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Deposition of Zinc Oxide on the Materials Used in Medicine. Preliminary Results

Abstract
This paper presents preliminary results of the direct deposition of nano- and microstructures of zinc oxide on materials used in medicine. The coatings were deposited on cotton gauze and polyamide fabric. During the research the biological activity of these materials was defined. Performed were also tests of doping the ZnO structures with silver obtained. The research has proved that there is a growth of zinc oxide structures both on the gauze and polyamide fabric. The nanostructures deposited on it did not become detached from the surface, even though the material was subjected to ultrasonic rinsing. In addition, good biocidal properties of both of the textile materials modified were found. Furthermore a complex surface analysis of catheters: vascular and urological was made. ZnO was deposited on catheters, but they were characterised by low adhesion.

Key words: *zinc oxide nanoparticles, cotton gauze, polyamide, catheters, bactericidal properties.*

Introduction

Nanotechnology is slowly entering into every aspect of life. Its influence is also seen in medicine, where it is used in modern diagnostic techniques, being the beginning of new medical treatment routines. Nanomaterials can be used for accurate administration of pharmaceuticals during medical treatment, including cancers, but also in the secretion of toll receptors in regenerative medicine [1 - 4].

A major problem that exists in medicine are infections following a break in the continuity of tissue, often leading to severe complications and,in extreme cases the patient's death. Commonly used dressing materials should be sterile and have good body fluid absorption. The most common dressing material used is cotton in the form of gauze and bandages. Cotton dressings adhere well to the wound, absorbing bodily fluids. However, in dressings saturated with body fluids, rapid development of bacteria takes place, which in extreme cases can cause serious infections, dangerous to the patient's health and life.

In many patients, an essential part of treatment is the use of vascular catheters, or in many other cases, urological catheters. After their application, a biofilm gets formed on the internal and external surface, with microorganisms constituting its vital part. Most commonly these include staphylococci, with a high resistance to most antibiotics.

In many scientific centres, research is being conducted on the modification of the surface of different textile materials used in medicine with the purpose of giving them bactericidal or bacteriostatic properties [5 - 7]. One of the better-known materials used for modifying the surface of textile materials utilised in medicine is nano-molecular silver [8]. Another one widely studied and used to modify the properties of textile materials is titanium dioxide [9]. On the other hand, there has been a biosafe and biocompatible material known for many centuries with both biocidal and drying properties - zinc oxide [10, 11]. Due to the variety of possible structures [12 - 15], ZnO has a wide range of applications in areas such as the abovementioned medicine, electronics, optoelectronics and pharmacology [16 - 19]. In literature, a significant amount of information can be found on the lack of toxicity of ZnO and its lack of adverse effects on human cells [20, 21]. The bioactivity of zinc oxide deposited on fibre products is comparable with the activity of silver, yet its price is lower and, most importantly, it does not cause a change in the product's colour [9, 22]. It was found that a layer of ZnO deposited on medical textile materials has strong antibacterial properties, effectively reducing the possibility of infections by *Escherichia coli* bacteria (*E. coli*), *Staphylococcus aureus* (*S. aureus*) and *Pseudomonas aeruginosa* (*P. aeruginosa*) - in patients undergoing hospitalisation [23]. Infections caused by the aforementioned gram-negative and gram-positive bacteria are difficult to treat and very dangerous for people with impaired immune systems [24 - 27]. For these reasons, researchers are trying to deposit zinc oxide utilising different methods with different textile materials in order to limit the growth of bacteria, fungi and viruses. Currently attempts are being made to modify textile materials by applying zinc oxide nanostructures to their surface, which are characterised by unique physicochemical properties [22, 28 - 30]. Various techniques are applied to the production of textile materials with new properties or to produce „smart" textile materials for unconventional applications, such as technical, biomedical or in the clothing industry. Due to the nature of textile materials, high-temperature methods or those that do not allow the modi-

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fication of materials with a large surface area cannot be applied. For these reasons, microencapsulation, hydrogel coating and sol-gel technology are among some of the techniques used for modifying the surface of textile materials [31 - 33]. A very simple method of obtaining zinc oxide coating on fabrics in order to absorb UV radiation was described by A. Becheri and others [34], where fabrics were soaked in isopropanol containing dispersed ZnO particles and gently mixed. Then the fabric was washed to remove excess particles and finally dried at 130 °C.

