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Dipping Time Influence on the UV Properties of Natural Textiles Treated via Sol-gel Method

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In this study lightweight 100 % cotton fabric was successfully modified by the sol-gel method to impart high ultraviolet radiation (UVR) blocking property to the fabric surface. The cotton fabric was dipped in the nanosol solution for 1, 5 and 10 minutes, dried at 90 ºC for 10 minutes with thermal post-treatment at 120 ºC for 2 minutes. Comparison of coatings of samples prepared using different dipping time was made. The durability of the treatment was investigated by performing repeated home laundering. Excellent durability of the treatment was obtained, which indicates about good adhesion between the coating and the fabric surface. Before and after laundering tests ultraviolet protective properties of the textile samples were determined according to the standard, results of samples with dipping time 10 minutes show that textiles after treatment with nanosol have excellent ultraviolet protection properties, as well after laundering tests (50 washing-drying cycles) still provide excellent ultraviolet protection.

Keywords: Cotton, Textile, Sol-gel method, Ultraviolet protection, Zinc oxide.

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1. INTRODUCTION

Natural fibres have been used throughout the ages to handcraft materials essential for human life and there is long history of modifying their properties to enhance their utility, durability and aesthetic appeal [1]. Nowadays, an advance in the knowledge of the fine structure and chemical composition of natural fibres has stimulated research and development into methods of improving their chemical and physical properties [1]. Natural fibres cannot be replaced by synthetic fibers due to their intrinsic biodegradable and wear comfort properties [1]. Among the most important advantages of natural fibers are: air permeability, hygroscopicity, no emission of harmful substances, no allergenic effect (except wool), no electrostatic charge accumulation (except wool), biodegradability, renewability, in some cases medicinal biocide properties. Cotton, wool, flax and silk are the main natural fibers in the clothing industry; cotton holds the main share approximately 80 % [1]. Application of natural fibres for advanced functional clothing allows to obtain green, safe and healthy products, environmentally and human friendly, that is products oriented towards specific consumer needs and requirements, such as UV protection, comfort, health, well-being and safety [2].

Since the appearance of the hole in the ozone layer and due to continuous decrease in the thickness of the ozone layer the ultraviolet intensity of solar radiation has increased. Nowadays the protection against skin cancer caused by UV radiation is of growing importance [3-5]. 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 [5-9]. 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 [5, 10].

There are both organic and inorganic UV blockers. The organic blockers are also known as UV absorbers as they absorb the UV rays, whereas the inorganic blockers such as TiO_2, ZnO etc. efficiently scatter both UVA and UVB [11]. Compared with organic UV absorbers, inorganic blockers are now preferred due to their properties such as non-toxicity, chemical stability under UV radiation, etc [11]. For the abovementioned reasons, zinc oxide seems to be ideal for the preparation of highly UV-protective, nanosol based coatings.

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 [12].

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 [13]. 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 [13, 14]. Nanosols prepared in this way are deposited on fibres / fabrics and dried at an low temperature to condense them into cross-linked lyogels containing a considerable content of liquid phase [13]. During further drying, the liquid phase is removed and a porous layer (xerogel) is formed on the fibre surface [13].

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 [13, 15]. Major advantage is the high degree of uniformity obtained; also advantage is the size of the substrates that can be coated the size is not limited [13]. 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 [13]. Thus the use of sol-gel coating for the preparation of protective coatings on the textile surface 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 for imparting the UV protective properties. During the experiment woven 100 % plain weave commercial cotton fabric 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 are 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. Tetraethoxysilane (TEOS, $C_8H_{20}O_4Si$), ethanol (C_2H_5OH), hydrofluoric acid (HF), deionized water and zinc acetate $Zn(CH_3COO)2{\cdot}2H_2O$ have been used for nanosols preparation. All chemical reagents were used as received.

2.3 Nanosol Preparation and Textile Coating Process

Nanosols were prepared by a controlled hydrolysis, by adding ethanol slowly into TEOS with continuous stirring at 50 °C temperature, after adding deionized water with hydrofluoric acid, stirred for 30 minutes, after mixed with the zinc acetate with continuous stirring 10 minutes at 50 °C temperature.

