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Cotton Textile Surface Investigation Before and After Deposition of the ZnO Coating by Sol-gel Method

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In the present research the commercial type of cotton textiles were modified by the sol-gel method to evaluate sol-gel technology suitability for cotton textiles. The nanosol was deposited on the cotton textile by dipping process; as well evaluation of the dipping process for thin zinc oxide coating deposition was made. The analysis of the coated textile surface was carried out by Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM) and energy dispersive X-ray (EDX) spectroscopy. Data received by SEM and EDX analyses evince that the deposited coatings are evenly distributed, not only on surface of yarns but in the depth of textile material as well and are resistant to the exploitation impact (laundry test). AFM analyse evince that the deposited zinc oxide coating constituted by spherical or ellipsoidal particles with 30-nm average diameter, assembled in larger clusters.

Keywords: Sol-gel, Zinc oxide, Thin films, Cotton textile, Nanosol, Surface modification.

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1. INTRODUCTION

Since the appearance of the hole in the ozone layer and due to continuous decrease in the thickness of the ozone layer the ultraviolet (UV) intensity of solar radiation has increased. Nowadays the protection against skin cancer caused by UV radiation is of growing importance [1-3].

The ultraviolet radiation (UVR) is composed of three types: UV-A (320-400 nm), UV-B (290-320 nm), and UV-C (100-290 nm). The UV-C radiation is absorbed by the ozone layer, however, the UV-A and UV-B reach the earth surface and cause serious health problems such as skin cancer, sunburn, and photo-aging [1, 3-9]. The UV-B radiation penetrates the upper skin layers (epidermis) while the UV-A radiation also reaches the deeper areas also (dermis) [1, 3, 4, 6, 10].

Therefore, special attention has been focused recently on the UV transmission of textile because of the growing demand in the marketplace for light-weight apparel that offers protection from UVR, while fostering comfort [3, 11]. When direct light shines onto a textile, a part of the radiation is reflected. The material will absorb a certain amount but the remainder can reach the skin [3, 4].

The absorption spectra of semiconductor such as zinc oxide show strong absorption in the UV region of the light spectrum but only very slight or no absorption of visible light [2, 3, 12, 13]. In comparison with the organic absorbers conventionally used in the textile industry, inorganic materials show no significant degradation and are therefore extremely stable and the oxides are classified as non-toxic materials [2, 3, 10-15]. Zinc oxide is harmless, that is why it is used in cosmetics such as suncreams. For the above-mentioned reasons, zinc oxide seems to be ideal for the preparation of highly UV-absorbing, nanosol based coatings [2, 3].

In addition to above mentioned textile materials have intrinsic properties that make them extremely valuable – they are flexible, light weight, strong, soft, etc. Because of this, they are excellent objects for imparting additional functionalities.

The present paper describes the deposition of zinc oxide thin-coatings by the sol-gel method on cotton textile substrates.

2. MATERIALS AND METHODS

2.1 Sol-gel Method

The sol-gel dip process is almost exclusively applied for the fabrication of transparent layers, primarily for the deposition of oxide films on float glass as a transparent substrate with a high degree of planarity and surface quality [16].

This method is based on the preparation of colloidal suspensions-nanosols – from appropriately selected precursors, mostly metal oxides or organometallic compounds such as metal or semimetal silicon-containing alkoxides. These compounds, which are subjected to hydrolysis in an acidic medium, are converted into corresponding hydroxides that are unstable and susceptible to further condensation processes. Nanosols prepared in this way are deposited on fibres / fabrics and dried at an elevated temperature to condense them into cross-linked lyogels containing a considerable content of liquid phase. During further drying, the liquid phase is removed and a porous layer (xerogel) is formed on the fibre surface [2, 17].

