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The effect of nano-titanium dioxide on the self-cleaning properties of TiO_2-PP composite fibers

Praripatsaya Panutumrong[1], Siripan Metanawin[1], Tanapak Metanawin[2]

[1]*Department of Textile Engineering, Faculty of Engineering, Rajamangala University of Technology Thanyaburi, PathumThani, Thailand*
siripan.m@en.rmutt.ac.th.
[2]*Department of Materials and Production Technology Engineering, Faculty of Engineering, King Mongkut's University of Technology North Bangkok, Bangkok, Thailand*
tmw@kmutnb.ac.th.

Abstract

This study aims to synthesis the self-cleaning fibers. The nano-titanium dioxide (TiO_2) were blend with the polypropylene (grade 561R) at 1wt%, 3wt%, 5wt%, 10wt%, 15wt% and 20wt%. The TiO_2-fibers were obtained from single screw extruder. The mechanical, thermal, rheology and self-cleaning properties were also investigated. The results showed that the tensile strength of the $nTiO_2$-PP fibers decreased with increasing of the amount of TiO_2. The presents of the TiO_2 in the PP fibers significantly showed the improving of the self-cleaning properties under sunlight and 20 watt of UV radiation. The TiO_2-PP fibers in presents of TiO_2 20wt% showed the best results of self-cleaning under 5 hours of the sunlight which the similar results were found under 5 hours of 20 watts of UV radiation.

Keywords: *Titanium dioxide, PP fiber, self-cleaning, polymer blend and polymer composite.*

1. INTRODUCTION

Many attention has been focused on the new materials that can demonstrate photocatalytic behavior under the proper illumination conditions for applications in textile technological fields.[1, 2] For this reason, titanium dioxide (TiO_2) has attracted great attention as a semiconductor photocatalyst due to its widely used materials, low cost, good stability, and ease of preparation.[3] One of an interesting application of TiO_2 is self-cleaning ability.[4, 5]

TiO_2 self-cleaning coatings are finding increasing applications in many fields, which now emerged in commercial products ranging from kitchen and bathroom ceramic tiles, and fabrics, to indoor air filters, window glass sections, furniture, painting and auto industry.[6-10] The mechanism of TiO_2 self cleaning ability is mainly based on TiO_2 photocatalysis, where photo-induced electron-holes catalyze reaction on the

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Corresponding Author: siripan.m@en.rmutt.ac.th
Tel. +66(0)2-549-3450 Fax +66(0)2-549-3452
Department of Textile Engineering, Faculty of Engineering, Rajamangala University of Technology Thanyaburi, PathumThani, Thailand

surface.[11-13] The thicknesses of the coatings are generally around 200 nm, which are deposited using various techniques such as sputtering,[14] electrophoretic deposition,[15] thermal oxidation,[16] chemical vapor deposition,[17] and wet coating[18].

Polypropylene (PP) is one of the most widely used synthetic fibers in textile industry, which is cheaper and stronger than the other synthetic fibers. Beside, PP can be use in various applications, for example, film, package, cover stock, cable, napkin, and so on. Particularly, it is used for carpet, automotive interior trim, etc.[19, 20]

In the last few decades, there has been increased interest in development of permanent self-cleaning on textile materials with a life cycle of 25–50 washings or more is an objective sought by the textile industry in the framework of new products classified as technical textiles.[6, 21] However, to date, no research has presented the PP-TiO_2 fibers nanocomposite. Therefore, in this research we designed an inorganic nanocomposite fibers which have self cleaning effect. For this purpose, we have prepared nanocomposite fibers using PP and nano TiO_2 with varying the concentration of TiO_2 nanoparticles.

2. EXPERIMENT

2.1 Materials

The polypropylene grade 561R was purchased from HMC polymer Company Limited. The TiO_2 CAS# 13463-67 was supplied by Chemipan Thai Co., Ltd. All other chemicals were used as supplied by the companies.

