50 *Egypt. J. Chem.* **59**, No. 5, pp. 819-831 (2016)

$ZnTiO_3$ Nanoparticles as Novel Multifunctional Finishing of Cotton Fabric

A. Farouk, S. Sharaf and A. Shalaby[*]
Textile Division, Textile Chemistry and Technology, Department of Preparation and Finishing of Cellulosic Fibers, National Research Centre,Scopus affiliation ID 60014618, 33 EL Bohouth st., Dokki,P.O. Box 12622,Giza, and [*]*Science and Technology Center of Excellence, Egypt.*

MULTIFUNCTIONAL textiles, a topic which is important from scientific and economic point of view will be the new direction for development of fabrics and clothing. Finishing of textiles with nanoparticles is a novel rout for creation of unique functions.It is well known that ZnO and TiO_2 possess UV-protection, antibacterial and photocatalytic properties, but there is no enough information concerning the similar behavior of $ZnTiO_3$. This provokes the interest to synthesize that compound and to examine its UV-protection and antibacterial properties in addition to its photocatalytic activity. In this study the synthesis and use of hybrid polymers loaded with $ZnTiO_3$ nanoparticles were presented. Hybrid polymerused here are based on 3-glycidyloxypropyltrimethoxysilane (GPTMS). $ZnTiO_3$ nanoparticles was used to impart cotton based fabric UV-protection, antibacterial and self-cleaning properties. The viability of the novel finishing as UV-protection will be dictatedby UV-Vis spectroscopy and byassessment of the ultraviolet protection factor (UPF). The antibacterial activity of these sol-gel derived hybrid materials will be researched against Gram-negative bacterium *Escherichia coli* DSMZ 498 and Gram-positive *Micrococcus lutues* ATCC 9341. Photocatalytic degradation (decolorization) of methylene blue (MB) in both $ZnTiO_3$ nanoparticles sol-gel solution /or on the coated fabrics was evaluated. The impact of this finishing technique on other fabric properties, *e.g.* air permeability, whiteness,and stiffness will be investigated.

Keywords: Zinctitanate, Multifunctional finishing, UV protection, Antibacterial , Sol-gel coating , Textiles , Hybrid polymers.

Zinc titanates have been explored for applications in numerous fields, for example, paint shade, gas sensor and reactant sorbent lately [(1-3)]. The ZnO– TiO_2 system still attracts the attention of researcher’ s importance in practical application [(4-6)]. It is well known that ZnO and TiO_2 possess UV protection and antibacterial properties [(6)], but there is no enough information concerning the similar behavior of $ZnTiO_3$. This provokes our interest to synthesize that compound and to evaluate its antibacterial and UV protection properties. Zinc titanate ceramics draws in the consideration of specialists because of their different applications as paint colors, sorbents, microwave dielectrics and catalysts (7) . There are several methods for preparing $ZnTiO_3$ nanoparticles, generally focused on conventional solid state reactions,mechanochemical initiation, precipitation and a few variations of the sol-gel method. Amid the late years, the sol-gel strategy has been viewed as a worthwhile one for the combination of nano powders with high virtue, ultra homogeneity, diminishment of the sintering temperaturev(8,9). That is the reason it was chosen keeping in mind the end goal to evade the $ZnTiO_3$ decay at high temperatures.

Researchers found that ZnTiO3 has photocatalytic and antibacterial properties (10-12) . Many researchers proved that $ZnTiO_3$ is stable from room temperature to 945º C, since this temperature is the temperature at which it can separate into $ZnTiO_4$ and Tio_2 (13).

The point of the present paper is to prepare $ZnTiO_3$ nanopowders by the sol-gel strategy. The study depends on trials utilizing Zn-acetate and $Ti(OEt)_4$ as principle precursors.

Experimental

Materials

The coating experiments were carried out using fabrics made of pure cotton (100%), mass per unit area 250 g/m^2 was supplied by Misr Company for Spinning and Weaving, Mehalla El Kobra, Egypt.

Chemicals

Zinc acetate dehydrate [Zn $(CH_3COO)_2.2H_2O$], citric acid monohydrate [$C_6H_8O_7.H_2O$] from Merck andtitanium ethoxide[Ti $(OCH_2CH_3)_4$]from Fluka AG were used. 3-Glycidyloxypropyltrimethoxysilane (GPTMS, 98%) was obtained from ABCR. Further chemicals used wereethanol[C_2H_5OH], ethylene glycol[$C_2H_6O_2$], methylene blue (MB), and hydrochloric acidHClfrom Merck.