With regard to the direct deposition of quasi-one-dimensional structures of ZnO on the surface of textile materials, only a few reports were found in world literature [23, 29, 30, 35 - 38]. ZnO nanostructures have been deposited on the surface of textile materials with the aim of obtaining a UV-absorbing material with antibacterial properties or a super-hydrophobic surface. The authors of research papers [39 - 43] used complex methods to apply the nanostructures of ZnO onto the surface of textile materials. A two-stage method of deposition of zinc oxide nano-rods on the surface of cotton fabrics was used by Wang and others [36]. During the first stage, seed layers were deposited onto the cotton surface by the dip-coating process repeated many times. After each immersion in a solution containing seeds, the cotton was annealed at 150 °C. During the second stage, on the thus-prepared cotton ZnO nanorods were deposited from an aqueous solution of zinc acetate and triethenamine. The process was carried out at room temperature for a few days, after which the samples were rinsed in water and dried at 60 °C.

In another paper, cotton and polyamide fabrics were examined due to their popular use in medicine as e.g. bandages and plasters [44]. Moreover in the literature there are many examples of surface modification of catheters in order to give them antibacterial properties. It can be achieved, for example, through modification using MgF_2 nanoparticles [45], silver nanoparticles [46 - 48], TiO_2 [49] or triclosan, which was used as an antimicrobial additive in the polymeric matrix [50]. However, there is still not enough information about the modification of catheters using ZnO nanoparticles [51]. Therefore besides the direct deposition of nano- and microstructures of zinc oxide on materials used in medicine such as cotton gauze and polyamide fabric, the authors made an effort to deposit ZnO on vascular and urological catheters. Attention was paid to differences between these two types of catheters. The authors also explained the problems with the deposition of ZnO.

The paper presents preliminary results concerning the possibility of direct deposition of nano- and microstructures of zinc oxide on cotton gauze, polyamide fabrics and catheters: central venous and urinary. Moreover the zinc oxide nanostructures obtained on the surface of the gauze and polyamide fabrics were doped with silver. The ZnO structure growth method applied by the authors of the paper is based on the synthesis method of one-dimensional structures devised by Vayssieres [43, 52, 53]. In this method, known as Chemical Bath Deposition - CBD, the growth process of quasi-one-dimensional structures of zinc oxide is carried out in an equimolar solution of the precursor of zinc ions (mostly nitrate) and hexamethylenetetramine (HMT) at an elevated temperature or 95 °C. The CBD is a new, extensively studied method of depositing the q-1D structures from water solution. Thanks to the CBD method, nanorods alongside other ZnO nanostructures with desired electrical and optical properties get deposited on clean and modified glass surfaces coated with indium-tin oxide (ITO) or on substrates of monocrystalline silicon.

Experimental

Using the modified CBD method, nano- and microstructures of ZnO were deposited directly on the surface of cotton gauze, polyamide fabric and two types of catheters: central venous and urological. Both catheters were made of polytetrafluoroethylene (PTFE). Nitrate(V) and zinc acetate, hexamethylenetetramine (HMT, urotropine, $C_6H_{12}N_4$) and silver acetate (pure) were used as primary substrates.

The ZnO deposition process was carried out in a true solution with a concentration of 0.1 mol/dm^3 with respect to the basic substrates, i.e. the precursor of zinc ions and the HMT. Silver acetate was used as an admixture, which was added to the true solution immediately before the process in the amount of 4% mol in relation to the concentration of zinc ions. The true solution can be subjected to a microwave field or placed in the dryer once the medium is put into the solution. The process was carried out at a temperature of 90 °C, at standard atmospheric pressure, for a duration of 9 hours. During the process there is a series of chemical reactions ultimately leading to the formation of zinc oxide. In the first stage HMT decomposes to ammonia and formaldehyde (1), whereas the zinc nitrate dissociates (2). Then the resulting ammonia undergoes electrolytic dissociation (3), and the resulting hydroxide ions react with the zinc ions to form zinc oxide (4), which in turn is deposited on the surface of the materials tested.

$$C_6H_{12}N_4 + 6H_2O \rightarrow \rightarrow 6CH_2O + 4NH_3 \quad (1)$$

$$Zn(NO_3)_2 \rightarrow Zn^{2+} + 2NO_3^- \quad (2)$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (3)$$

$$Zn^{2+} + 2OH^- \rightarrow ZnO\downarrow + H_2O \quad (4)$$

Immediately before the process, the materials were rinsed with ethanol using an ultrasonic washer, then in deionised water and finally dried in ambient atmosphere. The dry material was attached to special glass holders. Once the deposition process of zinc oxide was finished, the materials were rinsed in deionised water in an ultrasonic washer, and then in isopropyl alcohol. Once dry, a white precipitate of zinc oxide was visible on the surface of the cotton gauze, polyamide fabric and catheters.