Samples were prepared with zinc acetate concentration 5 %. The fabric samples were dipped into the prepared nanosol, immersed for 1, 5 and 10 minutes at room temperature. Subsequently, the samples were dried at 90 ºC for 10 minutes with thermal postreatment 120 ºC for 2 minutes.

2.4 Testing the Resistance of the Coated Samples to Laundering

The treated fabric samples were subjected to home laundering up to 50 cycles. Standard detergent (washing agent 5 g/l) without optical brighteners was used throughout the laundering cycles.

2.5 UV Protection Measurements

The UV protection factor (UPF) was measured using the Varian Cary50 Solascreen (Australia) according to the Australian / New Zealand Standard AS / NZS 4399 : 1996 [16]. UPF is the scientific term used to indicate the amount of ultraviolet (UV) protection provided to skin by fabric [7, 8]. The UV transmission measurements were performed according to EN 13758-1 : 2001 + A1 : 2006 [17]. From each sample group 4 samples were scanned for UV transmission protection (one scan totally consist of 6 measurements, 3 measurements from each of 2 different points of the sample surface) according standard for each sample two measurements are made from the machine direction and two from the cross machine direction [17].

2.6 Scanning Electron Microscopy (SEM)

Morphological changes as a result of sol-gel treatment of cotton fabric were investigated using scanning electron microscopy (SEM) Hitachi S-3400N (Japan).

3. RESULTS AND DISCUSSION

Graph in Fig. 1 indicates that dipping time has influence on the calculated UV protection factor: UPF of samples with the dipping time for 1 minute vary in range 37-47 (UPF rating 35-45), with the dipping time 5 minutes vary in range 40-48 (UPF rating 40-45) and with dipping time 10 minutes vary in range 52-65 (UPF rating 50+). That indicates that the best results – excellent UV protection properties of cotton fabric samples were obtained with the dipping time 10 minutes.

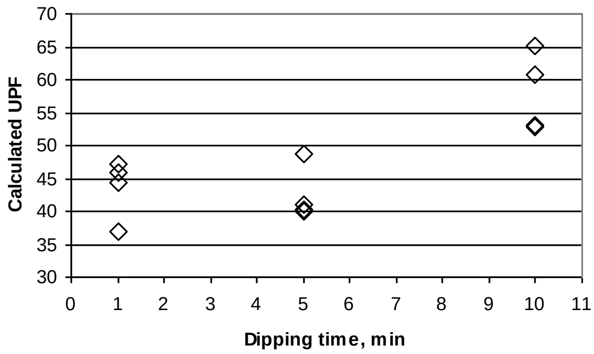

Fig. 1 – Calculated UPF of samples with 1, 5 and 10 minutes dipping time

The UPF of cotton textile coated with zinc oxide nanosol at dipping time 10 minutes increased by approximately 2,7 times to compare with UPF values of uncoated textile (Tab. 1) and offer excellent protection as UPF range corresponds to the standards rating "50 + UPF" (Table 1).

Moreover, it also means meeting the present day quality requirements for textiles in terms of personal safety UPF rating 50 + and the ability to withstand 50 washing-drying cycles without changing textile properties and defense capabilities.

The durability of the treatment to repeated home laundering was evaluated by performing 50 washing-drying cycles. There is unexpected increase of the calculated UPF after laundering cycles: the calculated UPF value increase after first washing cycle approximately by 3 times and after 50 washing cycles it is remain higher approximately by 1.3 times than calculated UPF of just coated samples (Table 1). The uncoated samples don't show the considerable increasing of the UPF after the washing. After first washing UPF rating of uncoated samples is in range from 20-25 UPF (before laundering 20 UPF), after 3, 5, 10 and 20 laundry fall in range 15-20 UPF after 50 washings in range 20-25 UPF. Washing increases the UPF of uncoated fabric because of shrinkage.

