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Synthesis and Application of Titanium Dioxide Nanoparticles on Cotton Fabrics for UV Protection

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ABSTRACT

In recent years, the requirements for the sun protection has increased dramatically with climate change specially in high UV index regions. This study was carried out to examine, test and enhance the ultraviolet protection of cotton fabric after applying titanium dioxide nanoparticles. Samples with different concentration of titanium dioxide nanoparticles were prepared by pad-dry- cure method and used in multiple test settings which investigated the presence and effectiveness of applied nanoparticles on fabric. Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-Ray diffraction (XRD), ultraviolet protection and tensile strength were used to investigate the resultant effect. The results demonstrated that titanium dioxide nanoparticles showed effective resistance against ultraviolet rays and provided excellent ultraviolet protection while, little increase in tensile strength of treated fabric was observed.

Keywords: UV protection, Titanium dioxide nanoparticles, SEM, XRD, EDS, pad-dry-cure

Introduction

The sunlight reaching Earth includes visible, ultraviolet (UV) and infrared rays (radiations). Scientists further divide the ultraviolet segment of the light spectrum into three regions i.e., the near, the far, and extreme UV. Among these radiations, extreme UV is considered as the most dangerous for living organisms. Long term exposure to UV could result in various physiological hazards on human body including permanent damage of skin cells as well as cancer. There has been a high risk of skin damage in the absence of suitable UV protection (EWG, 2016). With the passage of time, it has become very significant to consider the dangers executed by UV radiation in the ways of human lives, particularly in their clothing. One of the most important developments regarding the quantification of the protecting effects of textiles was the finding of the solar protection factor (SPF) by using spectroscopic measurements (Schindler and Hauser, 2004).

Skin is the major and most exposed organ of the human body as around 12-15% of the total body weight constitutes of it. Skin is also an important natural barrier against environmental hazards. Human skin constitutes of three cell layers i.e. epidermis (outer), dermis (middle) and subcutaneous fat (lower). However, the epidermis and dermis are able to totally absorb the ultraviolet radiations, but, the UV radiation with longer wavelength could penetrate deeper than the radiation of shorter wavelength. Similarly, UVA is also able to penetrate more deeply than UVB (Das, 2010). About 90% of non-melanoma skin cancers has been found to be the results of persistent and long exposure to UV radiation (Reinert, Fuso, Hilfiker & Schmidt, 1997). One of the most important skin protections technique against natural or artificial radiations is to wear appropriate clothing endorsed by medical and physician experts to reduce the negative effects of UV radiations on human skin (Davis et al., 1997).

Researches has revealed that textile clothing offers at least 5 times healthier protection than unadorned skin, which means that only less than 20% of the erythemogenic ultraviolet radiation could pass through the clothes, but it could still induce the burning of skin (Schlenker et al., 2000). The effectiveness for textile fabric against ultraviolet radiation depends on certain physical and chemical factors including, but not limited to, fibre type, weave design of fabric, weave density, cover factor, dyestuff used as well as fibre finishing (Azeem et al., 2017 and Stankovic et al., 2009). Silk and Cotton fibers have slight protection against UV radiations as the radiations easily penetrate through them without being absorbed or reflected. The TiO2 particles are known to absorb the UV radiations (Popov et al., 2005 and Trivedi and Murase, 2017). To quantify and evaluate the protection effectiveness of UV protection substances like UV protecting textiles and sunscreens, the sun protection factor is determined. SPF and UPF are developed for the measurement of the effectiveness of UV protective textiles, while SPF is primarily used for the assessment of sunscreens (Johnson, 2012). According to definition, the theoretically SPF (maximum) is the reciprocal of 1 minus the cover factor.

SPF max =

Ultraviolet Protective Factor (UPF) is defined as the ratio of the average effective UV radiations transmitted and calculated through air to average effective UV-R irradiance transmitted and calculated through the fabric. UPF can be calculated according to Equation.

UPF =

Where Eλ is the relative erythemal spectral efficacy, Sλ is the solar spectral irradiance (Wm−2 nm−1), Tλ is average spectral transmittance of the test sample (measured) and Δλ is measured wavelength interval (nm).