Since the growth of structures on the surface of the material depends on its quality, the roughness and wettability of catheters used was evaluated. Measurements of the surface roughness of the catheters were made using two profilometers: mechanical (Form Talysurf i120) and optical (Talysurf CCI). Parameters of the optical profilometer used in the study were as follows: measurement speed - up to 100 μm/s, field of view – 0.0025 mm^2 to 70 mm^2, measuring range (vertical) - 0.1 nm to 8 mm, vertical resolution - less than 0.1 nm Ra, and reproducibility - 0.01 nm. The parameter most measured was the arithmetic average deviation of the profile from the mean line – Ra. The mean line is the theoretical line at which the sum of the squared peak to the valley distances is the smallest. Contact angle measurements were performed using the so-called „sitting drop" method, used to evaluate the hydrophilicity of the flat surfaces. Measurements were performed at

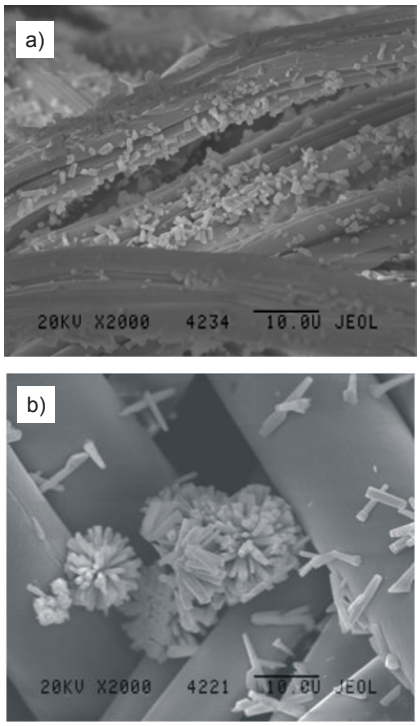

Figure 1. *Cotton gauze (a) and polyamide fabric (b) covered with micro- and nanostructures of zinc oxide.*

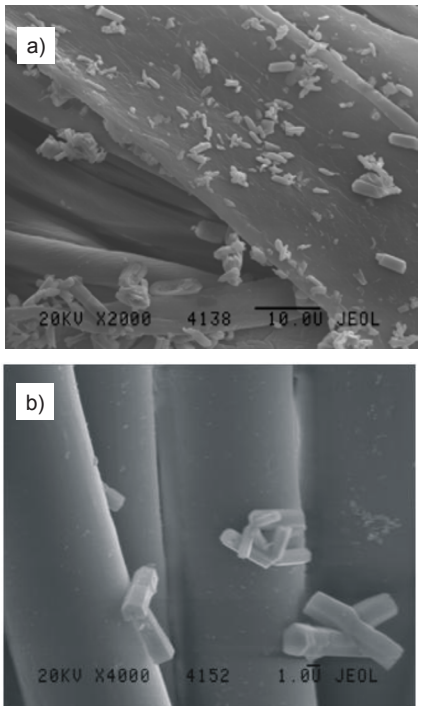

Figure 2. *Cotton gauze (a) and polyamide fabric (b) covered with zinc oxide nanostructures in a solution containing ions of silver.*

22 ± 2 °C, at standard atmospheric pressure and relative humidity of 50%.

The microstructure of zinc oxide layers deposited on the cotton and polyamide substrates and on the surface of catheters was examined using a scanning electron microscope, JSM 5800 LV, produced by Jeol (Japan), equipped with an X-ray microanalysis system - ISIS 300, by Oxford, with a semiconductor detector analysing characteristic X-ray radiation. The X-ray microanalysis system (MAR) allows a qualitative EDX analysis of elements from lithium (Li) to uranium (U). The crystallographic structure of the zinc oxide layers and structures was determined using a high resolution X-ray diffractometer, Phillips (the Netherlands), Materials Research Diffractometer (MRD) applying CuKα radiation. A conventional type of scan for powder materials was used, i.e. Θ/2Θ.

The biological activity of materials coated with nano-and microstructures of zinc oxide was examined for two bacteria: *E. coli* and *S. aureus*. For reliability, the tests were done using a liquid and solid medium, as described below.