2.2 Preparation of TiO_2 /PP composite

The PP pellets were dried at 80℃ overnight prior to compounding. The 1000g of PP pellets was mixed with 1wt%, 3wt%, 5wt%, 10wt%, 15wt% and 20wt% of TiO_2. The glycerol 4 drop was added into the mixture. The TiO_2 was blended with PP using ThermoHake PolyDrive (Single Screw Extruder). The extruder barrel-temperatures zones were set 160℃ 170℃ 1850℃ 200℃ and 210℃, respectively. The screw speed was 40 rpm. The obtained TiO_2/PP composites were passed through 5mm die and cut into pellet size.

2.3 Preparation of TiO_2/PP composite fibers by melt spinning technique

The TiO_2/PP composite pellets were mixed using ThermoHakePolyDrive. The barrel-temperatures zones were operated 160℃ 170℃ 1850℃ 200℃ and 210℃, respectively. The screw speed was 40 rpm. The melting composite exit from the spinneret was draw into the fiber shape. The obtained TiO_2/PP composites were passed through 5mm die and cut into pellet size.

2.4 Characterizations

2.4.1 Melt Flow Index

In order to investigate the Melt Flow Index of TiO_2-PP composite fibers, Melt Flow Index machine model XRL-400 was used to characterize the samples. The 6 gm of the samples were place in the machine and the temperature was set at 230 ℃.

2.4.2 Scanning electron microscope (SEM)

The SEM images were recorded by using JeolJSM-6510. The samples were coated with Pt.

2.4.3 Tensile strength or tenacity test

The tensile test of the fibers composite were performed on Instron 5560 universal testing machine. The speed of the cross head was 30mm/mm.

2.4.4 Differential scanning calorimeter (DSC)

Differential scanning calorimetry thermogram were measured on Netzsch DSC200. The samples were performed from -60°C to 200°C. The heating rate and cooling rate is 10°C/min.

2.4.5 Self cleaning Test

In order to investigate the self-cleaning characteristics of TiO_2-PP composite fibers, colorant stains were created on samples. Coffee stains were used as colorant organic stains. Aqueous solution of coffee stains was preparation by mixing 3 spoon of freeze-dried coffee in 50 mL of deionized water. The TiO_2/PP composites fibers were dipped into the solution for 5mins and then dried in ambient temperature and left in the oven at 60°C for 8 hrs. Stained samples were irradiated using a UV-A 20W lamp (Sylvania, Belgium), with 365 nm wave length radiation and light intensity of 0.2–0.4 l W cm)^2 for 5 hrs and under sunlight for 5 hrs.

3. RESULTS AND DISCUSSIONS

3.1 Fibers forming

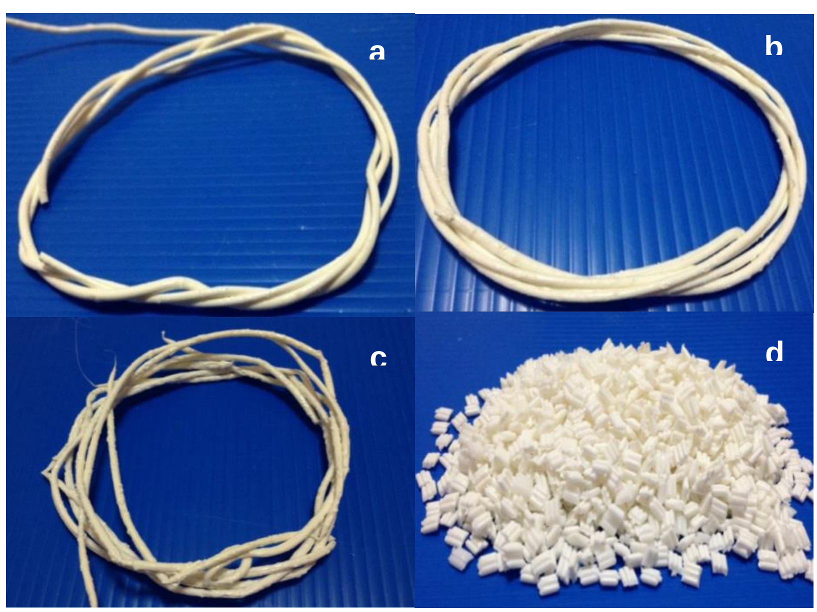

Figure 1. a) PP-10%TiO_2b)PP-15% TiO_2c)PP-20% $TiO_2$and d)PP-5% TiO_2Chip.

