageing of the skin. This means that UV protection must be provided against both UVB and UVA spectrums and trextile with UV protection propertie can be one of the problem solutions.

Natural cellulose fibres have excellent moisture bonding because of the high amount of the hydroxyl (-OH) groups, as a result they providing good microclimate under garment, at the same time attracting moisture and dirties from surrounding environment [13-15]. Hydrophobic textile surfaces are mainly produced in two ways, one is to create a rough structure of the surface and the other is to modify a surface by compounds with low surface free energy, like fluorine or silica containing compounds [16]. At the same time, the results of the numerous studies indicate that achieved functions have insufficient resistance to using and hydrothermal treatment processes.

For the textile coating nowadays use a wide range of technologies, each technology has both advantages and disadvantages. Several technologies for functional coating on natural cellulosic fibre textile theorethically and experimentally were investigated and compared in the frame of this research work. For textile coating widely use a powder or nanoparticles suspended in acrylic, polyurethane, polyvinyl acetate and acrylate binder. These methods are less than satisfactory for the using, for at least two reasons. First, binder or adhesive may entirely encapsulate the powder particles or nanoparticles, inhibiting their contact with fungi and bacteria, and making the textile useless as a fungicide and bactericide. Second, multiple laundering tends to weaken the binder or adhesive and loosen or remove the particles. Despite this nowadays, this method widely used for textile coating with nanoparticles, the most frequently with Ag and ZnO.

Anothert textile coating technology is electroless-plating technology that allows the easy formation of continuous and uniform metallic particles on the surface of a substrate in a complex shape, and can be performed on any type of textile – such as fibre, yarn, fabric without altering its structure or texture. In addition, electoless plating solutions are especially susceptible to impurities that effect the processing solution and cause reduced adhesion. As a result the metal coating only have a moderate adhesive strength on the surface of fabrics, therefore, metal coated fabrics have a weakness in that when the coated metal is exposed to air it may peel off. [17]. Furthermore, electroless-plating technology is multiple stage process with consumption of large amount of chemicals and yielding a large amount of effluent.

Magnetron sputtering technology offers a number of advantages over other technologies for textile materials: an abundance of deposition materials exists, such as metals, metal oxides and polymers, deposition takes place at low temperatures, deposited material adheres well to the fibrous substrates and different deposition materials can be combined.

Thermal vacuum evaporation is one more technology for textile surfaces coating. Nevertheless, the metallization process of the textile materials surface by thermal vacuum evaporation technology related with difficulties that caused by the textile intrinsic and metal coating formation characteristics as textile low thermal stability. Impurities on the textile surface – oils, waxes used in fabrics manufacturing process that interfered to obtain good metal coating and textile surface adhesion without pre-treatments, as well deposited coating thickness limited by metal internal stress caused by deposition of metal on the cold textile surface. The advantages of the thermal vacuum evaporation are fastness of the process, high repeatability and small consumption amount of the modificative material; as well, it is the process without yielding effluent. Technology also has disadvantages relatively high-energy consumption, restricted the use of metals and alloys with high boiling or melting points and low bonding strength with the substrate.

In order to improve the natural textile and coating adhesion, before coating textiles are exposed to the different types of the treatments. Another approach for adhesion improvement is presented by low-pressure plasma treatment that is a new developed in the last decade technology for natural textile modification the advantages of plasma technology are it potential environmental friendliness and energy conservation benefits in developing high-performance materials. Moreover, it is a dry process providing modification of the surface without using solvents or generating chemical waste. Furthermore, textile surface exposure to low-pressure plasma treatment results in the new properties achievement that hard to obtain with traditional textile treatments as, reactive surface increasing and surface structure changing.

Textile functionality enhancement can also be brought by sol-gel technology. Research experiments indicates that the main limitation of sol-gel technology application with respect to textiles is determined by the low thermal stability of the most textile materials that is usually below 200 °C, for many materials significantly lower, thermal treatment at temperature below 200 °C will form inorganic xerogels [18]. However, sol-gel technology conditions and treatment as well as composition of the sol can be adapted for the treatment of textiles with regard to the type of textile; as well, this technology promises the possibility to tailor surface properties to a certain extent, and to combine different functionalities in a single material. A crucial requirement for sol-gel technology using for textile coating application is a good bonding strength with the textile fibre in order to prevent the coating peeling off during the hydrothermal treatment and using processes. In the case of materials like cotton (cellulose) the adhesion of the sol-gel coating is easily improved by chemical condensation of silanol groups (Si-OH) with the hydroxyl (-OH) groups on the textile surface.

At the same time the application of sols can be carried out with techniques commonly used in the textile industry, finishing of textiles can, for example, be carried out by a simple dipping, spraying or padding process followed by thermal treatment. By spraying processing double-face effects can be obtained that allows manufacturing of textiles, for example, with one hydrophobic and one hydrophilic side. Besides the mentioned advantage of spray applications, the uniform spray application for large surfaces via continuous processung is a general problem, simultaneously incomplete coverage of the fibres might decrease the durability of the nanosol coatings applied.

There are less studies and articles with evaluation of adhesion of the textile surface with coatings implemented by the sol-gel technology. Mainly the coating stability to hydrothermal treatment was not evaluated at all, or only after few cycles that does not correspond with the standard requirements. Finally, in many research projects is mentioned a necessity to improve the coating bonding strength with textile substrate.

3. TECHNOLOGIES OF EXPERIMENT AND SAMPLE TESTING METHODS

3.1. Thermal vacuum evaporation technology

Thermal vacuum evaporation was carried out in a serial vacuum equipment UVN-2U. The maximum sample size is 5 x 6.3 cm. Experiments proved that a second long deposition allows obtaining 60 nm thick copper coating. In order to obtain of the thickest and smoothest copper coating, textile samples should be subjected to repeated depositions with or without modification/treatment with the low-pressure air plasma.

3.2. Magnetron sputtering technology

Magnetron sputtering was carried out in a serial vacuum equipment UVN-2 with an in-built self-made magnetron type of the sputtering equipment. The maximum sample size is 5.3 x 6.3 cm. There were seven fabric samples fixed on the rotating disk in the vacuum chamber. Before the deposition of the copper, the textile surface was treated with a plasma glow discharge, the optimum disk rotation rate of 20 min^{-1} was estimated for the prevention of the textile sample destruction during the sputtering process.

3.3. Sol-gel technology

Sols were synthesized using silica alkooxide tetraethylortosilicate $C_8H_{20}O_4Si$, ethanol and water added to perform the hydrolysis and condensation process, and hydrofluoric acid HF used as a catalyst of the process. Zinc acetate dihydrate $Zn(CH_3COO)_2 \cdot 2H_2O$ or zinc sulphate heptahydrate $ZnSO_4 \cdot 7H_2O$ was used as the modifier of the sol-gel system.

Sols were synthesized by the following two methods:

1. By adding ethanol into TEOS slowly with continuous stirring, after added deionized water and HF, stirred intensively for 30 minutes, to obtain a homogeneous solution, then mixed with zinc acetate dihydrate (ZAD) or zinc sulphate heptahydrate (ZSH) with continuous stirring for another 10 minutes,
2. By adding ethanol into TEOS slowly with continuous stirring, after added deionized water and HF, stirred intensively for 30 minutes at 50 °C temperature, to obtain a homogeneous solution, then mixed with ZAD or ZSH with continuous stirring for another 10 minutes at 50 °C temperature.

The textile samples were modified by the dip-coating process in the prepared sols: 2.5, 5, 7.5 and 10 wt. % ZAD sol, or 2.5, 5, 7.5, and 10 wt. % ZSH sol with 0.2 M and 0.1 M TEOS. After the treatments, the samples were dried in an oven with the following thermal post-treatment, followed by the eposure to the prolonged low temperature thermal treatment the drying and thermal post-treatment were combined.

3.4. Methods of sample testing

The following tests were performed in order to test the properties of the modified textile:

- A surface structure analysis by scanning electron microscopy (SEM),
- A coating composition analysis by energy dispersive x-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD),
- A surface topography analysis by atomic force microscopy (AFM),
- The determination of the coating adhesion to hydrothermal treatment in accordance with EN ISO 105C10-AO1:2006,
- The determination of the abrasion resistance of coatings and fabrics by the Martindale method in accordance with EN ISO 12947-2:2000/AC,
- The determination of the antimicrobial properties against nosocomial pathogenic micro-organisms by the Parallel streak method in accordance with AATCC 147-2004:

- *Staphylococcus aureus* gram-positive bacteria, due to the presence of virulence factors can penetrate in a human organism and cause some heavy hospital (nosocomial) and in public environments acquired infections, it is also a frequent aerobe micro-organism found to the patients with wound infections and abscesses [19, 20];
- *Pseudomonas aeruginosa* gram-negative bacteria that is a well known micro-organism in the medical practice, that is found in soil, water, skin flora and most man-made environments; it shows significant activity in a variety of implant colonization, it is a frequent cause of nosocomial infections, such as, the skin and soft tissue, wound infections [21, 22];
- *Escherichia coli* gram-negative bacteria that can cause urinary tract infections and wound and nosocomial infections [20];
- *Candida albicans* microscopic fungus that can cause nosocomial infections [21].