There are many determinant factors that should be considered as mentioned earlier, for example, the fiber content, thickness, fabric construction, GSM and air permeability attributed to UV protection offered by the fabric. Moreover, the UV protective properties of a fabric can be improved by applying chemical finishing treatment afterwards (Rupp, Bohringer, Yonenaga & Hilden, 2001). Different dyes and optical brightening agents are also found in previous researches for UV protection of fabrics. UV absorbers are the organic or inorganic compounds which can absorb the UV radiation in the wavelength range of 290-360 nm. The most commonly used UV absorbers are titanium dioxide in particle form due to their high efficiency in UV absorption (Achwal, 1995).

Biosynthesis of TiO2 nanoparticles has been reported by using bacterium Bacillus subtilis (Rahuman et al., 2011). TiO2 nanoparticles were made via low temperature sucrose ester micelle- mediated, hydrothermal processing route using titanium iso-propoxide as a precursor (Thangavelu, Annamalai & Arulnandhi, 2013). TiO2 nanoparticles were synthesized using optimized biomass of Planomicrobium, which was isolated from melted ice (Anwar et al., 2010). A hydrothermal method was used for the fabrication of tungsten trioxide nano rods to analyze its ultraviolet resistance and electrostatic properties (Azeem et al., 2016). Recent study about UV protection done by mathematical modelling of fabric construction parameters and model showed satisfactory results to be used for UV protection (Azeem et al., 2017).

The main disadvantage of previously used UV protectors was their degradation behavior and thus, were not a sustainable solution to UPF and SPF specifically, in ozone depleted areas. So, in this study, we successfully applied titanium dioxide nano particles on cotton fabric which not only resists the UV transmission, but also reflects the visible and IR radiations. Owing to high refractive index of TiO2 and transfer of destructive UV energy absorbing capability into heat avoid discoloration that mostly caused drastically due to UV radiations.

Experimental

Materials

Fabric

A bleached 100% cotton fabric was used in this study. The fabric was taken from the textile chemistry lab National Textile University, Faisalabad. The specifications of the fabric are given in Table 1.

Table 1. Fabric specification

No.	Parameters	Units	Values
1	Warp Count	Ne	20
2	Weft Count	Ne	20
3	Ends/Inch	-	116
4	Picks/Inch	-	56
5	Areal Density	g/m2	200
6	Weave	Twill	-

Chemicals and auxiliaries

Different types of chemicals and auxiliaries were used during working for preparation of TiO2 nanoparticles. Names and information about those chemicals and auxiliaries are given in Table 2.

Table 2. Chemicals and auxiliaries

Sr. No.	Name	Function	Chemistry	Manufacturer
1	TTIP	Formation of TIO_2	$Ti\{OCH(CH_3)_2\}_4$	Aldrich
2	Ethanol	hydrolysis	C_2H_5OH	Merck
3	Acetic Acid	Maintain pH	CH_3COOH	Merck
4	Distilled Water	Medium	H_2O	TP lab

Table 3. Production/Processing equipment used in this study

S. No.	Name of Equipment
1	Ultrasonic Bath
2	Pyrex Beakers
3	pH Meter
4	Padder
5	Stenter
6	Micropipette

Equipment

Processing Equipment

Lab scale practical was done to carry out or prepare titanium dioxide nanoparticles and the apparatus used in that practical is enlisted in Table 3.

Testing Equipment

For confirmation and characterization of titanium dioxide nanoparticles on the fabric different types of test were done. The apparatus used for testing is described in the Table 4.

Table 4. Testing equipment used in this study

S. No.	Name of Equipment	Model	Manufacturer
1	Scanning Electron microscopy	QUANTA 250	FEI
2	X- ray Diffraction	Panalytical	XPERT PRO
3	UV/VIS Spectrophotometer with SPF M550	Spectronic Camspec	
4	Tensile strength tester	KG-300	DAIEI KAGAKU SEIKI SEISA-KUSHO Ltd.

Methods

Preparation of titanium dioxide nanoparticle solution

The solution was prepared into two steps, in first step Titanium (IV) isopropoxide (TTIP) was mixed with ethanol and then the mixture of TTIP and ethanol was added into water. 15 ml of ethanol was taken in a beaker and the required quantity of TTIP was added in ethanol with adequate stirring.