The TiO_2/PP fibers composite containing %1wt-20%wt of TiO_2 were produced using ThermoHake PolyDrive. The TiO_2/PP polymer compounds were obtained. The results of the extrusion instabilities of the compound were investigated. It was found that TiO_2/PP compound containing %1wt-10%wt of TiO_2 demonstrated the smooth skin, as seen in Figure 1a. However, the sharkskin were found when increased the loading amount of TiO_2 more than 10%, as shown in Figure 1(b-c). The compounds were cut into pellet size, as presented in Figure 1d. The fibers were form by melt spinning extruder, as shown in Figure 2. It was found that the TiO_2/PP fibers composite containing %1wt-10%wt of TiO_2 wereable to form the smooth fiber. On the other hand, the compound containing more than 10%wt of TiO_2 demonstrated the unsmooth fibers.

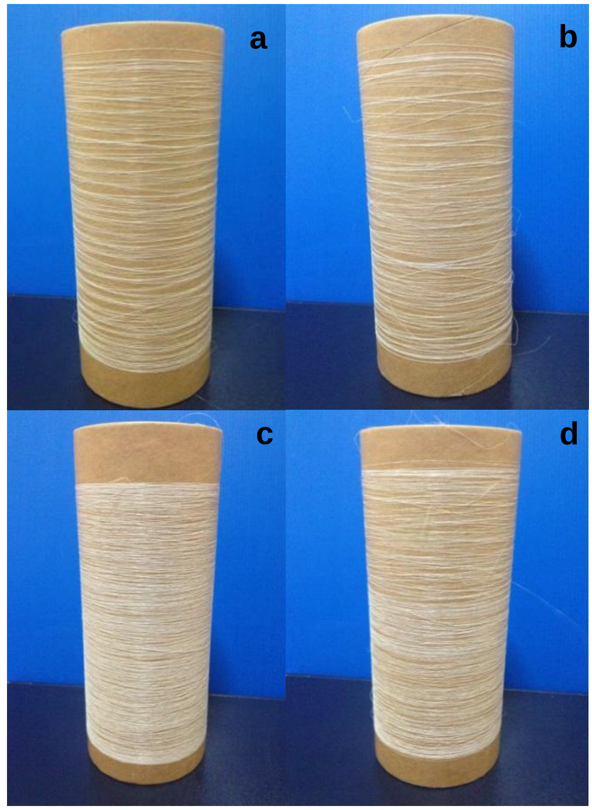

Figure 2. a) PP-1% TiO_2Fiber, b)PP-3% TiO_2Fiber, c)PP-10% TiO_2Fiber and d)PP-20% TiO_2Fiber.

3.2 Characterization of TiO_2 -PP composite fibers.

3.2.1 Melt Flow Index

The melt flow indexes of TiO_2/PP composites were investigated. The results show that the melt flow indexes of the TiO2/PP composite were similar with all of the samples, as seen in the Figure 3. The nanoTiO_2 did not affect the melt flow index of the composite due to the size of the particle very small.