Preparation process

The sol-gel method was employed to prepare TiO_2, ZnO and $ZnTiO_3$ at room temperature by using different chemical reagents and special equipment. Zinc acetate (ZnAc) and titanium ethoxideas starting materials were used. The precursors were dissolved in ethanol at room temperature under vigorous stirring to guarantee the occurrence of hydrolysis processes. The citric acid, ethylene glycol and hydrochloric acid were added. By drying at 110 $^{\circ}$C for 5 hr, a white xerogel was obtained. Subsequently, the obtained xerogel was subject to evaporation, drying and calcination at 400, 500 and 550°C for 1 hr respectively using globar-heated electrical furnace.

Preparation of GPTMS sols

10 ml GPTMS are dissolved in 100 ml solvent before hydrolysation using 0.01M hydrochloric acid. The resulting sol is stirred for at least 3hr to form the basis sol.

Preparation of the hybrid polymer

Before finishing of textiles the zinc titanate dispersion and the GPTMS sol were mixed in different ratios finally 1-methylimidazol (0.5 ml/10 ml GPTMS) was added as a catalyst for the cross-linking reaction of the epoxy group of the GPTMS.

Coating process

The hybrid polymer sol was applied to the fabrics by a pad-cure-method. The coating was carried out by a padding process with laboratory padder to a wet pick up of 100%. After padding samples were dried in a labcoater (Mathis, Switzerland) at 130 °C for 30 min before it was washed to remove residual by-products.

Tests and analysis

UV protection factor

UV– vis spectrum was recorded on Perkin Elmer Lambda 3BUV– Vis spectrometer. Ultraviolet protection factor (UPF) wasmeasured using UV Shimadzu 3101 PC-Spectrophotometer. UVProtection and classification according to AS/NZS 4399:1996 were evaluated (38).

Antimicrobial testing

The antimicrobial activity of the coated fabrics was tested against the Gram-negative bacterium *Escherichia coli* and the Gram– positive *Micrococcus luteus* using Tetrazolium/formazan test (TTC).

Also, the antimicrobial activity of the prepared sol was evaluatedusing agar diffusion test according to AATCC Standard TestMethod 147-1988.

Scanning electron microscopy SEM/EDX analysis

The particles morphology in the calcinated samples at 500°C was investigated using Scanning Electron Microscopy. Samples for SEM/EDX were taken using FEI INSPECTS Company,Philips, Holland environmental scanning without coating. Elemental microprobe and elemental distribution mapping techniques were used for analyzing the elemental constitution of solid samples. An elemental analysis of the particles was implemented bya SEM equipped with an energy dispersive spectroscope (EDX), which can provide a rapid qualitative and quantitative analysis ofthe elemental composition.

XRD

XRD patterns of $ZnTiO_3$were recorded on a Philips PW 3050/10model. The samples were recorded on a Philips X-Pert MMP diffractometer. The diffractometer was controlled and operated by a PCwith the programs P Rofit and used a MoK source with wavelength 0.70930˚A, operating with Mo-tube radiation at 50 kV and 40 mA.

Fabric whiteness

Whiteness index was evaluated with a Color- Eye 3100 Spectrophotometer from SDL Inter.

Air permeability

It was tested using air permeability tester (21443, FRANK) according to DIN 53887.

Stiffness

It was tested using Shirley stiffness tester according to DIN 53362.

Result and Discussion

The sol-gel strategy has been decided for the synthesis because of the upsides of this system in particular: fine molecule size, straightforward compositional control and low handling temperature. The main precursors were titanium ethoxide with zinc acetate according to the schemes of the preparation (Fig.1) . Titanium ethoxide was picked on the grounds that it is realized that the transition metal alkoxides are highly reactive because of the existence of highly electronegative OR groups that stabilize the metal in the highest oxidation state and let the nucleophilic attack to the metal possible [9].