Then, 250 ml double distilled water was taken in a separate beaker and placed on ultrasonic bath. The prepared mixture of ethanol and TTIP was added gradually in the above water and sonication was done till a homogeneous mixture was obtained. Throughout the process, pH of homogeneous mixture was maintained at 3. Table 5 gives information about the number and types of the experiment.

Table 5. Concentration of TTIP and number of experiments

Sr. No.	TTIP (ml)	Ethanol (ml)	Water (ml)	pH
1	0.4	15	250	3
2	1	15	250	3
3	1.2	15	250	3
4	1.4	15	250	3
5	1.8	15	250	3
6	5	15	250	3
7	15	15	250	3

Fabric treatment with prepared solution
Pad-Dry-Cure root was applied to the fabric. Briefly, the fabric was dipped in solution and padded through rollers twice for homogeneous distribution of the solution on fabric with a pick- up of 80%. After padding, the fabric was dried at 120°C for 3 min. From previous literature, it was noticed that there is no need for an external material except for high temperature for the attachment and binding of TiO2 nanoparticles to the cotton fabric since TiO2 nanoparticles are presumed to be bound with cotton through ester bonding over the non-homogeneous irregular structure of the cotton (Abbas et al., 2018) and ionic potential build on cellulose during wet treatment (Zhang et al., 2019) and complete removal of water so that nanoparticles are readily adsorbed by weak chemical forces and absorbed in the interstices of cellulose fibres (Ramirez et al., 2019). So, after drying the fabric was further cured for esterification at 155°C for 5 min. A different piece of fabric was used for each type of solution.

Testing Methods
SEM, X-ray diffraction and ultraviolet (UV) protection tests were done on the fabric to check the presence and effect of titanium dioxide particles. SEM and X-ray diffraction tests were used for characterization and presence of titanium dioxide nanoparticles on the fabric, while UV protection test give the information about the effectiveness of nanoparticles.

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS)
This test was performed with a focused beam of high energy electron that magnifies the images and precisely measures very small features and objects. It is mostly used for qualitatively or semi- quantitatively determining chemical composition, crystalline structure and crystal orientation.

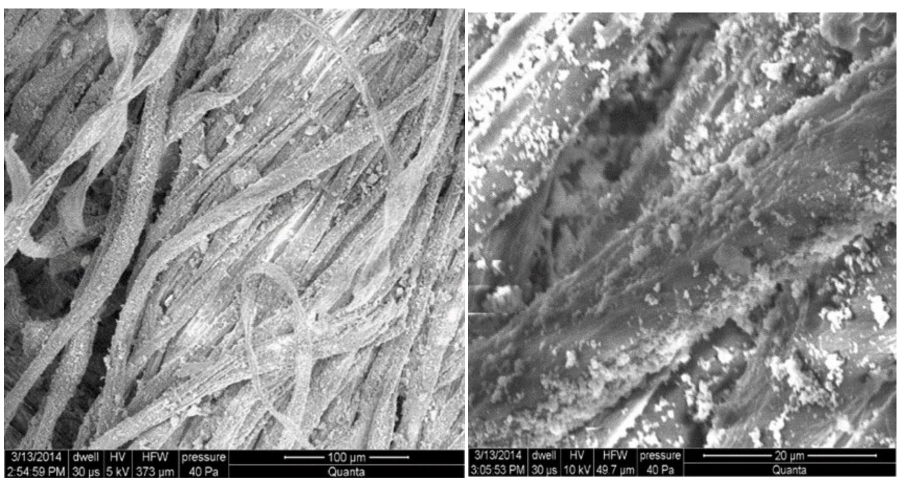
X-ray diffraction (XRD)
X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystal structure, chemical composition and physical properties of materials and thin films. The X-ray diffraction (XRD) analysis of prepared sample titian treated fabric was done using a diffractometer, Cu Kα X-rays of wavelength (λ) =1.5406 Å and data was taken for the 2θ range of 10o to 70o with a step of 0.1972o.

Ultraviolet protection (AATCC 183)
Ultraviolet protection of a fabric gives information about how much a fabric gives protection from UV rays which are dangerous for human beings. AATCC 183 method defines the UPF rating for a fabric/textile as the ratio of UV measured

without the protection of the fabric (compared to) with protection of the fabric.