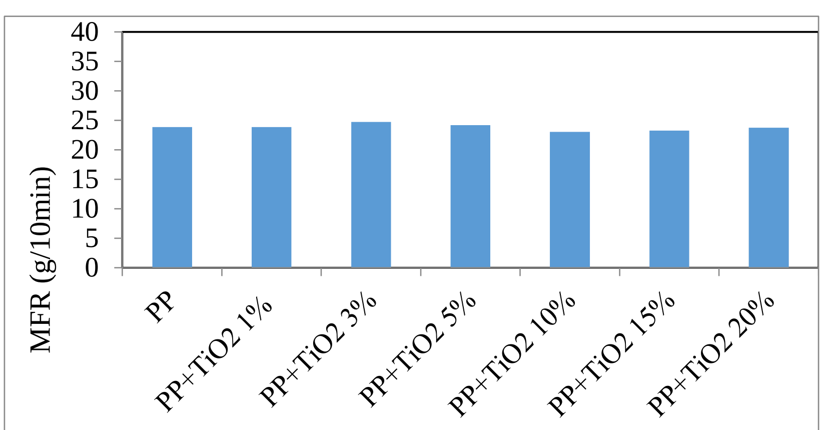

Figure 3. Melt flow index of PP fibers and PP+TiO_2 fibers composite from 1%wt-20% of TiO_2.

3.2.2 Scanning electron microscope

The images of the cross section and the surface of the TiO_2/PP composite fibers were investigated using Scanning Electron microscope. The surfaces of the composite fibers were observed. It was noticed that not only the surface of the composite fibers containing 3%wt of TiO_2 were well dispersed (Figure 4) but also the cross-section of the composite fibers containing 1%wt-5%wt TiO_2 were well dispersed in the fibers, as seen in Figure 5(b-d). However, the SEM images of TiO_2/PP containing 3%wt of TiO_2s tarted to show a few agglomeration of TiO_2, as illustrated in Figure 5c. Thus, the agglomeration of TiO_2 could be occur when increased the amount of TiO_2.

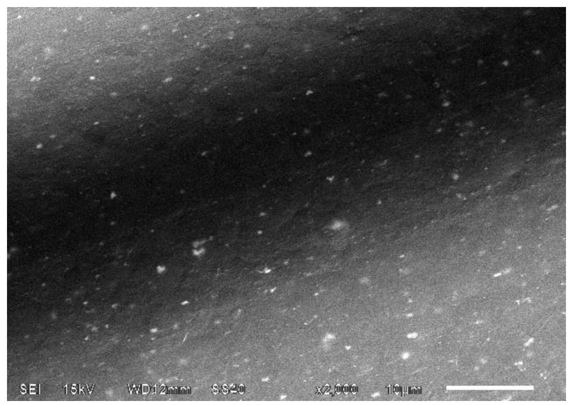

Figure 4. SEM images at the surface of the TiO_2/PP composite fibers containing 3%wt of TiO_2