* The determination of the antimicrobial properties against micro-organisms causing cellulosic textile destruction, the tests based on the Parallel streak method (AATCC 147-2004):
  - *Pseudomonas fluorescens* bacteria, it is a producing array of the extracellular hydrolytic enzymes resulting in cellulose textile destruction, furthermore, the bacteria can cause degradation by using the plant tissue components, e. g., carbohydrates, fatty acids and oils [23, 24];
  - *Trichoderma viride* microscopic fungi mycelium that can formed enzymes (cellulase and chitinase) that cause destruction of the cellulose and chitin [2, 25, 26];
  - *Saccharomyces cerevisiae* yeast, is a micro-organism of the fungi kingdom and it is known with for a long history of safe use, during the fermentation process, the yeast converts carbohydrates to CO_2 and ethanol. *S. cerevisiae* explored as a model of eukaryotic organisms [23, 27].
* The determination of the micro-organisms adhesion on the textile surface:
  - *Pseudomonas aeruginosa* gram-negative bacteria that is well known micro-organisms in the medicine practice, that is found in soil, water, skin flora and most man-made environments; it shows significant activity in a variety of implant colonization, it is a frequent cause of nosocomial infections, for example skin and soft tissue, wound infections [21, 22];
  - *Staphylococcus epidermidis* gram-positive bacteria, it is a part of normal skin flora, it shows significant activity in a variety of implant colonization (from piercings to

artificial heart etc.), it causes nosocomial infections to the immunosuppressed patients [22].

- The evaluation of the UV protection and UPF classification using certified equipment Varian Cary 50 Solascreen (Australia) in accordance with Australian/ New Zealand Standard AS/NZS 4399:1996 and European Standard EN 13758-1:2001+A1:2006: E,
- The determination of the permeability of textile to air using certified equipment Air Permeability Tester III FX 3300 (TEXTEST Instruments, Germany) in accordance with Europe Standard EN ISO 9237:1998,
- The determination of liquid sorption by the drop test in accordance with Polish Standard PN-91 P-04746,
- The determination of hygroscopicity in accordance with Polish Standard PN-80 P-04635;
- The contact angle measurements by the drop method using an optical tensiometer Theta Attension (Finland).

4. RESULTS

4.1. Microstructure of the cotton textile surface modified by thermal vacuum evaporation technology

SEM micrograph (Fig. 1a) illustrates that the copper coatings deposited by the thermal vacuum evaporation technology on the cotton textiles surface are without defects. After only one second long deposition, the copper coating is distributed evenly, not only on the surface of yarns/fibers, but throughout the depth of the textile structures. After one cycle of the hydrothermal treatment on the coated textile some micro defects can be observed (Fig. 1b), these defects can reduce the stability of the coating during the continuous using and hydrothermal treatment processes.

a) **b)** **c)**

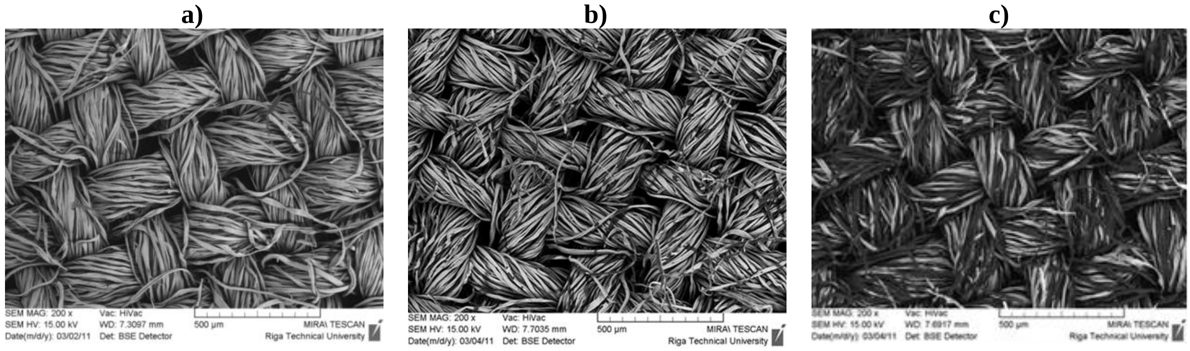


Fig. 1 The copper coating structure on the cotton textile surface deposited by thermal vacuum evaporation technology, copper coating thickness 60 nm (deposition time 1 s):
a) coated, b) after one cycle of hydrothermal treatment, c) after one cycle of the hydrothermal treatment: with plasma treatment 3 min before deposition

The low-pressure air plasma treatment of the cotton textile before coating has a negative effect on the coating adhesion on the cotton textile substrates (Fig. 1c).

a) **b)** **c)**

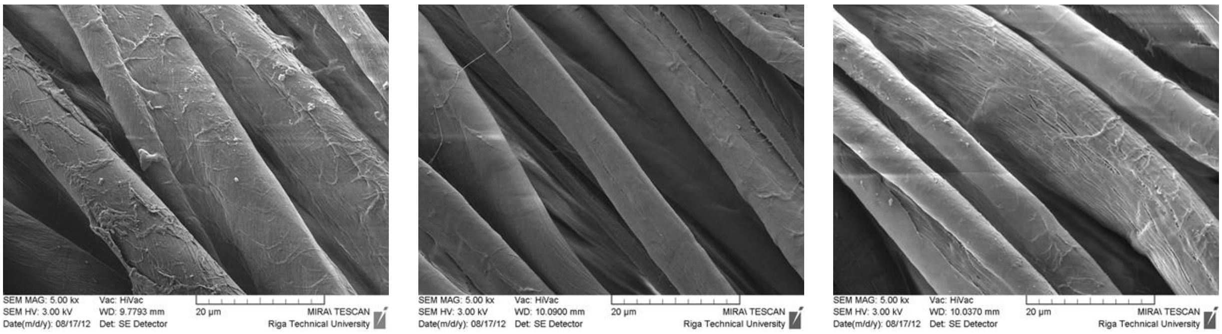


Fig. 2 Influence of the plasma treatment on cotton textile fibre
a) original cotton fibres, b) plasma treatment 30 s c) plasma treatment 3 min

SEM micrographs (Fig. 2) reveal that low-pressure air plasma changes the cotton fiber surface relief: the original cotton fiber surface (Fig. 2a) generally becomes smoother after being subjected to only 30 s of plasma treatment (Fig. 2b) so the changes in fiber roughness can be explained as worsening to the coating adhesion with the textile surface. With increasing of the plasma treatment time, starting from three minutes long treatment, there is not only relief smoothening, but also fibre destruction observed (Fig. 2c).

4.2. Microstructure of the cotton textile surface modified by thermal vacuum evaporation technology

SEM micrograph of the cotton textile samples surface (Fig. 3a) illustrates that the copper coatings deposited by the magnetron sputtering technology on the cotton textiles surface are dense, uniform, without defects, there are no flaking-off of the coating observed, and the copper deposited on the textile surface without changing the textile surface structure and texture.

a) **b)**

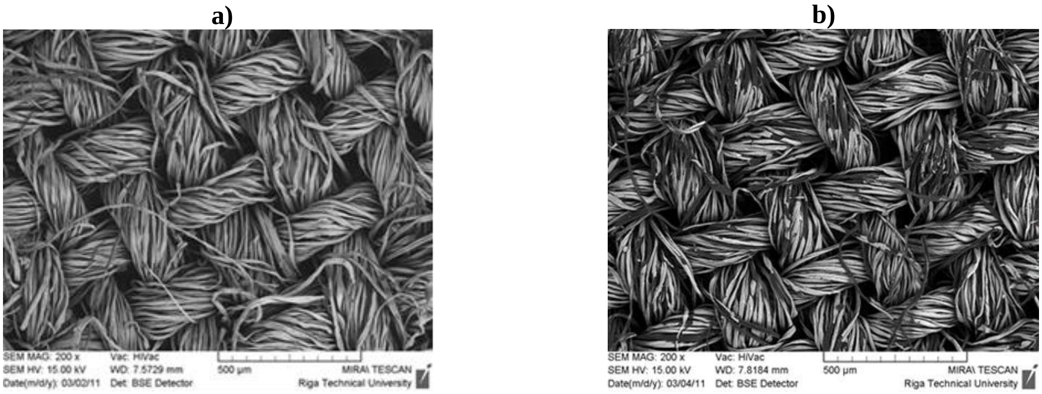


Fig. 3 The copper coating structure on the cotton textile surface deposited by magnetron sputtering technology, coating thickness 90 nm, deposition time 60 s (one sample exposition time 4.5 s):
a) coated, b) after one cycle of the hydrothermal treatment

After one cycle of the hydrothermal treatment on the coated textile surface, some micro defects can be observed (3. att., b) that evince that 100 % of the cotton textiles coated with copper by the magnetron sputtering technology during the usage process should not be subjected to hydrothermal treatment.

4.3. Microstructure, composition and topography of the cotton textile surface modified by the sol-gel technology

SEM micrographs illustrate that on the surface of the cotton textile modified by 0.2 M TEOS sol that was synthesized by the optimized method (No. 2) regardless of the ZAD concentration, there was a very thick and poor quality coating obtained (Fig. 4a). The EDX analysis evinces that on the textiles surface modified by 0.2 M TEOS sol, there is a relatively high percentage weight of silica (average of 7 %), that is 2 times more than on the surface modified by 0.1 M TEOS sol with the same ZAD concentrations. It can explain why the coatings received are thicker after the modification of textiles by 0.2 M TEOS sol regardless of the ZAD concentration.