Tensile Strength
Tensile strength of treated fabric was calculated to investigate the effect of TiO2 nanoparticles on mechanical properties of twill weave cotton fabric. The stander test method that was followed for determination of tensile strength was ASTM D5034.

Results and Discussion
Scanning Electron Microscopy (SEM)
Scanning Electron Microscopy (SEM) analysis was done to investigate and characterize the presence of titanium dioxide nanoparticles on the treated fabric. The Figures 1 (a) and 1 (b) are of treated cotton fabric which shows the presences of titanium dioxide powder on fabric. The concentration of Titanium IV iso-propoxide (TTIP) for this fabric was 5ml per 250ml of water. Figure 1 (a) was taken at zoom of 400X while, the second Figure was taken at 3000X. Figure 2 is of untreated cotton fabric; as clear, there is a large difference of picture appearance with respect to concentration of titanium dioxide nanoparticles powder. The zoom of this picture is also 400X. The particles of the first two pictures display the presence of titanium dioxide nanoparticles whereas, there are no such particles in Figure 2 which represents untreated or control fabric.



(A) **(B)**

Figure 1. SEM image of TTIP treated cotton fabric (a) at 400X (b) at 3000X

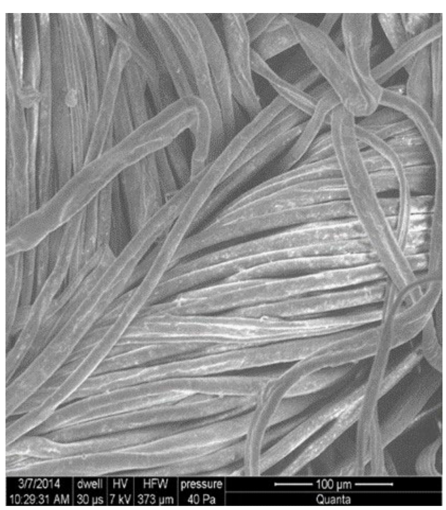


Figure 2. SEM image of untreated cotton fabric at 400X

Energy dispersive spectroscopy (EDS)

This test was done to investigate whether the powder present on the fabric is titanium or not. The results of energy dispersive x-ray spectroscopy (EDX) with at 2% and 5% concentration of TTIP are shown in the Figure 3 and 4 respectively. The EDX analysis confirmed the presence of titanium dioxide on the treated fabric.

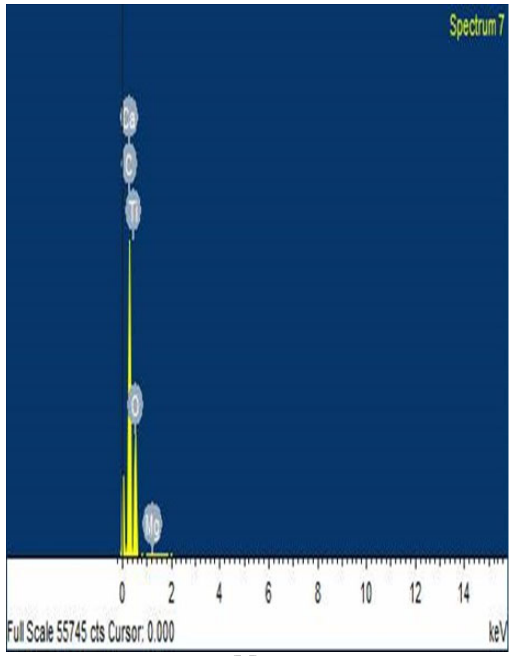


Figure 3. EDX pattern of 2% concentration of TTIP

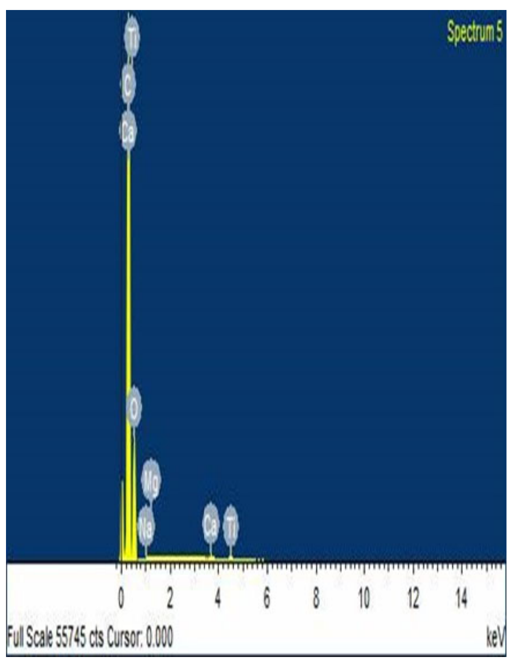


Figure 4. EDX pattern of 5% concentration of TTIP

X-ray diffraction (XRD)