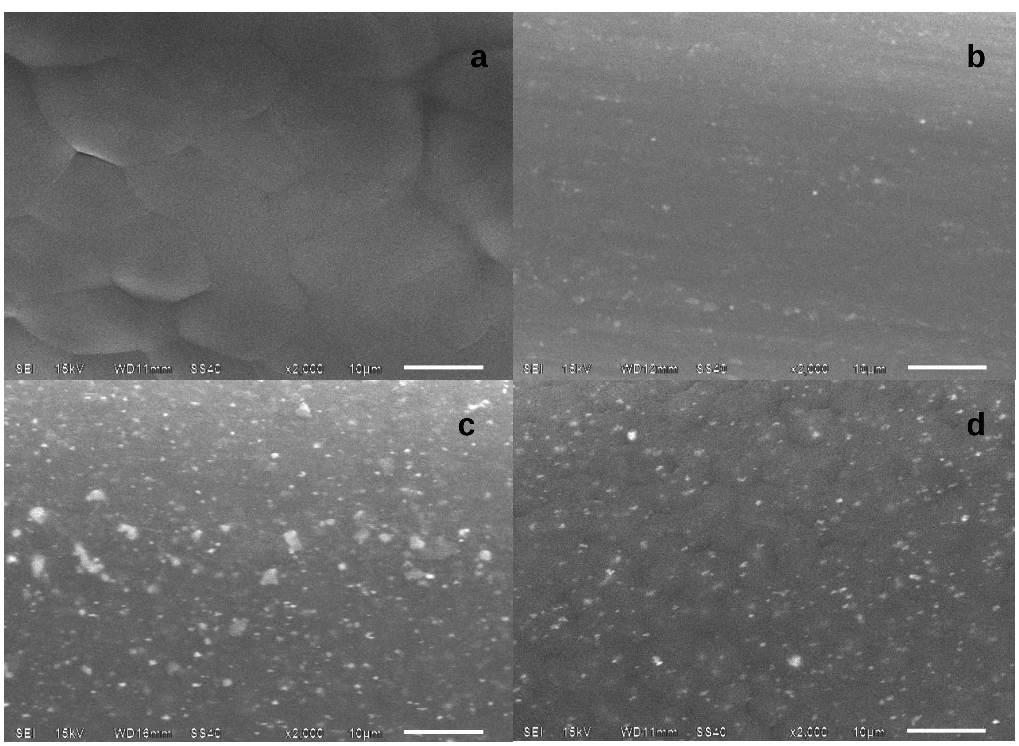

Figure 5. Cross-section SEM images of the a) PP fibersb) TiO_2/PP fiber compositewith 1%wtof TiO_2 c) TiO_2/PP fiber composite with 3% $TiO_2$and d) TiO_2/PP fiber composite with 5% wt of TiO_2

3.2.3 Tensile Strength or Tenacity of the fibers

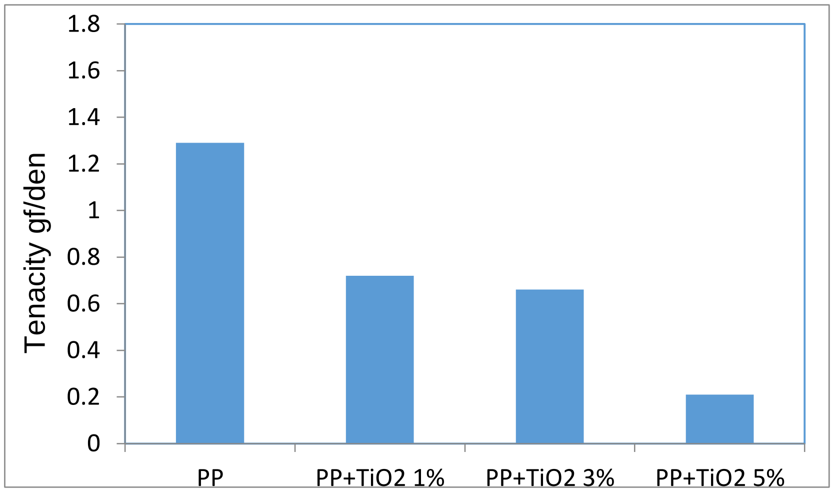

Figure 6. Tenacity of the PP fiber and TiO_2/PP composite fibers containing 1%wt, 3%wt and 5%wt

The tenacity of the TiO_2/PP fibers composite containing 1%wt, 3%wt and 5%wt of TiO_2 were performed on the Instron 5560 universal testing machine. The results of the tenacity test were shown in Figure 6. The tenacity tests of the PP fibers were 1.29 gf/den. The tenacity of the fiber composite containing 1wt% and 3wt% of TiO_2 decreased 45% and 49%, respectively. Moreover, the TiO_2/PP containing 5%wt of TiO_2 were lowest at 0.21gf/den. On the other hand, the tenacity of the TiO_2/PP fibers composite containing 10%wt-30%wt of TiO_2 could not pass the test due to the fibers vey brittle. It was confirmed that tenacity of the fiber decreased when increased the TiO_2 in the fibers.

3.2.4 Differential Scanning Calorimetry (DSC)

The melting point, crystallinity temperature and % crystallinity of the TiO_2/PP fibers composite were explored using Differential Scanning Calorimetry. There were no significant difference of themelting temperature when increase the amount of TiO_2 from 1wt% to 30wt% as shown in Table 1.The crystallinity temperature were slightly increased when raised the loading amount of TiO_2 in the fibers composite. However, the %crystallinity of the fibers composite dramatically decreased when increased 1%wt of TiO_2. After increasing the amount of the TiO_2 from 1%wt to 30wt%, the % crystalinity were slightly fluctuated. It was concluded that the TiO2 could be affected the % crystalinity.