One of the advantages of this method is the possibility of preparing thin layers on various materials, as well as the sol-gel layers can cover all fibres with enough high adhesion [18]. Major advantage is the high degree of obtained uniformity; another advantage is the

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unlimited size of the substrates that can be coated [16]. The thickness of the coatings applied to the fiber surface is mainly in the range of several nanometers to micrometers, besides the flexibility of a coating is directly related to its thickness [2]. Thus the use of sol-gel coating for the preparation of protective coatings seems to be appropriate.

2.2 Materials

In the present study sol-gel method was evaluated in terms of the deposition of zinc oxide thin films on the commercial cotton textile substrate. During the experiment woven 100 % plain weave commercial cotton fabric with surface density 50.91 g/m^2 from yarns of linear density 8.4 Tex, the thickness of the fabric 0.21 mm (the measurement was taken by the textile fabric thickness tester "TH-25") was subjected to coating by sol-gel method.

Cotton is a cellulosic fibre with a high ratio of hydroxyl groups that make it hydrophilic and that is available for polar interaction or potential surface reactions. In addition cotton is unique in features such as its biodegradability, water absorbency, comfort and thermostatic capacity [19].

2.3 Textile Surface Preparation

In order to provide good interfacial contact between the fibre surface and the deposited zinc oxide coating and to remove dust, organic matter and oils used in the textile production from the textile surface, cotton textile samples were washed at temperature 90 °C with detergent without any optical brighteners.

2.4 Nanosol Preparation and Textile Coating Process

Tetraethoxysilane (TEOS, $C_8H_{20}O_4Si$), alcohol (C_2H_5OH), hydrofluoric acid (HF), deionized water and Zn $(CH_3COO)_2 \cdot 2H_2O$ have been used for nanosols preparation.

Nanosols were prepared by a controlled hydrolysis, by adding ethyl alcohol slowly into TEOS with continuous stirring, after adding deionized water and hydrofluoric acid, stirred for 30 minutes, after mixed with the zinc acetate with continuous stirring 10 minutes.

The process was performed at room temperature. The obtained nanosols were clear and homogeneous.

Raw and commercial fabric samples were prepared with TEOS concentration 2% and zinc acetate concentration 2.5 % to evaluate the coating quality.

The fabric samples were dipped into the prepared nanosol, immersed for 10, 20 and 30 minutes at room temperature. Subsequently, the samples were dried at 50 °C for 10 minutes and after cured in an oven at 120 °C for 5 minutes.

2.5 Testing the Resistance of the Coated Samples to Laundering

For evaluation of the exploitation impact on the zinc oxide coating laundry test was carried out, the samples from all groups were washed at temperature 40 °C with detergent without optical brighteners. Drying was carried out on a horizontal surface.

2.6 SEM and EDX Analysis of the Coated Samples

The morphological changes of the natural textile as a result of coating with zinc oxide and after its washing have been investigated using scanning electron microscope SEM (Tescan, Mira//LMU Schottky).

EDX spectroscopy was used for the analysis of the elemental composition of the coated textile samples before and after laundry test.

2.7 AFM Analysis

Surface treatments of textile fibers, yarns or fabrics play an important role in their processing and end-use. The AFM seems a very valuable tool for investigating the effect of different fiber surface treatments and their impact on the final textile material properties.

The AFM uses a sharp probe which has a nanosize tip mounted on a flexible cantilever to lightly scan across a specimen surface at the end of the cantilever [20]. The microscope operates by measuring attractive or repulsive forces between the tip and specimen, where the forces cause the tip to deflect [20]. This deflection can be recorded using a laser focused on the top of the cantilever and reflected on to photodetectors [20]. The photodetector signals are used to map the surface characteristics of specimens with resolutions down to nanoscales [20].

The AFM measurements were carried out with a commercial instrument (Solver-PPO).