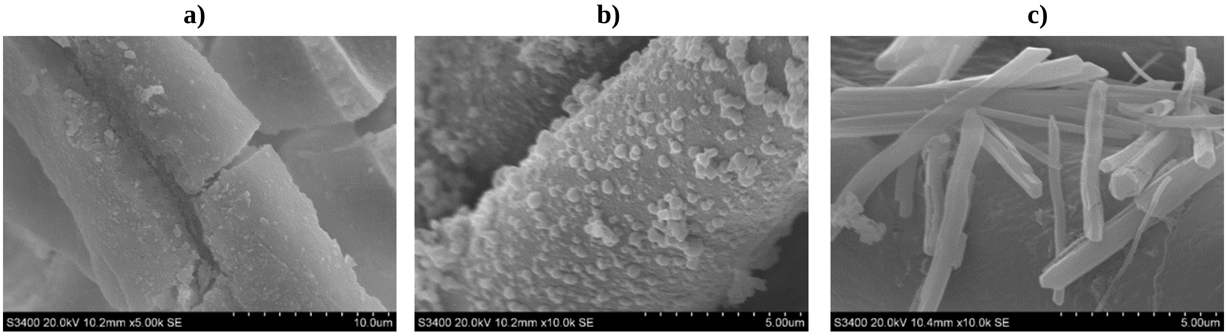


Fig. 4 The coating structure changes depending on the composition of the sol, thermal post-treatment 120 °C at temperature 2 min:
a) 5 wt. % ZAD (0.2 M TEOS) sol, b) 5 wt. % ZAD (0.1 M TEOS) sol, c) 5 wt. % ZSH (0.1 M TEOS) sol

By reducing of the TEOS concentration up to 0.1 M regardless of the ZAD concentration (5 wt.% or 7,5 wt.%), there was a thin, evenly distributed coating obtained consisting from single particles and particles agglomerates, at some spaces it agglomerates consolidates and form unregular several micrometer flat and/or long clusters on the textile surface (Fig. 4b). On the cotton textile surface modified with ZSH sol, there was a different coating structure observed, on the fibres surface there were some visible nanorods (nanowires) and pronounced signs of the fibre destruction (Fig. 4c, Fig. 5a and b).

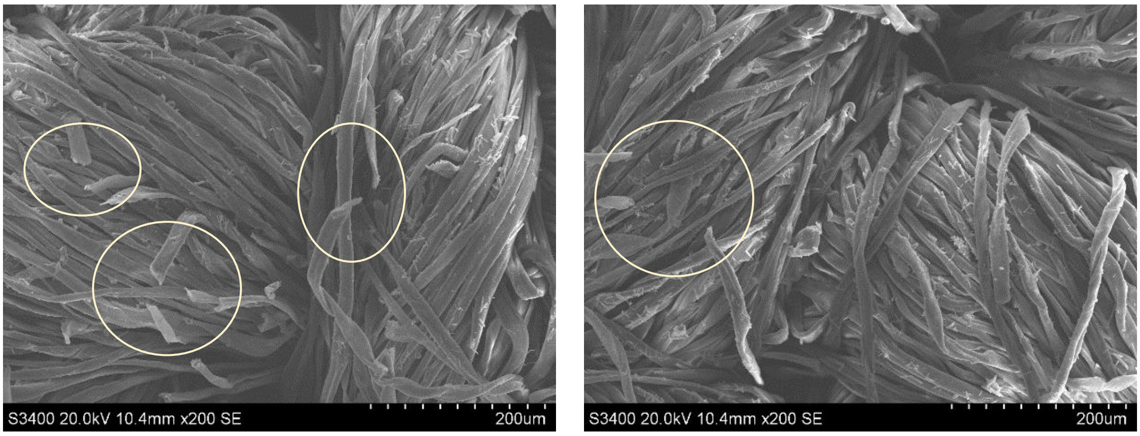


Fig. 5 The cotton textile modified by 5 wt. % ZSH (0.1 M TEOS) sol (thermal post-treatment at 120 °C temperature 2 min.)

After the first cycle of the hydrothermal treatment, the consolidation of the textile surface coating was observed, due to the self-assembly of the aggregates, as a result increasing the coating thickness and possible chemical composition changes, as indicated by the EDX analysis (Fig. 6a - d).

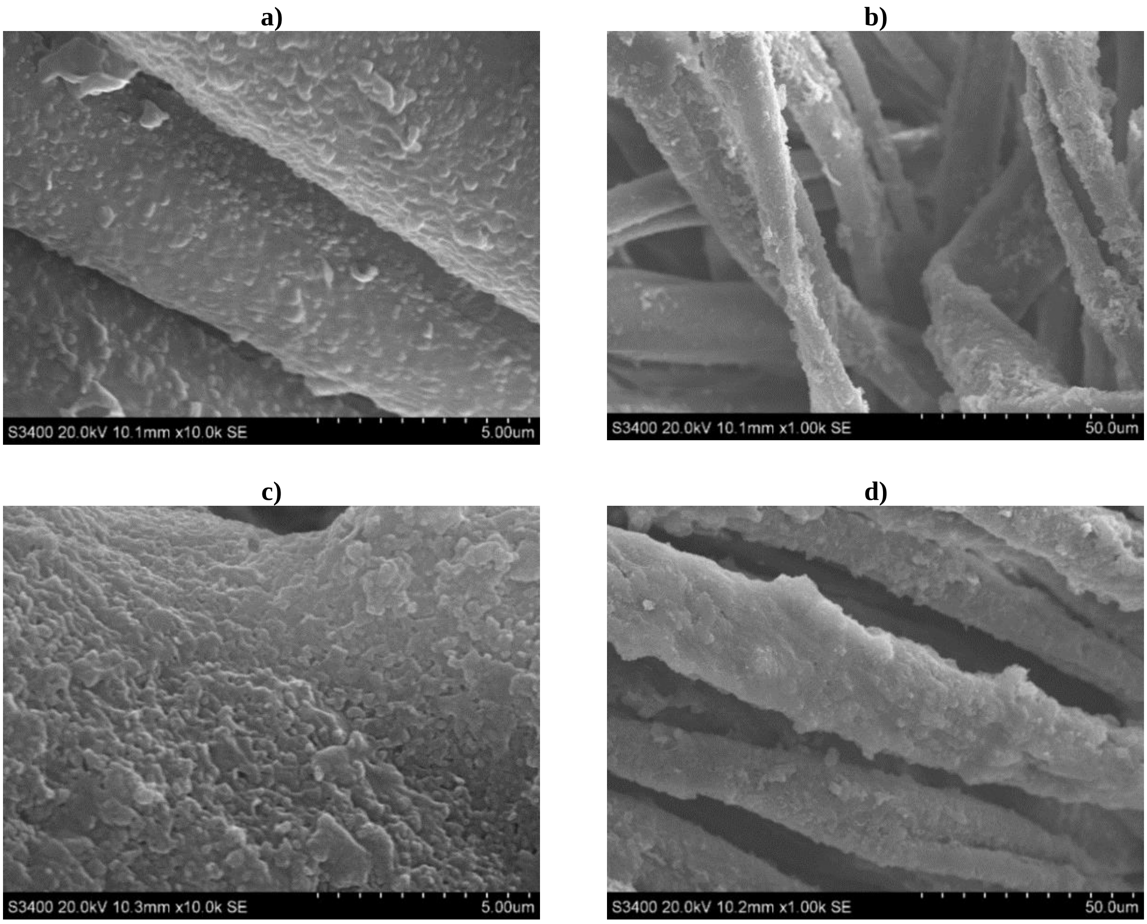


Fig. 6 The coating structure of the cotton textile modified by 7.5 wt. % ZAD (0.1 M TEOS) sol (thermal post-treatment 120 °C at temperature 2 min)

a-b) after one cycle of the hydrothermal treatment, c-d) after 50 cycles of the hydrothermal treatment

One of the reasons why the coating has been changing is that within the study applied thermal post-treatments were below 200 °C, which forms mainly amorphous structures, because for the crystalline structures are necessary thermal post-treatment at temperature higher than 400 – 500 °C [17, 26]. Since, the amorphous coatings compared to crystalline are less stable, the hydrothermal treatment could have led to the irreversible changes in the coating structure.