Samples prepared with dipping time 10 minutes after

Table 1 – Laundering effect un the UV protection properties of the samples with dipping time 10 minutes

Samples	Calculated UPF	UVA transmission, %	UVB transmission, %	UVR rating
Non-coated	19.929	3.875	4.059	15 / 20
Coated	59.347	1.318	1.162	50+
1 washing	179.678	0.334	0.260	50+
3 washing	74.139	1.502	1.162	50+
5 washing	64.812	1.431	1.291	50+
10 washing	61.747	1.373	1.367	50+
20 washing	66.149	1.352	1.278	50+
50 washing	75.680	1.698	1.081	50+

1, 3, 5, 10, 20 and 50 washing-drying cycles have UPF rating 50+ (Excellent protection) (Table1). The unexpected increase of the UPF during laundering is an interesting phenomenon and further studies are necessary to indicate the effect of water and detergent on the structure of formed coating on the cotton fabric surface, the same increasing of UPF after the laundering is mentioned in other authors works [5]. Polymerization of silicon alkoxide can lead to the complex branching of polymer, because a fully hydrolyzed monomer $Si(OH)_4$ can branch or bond in four different directions. Alternatively, under certain conditions such as low water concentration, for example, fewer than four of the – OH groups will be capable of condensation, so relatively little branching will occur. As the mechanisms of hydrolysis and condensation, and the factors that influence the structure toward linear or branched structures are the most critical issues of sol-gel processes, during the first washing branching of the left silicon polymer groups seems still in process due to environment rich in water and further Si replacements occur. As a result UPF of fabric increases.

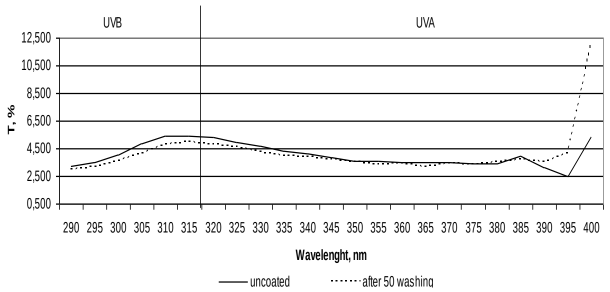

Fig. 2 – UVA and UVB transmission of uncoated sample

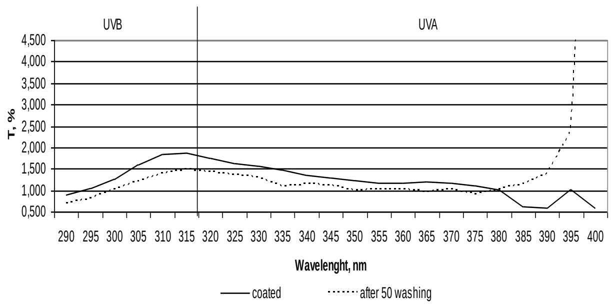

Fig. 3 – UVA and UVB transmission of sample with dipping time 10 minutes

The durability and stability of the treatment to multiple home laundering indicates about good adhesion between the coating and the fabric surface, as well treatment imparted excellent UVR protection to the cotton textile in both regions of UVR – UVA and UVB (Fig. 2 and Fig. 3)

3.1 Scanning Electron Microscopy

Morphological changes as a result of sol-gel treatment of cotton fabric were investigated using scanning electron microscopy (SEM) Hitachi S-3400N (Japan). Figures 4 and 5 show the morphological changes induced by the different dipping time of textile samples. Figures 4 and 5 indicate that the cotton samples treated by nanosol have sufficiently even coating without visible defects. SEM micrograph Figure 4 illustrate the treated cotton fabric, on fibres can notice the presence of silica particles that was proofed by EDX analysis of treated samples in previous experiment [5,12]. SEM micrograph Figure 5 indicates that after 50 washing-drying cycles received coating became thicker, as well increased the roughness of coating, it can explained the increasing of UPF after washing-drying cycles.