- Method I – in liquid medium: Material samples were placed in full Mueller-Hinton broth (3 ml) containing 3×10^6 bacterial cells/ml. Such samples were incubated at 37 °C for 24 hours. After that time, the optical density value of the resulting culture was read and the results obtained were compared with data received from cultures bred under the same conditions but without the presence of the test material.
- Method II – in solid medium: Material samples were placed on the sur-

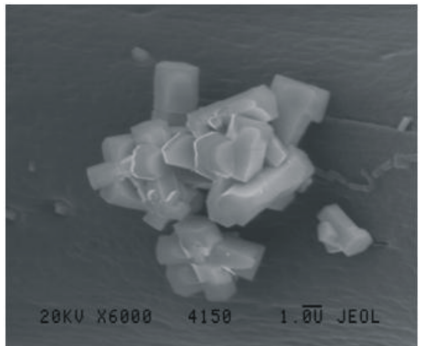

Figure 3. *Shape of ZnO structures formed on polyamide fabric in a solution containing ions of silver.*

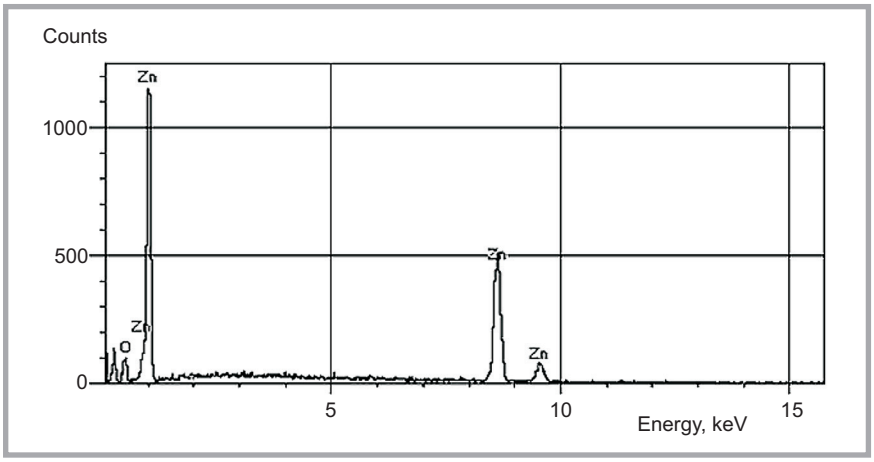

Figure 4. *Results of EDS analysis of structures deposited on the surface of the cotton gauze.*

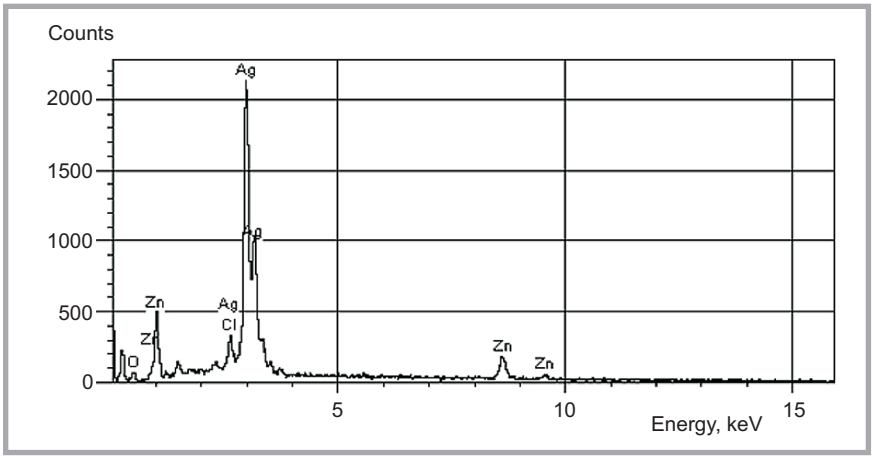

Figure 5. *Results of EDS analysis of Ag-doped ZnO structures deposited on the surface of the cotton gauze.*

face of a solid substrate following the Mueller-Hinton, where 1ml of each test overnight bred bacteria cultures containing 3×10^6 cells/ml was previously seeded. Samples were incubated for 24 hours at 37 °C. The objective was to find out whether an inhibition of bacterial growth around the test sample could be observed. The presence of bacterial growth inhibition zone indicates the quality of bactericidal properties of the material.

Results and discussion

Tests of the microstructure made using a scanning electron microscope showed that the number, shape and size of the structures of zinc oxide deposited strongly depend on the type of material on which the layer grew and on the presence of additives (***Figures 1 - 2***).

Nano- and microrodes of zinc oxide were formed on the surface of the cotton gauze and polyamide fabric. In the case of the growth process of the nanostructures on cotton gauze in the presence of silver ions, the formation of nanorod agglomerates was observed (***Figure 2.a***). Furthermore both on cotton gauze and polyamide fabrics the shape of the nanorods formed in a solution containing ions of silver is not as repetitive nor as symmetrical as in the case of synthesis without the presence of these ions (***Figures 2 - 3***).