4.3.1. The energy dispersive x-ray analysis (EDX)

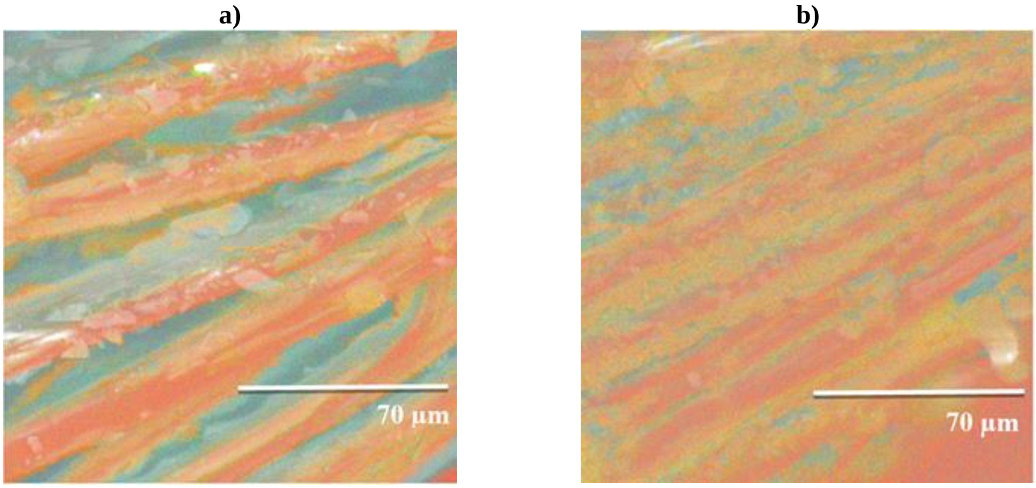


Fig. 7 The distribution of the chemical elements F, Si, Zn in the coating of the modified cotton textile surface (thermal post-treatment at 120 °C temperature 2 min.)
a) 5 wt. % CAD (0.1 M TEOS) sol, b) 7.5 wt. % CAD (0.1 M TEOS) sol

The EDX analysis indicates that in the coatings of the cotton textile surfaces treated with ZAD sol: the F, Si and Zn functional elements are sufficiently evenly distributed on the treated textile fibers after the treatment with both 5 wt. % and 7.5 wt. % ZAD (0.1 M TEOS) sols (Fig. 7a, b).

After 50 cycles of hydrothermal treatment of the textiles treated with ZAD, the percentage mass of the F, Si and Zn functional elements reduced significantly, but the Zn functional elements (Fig. 8) were still prevailing, which ensure such properties as the UV protection and antimicrobial activity.

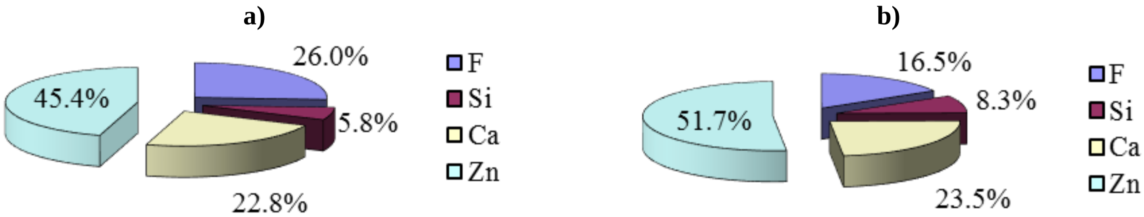


Fig. 8 Relative percentage weight of the chemical elements on the surface of textile treated by 7.5 wt.% ZAD (0.1 M TEOS) sols, after 50 cycles of hydrothermal treatment
Thermal post-treatment: a) at 120 °C temperature 2 min., b) at 90 °C temperature 30 min.

4.3.2. The Fourier transform infrared spectroscopy (FTIR)

From the obtained data can be concluded that during textile treatment by the sol-gel method with thermal post-treatments regimes used in work (from 90 °C to 200 °C), probably, occurs a partial decomposition of the zinc acetate dihydrate and basic zinc compound formation. The functional coating primarily consist from zinc acetate and probably from insoluble basic zinc compounds or zinc oxide in amorphous phase. FTIR analyses confirms the presence of Si compounds in the resulting material. As distinct from EDX data, the presence of the fluorine compounds in the treated textiles and sol powders (dried at 100 and 200 °C) is difficult to identify by the FTIR. In order to determine the exact chemical composition of the sample coatings further in-depth studies are necessary.

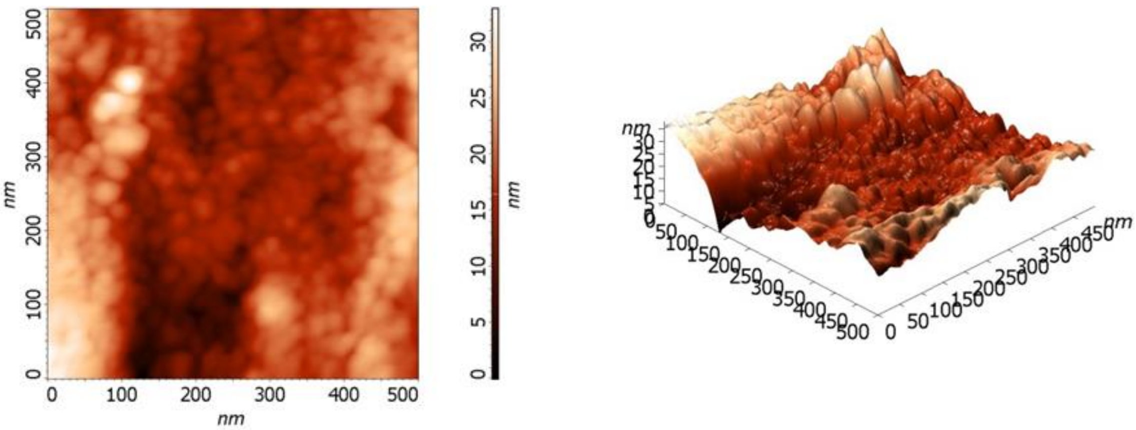
4.3.3. The X-ray Diffraction (XRD)

XRD analyses data evince that crystalline phase of the ZnO appears starting from the temperature 300 °C, in the range of the temperature from 300 to 500 °C SiO2 is also obtained, from the 400 °C begins the formation of the willemit - $Zn_2(SiO_4)$. At lower temperatures - 100 and 200 °C - occurs a partial decomposition of the zinc acetate dihydrate and basic zinc compound formation. The functional coating primarily consist from zinc acetate ($C_4H_6O_4Zn$), silica compounds: $H_2Si_3O_7(H_2O)$ and $H_2Si_{14}O_{29}\cdot 5.4H_2O$ and probably from insoluble basic zinc compounds in amorphous phase. Alike FTIR analyses, the presence of the fluorine compounds in the treated textiles and sol powders (dried at 100 and 200 °C) is difficult to identify by the XRD. In order to determine the exact chemical composition of the sample coatings further in-depth studies are necessary. It should be noted that the obtained data correlate with the results obtained from FTIR analysis.

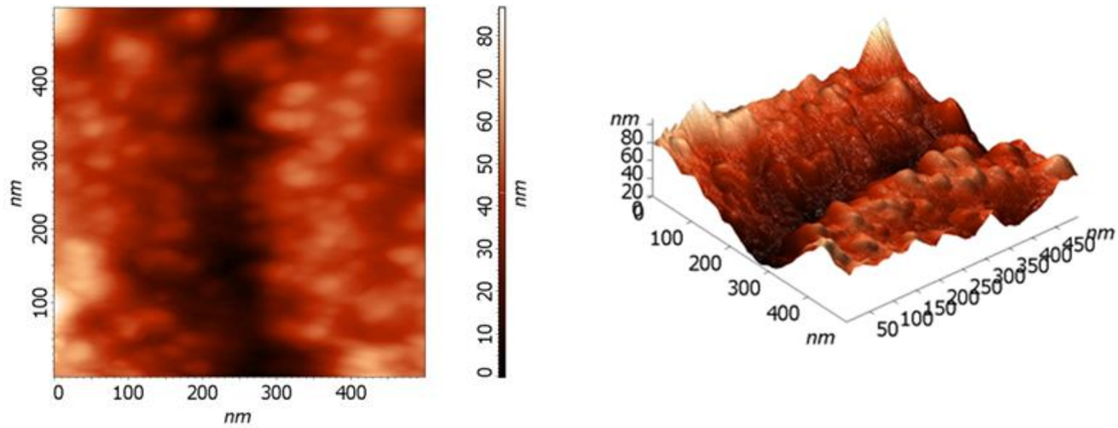
4.3.4. The Surface topography by the atomic force microscopy (AFM)

AFM topographic pictures illustrates that after the cotton textile treatment with sol within the ZAD concentrations 5 wt.% - 7.5 wt.% (0.1 M TEOS), the coatings obtained constituted by spherical or ellipsoidal particles, assembled in larger clusters (Fig. 9a, b). The pictures also reveals that the particles are more or less evenly distributed; there are even some obvious aggregations at the fiber surface (Fig. 9a, b).

a)



b)



9. Fig. The topographic pictures of the cotton textile treated by sol
a) 5 wt.% ZAD (0.1 M TEOS) sol, b) 7.5 wt.% ZAD (0.1 M TEOS) sol

4.4. Evaluation of the coating and cotton textile resistance to abrasion

Coatings deposited by the *thermal vacuum evaporation* and *magnetron sputtering technology* have relatively low bonding strength with the cotton textile surface, hence, the modified textile materials with antimicrobial copper coatings can be integrated in the single-use medical products that are not to be subjected to constant abrasion.

The textile modified by *ZSH sol* has very low abrasion resistance, thereby, within the parameters of the sol-gel technology used in the study, ZSH sols are not appropriate for the modification of cotton textile surfaces.