Table 1. Thermal properties of the melting point, crystallinity temperature and % crystallinity of the TiO_2/PP fibers composite containing 1%wt-30%wt of TiO_2

	T_m	T_c	%Crystallinity
PP	167.8	114.7	40.5
PP-1%TiO_2	168.0	115.0	6.6
PP-3%TiO_2	169.2	116.1	8.3
PP-5%TiO_2	168.5	116.0	7.0
PP-10%TiO_2	165.8	119.5	4.5
PP-15%TiO_2	166.5	122.0	6.8
PP-20%TiO_2	166.5	122.0	7.3

3.2.5 Self cleaning Test

The self-cleaning properties of the TiO_2/PP fibers composite stained with coffee were investigated under sunlight and 20watt UV radiation. The result shown that the coffee stained on the composite fibers were decreased the stain color when increased loading amount of TiO_2 from 1%wt to 30%wt. The coffee stain on TiO_2/PP fiber containing 20%wt of TiO_2were relatively removed under sunlight and 20watt UV radiation.

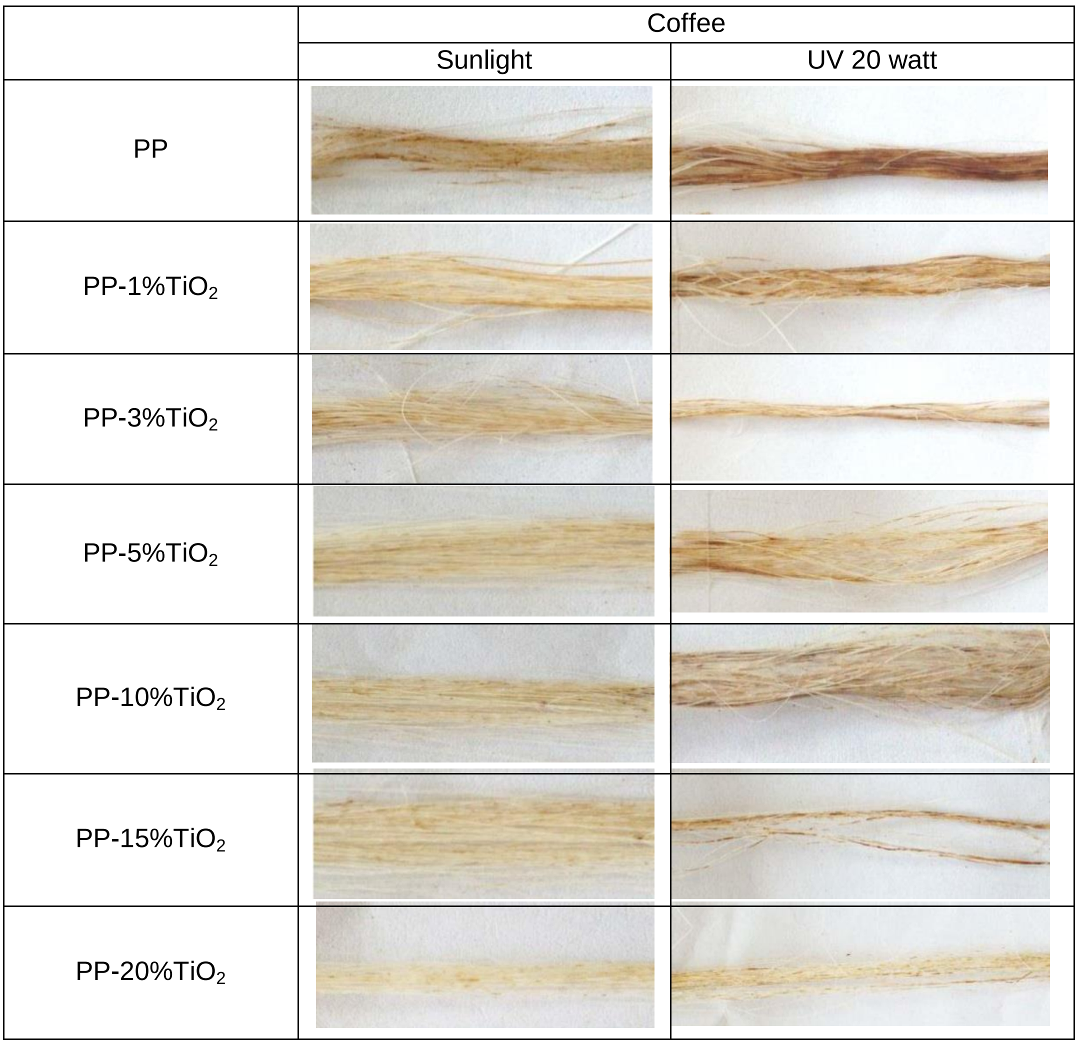

Figure 7. The photography of the self-cleaning test of the PP fibers and TiO2/PP fibers composite containing 1%wt-20wt% of TiO_2 stained with coffee under sun light and 20 watt UV radiation.

4. CONCLUSION

The aim of this study was to study the self-cleaning properties of PP-TiO_2 fibers. Variation of the TiO_2 content in the PP fibers composite resulted in self-cleaning properties of the fibers. With increase in the amount of TiO_2 in PP fibers composite, the self-cleaning properties of the PP fibers composite gradually increase. The Melt Flow Index of the TiO_2-PP fibers composite also provides proof of well blending. SEM micrographs show the fracture surface of the TiO_2 fibers composite at different ratio. The tensile properties of the TiO_2-PP fibers results provide further evident to proof that this fibers composite able to make a textile products.

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REFERENCES