3. RESULSTS AND DISCUSSION

3.1 SEM Micrographs Analysis

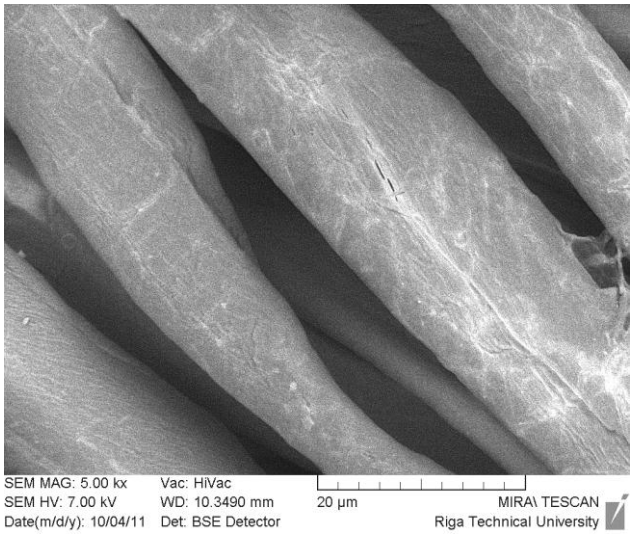
Fig. 1 (a, b, c) illustrates micrographs of the coated fabric samples depending on the time of dipping in nanosol 10, 20 and 30 minutes.

On the surfaces of the samples dipped in nanosol for 20 and 30 minutes (Fig. 1b, c) were formed agglomerated particles and bridges between fibres.

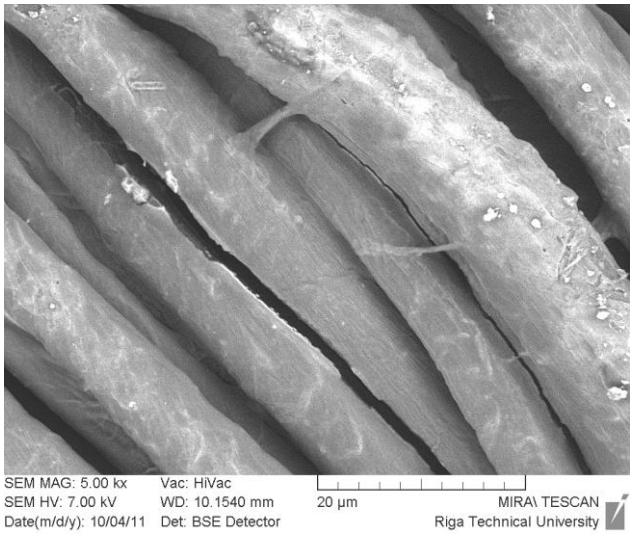
The formation of small bridges can be tolerated to a certain extent – these will break during use, leaving small fins (Fig. 1b). Large bridges (Fig. 1c) may cause problems, since during stress an exfoliation of the coating material can be observed, leaving the bare fiber surface. Such defects are critical for barrier coatings that are applied to protect fiber material in aggressive atmospheres [2].

After reducing of the dipping time till 10 minutes qualitative, distributed evenly, not only on surface of yarns but in the depth of textile material as well, zinc oxide coating was received (Fig. 1a and Fig.2a, b).

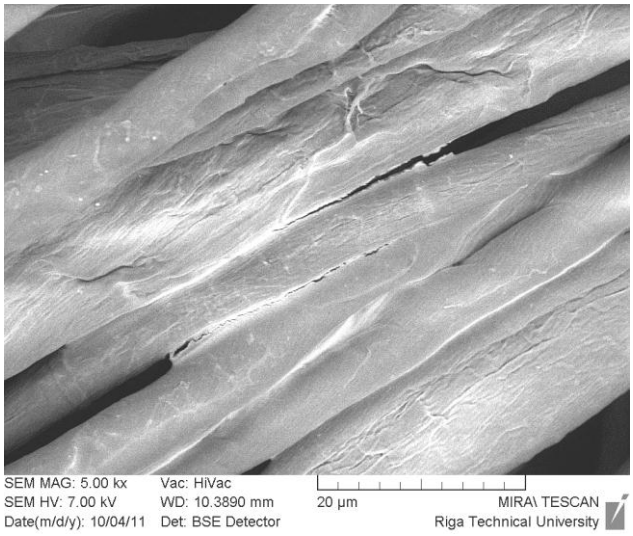
From the micrographs observations, follows that zinc oxide nanosols can be deposited on cotton textiles in the form of thin elastic coating, which completely and uniformly cover the fibres surfaces, as it is clearly seen in the SEM image (Fig. 2).



