Journal of Applied Sciences Research, 9(3): 1731-1742, 2013
ISSN 1819-544X
This is a refereed journal and all articles are professionally screened and reviewed

ORIGINAL ARTICLES

Effect of Surface Activation Method of PET and PET/C Blended Fabrics on its Functional Finishing with TiO_2 Nanoparticles

[1]Shalaby, S.E., [1]Abo El-Ola, S.M., [1]AL-Blakocy, N.G., [1]Beliakova, M.K., [2]Afify, H.

[1]Textile Research Division, National Research Centre, Giza, Egypt
[2] Physics Division , National Research Centre, Egypt

ABSTRACT

Recent studies indicate that treatment of hydrophobic fibers by plasma can significantly enhance the binding efficiency of TiO_2 nanoparticles. However, up till now this approach has not been applied on industrial scale. Therefore it seems of great interest to clarify the possibility of applying the chemical activation method as a practical alternative to the plasma approach. Stemming from the above mentioned, the present work discuses the effect of applying Dielectric Barrier Discharge (DBD) plasma and alkali hydrolysis, on the functional finishing of PET and PET/C blended fabrics with TiO_2 nanoparticles. Characterization of the so finished PET fabrics was carried out through Scanning Electron Microscopy (SEM), Energy Dispersion Emission X-ray (EDX), Infrared Spectroscopy (FT-IR), and X-ray Diffraction (XRD). SEM shows a more uniform distribution of TiO_2 on the PET fabrics activated with alkali hydrolysis. EDX and FT-IR Spectroscopy have confirmed that TiO_2 is chemically bonded to polyester fabrics. The effect of surface activation method on the multifunctionality of PET fabrics was evaluated by analyzing its antimicrobial activity and UV protection efficiency. The level of UV protection was verified by the UV protection factor (UPF) of fabrics. The antimicrobial activity was tested against Gram- positive *B. mycoides*, Gram-negative *E. coli* and nonfilamentous fungi *Candida albicans*. It has been found that PET fabrics activated with alkali hydrolysis loaded with TiO_2 nanoparticles showed better antimicrobial activity and UV protection efficiency compared to the plasma activated fabrics. The advantage of alkali treated fabrics became even more prominent after washing test. These fabrics exhibited outstanding antimicrobial activity and UV protection efficiency even after five washing cycles, indicating excellent laundering durability.

Key words: PET fabrics, alkali hydrolysis, DBD plasma, TiO_2 NP, Sol-Gel, EDX, SEM, FT-IR, Antimicrobial, and UPF.

Introduction

Recent trends in textile industry are oriented towards development and manufacturing of high added value products with multifunctional properties. The application of nanoparticles to textile materials has been the subject of several studies aimed at producing finished fabrics with different performances (Lee, *et al* 2003; Xin, *et al* 2004; Wang, *et al* 2005; Becheri, *et al* 2002; Mihailvoic, *et al* 2008; Mihailvoic, *et al* 2010;Ilicm *et al* 2009 and Mejia, *et al* 2011). This is mainly due to the fact that conventional methods used to impart different properties to fabrics often do not lead to permanent effects, and will lose their functions after laundering or wearing. Nanoparticles can provide high durability for treated fabrics, with respect to conventional materials, because they posses large surface area and high surface energy that ensure better affinity for fabrics and lead to an increase in durability on the textile functions (Becheri, et al 2002).

Several recent studies reported the promising potentials of nontoxic and inexpensive TiO_2 nanoparticles for imparting multifunctional properties to different textile materials (Bozzi, et al 2005; fu, et al 2005; Stamate and Lazar, 2007; Han and Yu, 2006; Qim et al 2007 and Meilert, et al 2005). The compatibility of TiO_2 nanoparticles with fiber surface chemical functionalities is one of the most important prerequisites for obtaining stable composite system and long-term durability effects (Mihailvoic, et al 2010). The tailoring of desirable fiber surface from the standpoint of its chemical functionality and improvement of TiO_2 nanoparticles binding efficiency has recently gained much scientific interest. Recent studies indicated that treatment of hydrophobic fibers by low-pressure plasma and corona at atmospheric pressure can significantly enhance the binding efficiency of TiO_2 nanoparticles (Mihailvoic, *et al* 2008; Bozzi, *et al* 2005 and Qi, *et al* 2007). However, uptill now this approach has not been applied on industrial scale. It is well known that the main players in binding TiO_2 nanoparticles are hydroxyl and particularly carboxylic groups. It was shown that the introduction of additional carboxylic groups to wool has likely induced more efficient binding of TiO_2 nanoparticles and more