The XRD test was used to check the crystallinity of the material which was applied on fabric during study. The XRD pattern gives information about crystallinity of the substrate as well as of applied powder. Figure 5 displays the XRD graph of titanium dioxide treated cotton fabric. Two main peaks can be observed in the graph. The peak at 17 is of cellulose while, the peak at 25 is of titanium dioxide nanoparticles. This peak confirms the presence of nanoparticles on fabric.

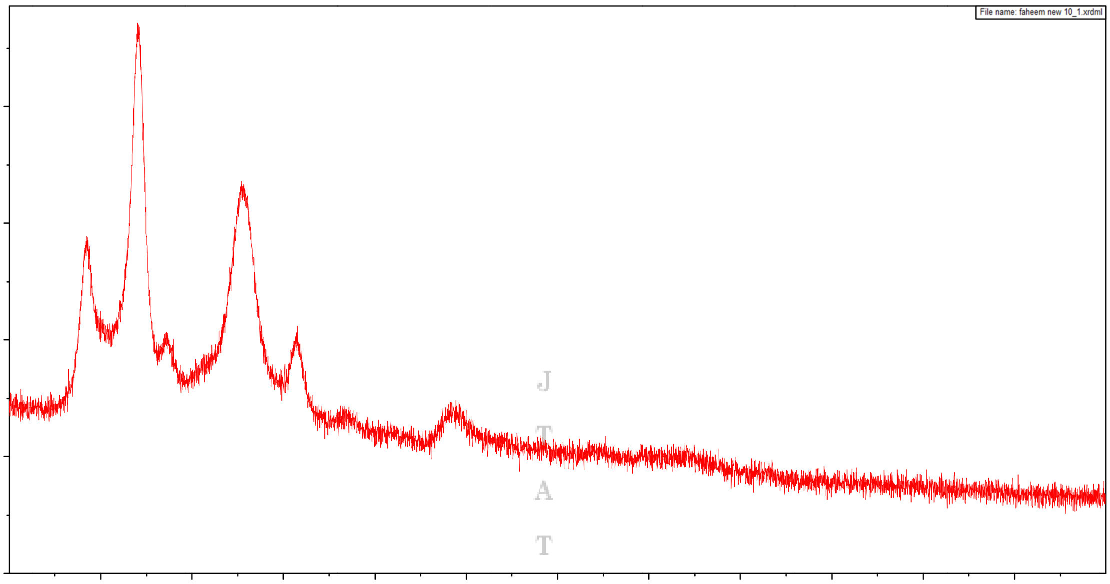


Figure 5. XRD pattern of titanium dioxide nanoparticles treated cotton

Ultraviolet Protection

TiO2 has a natural attribute of UV-absorption property, that could be clarified by the solid band theory. It is a type of semiconductor oxide having a large band gap between its high-energy conduction band and low-energy valence bands. The electrons would get the energy of the photons and so excited to cross the band gap to produce holes and electrons pairs, when TiO2 is illuminated by light with energy higher than its band gaps. These excited holes and electrons then result in two notes: either combining with other electrons or holes or captured by the surrounding TiO2 and starting the oxidation and reduction reactions. The former clarifies how the UV-defender TiO2 works, while the last uncovers the mechanism of TiO2 as a light catalyzer.

Ultraviolet protection test is the fundamental test of this practice; the result of this test will demonstrate how successful the treated fabric is for UV protection. These results of the UV protection test are shown in the Table 6. We assume that with the increase of concentration TTIP, there is decrease in particle size, due to this reduction of particle size the surface area of particles increase and they reveal much protection or resistance against UV rays.