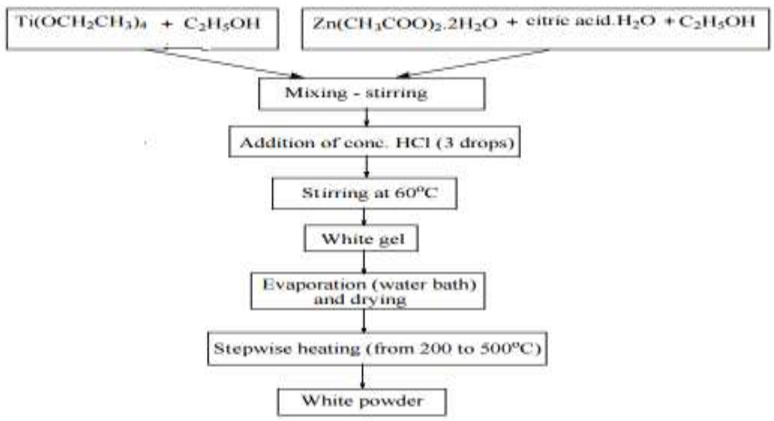


Fig. 1. Synthesis of $ZnTiO_3$ by sol-gel method .

Such alkoxides are utilized as forerunners as a part of sol-gel handling considering that they are firmly electrophilic and in this manner less steady toward hydrolysis, buildup, and other nucleophilic responses. Besides, the gathering R from $Ti(OR)_4$ impacts the morphology (molecule size and surface zone) and the crystallization behavior of final gel [(9)].

Titanium ethoxide and zinc acetate precursors were dissolved in ethanol or ethylene glycol with addition of citric acid as indicated in the way of the scheme of the preparation (Fig.1) . The hydrolysis process is fundamentally enhanced if directed at pH ≠ 7. Hence, adding acid (HCl (aq)) or base (NH_4OH) invigorates this procedure. After the hydrolysis the acidity of the sol is neutralized slowly to approx. pH=7, which stimulates the gelation process. At this stage a mechanically unstable "wet" gel is formed. Drying of wet gels prompts xerogels ("dry gels") even at ambient temperatures. So few drops HCl were added in some schemes to stimulate the hydrolysis and condensation reactions in order to obtain gel or precipitate at the end of the reactions. The as obtained gel or precipitate was transferred into a porcelain crucible and putt in water bath to evaporate the excess of water then dried on a hot plate (≈100 ^{o}C). After that a sequence of heating at 200 ^{o}C, 300^{o}C, 400 ^{o}C, 500 ^{o}C and 550 ^{o}C were done so as to evaporate the organics and to start the crystallization of the powders. The phase formation and structural transformation were followed by X-ray phase analysis.

X-ray

The X-ray diffraction pattern of that sample is shown in Fig. 2. As it is seen at 400°C the sample preserves its amorphous condition, but at 500 °C the strongest peaks of $ZnTiO_3$ (JCPDS 39-0190) (the three strongest lines 2.54; 2.97; 1.49) appeared. In order to check the temperature influence on the sample an additional heat treatment at 550 °C was made. It leads to increasing the peaks intensity.

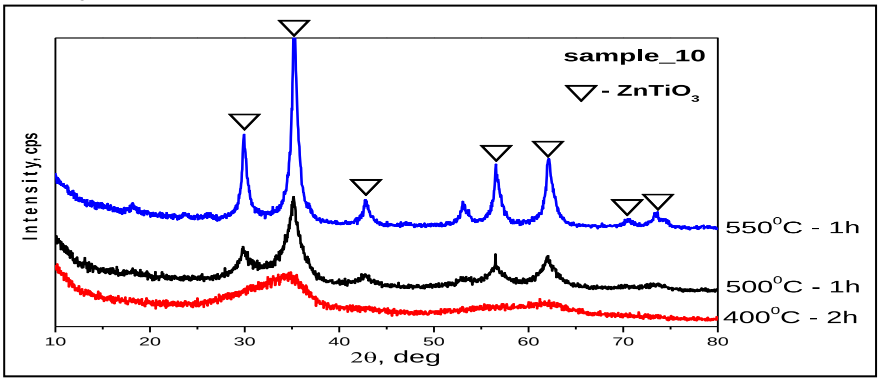


Fig. 2. XRD patterns of the $ZnTiO_3$ sample heat treated at 400, 500 and 550°C.