a



b



c

Fig. 1 – SEM micrographs of the coated textile samples, dipping time 10 min (a); 20 min (b); 30 min (c)

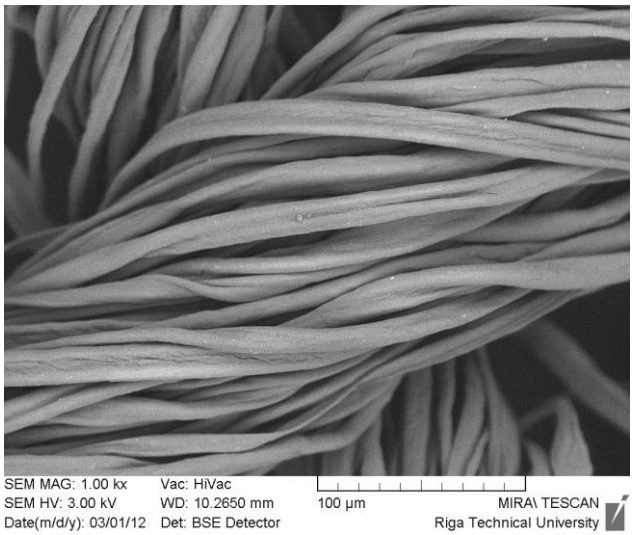


Fig. 2 – SEM micrographs of the coated textile samples, dipping time 10 minutes

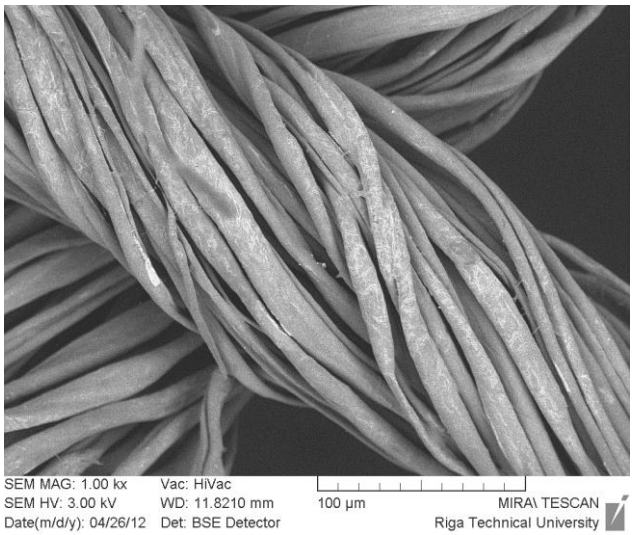


Fig. 3 – SEM micrographs of the coated textile samples after laundry test

SEM micrograph Fig. 3 reveals that received zinc oxide thin-coatings are resistant to exploitation impact (laundry test) the coatings on the cotton samples still are distributed evenly on the fibres surface and without significant defects.

3.2 EDX analysis

EDX analysis was used for the analysis of the elemental compositions of samples after the samples coating. From EDX analysis of the samples coated with nanosol are visible that the main elements of the surface species of treated cotton textile samples are C, Zn, O, F and Si (Fig. 4).

The EDX analysis (Tab. 1) of the coated samples after laundry test evince that the percentage weight of zinc on the surface of the samples coated by nanosol with dipping time 10 minutes remained almost the same like in previous laundry test.