Before examination of the microstructure using a scanning electron microscope the cotton gauze and polyamide fabric were rinsed in deioniaed water. The presence of structures grown directly on the surface shows good adhesion to the substrate.

The study of the composition of zinc oxide structures deposited on the materials studied conducted with an X-ray microprobe showed that the crystallites are composed of only two elements: oxygen and zinc (***Figure 4***) or contain silver (***Figure 5***), when synthesis was performed in the presence of silver ions.

The analysis using High Resolution X-ray diffraction of the crystal structure of zinc oxide deposited on the surface of cotton and polyamide has shown that it is zinc oxide of the wurtzite structure type (***Figure 6***). The test results are consistent with the literature data presented in the work of Y. -N. Xu and W. Y. Ching [54].

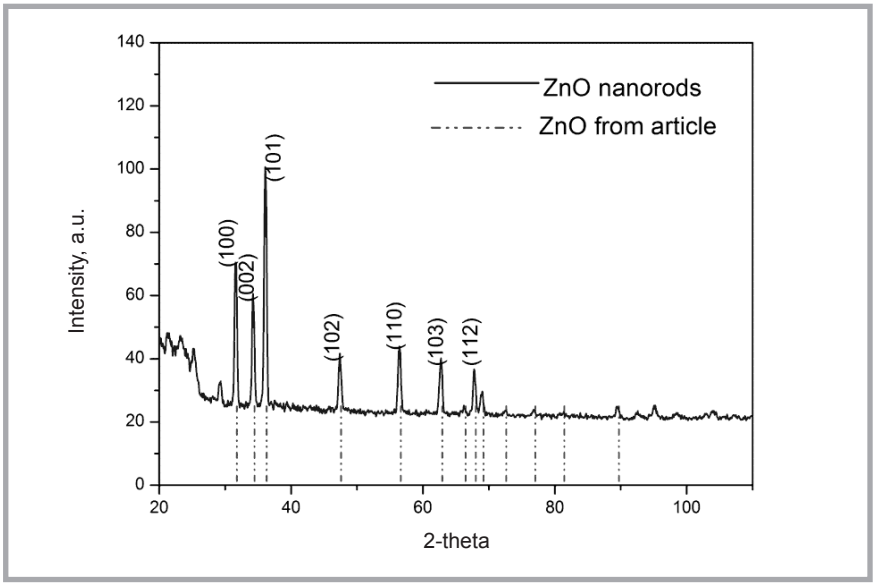

Figure 6. *X-ray diffraction pattern of ZnO structures synthesised on the surface of the cotton gauze.*

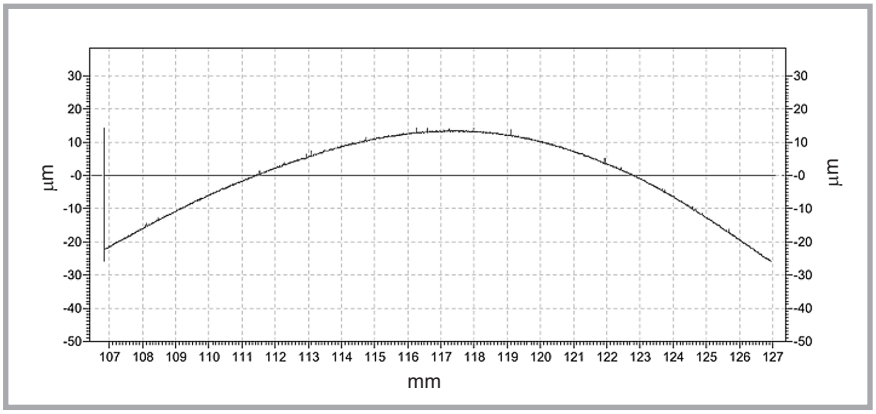

Figure 7. *Transverse surface profile of the central venous catheter determined using a mechanical profilometer.*

Table 1. *Results of the antibacterial activity of structures deposited on the surface of the gauze and polyamide fabric.* ***Note:*** *The table shows averaged results of measurements of three samples. Measurement error is estimated to be approximately 2 - 5%.*

Type of sample	% of bacteria killed	
	Escherichia coli	*Staphylococcus aureus*
Cotton gauze	0	0
Cotton gauze + ZnO	39	40
Cotton gauze + ZnO + Ag	33	64
Polyamide fabric	0	0
Polyamide fabric + ZnO	100	63
Polyamide fabric + ZnO+ Ag	100	75

Studies performed with two methods of testing the antibacterial activity of cotton gauze and polyamide fabric covered with nano- and microstructures of zinc oxide showed that it has good bactericidal activity in the case of both strains studied (***Table 1***).