Modification of the cotton textile surfaces by 5 wt. % and 7.5 wt. % *ZAD* (0.1 M TEOS) *sol* provide excellent abrasion resistance of the textile, the level of the abrasion resistance can be adjusted by the thermal post-treatment temperature.

4.5. Antimicrobial properties of the modified cotton textiles

4.5.1. Pathogenic micro-organisms

It was proved experimentally that the cotton textiles coated with nano-level copper coating by the *thermal vacuum evaporation* provide antimicrobial activity against:

- The gram-positive bacteria at the maximum micro-organisms concentration *Staphylococcus aureus ATCC 25923* ($4.3 \cdot 10^8$ CFU ml^{-1}) and gram-negative bacteria *E. coli ATCC 25922* ($7.1 \cdot 10^8$ CFU ml^{-1}) (Fig. 10a) with the coating of 180 nm;
- The gram-negative bacteria at the ten times lower micro-organisms concentration *Escherichia coli ATCC 25922* ($7.1 \cdot 10^7$ CFU ml^{-1}) and *Pseudomonas aeruginosa ATCC 10145* ($3.9 \cdot 10^7$ CFU ml^{-1}) (Fig. 10b) with the coating of 120 nm;
- The gram-positive bacteria at the ten times lower micro-organisms concentration *S. aureus ATCC 25923* ($4.3 \cdot 10^7$ CFU ml^{-1}) and gram-negative bacteria *E. coli ATCC 25922* ($7.1 \cdot 10^7$ CFU ml^{-1}), as well as *P. aeruginosa ATCC 10145* ($3.9 \cdot 10^7$ CFU ml^{-1}) (Fig. 10b) with the coating of 180 nm.

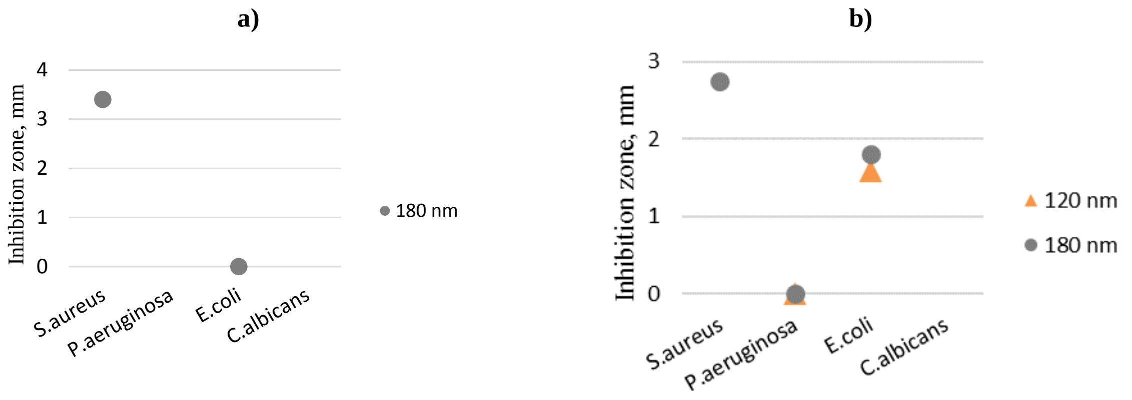
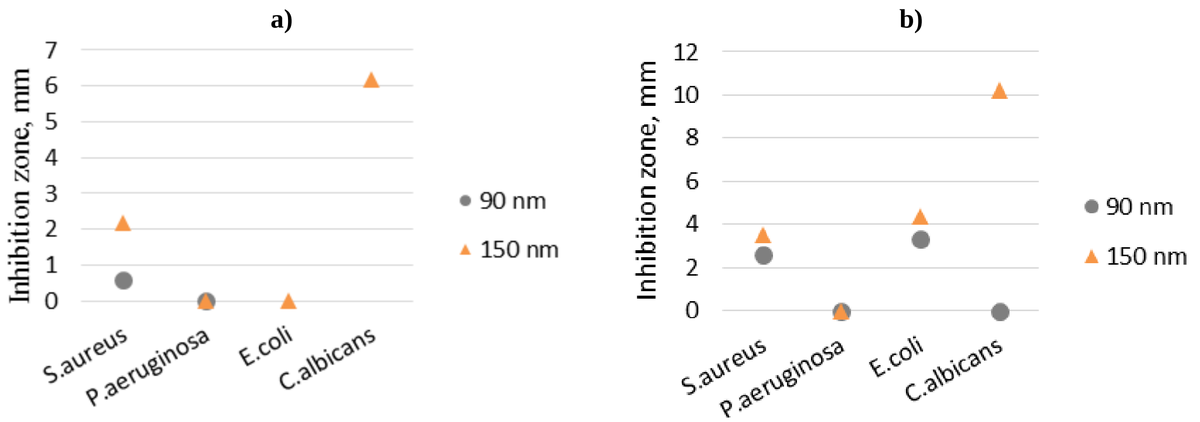


Fig. 10 Inhibition zone

a) maximum concentration of micro-organisms, b) ten time lower concentration of micro-organisms. 0 – under the samples was not observed micro-organisms growing, samples have antimicrobial activity

At the both concentrations, the microscopic fungus *Candida albicans ATCC 60193* ($8.2 \cdot 10^6$ CFU ml^{-1} and $8.2 \cdot 10^5$ CFU ml^{-1}) shows resistance against the copper coating deposited by the thermal vacuum evaporation technology.

The cotton textiles coated with nano-level copper coating by the *magnetron sputtering technology* provide antimicrobial activity against:



11. Fig. Inhibition zone

a) maximum concentration of micro-organisms, b) ten time lower concentration of micro-organisms. 0 – under the samples was not observed micro-organisms growing, samples have antimicrobial activity

- The pathogenic micro-organisms at the maximum concentration – the gram-positive bacteria *S. aureus ATCC 25923* ($4.3 \cdot 10^8$ CFU ml^{-1}), gram-negative bacteria *P. aeruginosa ATCC 10145* ($3.9 \cdot 10^8$ CFU ml^{-1}) (Fig. 11a) with the coating of 90 nm;
- The pathogenic micro-organisms at the maximum concentration – the gram-positive bacteria *S. aureus ATCC 25923* ($4.3 \cdot 10^8$ CFU ml^{-1}), gram-negative bacteria *P. aeruginosa ATCC 10145* ($3.9 \cdot 10^8$ CFU ml^{-1}), gram-negative bacteria *E. coli ATCC 25922* ($7.1 \cdot 10^8$ CFU ml^{-1}), microscopic fungus *C. albicans ATCC 60193* ($8.2 \cdot 10^6$ CFU ml^{-1}) with the coating of 150 nm.

After reducing the micro-organisms concentration ten times and the copper coating of 90 nm provides antimicrobial activity against all micro-organisms mentioned above (Fig. 11b).

The cotton textiles modified by the *sol-gel technology* provide antimicrobial activity against all nosocomial pathogenic microorganisms tested at the maximum concentration already after the treatment with 5 wt.% CAD (0.1 M TEOS) sol: the gram-positive bacteria *S. aureus ATCC 25923* ($4.3 \cdot 10^8$ CFU ml^{-1}), gram-negative bacteria *P. aeruginosa ATCC 10145* ($3.9 \cdot 10^8$ CFU ml^{-1}) and *E. coli ATCC 25922* ($7.1 \cdot 10^8$ CFU ml^{-1}), and microscopic fungus *C. albicans ATCC 60193* ($8.2 \cdot 10^6$ CFU ml^{-1}) (Fig. 12a and Fig. 13). Furthermore, against the wound infection, abscesses widely causing agent – the gram-positive bacteria *S. aureus ATCC 25923* ($4.3 \cdot 10^8$ CFU ml^{-1}), antimicrobial activity maintained after 10 cycles of the hydrothermal treatment of the modified textiles; but if the textile is modified by 7.5 wt.% CAD sol, then the activity remained also after 50 cycles of the hydrothermal treatment.

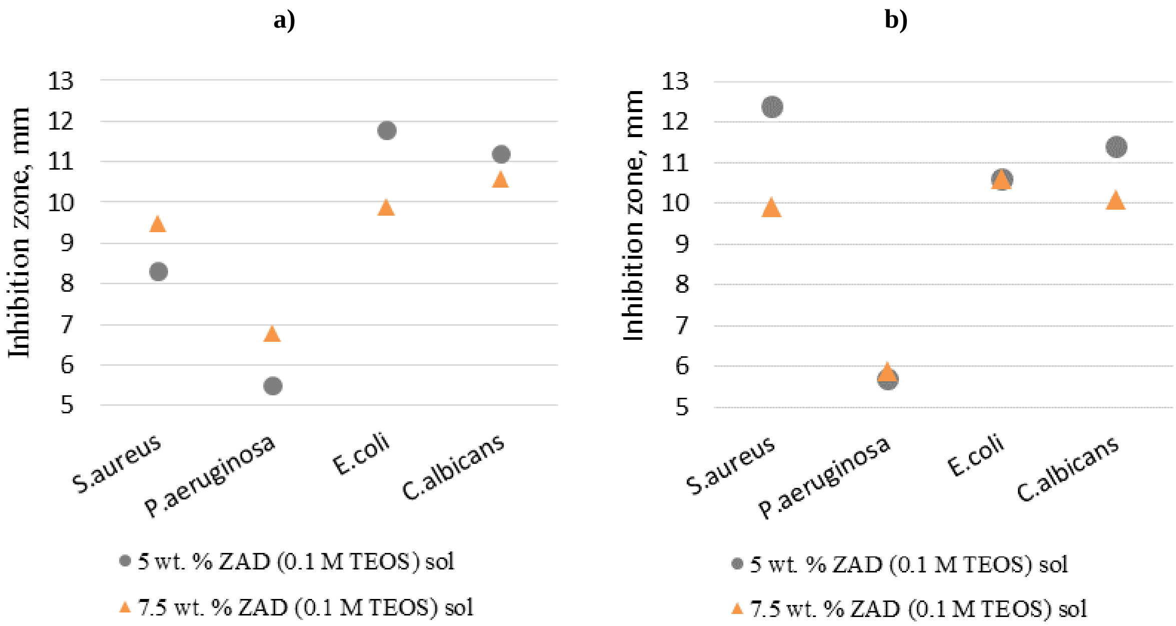


Fig. 12 Inhibition zone
a) maximum concentration of micro-organisms, b) ten time lower concentration of micro-organisms