TEM

Figure 3. shows the morphology of ZnTiO3 nanoparticles since the size of the particles is between 25-50 nm.

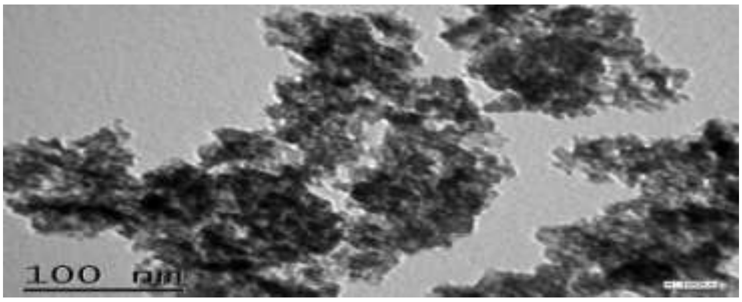


Fig.3.TEM image of $ZnTiO_3$.

SEM – EDX analysis of cotton fabric coated with$ZnTiO_3$

Some regular SEM micrographs of the sol– gel treated cotton fabrics are accounted for in Fig. 4. Generally, homogeneous and conservative film is covering the fiber.

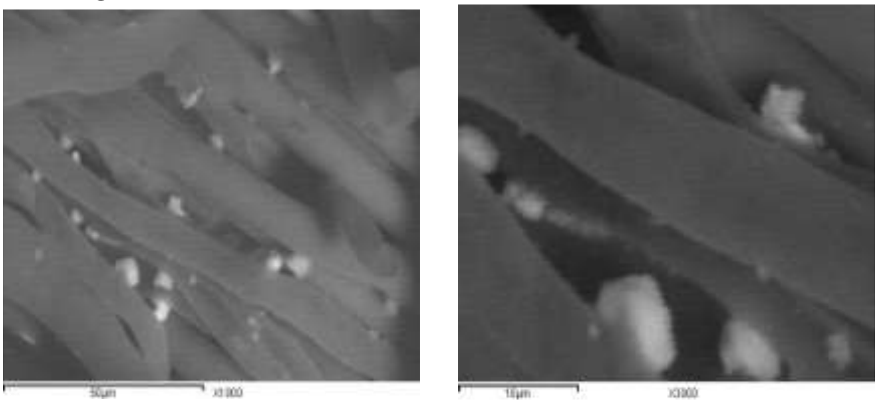
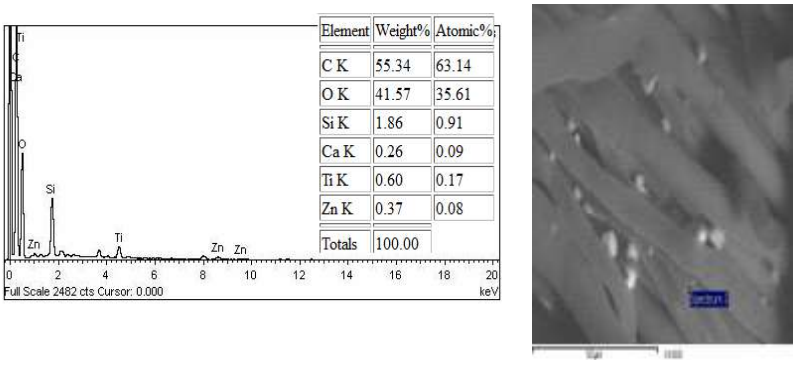


Fig. 4. SEM micrographs of $ZnTiO_3$/GPTMS treated fabric.

An essential examination of the particles was executed by SEM equipped with an energy dispersive X- ray spectrum [EDX], which can give a fast quantitative investigation of the elemental composition. Figure 5 depicts the quantitative analysis for cotton fabric treated with $ZnTiO_3$nanoparticles which confirms that the nanostructure contains about, carbon 55.34%, oxygen41.57%, and titanium0.6%, zinc 0.36% and silicon 1.86%.The homogeneity of dispersion of the inorganic coatings relies on the metal utilized in the sol– gel procedure. As pointed out by the elemental maps (Fig.

6) very high level of Ti distribution was observed while the distribution of Zn appears to be less homogeneous and thick when compared with Ti.