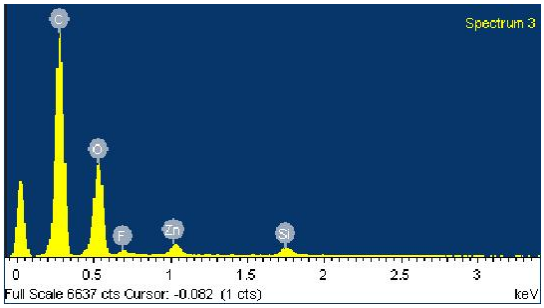


Fig. 4 – EDX spectrum after sol-gel treatment

Table 1 – EDX analysis – elemental weight in %

Samples	C	O	F	Si	Zn
Uncoated	46.67	53.31	-	-	-
Coated samples, dipping time 10 min	62.62	29.96	2.81	1.26	3.35
Coated samples (dipping time 10 min) after laundry test	43.83	46.10	0.06	6.71	3.30

3.3 AFM Analysis

Fig. 5 and 6 illustrate topography of the non-coated and coated fabric samples. Samples from polyamide before and after coating were prepared for investigation of the textile samples fibre surface topography changes by AFM because the natural thread consists of thin fibers that interfere with natural textile surface investigation by AFM.

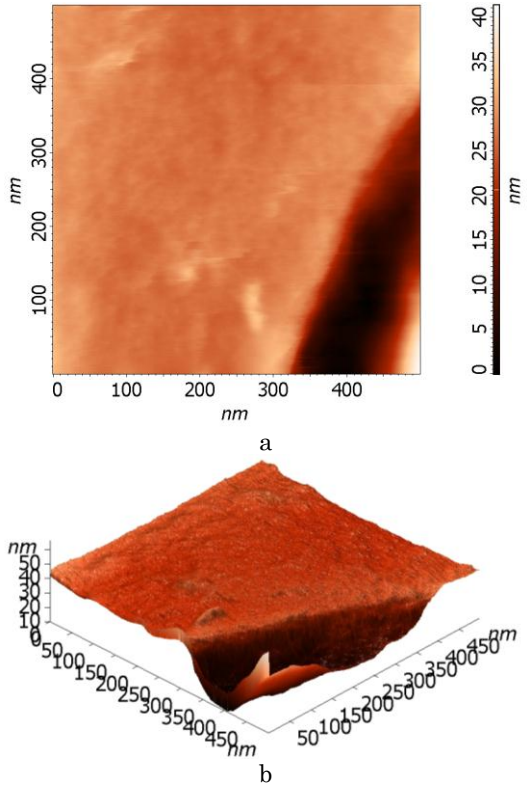


Fig. 5 – AFM topography of the non-coated textile samples (a) and 3D image (b)