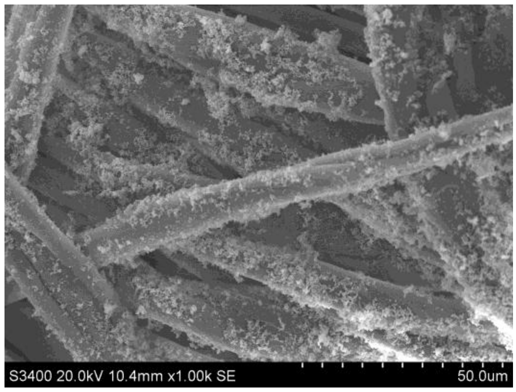

Fig. 4 – SEM micrograph of treated cotton fabric

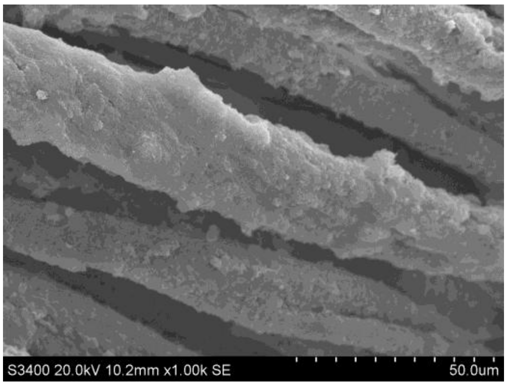

Fig. 5 – SEM micrograph of cotton fabric after 50 washing-drying cycles

4. CONCLUSIONS

Lightweight cotton fabric surface was successfully modified with zinc based nanosol. The UPF increases with the dipping time increase in range from 1 minute (UPF rating 35-45 UPF) to 5 minutes (UPF rating 40-45 UPF) and highest UVR protection factor values were obtained with dipping time 10 minutes (UPF rating 50+ UPF).

Spectrophotometer analyses show that with the zinc acetate concentration 5 % in the nanosol and dipping time 10 minutes, the deposited coating on textile is distributed evenly and is resistant to exploitation process (laundry test) as after multiple washing processes the UPF rating remain 50+ (Excellent protection). If compared to the standards, it is an excellent protection towards UV radiation. Moreover, it also means meeting the present day quality requirements for textiles in terms of personal safety and the ability to withstand 50 washing-drying cycles without changing textile properties and protection capabilities.

Unexpected increase of the calculated UPF during laundering cycles is established: the calculated UPF value increase after first washing cycle approximately by 3 times and after 50 washing cycles it remains superior by approximately 1.3 times compare to the UPF of just coated samples. At the same time the tests of uncoated samples doesn't show the considerable increase of UPF values after washing.

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REFERENCES

1. *Handbook of Natural Fibres* (Ed. M. Kozlowski) (London: Woodhead Publishing Limited: 2012).
2. M. Zimniewska, J. Batog, E. Bogacz, B Romanowska, *J. Fiber Bioeng. Informatics* **5**, 321 (2012).
3. B. Mahlting, T. Textor, *Nanosols and Textiles* (Singapore: World Scientific Publishing: 2008).
4. *Surface Modification of Textiles* (Ed. Q. Wei) (London: CRC Press: 2009)
5. S. Vihodceva, S. Kukle, *J. Riga Tech. Un. Mat. Sci. Clothing Tech.* **6**, 19 (2011).
6. A. Farouk, T. Textor, E. Shollmewer, A. Tarbuk, A.M. Grancacic, *AUTEX Rsrch. J.* **10**, 58 (2010).
7. N. Abidi, E. Hequet, S. Tarimala, *J. Appl. Polym. And Sci.* **104**, 111 (2007).
8. M. Akgun, *Pr. Of the Int. Scien. Conf. UNITECH* 301 (2010).
9. S.M. Salah, *Affrican J. of Agricalt. Rsrch.* **6**, 4746 (2011).
10. S. Kathirvelu, L.D. Souza, B. Dhurai, *J. Riga Technol. Un. Mat. Sci. Clothing Tech.* **34**, 267 (2009).
11. R. Paul, et al., *Textile Rsrch. J.* **80**, 454 (2009).
12. S. Vihodceva, S. Kukle, *J. Riga Technol. Un. Mat. Sci. Clothing Tech.* **7**, 69 (2012).
13. T. Mikolajczyk, *Fibers Textiles in East. Europe* **18**, 39 (2010).
14. J. Alongi, M. Ciobanu, G. Malucelli, *Carbohydrate Polym.* **87**, 2093 (2012).
15. A. Chladova, et al., *Pr. Of the 7th Int. Conf. TEXSCI* (2010).
16. *Australian / New Zealand Standard*, AS / NZS 4399 : 1996 (1996).
17. *European Standard*, EN 13758-1 : 2001 + A1 : 2006 (2006).