Element	Weight%	Atomic%
C K	55.34	63.14
O K	41.57	35.61
Si K	1.86	0.91
Ca K	0.26	0.09
Ti K	0.60	0.17
Zn K	0.37	0.08
Totals	100.00	

Fig. 5. EDX spectra of $ZnTiO_3$/GPTMS treated fabric.

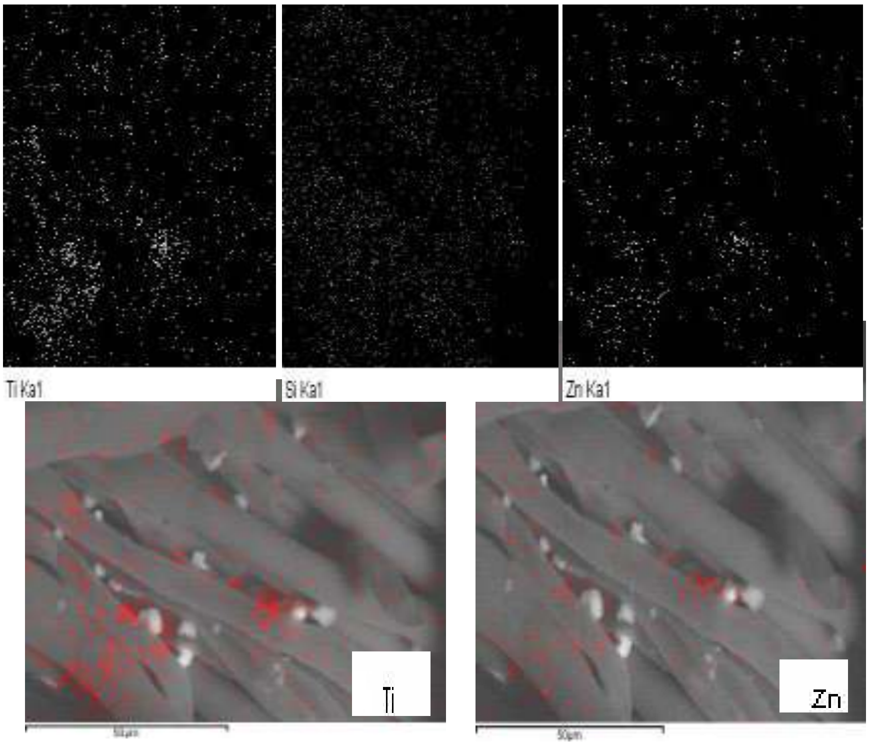


Fig. 6. Element maps of $ZnTiO_3$/GPTMS treated cotton fabrics.

UV protection for treated cotton fabrics

The treatments laundry testwere carried out for the durability of, since all samples were washed before the UV transmission was measured. The relating information for the coated cotton fabrics are outlined in Table 1 demonstrating changes in the absorption characteristics of the treated samples which expressed as UPF value contrasted with the untreated fabrics.

From the table it can be seen that untreated cotton fabric give only moderate UV protection.Treatment with GPTMS or $ZnTiO_3$nanoparticles results in good UV protection, but treatment with $ZnTiO_3$/GPTMS yields excellent protection.

TABLE 1. UPF value of treated fabrics.

Substrate	Upf value	Uv protection
Blank cotton	13	moderate
Cotton Fabric treated WithGPTMS	17	Good
Cotton Fabric treated With$ZnTiO_3$	22	Good
Cotton Fabric treated With$ZnTiO_3$/GPTMS	75	Excellent

Antibacterial efficiencyof treated cotton fabrics

Tetrazolium/formazan-test method TTC

The antibacterial activities of the cotton treated fabric samples were assessed against *E.coli* and *M. lutues* utilizing the TTC test technique.