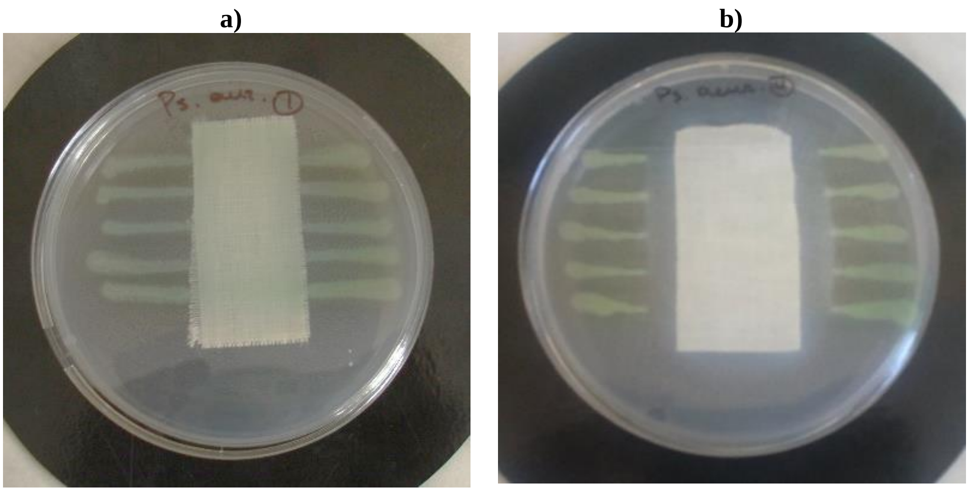


Fig. 13 Parallel streak method results against *P.aeruginosa ATCC 10145*
a) untreated cotton textile, b) cotton textile treated by 5 wt.% ZAD (0.1 M TEOS) sol

4.5.2. Micro-organisms causing cellulose textile destruction

The cotton textiles coated with the nano-level copper coating by the *thermal vacuum evaporation* provide antimicrobial activity against:

- The microscopic fungus *Trichoderma viride* ($3.1\cdot10^5$ CFU ml^{-1}) and yeast *Saccharomyces cerevisae 14* ($2.8\cdot10^5$ CFU ml^{-1}) with the coating of 60 nm.

Within the copper coating thickness deposited by the thermal vacuum evaporation exposed to analysis, there is not observed antimicrobial activity against the bacteria *Pseudomonas fluorescens AM11* ($1.7\cdot10^6$ CFU ml^{-1}).

The cotton textiles coated with the nano-level copper coating by the *magnetron sputtering technology* provide antimicrobial activity against:

- The bacteria *P. fluorescens AM11* ($1.7\cdot10^6$ CFU ml^{-1}), microscopic fungus *T. viride* ($3.1\cdot10^5$ CFU ml^{-1}) and yeast *S. cerevisae 14* ($2.8\cdot10^5$ CFU ml^{-1}) with the coating of 150 nm.

The cotton textiles modified by *5 wt. % and 7.5 wt. % CAD (0.1 M TEOS) sol* (Fig. 14, Fig. 15) provide antimicrobial activity against:

- all cellulose destruction causing micro-organisms tested – the bacteria *P. fluorescens AM11* ($1.7\cdot10^6$ CFU ml^{-1}), microscopic fungus *T. viride* ($3.1\cdot10^5$ CFU ml^{-1}) and yeast *S. cerevisae 14* ($2.8\cdot10^5$ CFU ml^{-1}). The antimicrobial activity remained after 96 h of inhibition (for 4 days) that indicate about strong antimicrobial activity.

Antimicrobial activity against the bacteria *P. fluorescens AM11* ($1.7\cdot10^6$ CFU ml^{-1}) remained after 10 cycles of the hydrothermal treatment and after 50 cycles of the hydrothermal treatment against yeast *S. cerevisae 14* ($2.8\cdot10^5$ CFU ml^{-1}).

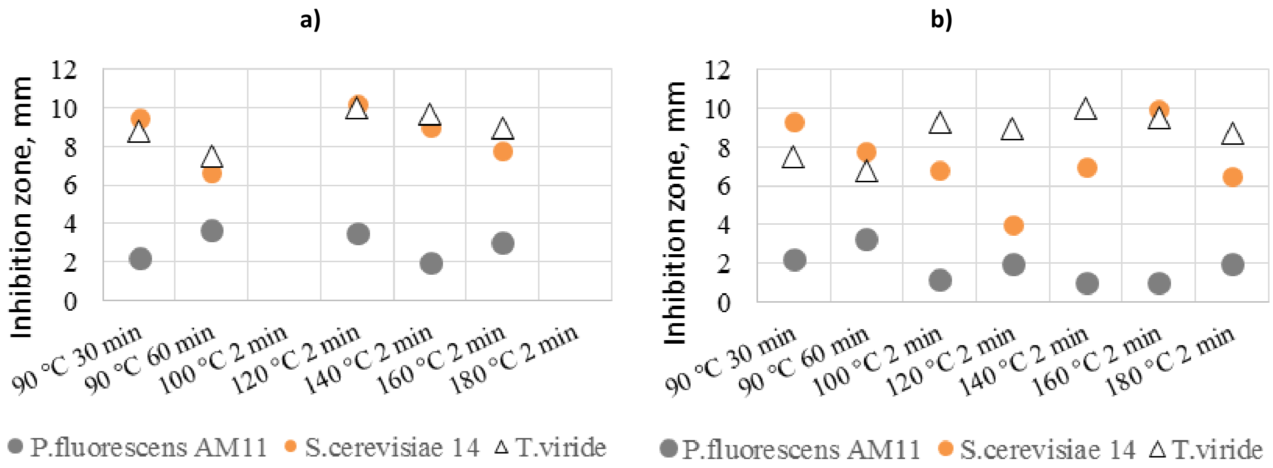


Fig. 14 Inhibition zones after 96 h incubation of cotton treated by ZAD sol
a) 5 wt. % ZAD (0.1 M TEOS) sol, b) 7.5 wt. % ZAD (0.1 M TEOS) sol