Correspondence Author: S.E. Shalaby, Textile Research Division, National Research Centre, Giza, Egypt
E-mail: samyshalaby40@yahoo.com

uniform coating of the fiber surface, which in turn resulted in enhanced self-cleaning efficiency. Meilert *et al* 2005 have used commercially available nontoxic and low cost saturated polycarboxylic acids as chemical spacers to attach TiO_2 nanoparticles to cotton (Meilert, *et al* 2005). Dauod *et al* 2008 reported that acylation of wool fibers with non-toxic succinic acid anhydride led to an increase in reactivity toward anatase nanoparticles.

Stemming from the above mentioned and from the fact that, industrial wet processing line for natural and man-made fibers includes scouring the fabrics in alkaline solution, which leads to the creation of additional carboxylic groups in PET macromolecule, it seems of a great interest to clarify the possibility of applying the chemical activation method as a practical alternative to the plasma approach. Therefore the present work discuses the effect of applying Dielectric Barrier Discharge (DBD) plasma and alkali hydrolysis, as treatment for fiber surface activation of PET and PET/C blended fabrics, on its functional finishing with TiO_2 nanoparticles.

Experimental:

2.1. Materials:

- Bleached polyester 100% Trevira (165 gr/m^2), polyester/cotton (50:50) blend woven fabric (236 gr/m^2), and polyester nonwoven fabric (117.7 gr/m^2; 1.03-mm thickness) were used throughout this work. All types of used fabrics were provided by local textile industries.
- All chemical used in this work (titanium tetra – isopropoxide (TIP), nitric acid, ethyl alcohol and hydrochloric acid were purchased from Fluka and have been used as received.
- *Bacillus mycoides* (*B. m*) (Gram positive bacterium), *Escherichia coli* (*E.c*) (Gram negative bacterium), and *Candida albicans* (*C.a*) (nonfilamentous fungus) were used for estimation of antimicrobial potency of control and treated samples. Microorganisms were obtained from the culture collection of the Microbial Chemistry Department, Division of Genetic Engineering and Biotechnology, National Research Centre of Egypt.

2.2. Methods:

- *Preparation of TiO_2 Colloid Solution:*

The TiO_2 –gel containing TiO_2 particles was prepared as follows: Titanium tetraisopropoxide (TIP) (20 ml) was added drop wise to 300 ml of 2-propanol acidified with 1 ml of concentrated HNO_3 and cooled to 0^oC. This solution was stirred for 1 h to achieve the total dissolution of resulting polymeric chains and produce a transparent solution (*Bozzi, et al 2005)*.

- *Preparation of Activated PET:*

Two different methods were used to activate polyester fabrics:

(a) Polyester woven and nonwoven fabrics of 10 cm diameter were pretreated in DBD – plasma cavity at constant discharge conditions (electrode gap distance 3 cm, plasma treatment time 10 minutes , input voltage 3w, input frequency 50 Hz, electric current 1.5 mA) and under various gaseous environments (air, oxygen , oxygen/ argon 50:50, and argon) .

(b) Polyester fabrics were partially hydrolyzed according to the method described by Shalaby, *et al* 2007.

- *Loading of PET Fabrics with TiO_2 Nanoparticles:*

Plasma or alkali pre treated PET textiles samples were immersed in TiO_2 colloidal solution, squeezed to the required pickup percent, dried in air at 22^oC (room temperature) for 24 hours and then cured in an oven at 130^oC for 15 minutes. The PET samples were then washed with distilled water to remove TiO_2 particles that did not attach to the fabric surface. In order to evaluate the TiO_2 nanoparticles adhesion to the PET textiles, the treated woven and nonwoven fabrics were washed five cycles according to the standard AATCC test method (61-1989).