[1] Niedermeier, M.A., et al., "Combining mixed titania morphologies into a complex assembly thin film by iterative block-copolymer-based sol–gel templating," *Nanotechnology*, Vol. 23, No. 14, pp. 145602 −145610, 2012.
DOI: 10.1088/0957-4484/23/14/145602

[2] Athanassiou A, et al., "Reversible wettability of hybrid organic/inorganic surfaces of systems upon light irradiation/storage cycles," *International Journal of Nanomanufacturing*, Vol. 6, No. 1/2/3/4, pp. 312-323, 2010.
DOI: 10.1504/IJNM.2010.034793

[3] Fateh, R., R. Dillert, and D. Bahnemann, "Self-Cleaning Properties, Mechanical Stability, and Adhesion Strength of Transparent Photocatalytic TiO2–ZnO Coatings on Polycarbonate," *Applied Materials & Interfaces*, Vol. 6, No. 4, pp. 2270-2278, 2014.
DOI: 10.1021/am4051876

[4] Kapridaki, C. and P. Maravelaki-Kalaitzaki, "TiO2-SiO2-PDMS nano-composite hydrophobic coating with self-cleaning properties for marble protection," *Progress in Organic Coatings*, Vol. 76, Issues 2-3, pp. 400-410, 2013.
DOI:10.1016/j.porgcoat.2012.10.006

[5] Y. Paz, et al., "Photooxidative self-cleaning transparent titanium dioxide films on glass," *Journal of Materials Research*, Vol. 10, No. 11, pp. 2842-2848, 1995.
DOI: http://dx.doi.org/10.1557/JMR.1995.2842

[6] Karimi, L., et al., "Effect of Nano TiO 2 on Self-cleaning Property of Cross-linking Cotton Fabric with Succinic Acid Under UV Irradiation," *Photochemistry and Photobiology*, Vol. 86, Issue 5, pp. 1030-1037, 2010.
DOI: 10.1111/j.1751-1097.2010.00756.x

[7] Yaghoubia, H., N. Taghaviniab, and E.K. Alamdaria, "Self cleaning TiO2 coating on polycarbonate: Surface treatment, photocatalytic and nanomechanical properties," *Surface and Coatings Technology*, Vol. 204, Issue 9-10, pp. 1562-1568, 2010.
DOI:10.1016/j.surfcoat.2009.09.085