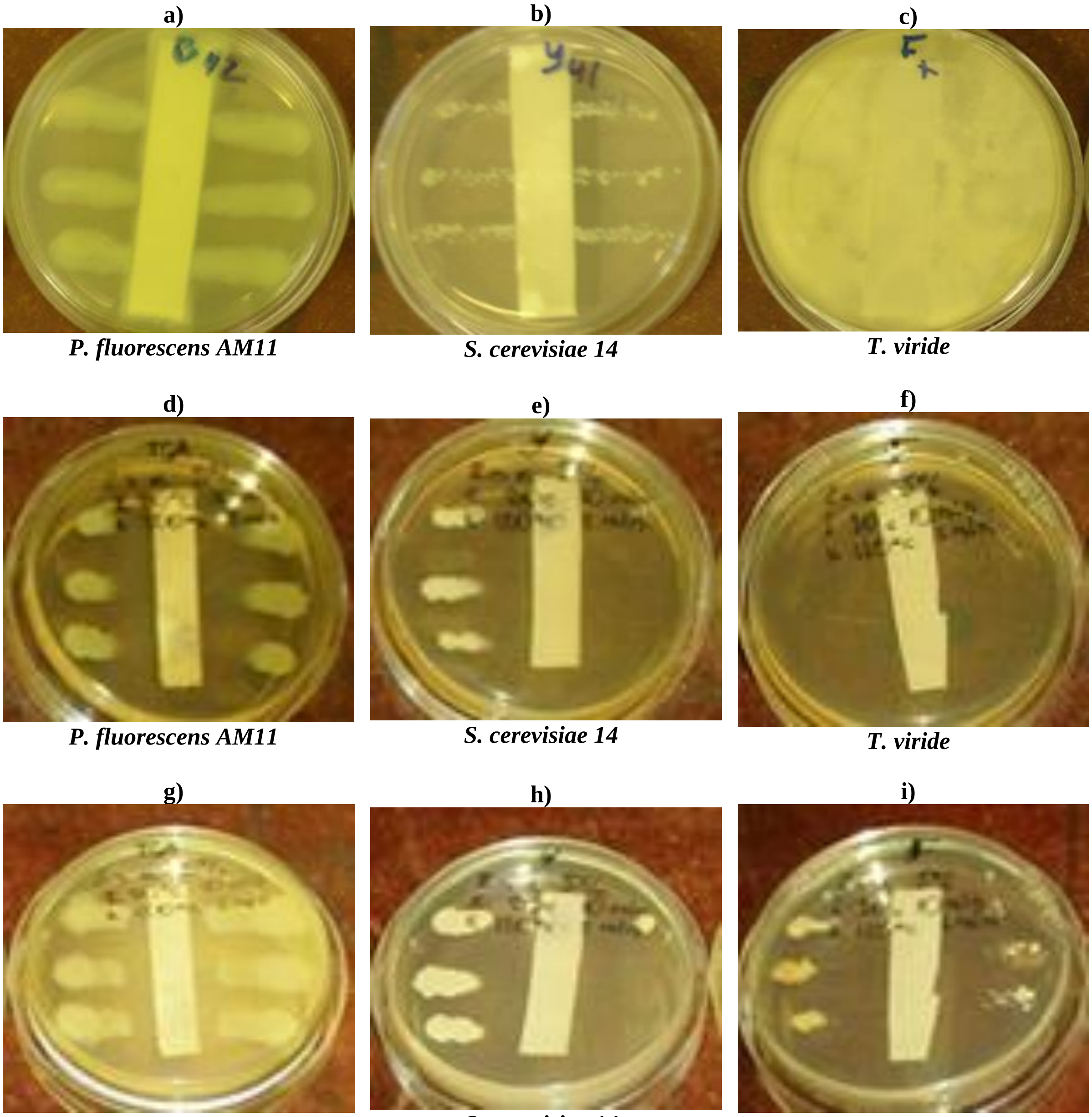


Fig. 15 Visualization of the results obtained by tests based on a parallel streak method
Upper row (a-b): untreated samples after 24 h of incubation and c) after 96 h of incubation; middle row (d-f): samples treated by 5 wt. % ZAD (0.1 M TEOS) sol after 24 h of incubation; lower row (g-i): samples treated by 5 wt. % ZAD (0.1 M TEOS) sol after 96 h of incubation

4.5.3. The micro-organism adhesion on the textile surface

The adhesion of such nosocomial pathogenic micro-organisms as the gram-negative bacteria *P. aeruginosa ATCC 27853* (10^2 CFU ml^{-1}) and gram-positive bacteria *S. epidermidis ATCC 12228* (10^2 CFU ml^{-1}) was prevented by:

- cotton textiles with the copper coating of 60 nm deposited by the *thermal vacuum evaporation technology*;
- cotton textiles with the copper coating of 90 nm deposited by the *magnetron sputtering technology*;

– cotton textile modified by *5 wt. % and 7.5 wt. % ZAD (0.1 M TEOS) sol*, as well after 50 cycles of the hydrothermal treatment.

4.6. UV protection of the modified textile

The cotton textile treatment by 7.5 wt.% ZAD (0.1 M TEOS) sol provides excellent UV protection – the 50+ UPF Category (Fig. 16), blocking both the UVB and UVA spectrums and maintaining full protection ability also after 50 cycles of the hydrothermal treatment (Fig. 17).

Also treatment by 5 wt. % ZAD (0.1 M TEOS) sol allows obtaining the 50+ UPF Category for the tested cotton textile, however, during modification it is necessary to reckon with stricter restrictions in the thermal post-treatments (Fig. 16).

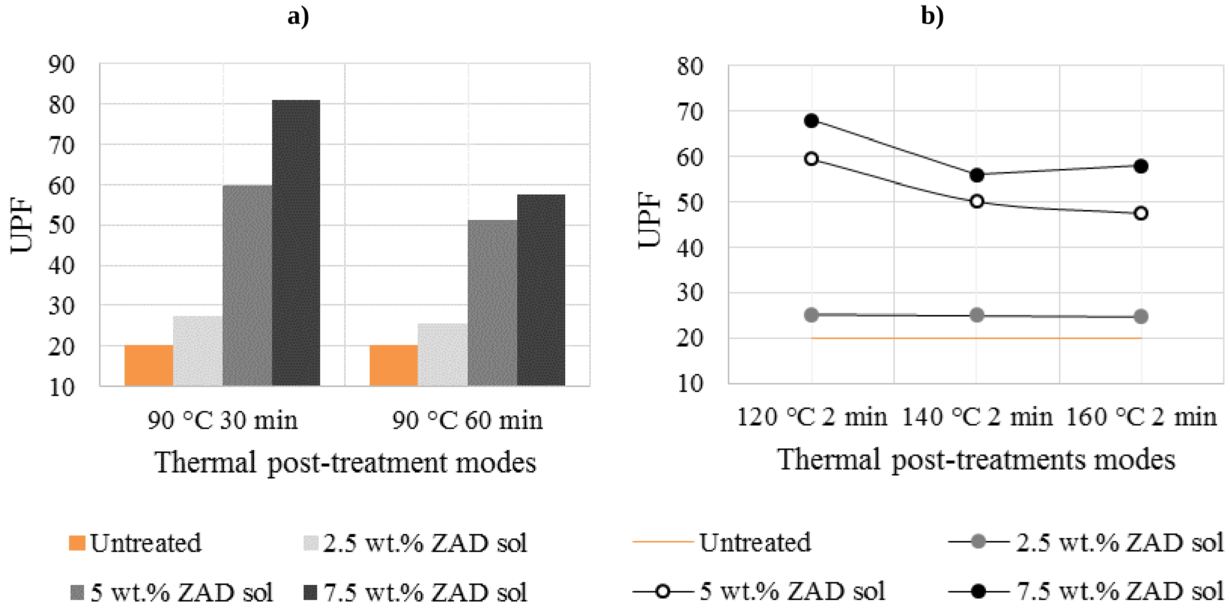
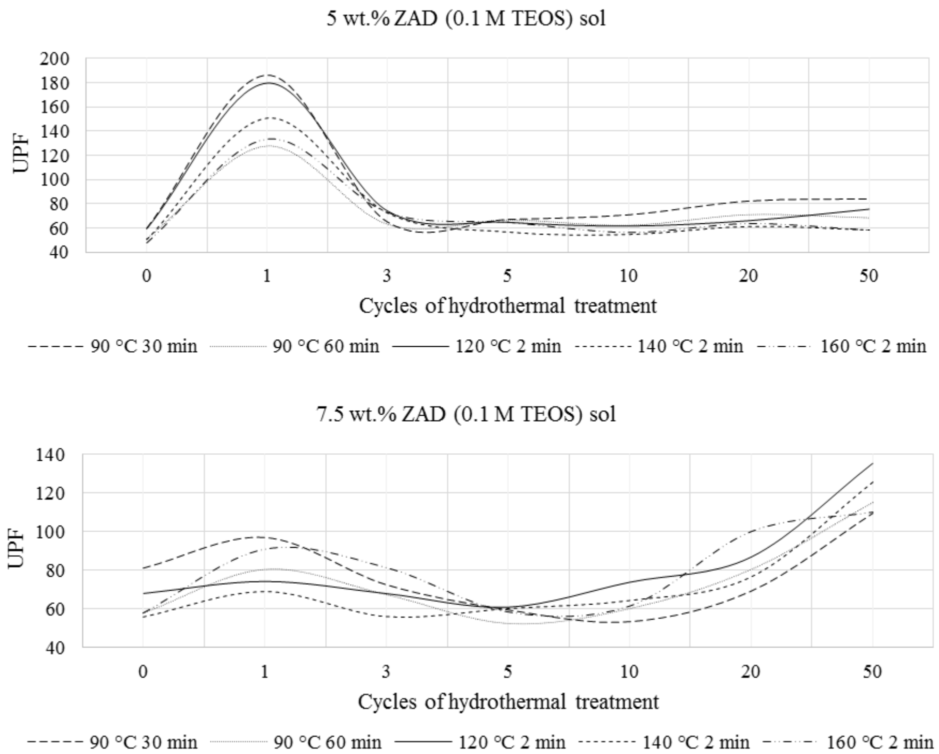


Fig. 16 UV protection depending on ZAD concentration (0.1 M TEOS)

The durability of the cotton textile coating (ZAD sol) to multiple hydrothermal treatment indicates that a very good bonding strength between the coating and the cotton textile surface is obtained, which is significant for sol-gel to practical application of sol-gel in the textile industry (Fig. 17).



17. Fig. UPF values of the modified textiles after hydrothermal treatment

4.7. Permeability of the modified textiles to air and hygroscopicity

The copper coatings within the range of the thickness from 30 nm to 210 nm deposited on the cotton textile surface by *the thermal vacuum evaporation* and *magnetron sputtering technology* practically without changing the textile air permeability, this means, that the coatings deposited within the analyzed thickness makes no changes to the textile surface texture and structure and maintains the intrinsic properties of textiles.