2.3. Analysis:

- Carboxylic content was determined according to the method described by Daul, *et al* 1953.
- Antimicrobial activity of PET fabrics loaded with TiO_2 nanoparticles was quantified using the following methods:

J. Appl. Sci. Res., 9(3): 1731-1742, 2013

1. Disk diffusion method:

in this method the antimicrobial potency by diffusion was quantified by measurement in millimeters of the width of the zone of growth inhibition around the sample according to AATCC standard test method (Koneman, *et al* 1997).

2. Shake Flask method:

in this case the antimicrobial activity of immobilized antimicrobial agents is determined under dynamic contact conditions according to ASTM standard test method 2149 (2001).

- Fiber morphology was characterized by scanning electron microscopy (SEM, JEOL JSM T2O). Electron dispersion Emission X-ray (EDX) mode was applied for the elemental composition analysis. Gold layer was deposited on the samples before the analysis.
- The chemical structure of unloaded and loaded with TiO_2 nanoparticles PET samples was determined using the Fourier Transformation Infrared (FT-IR) spectrometer, model NFXUS 670, NICLET USA. The measurements were carried in the spectral range from 4000 to 500 cm^{-1}. Reflection percentage measurement technique (R %) was applied to all investigated samples.
- The surface chemical composition of polyester fabrics was analyzed by XRD. The XRD spectra were obtained from the analytical EMPYREM2 (Netherland) with Cu radiation (λ= 1.5406 Å), the tube operated at 45 KV, and 30 mA, 2θ=10-60, step size=0.026, step time 20 sec/step.
- Ultraviolet Protection Factor (UPE) was determined using UV-Shimadzu 3101 PC Spectrophotometer. It is a double beam direct ratio measuring system. It consists of photometer unit and a PC computer. The UPF values were automatically calculated on the basis of the recorded data in accordance with Australia/ New Zealand standard AS/NZS 4395:1995 (Gambichler, *et al* 2001)

UV protection and classification according to AS/NZS 4395:1996

UVP	UPF classification
Excellent	40, 45, 50, 50+
Very good	25, 30, 35
Good	15, 20
Non- ratable	5, 10

Results and Discussion

In Sol-gel synthesis technique, TiO_2 nano-sol was formed in a single step by continuous stirring of mixture of TIP with 2-propanol in acidic medium (HNO_3) solution. This nano-sol was applied directly on the PET fabrics and the nano- TiO_2 is generated in – situ during the hydrothermal treatment. During this synthesis the following chemical reactions occur:

$$Ti\ (O\text{-}ipr)_4 + H_2O \rightarrow Ti(OH)_4 + 4\ prOH \quad (i)$$

$$Ti\ (OH)_4 \rightarrow TiO_2 + 2H_2O \quad (ii)$$

To evaluate the effect of the method applied for surface activation on binding efficiency of nanoparticles, PET fabrics were initially treated by dielectric barrier discharge (DBD) plasma, in one hand, and with alkali solution, on other hand before loading with TiO_2 nanoparticles. X-ray photoelectron Spectroscopy (XPS) analysis was applied to investigate what functional groups were formed by the plasma treatment has reviled that the functional group distribution of the original PET fabrics before plasma treatments, consisted of 76.72% C-C and C-H groups, 9.81% C-O group and 2.96% O-C=O group. After the plasma treatment, the concentration of the oxidized carbon components (C-O and O-C=O) increased to 12.4% and 8.21% for the C-O and O-C=O groups, respectively, whereas the concentration of the C-C and C-H decreased to approximately 68.21% [Ilic, *et al* 2009 and Onssuratoom, *et al* 2010). These results reveal that air DBD plasma mainly affects the C-C and C-H groups on the PET surface to form more C-O and O-C=O groups .