[8] Ohkoa, Y., et al., "Photoelectrochemical Anticorrosion and Self-Cleaning Effects of a TiO2 Coating for Type 304 Stainless Steel," *Journal of the Electrochemical Society*, Vol. 148, No.1, pp. B24-B28, 2001.
DOI: 10.1149/1.1339030

[9] Gopal K. Mora, et al., "A room-temperature TiO2-nanotube hydrogen sensor able to self-clean photoactively from environmental contamination," *Journal of Materials Research*, Vol. 19, Issue. 2, pp. 628-634, 2004.
DOI: http://dx.doi.org/10.1557/jmr.2004.19.2.628

[10] Quagliarini, E., et al., "Self-cleaning and de-polluting stone surfaces: TiO 2 nanoparticles for limestone," *Construction and Building Materials*, Vol. 37, pp. 51-57, 2012. DOI:10.1016/j.conbuildmat.2012.07.006

[11] A. Fujishima, X. Zhang, and D.A. Tryk, "T iO2 photocatalysis and related surface phenomena," *Surface Science Reports*, Vol. 63, Issue 12, pp. 515-582, 2008. DOI:10.1016/j.surfrep.2008.10.001

[12] A. Fujishima, T.N. Rao, and D.A. Tryk, "Titanium dioxide photocatalysis," *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, Vol. 1, Issue 1, pp. 1-21, 2000. DOI:10.1016/S1389-5567(00)00002-2

[13] A. Fujishima and X. Zhang, "Titanium dioxide photocatalysis:present situation and future approaches," *Comptes Rendus Chimie*, Vol. 9, Issue 5-6, pp. 750-760, 2006. DOI:10.1016/j.crci.2005.02.055

[14] K.O. Awitor, et al., "Photo-protection and photo-catalytic activity of crystalline anatase titanium dioxide sputter-coated on polymer films," *Thin Solid Films*, Vol. 516, Issue 8, pp. 2286-2291, 2008. DOI:10.1016/j.tsf.2007.08.005

[15] T. Moskalewicz, A. Czyrska-Filemonowicz, and A.R. Boccacini, "Microstructure of nanocrystalline TiO2 films produced by electrophoretic deposition on Ti–6Al–7Nb alloy," *Surface & Coatings Technology*, Vol. 201, Issue 16-17, pp. 7467-7471, 2007. DOI:10.1016/j.surfcoat.2007.02.016

[16] Saeki, I., et al., "The Photoelectrochemical Response of TiO2 - WO 3 Mixed Oxide Films Prepared by Thermal Oxidation of Titanium Coated with Tungsten," *Journal of The Electrochemical Society*, Vol. 143, No. 7, pp. 2226-2230, 1996. DOI: 10.1149/1.1836984

[17] A. Brevet, et al., "Thermal effects on the growth by metal organic chemical vapour deposition of TiO thin films on (100) GaAs substrates," *Surface and Coatings Technology*, Vol. 151 - 152, pp. 36-41, 2002. DOI:10.1016/S0257-8972(01)01586-9

[18] M. Sasani Ghamsari and A.R. Bahramian, "High transparent sol–gel derived nanostructured TiO2 thin film," *Materials Letters*, Vol. 62, No. 3, pp. 361-364, 2008. DOI: 10.1016/j.matlet.2007.05.053

[19] ukhtar, A.M., *Polypropylene Fibers*, New York: Elsevier Science Publishing Company Inc., 1982.

[20] Washino, W., *Funtional Fibers: Trends in Technology and Product Development in Japan*, Toray Research Center Inc., 1993, Japan**.**

[21] Yuranova, T., et al., "Self-cleaning cotton textiles surfaces modified by photo-active SiO 2 ⁄ TiO 2 coating," *Journal of Molecular Catalysis A: Chemical*, Vol. 244, Issue 1-2, pp. 160-167, 2006. DOI: 10.1016/j.molcata.2005.08.059