The test results evince that the air permeability of textiles after being subjected to treatment by *sol-gel technology* reduced. However, also after 50 cycles of the hydrothermal treatment, the tested cotton textile samples, according to the standards applied to the clothing, which is in close contact with skin, provide comfort to the group from the three years of age. But the hygroscopicity tests results evince that the textile samples provide comfort from the age of 14 years, if textile is modified by 5 – 7.5 wt. % ZAD (0.1 M TEOS) sol. In the number of other applications, where is necessary UV and antimicrobial protection and surface water-repellency (interior textiles, outdoor textiles) were to be achieved, these restrictions are irrelevant

4.8. Liquid (water) sorption of the modified textiles

The textile water sorption before coating by the *thermal vacuum evaporation* and *magnetron sputtering* depends on the textile structural parameters – density, thickness and porosity; water sorption velocity of the untreated textiles varying from 5 to 20 ± 0.001 s. After coating the textile with copper, the water sorption velocity has been decreased within from 2 to 5 minutes. That indicates that the thickness of the coating and technology practically are has no practical effect on the water sorption of the textile.

After the cotton textile treatment by *5 wt. % or 7.5 wt. % ZAD (0.1 M TEOS) sol*, the water sorption velocity was decreased from 11 ± 0.001 s to > 30 minutes (Fig. 18). The number of cycles of the hydrothermal treatment has not affected the water sorption velocity of the textiles modified by 7.5 mas. % ZAD (0.1 M TEOS) *sol*, the sorption velocity remains > 30 minutes; sorption velocity of the textile modified by 5 mas. % ZAD (0.1 M TEOS) *sol* was decreased only after 50 cycles of the hydrothermal treatment up to 2 minutes.

a) **b)**

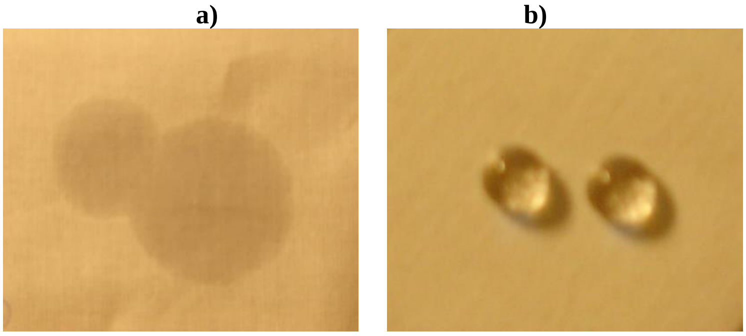


Fig. 17 Liquid sorption
a) untreated, b) after treatment by 5 wt.% ZAD (0.1 M TEOS) sol

1.8. Contact angle of the modified textiles

The cotton textile treatment by 5 wt. % ZAD (0.1 M TEOS) sol provides the water-repellent properties, also after 20 cycles of the hydrothermal treatment. The cotton textile treatment by 7.5 wt. % ZAD (0.1 M TEOS) sol provides the water-repellent properties to cotton textiles even after 50 cycles of intensive hydrothermal treatment, which also ensures self-cleaning of the surface and reduces the risk of the infections (Fig. 18. and Fig. 19).

a) **b)** **c)**

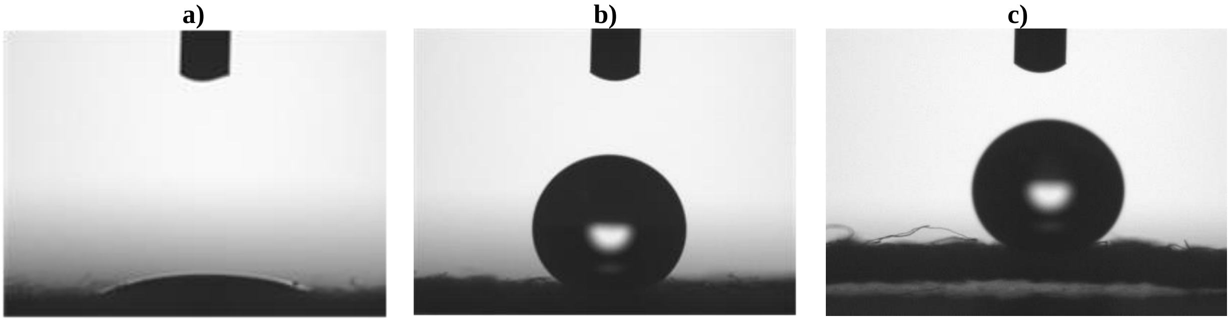


Fig. 18 Cotton textile surface wettability process (drop 5µL)
a)untreated b) treated by 7.5 wt.% ZAD (0.1 M TEOS), b) treated by 7.5 wt.% ZAD (0.1 M TEOS) after 50 cycles of the hydrothermal treatment

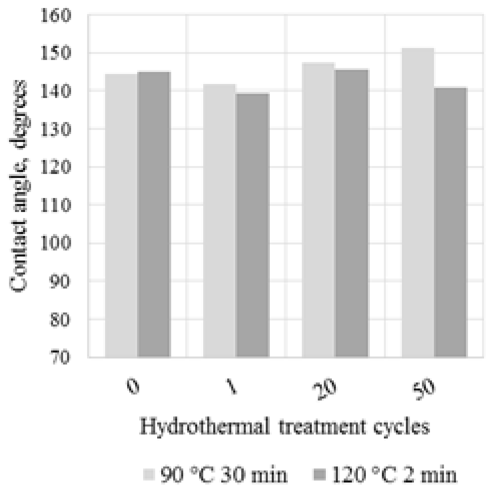
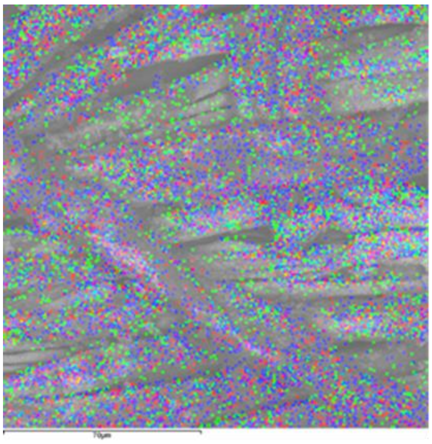


Fig. 19 Contact angle of the cotton textiles modified by 7.5 wt. % ZAD (0.1 M TEOS) sol



20. Fig. The distribution of the chemical elements **F**, **Si**, **Zn** in the coating of the modified cotton textile surface

5 wt.% ZAD (0.1 M TEOS) sol; thermal post-treatment at 90 °C temperature 30 min.

As it was mentioned previously, the hydrophobic textile surfaces are mainly produced in two ways, one is to create a rough structure of the surface and the other is to modify a surface by compounds with low surface free energy, like fluorine or silica containing compounds [16]. The EDX chemical element analysis evinces that in addition to the rough surface of the coating, within the studies, the synthesized compositions and modification technologies by sol allow to obtain coatings with not only the Si un Zn containing functional groups, but also the F containing functional groups which have low surface energy (Fig. 20). After 50 cycles of the hydrothermal treatment of the modified textile by 5 wt. % ZAD (0.1 M TEOS) sol, the F percentage weight has been decreased at least 8 times in comparison with the modified textiles before hydrothermal treatment. While on the surface of the modified textiles by 7.5 wt. % ZAD (0.1 M TEOS) sol, the F percentage weight has been decreased maximum 3 times, but the Si content for textiles modified with both ZAD concentrations becomes the same that can explain the increase of wettability of the textile surface modified by 5 wt. % ZAD (0.1 M TEOS) sol after the hydrothermal treatment. This suggests that exactly F containing functional groups provide the modified textile surface sustainable water-repellent (hydrophobic) properties during use, if the cotton textile surface has been modified by 7.5 wt.% ZAD (0.1 M TEOS) sol, since it provides the sufficient concentration of F, even after 50 cycles of the hydrothermal treatment.

CONCLUSIONS

1. Neither the thermal vaccum evaporation, nor magnetron sputtering technology can provide durable coating with natural fiber materials capable of resistance to the hydrothermal treatment and friction. However, a number of other applications can be found,in sinlge-use medical products including various types of antimicrobial dressing and patches, partly replacing the antibacterial textiles coated with silver. Moreover, the applied technology proves to be economically advantageous since copper is much cheaper than silver.
2. The author of the present paper applied the sol-gel method to the cotton textile processing. Sol compound concentration range, textile thermal post-treatment temperature-time regime and was described. It was experimentally proved that the developed method allows obtaining textiles, which combine hydrothermal treatment resistant properties: they are anti-microbial, UV-protective and water-repellent (waterproof).
3. Extensive full-scale tests in accordance with the strict standards of sol-gel technology demonstrate the ability of modified textiles to perform the functions assigned both after the coating and repeated cycles of hydrothermal treatmen. The obtained results confirm the estimated coverage of sustainability; moreover, the acquired knowledge provides the option of adjusting the intensity of the properties in accordance with the intended use.
4. The samples processed in sol-gel technology with the coating containing amorphs Si and Zn demonstrated the highest antimicrobial activity in terms of the growth of microorganisms in all the performed tests, whereas the samples covered with Cu coatings obtained by thermal vacuum evaporation and magnetronsputtering technology indicated lower antimicrobial activity.
5. It is supposed that the acquired know-how of thermal vacuum evaporation and magnetron sputtering processes, as well as the application of sol-gel technology to the

textile surface modification, technological parameters, the resulting effects and their sustainability will greatly intensify the future research and promote industrial technology development.

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