In addition, the microbiological studies conducted showed that the bactericidal effect of the additive of silver nanostructures obtained depends on the type of bacteria. The silver additive caused a significant increase in bactericidal prop-

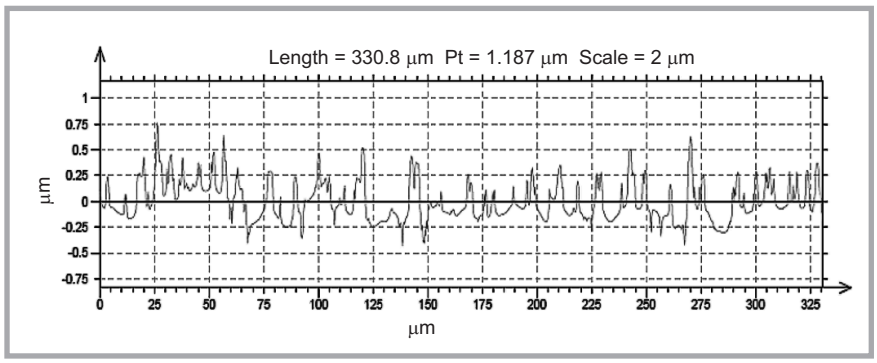

Figure 8. *Surface roughness of the central venous catheter determined using the optical profilometer after shape profile filtration.*

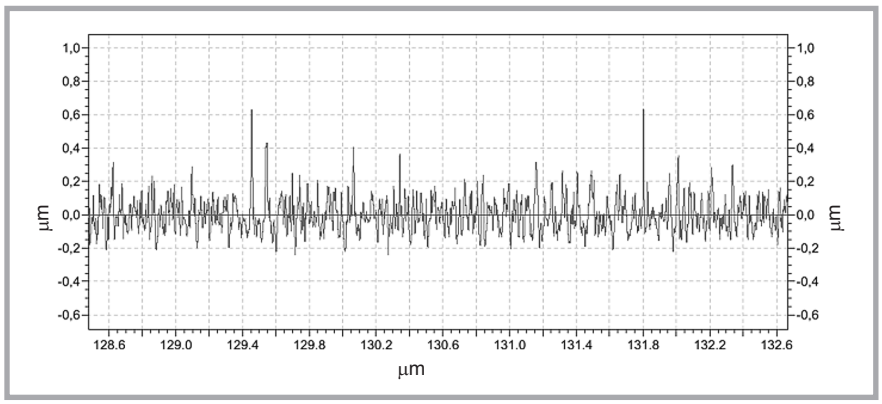

Figure 9. *Surface roughness of the central venous catheter determined using the mechanical profilometer after shape profile filtration.*

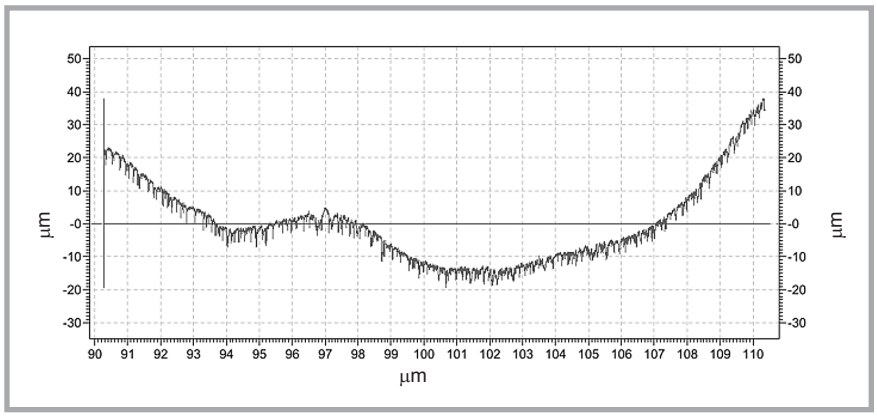

Figure 10. *Transverse surface profile of the urological catheter determined using a mechanical profilometer.*

erties against *S. aureus*, whereas with *E. coli*, the effect is hardly visible for cotton gauze. On the other hand great bactericidal properties against *E. coli* are shown by polyamide fabric covered with ZnO, in which the addition of silver was not needed.

The ruggedness test of both catheters was performed several times in order to obtain results of high reliability. It was noted that central venous catheters have a very smooth surface (***Figure 7***, see page 129 and ***Figures 8 - 9***). It was also found that the greatest surface smoothness deviation of the catheter was about 0.75 μm. Such a great smoothness of the central venous catheter hinders the formation of cell biofilm when used in medicine. The results of surface roughness tests conducted using optical and mechanical profilometers showed a high degree of conformity (***Figures 8 - 9***).