Effect of TTIP on UPF

The relation of TTIP and UPF was given in the Figure 6, which shows that as the concentration of TTIP increases in the solution, the ability of ultraviolet protection of the fabric increases. This can be expressed as x number of particles are present for protection against y number of UV-rays. If the number of particles increases, but the number of rays remains constant than the UV protection will increase.

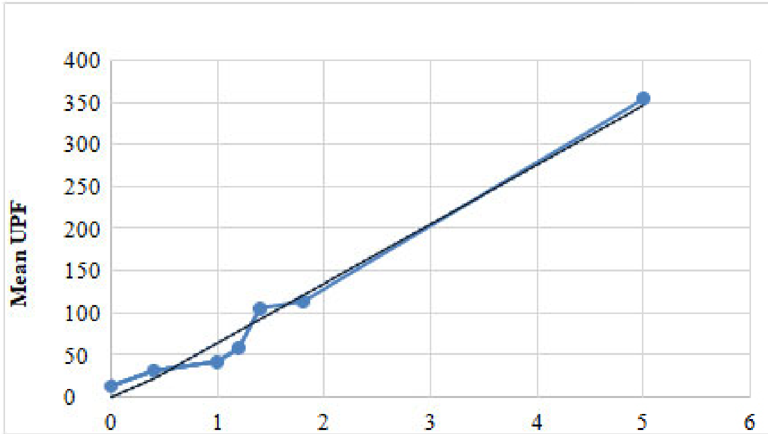


Figure 6. EffectToTf ITPTcIoPncco. (nmcel/n2t5r0atmioln) on UPF

Effect of TTIP on UVA Blocking
The relationship between the concentration of TTIP and UVA blocking is given in the Figure 7. This Figure explains the relationship between the concentration of TTIP and the UVA blocking. As the concentration of TTIP is zero the percentage of UVA blocking is 86 it is due to compact weave structure of the fabric (Twill). With the increase of TTIP concentration, the UVA blocking also increases. As the concentration of TTIP is 5, the UVA blocking percentage is 97, as the concentration of TTIP increases up to 15 there is no further increase in UVA blocking because the remaining percentage of UVA blocking pass through the inter yarn spaces present in the fabric. To achieve 100% UVA blocking the cover factor of the fabric must be 1.

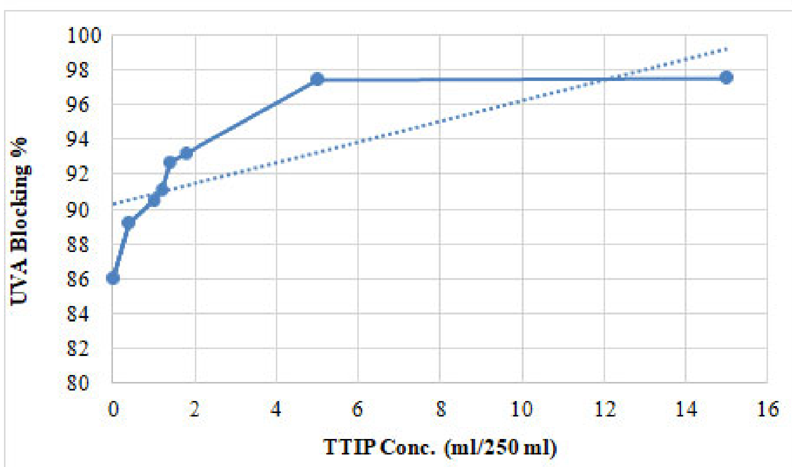


Figure 7. Effect of TTIP concentration on UVA blocking

Effect of TTIP on UVB Blocking
The relationship between the concentration of TTIP and UVB blocking is given in the Figure 8. This Figure explains the relationship between the concentration of TTIP and the UVB blocking. As the concentration of TTIP is zero, the percentage of UVB blocking is 94. With an increase of TTIP concentration, the UVB blocking also increases. As the

concentration of TTIP is 1.8, the UVB blocking percentage is 100 as the concentration of TTIP was increased up to 5, but there is no further increase in UVB blocking.