This test serves as showing framework for the determination of the suitability of bacterial cell, since absorbance of formazane is straightforwardly relative to the measure of living microscopic organisms. Figure 7 demonstrates the antibacterial action (which was communicated by formazan absorbance values) for cotton fabrics treated with various $ZnTiO_3$ nanoparticle focuses (0.25%, 0.5 % and 0.75%)(w/v) in GPTMS-sol. We notice a highly reduction of the essential cells due to the existence of $ZnTiO_3$-filled sol. By increasing the amount of the $ZnTiO_3$ within the hybrid polymer, the antibacterial activity increases. Since the higher the $ZnTiO_3$ concentration, the lower the formazan absorption value (*i.e.*, more microbes are executed) which shows the higher antibacterial action.

a b c d e

Fig.7. TTC test method of (a) blank, (b) GPTMS, (c) 0.25% $ZnTiO_3$/GPTMS, (d) 0.5% $ZnTiO_3$/GPTMS and (e) 0.75% $ZnTiO_3$/GPTMS against *E.coli.*

Disc diffusion method

Antibacterial impact of cotton treated fabrics against *E.coli* and *M. lutues* as hindrance zones, assessed by the circle dissemination examine is shown in Fig. 8. There is a reasonable zone of hindrance inside and around the examples completed with $ZnTiO_3$/GPTMS hybrid polymer compared with the untreated or only treated with GPTMS fabric.

(a) M.lutues

(b) E.coli

Fig. 8. The disc diffusion test of high $ZnTiO_3$ concentration for the growth inhibition of: (a)*M.lutues* and (b) *E.coli*. (1) Untreated fabric, (2) fabric treated with GPTMS, (3) fabric treated with $ZnTiO_3$/ GPTMS (0.75%)(w/v).

Photocatalytic property of $ZnTiO_3$ nanoparticles

The charge division of electrons and holes was advanced and the recombination of the hole– electron sets was diminished due to the coupling impact of zinc oxide and titanium dioxide in the grain-like composite nanoparticles. As an outcome, the $ZnTiO_3$ nanoparticles demonstrated high photocatalytic activity in the treatment of natural contaminated water [10].

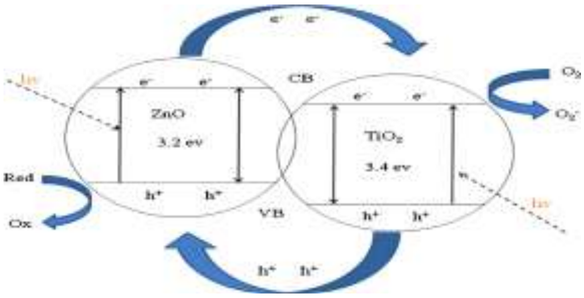


Fig.9. Assumed diagram of charge separation of Zinc oxide/Titaniananomaterials [10].

Photocatalytic activity of $ZnTiO_3$ nanoparticles toward photodegradation of methylene blue (MB) was evaluated under UV light irradiation. The results indicate that zinc titanate nanoparticles exhibit high photocatalyticacion.

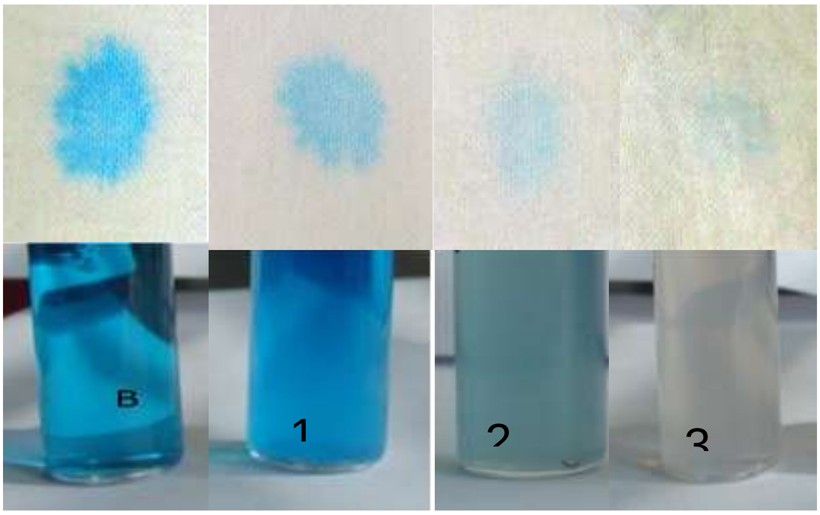


Fig. 10. Decolorization of MB dye after 30 min UV irradiation. Since B: Blank methylene blue, (1) methylene blue with GPTMS, (2) methylene blue with 0.5 % $ZnTiO_3$/GPTMS and (3) methylene blue with 0.75 % $ZnTiO_3$/GPTMS.