The surface roughness of urological catheters, in contrast to the surface of central venous catheters, is much greater (***Figures 10 - 11***). It was found that the maximum deviations from the surface smoothness of the catheters, determined both across and longitudinally (***Figure 11***), amounts to about 4 μm. Again the surface roughness results obtained with the use of optical and mechanical profilometers showed a high degree of conformity.

As work was conducted on the growth of zinc oxide structures of materials used in medicine from an aqueous solution, the surface wettability of these materials was rated. Measurement of the contact angle Θ_C is one of the parameters allowing to pre-determine the degree of adhesion of ZnO nanostructures formed on the substrate. The study investigating hydrophilic properties of the catheters showed that the biggest contact angle is observed for the surface of the central venous catheter, which is about 110° (***Figure 12.a,*** see page 24). The contact angle of the surface of urological catheters is much smaller, at around 70° (***Figure 12.b***).

The test results are in line with those expected, as Young's ***Equation 5*** describes the dependence of the angle formed by the „sitting drop" on the surface of a solid depending on the energy state of the interface:

$$\gamma_{LA} \cdot \cos\Theta = \gamma_{SA} - \gamma_{SL} \qquad (5)$$

where:

Θ - contact angle formed by a drop of liquid (L) on the surface of a solid (S),

γ_{LA} - surface tension between the liquid drop (L) and air (A),

γ_{SA} - surface tension between the surface of a solid (S) and air (A),

γ_{SL} - surface tension between the surface of a solid (S) and drop of liquid (L).

The surface tension between the liquid drop (L) and the air (A) and between the surface of a solid (S) and the air (A) does not depend on the development of the surface of the solid. The value of surface tension between the solid and the liquid depends on this parameter, increasing with an increasing degree of surface development. Consequently if the surface contact angle of the urological catheter is smaller, its surface is more hydrophilic.

Based on the above-mentioned research, the authors concluded that on the surface of the urological catheter, ZnO nanostructures will grow showing

good adhesion. Unfortunately despite positive results of the surface roughness and contact angle, the deposition process of one-dimensional structures of zinc oxide on the surface of both PTFE catheters occurred differently. On their surface singular hexagonal structures were not formed, whereas the surface of the central venous catheter was covered with very tightly packed zinc oxide nanostructures, but of weak adhesion (***Figure 13.a***).

On the other hand when a layer of zinc oxide was deposited on the surface of the urological catheter, it seemed to be composed of structures resembling flakes, which also showed poor adhesion (***Figure 13.b***).

The differences in the microstructure of the zinc oxide layers deposited on the surface of the catheters may be due to their chemical composition. Both catheters are commercially available and vary in colour. The central venous catheter is white, while the urological catheter is yellow, indicating that in addition to the base component, PTFE contains modifying substances which influenced the growth kinetics of the zinc oxide nanostructures. Because of the poor adhesion of zinc oxide nanostructures to the surface of both types of catheters, no assessment of the antibacterial activity of ZnO layers grown on the surface of these catheters was made. According to the authors, in order to improve the adhesion level of the layers of ZnO to the surface of catheters it is necessary to perform additional processes of modification, e.g. through activating the surface of the catheter in plasma.

Conclusions

A technology was developed for the direct deposition of zinc oxide micro- and nanostructures, both pure and doped with silver, on cotton gauze and polyamide fabric as well as on two types of catheters made of PTFE. Nanostructures were deposited by the chemical bath technique (CBD) directly onto the surface of the materials. The adhesion of ZnO nanostructures to the surface of the cotton gauze and polyamide fabric was very good. The nanostructures deposited on them did not become detached from the surface, even though the material was subjected to ultrasonic rinsing. A comprehensive study of the nanostructures which grew on the surface of the cotton gauze and polyamide fabric was conducted. Their microstructure, chemical composition and crystal structure were all examined along with the biological activity of the materials for use in medicine.