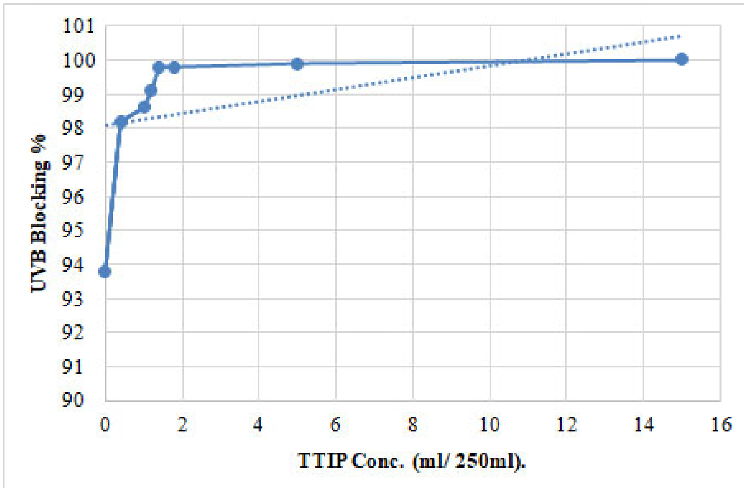


Figure 8. Effect of TTIP concentration on UVB blocking

Tensile strength

The tensile strength test was done to investigate the mechanical properties of the fabric to measure the effect of particles on the tensile strength of fabric. The results of the tensile strength test are given in the Table 6. Table is showing that the tensile strength of the fabric increases with increase in concentration of TTIP in solution. The Figure 9 also shows the relation between TTIP concentration and tensile strength of the fabric Maximum value of 90 MPa is achieved at 9% TTIP loading.

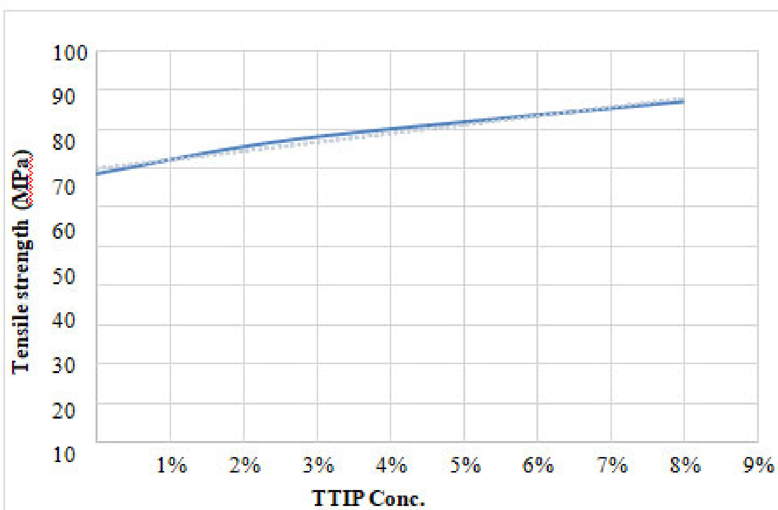


Figure 9. Effect of TTIP concentration on Tensile strength

As the concentration of TTIP increases, the tensile strength also increases. This is due to the filling of inter yarn spaces in fabric due to this the friction between yarns produced and they resist to elongate (Rahman, Solaiman, and Khalil, 2014) and also, stiffness of fabric increases which increases the tensile strength of fabric (Nilakantan et al., 2012).

Conclusion

In this study, TiO_2 nanoparticles were successfully synthesized and applied on 100% cotton fabric to enhance its UV protection. Good UV protection was observed and a nearly direct relation between UPF and concentration of titanium dioxide was seen. At a very low concentration of TTIP i.e., 5 ml/250 ml, mean UPF value was above 350. Even at the low concentration of TiO_2, in case of rendering UVA and UVB, the treated fabric showed excellent blocking percentage of about 98% at 5 ml/250 ml and nearly 100% at 2 ml/250 ml. It not only increased UPF, but also improved tensile strength as depicted in the results.

Conflict of Interest

We, the all authors verify and declared that there is no conflict of interest among any contributor or other organizations.

References

Abbas, M., Iftikhar, H., Malik, M. H., and Nazir, A. (2018). Surface Coatings of TiO2 Nanoparticles onto the Designed Fabrics for Enhanced Self-Cleaning Properties, Coatings, 8(1), 35.

Achwal, W. B. (1995). Use of UV Absorbers in Textiles, Colorage, 42, 44-45.