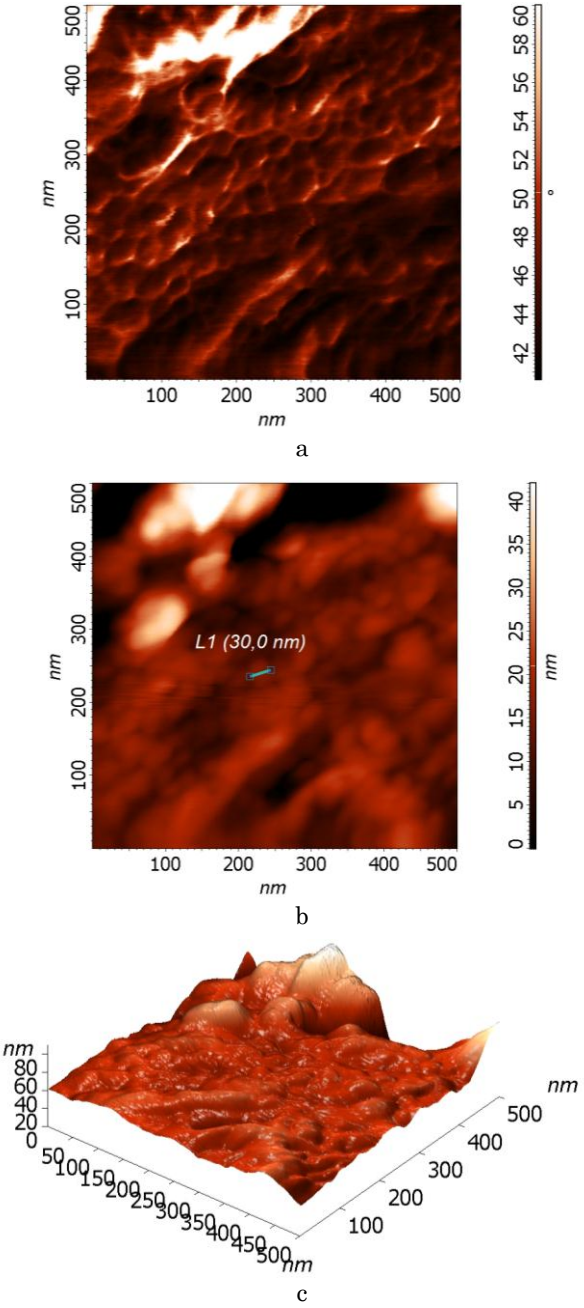


Fig. 6 – AFM topography of the coated textile samples zinc acetate concentration 2,5 %, dipping time 10 minutes (a), (b) and 3D image (c)

Fig. 5 illustrates image of non-coated textile thread surface, the textile thread surface without coating shows relatively flat surface with some microdefects.

Fig. 6a and 6b illustrate images of the deposited zinc oxide coating constituted by spherical or ellipsoidal particles with 30-nm average diameter, assembled in larger clusters. AFM image also reveals that the nanoparticles are more or less evenly distributed; there are even obvious aggregations in the image.

Table 3 represents the textiles thread surface roughness changes after the coating deposition, from Table 3 data can be seen that roughness increased after the deposition of zinc oxide coating.

Table 3 – AFM analysis – the textile sample surface roughness before and after coating

	Non-coated	Coated
Max	56,49	90,67
Min	0	0
Ten point height	28,02	45,43
Average	27,29	44,08
Average Roughness	4,39	5,62
Entropy	7,93	9,22

4. CONCLUSIONS

The zinc oxide coatings were deposited on the textile surface by sol-gel method without deterioration of textile intrinsic properties, such as flexibility and softness etc. SEM micrographs and AFM images evince that the zinc oxide coating is not a flat film on the cotton textile surface, but coating constituted by spherical or ellipsoidal particles with 30-nm average diameter, attempted in larger clusters, as well deposited on fibres without changing the textile surface structure and trim. AFM is powerful technique for not only detecting nanoscale surface changes, but also for providing quantitative information.

Based on the SEM, AFM and EDX analyses it is concluded that with concentration of the TEOS 2 % in the nanosol and dipping time 10 minutes, the received textile coating:

– is distributed evenly, not only on surface of yarns but in the depth of textile material as well;

– is resistant to exploitation process (laundry test), after process it is still without significant defects, besides the elemental percentage weight of the samples has not changed.

The sol-gel method has to be adapted for the treatment of textiles because of textile low heat resistance; a thermal post-treatment at higher temperatures should be avoided to reduce degradation and deformation of the textile materials, and has to be adapted with regard to the type of textile coated and to the applied nanosol. Experiment results show that a moderate thermal post-treatment at 120 °C after the nanosol applied to the cotton textile is appropriate for the cotton textile samples coated by sol-gel method.

The sol-gel method for nanosol preparation used in this research to implement zinc oxide coating on the cotton fabric surface is a simple process that can be easily transferred to the textile industry. Nanosol can be also applied by conventional coatings techniques used in the textile industry – the application can be implemented by simple dipping process.

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