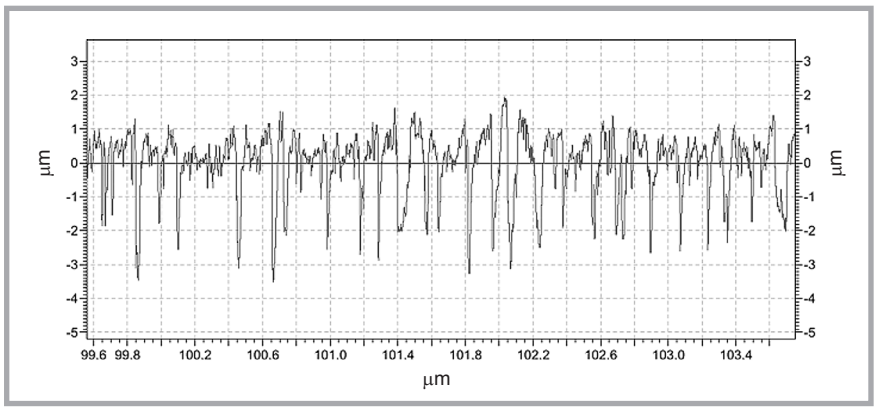

Figure 11. *Surface roughness along the urological catheter determined using a mechanical profilometer after shape profile filtration.*

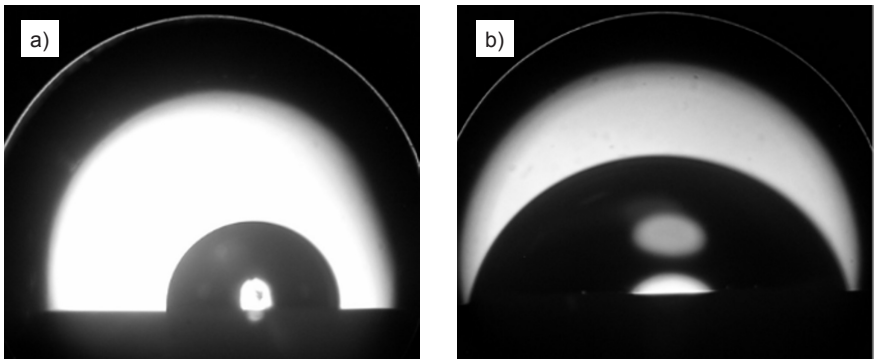

Figure 12. *Contact angle of the catheters: a) central venous, b) urological.*

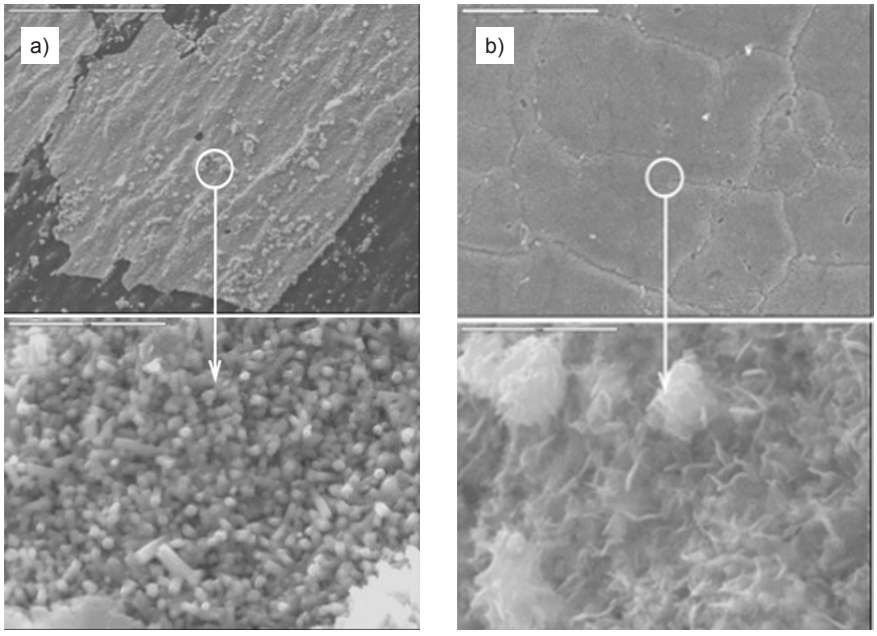

Figure 13. *Microstructure of the surface of the central venous (a) and urological (b) catheters coated with zinc oxide. Magnification: 500× and 10 000×.*

Also on the surface of the catheters, both the ones characterised by very good smoothness as well as those with a rougher structure, structures were deposited. However, their adhesion to the substrate was very weak, which resulted in ZnO dropping off the surface of catheters

already in the rinsing process. It seems that in order to improve the adhesion of zinc oxide nanostructures to the surface of catheters, their surface would need to be activated, e.g by plasma.

Microbiological studies on *E. coli* and *S. aureus* showed that the resulting structure of pure as well as doping with silver zinc oxide, with which the cotton gauze and polyamide fabric was covered, has good bactericidal properties. In the case of polyamide fabric covered only using ZnO significant antibacterial properties against *E. coli* were noticed. Authors believe that such modification of dressing materials can increase their effectiveness in the treatment process.

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