Anwar, N. S., Kassim, A., Lim, H. N., Zakarya, S. A., and Huang, N. M. (2010). Synthesis of titanium dioxide nanoparticles via sucrose ester micelle-mediated hydrothermal processing route, Sains Malaysiana, 39, 261-265.

Azeem, A., Ashraf, M., Munir, U., Sarwar, Z., Abid, S., and Iqbal, N. (2016). Synthesis of Tungsten Oxide Nanorod, Its Application on Textile Material, and Study of Its Functional Properties, Journal of Nanotechnology, 2016, 1-7.

Azeem, A., Nazir, A., Abid, S., Sarwar, Z., and Munir, U. (2017). Modelling of fabric structure and shade for UV protection properties using full factorial design, The Journal of Textile Institute, 108, 1800-1807.

Das, B.R. (2010). UV Radiation Protective Clothing, The Open Textile Journal, 3, 14-21.

Davis, S., Capjack, L., Kerr, N., and Fedosejevs, R. (1997). Clothing as Protection from Ultraviolet Radition: Which fabric is most effective?, International Journal of Dermatology, 36, 374-379.

EWG Sunscreen Guide. (2016). EWG's analysis of UV protection offered by U.S. sunscreens.

EWG research.; https://www.ewg.org/sunscreen/report/imperfect-protection/#.Wxj088K-nIU

Johnson, S. L. (2012). Transmittance or Blocking of Erythemally Weighted Ultraviolet Radiation through Fabrics, AATCC TECHNICAL MANUAL, 87, 323-326.

kirthi, A. V., Rahuman, A. A., Rajakumar, G., Marimuthu, S., Santoshkumar, T., Jayaseelan, C., Elango, G., Zahir, A. A., Kamaraj, C., and Bagavan, A. (2011). Biosynthesis of titanium dioxide nanoparticles using bacterium bacillus subtiles, Material letters, 65, 2745-2747.

Popov, A. P., Priezzhev, A. V., Lademann, J., and Myllyl, R. (2005). TiO2 nanoparticles as an effective UV-B radiation skin-protective compound in sunscreens. Journal of Physics D: Applied Physics, 38, 2564.

Rahman, M. M., Solaiman, M., Khalil, E. (2014). Effect of Titanium Dioxide Treatment on the Properties of 100% Cotton Knitted Fabric, American Journal of Engineering Research, 3(9), 87-90.

Reinert, G., Fuso, F., Hilfiker, B., and Schmidt, E. (1997). UV-Protecting Properties of Textile Fabrics and their Improvenment, Textile Chemicals and Colourants, 29, 36-43.

Ramirez, L, Gentile, S. R., Zimmermann, S., and Stoll, S. (2019). Behavior of TiO2 and CeO2 Nanoparticles and Polystyrene Nanoplastics in Bottled Mineral, Drinking and

Lake Geneva Waters. Impact of Water Hardness and Natural Organic Matter on Nanoparticle Surface Properties and Aggregation, Water, 11(4), 721;

https://doi.org/10.3390/w11040721Rupp. J., Bohringer, A., Yonenaga, A., and Hilden, J. (2001). Texiles for protection against Harmful Ultraviolet Radiation, Internatonal Textile Bulletin, 6, 8-20.

Schindler, W., & Hauser, P. J. (2004). Chemical finishing of textiles. Cambridge: Elsevier. Schlenker, U., Rohwer, W., Martin, H., and Schuh. E. (2000). Facts and Fiction on Ultraviolet Protection by Clothing, Radiation Protection Dosimetry, 91, 255-259.

Stankovic, S. B., Popovic, D., Poparic, G. B., and Bizjak, M. (2009). Ultraviolet Protection Factor of Gary-state Plain Cotton Knitted fabrics, Text Res J 79:1034-1042.

Thangavelu, Annamalai, K. R., and Arulnandhi, D. (2013). Prepartion and charcterization of nanosize titanium dioxide powder by sol-gel precipetation, International Journal of emerging technology and advance engineering, 3, 636-639.

Trivedi, M., and Murase, J. (2017). Chapter 4: Titanium Dioxide in Sunscreen, Intech Publishers.; http://dx.doi.org/10.5772/intechopen.68886