Impact of $ZnTiO_3$sol on the performance properties of the fabrics

It is essential to think about the impact of this treatment on the performance properties of the fabrics contrasted with the untreated fabrics.

The impacts of the sol treatment for the level of whiteness and for the air permeability were researched and the relating information isshown in Table 2.

We can notice that there is no worsening of the air permeability but there is a slight improvement. Also, the whiteness of the fabrics is slightly decreased but in a tolerable level. The increase of the bending stiffness values was recorded by increasing the concentration of $ZnTiO_3$, this is because of the higher uptake of the hybrid polymer on cotton surface, as a result of the increasing of solid content for sol with higher amount of$ZnTiO_3$.

TABLE 2. Effect of higher concentrations of $ZnTiO_3$– sol on some performance properties of cottonsubstrate.

Cotton substrate	Air permeability l/dm^2*min.	Degree of Whiteness (Berger)	Bending Stiffness ($cNcm^2$)
Untreated	254.8	62.1	14.18
ZnTiO3/ GPTMS-sol (0.25%)	256.2	59.1	15.36
ZnTiO3/ GPTMS-sol (0.5%)	254.3	58.9	16.72
ZnTiO3/ GPTMS-sol (0.75%)	252.0	61.2	17.87

Conclusion

The $ZnTiO_3$nanoparticles were synthesized and utilized to prepare functional coating for inorganic-organic hybrid materials. The resulting finished fabrics achieved higher UV protection, antibacterial activity, and self-cleaning properties without affecting the mechanical properties of the fabrics.

References

1. **Wang, L., Kang, H. Xue, D. and Liu, C.,** *J. Cryst. Growth,* **311**, 611– 614. (2009).

2. **Liu, Z., Zhou, D., Gong, S. and Li, H.,** *J. Alloy Compd.* **475,** 840– 845. (2009).

3. **Chaouchi, A., d' Astorg, S., Marinel, S. and Aliouat, M.,** *Mater. Chem. Phys.* **103**, 106– 111. (2007).

4. **Farouk, A., Textor, T. and Schollmeyer, E.,** Sol-gel derived inorganic-organic hybrid polymers filled with ZnO nanoparticles as ultraviolet protection finish for textiles. *AUTEX Research Journal,* **Vol. 9**, No.4, December (2009).

5. **Farouk A., Textor T. and Schollmeyer E.,** ZnO-modified hybrid polymers as an antibacterial finish for textiles. *Textile Research Journal*. published online 15 July (2013).

6. **Ibrahim, N. A., Refai, R. and Farouk, A.,** Novel approach for attaining cotton fabrics with multi-functional properties. *J. of Industrial Textiles,* **40**, 1, (2010).

7. **Shalaby, A., Dimitriev, Y., Iordanova, R., Bachvarova-Nedelcheva, A. and Iliev, Tz.,** *Journal of the University of Chemical Technology & Metallurgy;* Vol. 46 Issue 2, p137. (2011).

8. **Shalaby, A., Dimitriev, Y., Iordanova, R., Bachvarova-Nedelcheva, A. and Iliev, Tz.,** *Journal of Optoelectronics and Biomedical Materials* Vol. 3 Issue 2, p. 39-44. April- June (2011).

9. **A. Stoyanovah. Hitkova, A. Bachvarova-NedelchevAa, R. IordanovAa, N. Ivanova, M. Sredkova,** *Digest Journal of Nanomaterials and Biostructures,* **Vol**. **7**, No. 2, 777 – 784. April - June (2012) .

10. **Mohammad Hossein Habibi and Maryam Mikhak,** *Applied Surface Science,* **258,** 6745-6752. (2012).

11. **Iordanova, R., Bachvarova-Nedelcheva, A., Dimitriev, Y. and Iliev, Tz.** *Bulgarian Chemical Communications,* Volume **43** , No. 3 (pp. 378 – 382) (2011).

12. **Ya-wen Wang, Pei-Hong Yuan, Cai-Mei Fan, Yan Wang, Guang-Yue Ding and Yun-Fang Wang,** *Ceramics International* , **38,** 4173-4180. (2012).

13. **Obradovic, N. Stevanovic, S. and Ristic, M. M.,** *Powder Metallurgy and Metal Ceramics,* **47**, 1-2, (2008).

(*Received* ;
accepted)