The above mentioned results were experimentally confirmed by the determination of function groups existing on the surfaces of PET fabrics before and after the activation step. It was found (Table 1) that surface activation leads, in general, to an increase in carboxylic content for PET fabrics, irrespective of the method applied for activation. Plasma treatment brings about an outstanding increase in carboxylic content from 2.95 to 38.50 meg/100 gr fabric and from 5.0 to 43.2 for PET and PET/cotton blend fabrics, respectively. This is in contrast with 11 meq/100gr fabrics and 22.4 meq/ 100 gr fabrics in case of partially hydrolyzed with alkali water solution PET and PET/C blend fabrics.

The presence of TiO_2 nanoparticles on the surface of PET fabrics was confirmed by SEM analysis performed in EDX mode. EDX spectra of the PET fabrics loaded with TiO_2 nanoparticles following the washing step are shown in Figures 1 and 2. On the basis of these spectra, it is noteworthy to conclude that the deposited material consisted of Ti and oxygen. This shows that even after five washing cycles (25 home washings), TiO_2 is still present on the PET fabrics surface (Table 1). EDX measurements also reveal higher Ti content on hydrolyzed PET/C fabrics (6.76 atomic %). This means that TiO_2 nanoparticles have sufficient adhesion towards the activated PET fabrics either by plasma or by alkali treatments.

Characterization of PET Fabrics Loaded with TiO_2 Nanoparticles:

It would be of interest to find out whether the coating or immobilization of TiO_2 nanoparticles on activated fabrics is through physical or chemical interactions. Therefore, characterization of the so finished PET fabrics was carried out through scanning electron microscope (SEM), FTIR and X-ray diffraction measurements (XRD).

SEM:

The surface topography of PET fabrics was investigated using SEM technique (Figure 3). Based on the images seen in Figure 3 the following can be concluded:

1- The surfaces of untreated PET and PET/C fabrics are clean and smooth [Figure 3 (a) and (b)].

2- The treatment of the fabrics with TIP leads to the formation of some precipitation on the surface of treated fabrics. The shape and the size of such precipitation vary according to the fabrics used during the plasma treatment as follows:

(a) The plasma treatment of PET fabrics in the presence of air followed by loading with TiO_2 nanoparticles leads to the formation of a thick layer on the surface of fabrics in the form of coating with cracks perpendicular to fiber axis (Figure 3c). These findings are in full agreement with the data obtained by EDX technique. It is worth mentioning that washing for 5 cycles has led to a decrease in the number of cracks and partial disappearance of the precipitates (Figure 3d).

Table 1: The effect of surface Activation Method on Both Carboxylic Content and Amount of TiO_2 NanoparticlesLoaded on PET Fabrics

Surface Activation Method		Fabrics								
		PET			PET/Cotton			PET nonwoven		
		Carboxylic content (meq/100 gr fabric)	Ti content (Atomic %) Estimated by EDX after washing Cycles:		Carboxylic content (meq/100 gr fabric)	Ti content (Atomic %) Estimated by EDX after washing Cycle:		Carboxylic content (meq/100 gr fabric)	Ti content (Atomic %) Estimated by EDX after washing Cycles:	
without		2.95	0.0		4.99	0.0		2.15	1*	5*
									0.0	
Plasma	Air	38.49	1*	5*	43.22	8.56	1.36	46.9	10.58	0.41
			8.82	1.83						
	O_2	36.48	1*		29.45	1*			1*	
			3.97			4.37		34.49	5.01	
	Ar	34.88	3.6		28.65	2.68		32.78	1.24	
	O_2/ Ar	29.88	0.93		35.64	1.69		34.59	0.8	
Alkali Hydrolysis		10.91 (Wl**=28%)	5*		22.38 (Wl**=19%)	5*		-	--	
			2.88			6.76				

Plasma Treatment Condition:

Electrode Gap Distance, 3 mm; Treatment Time, 10 min.; power, 3 w.; frequency, 50 Hz; I, 1.5mA

Alkali Hydrolysis Treatment Conditions:

[NaOH], 1.5 mol/L; Time, 60 min.; Temperature, 100 ^oC ; M:L ,1.50

Sol-gel Treatment Conditions:

[Titanium isopropoxid], 3.3×10^{-1} mol/L; curing time, 15 min; curing Temperature, 130 ^oC, *According to AATCC Method (61- 1989), ** weight loss

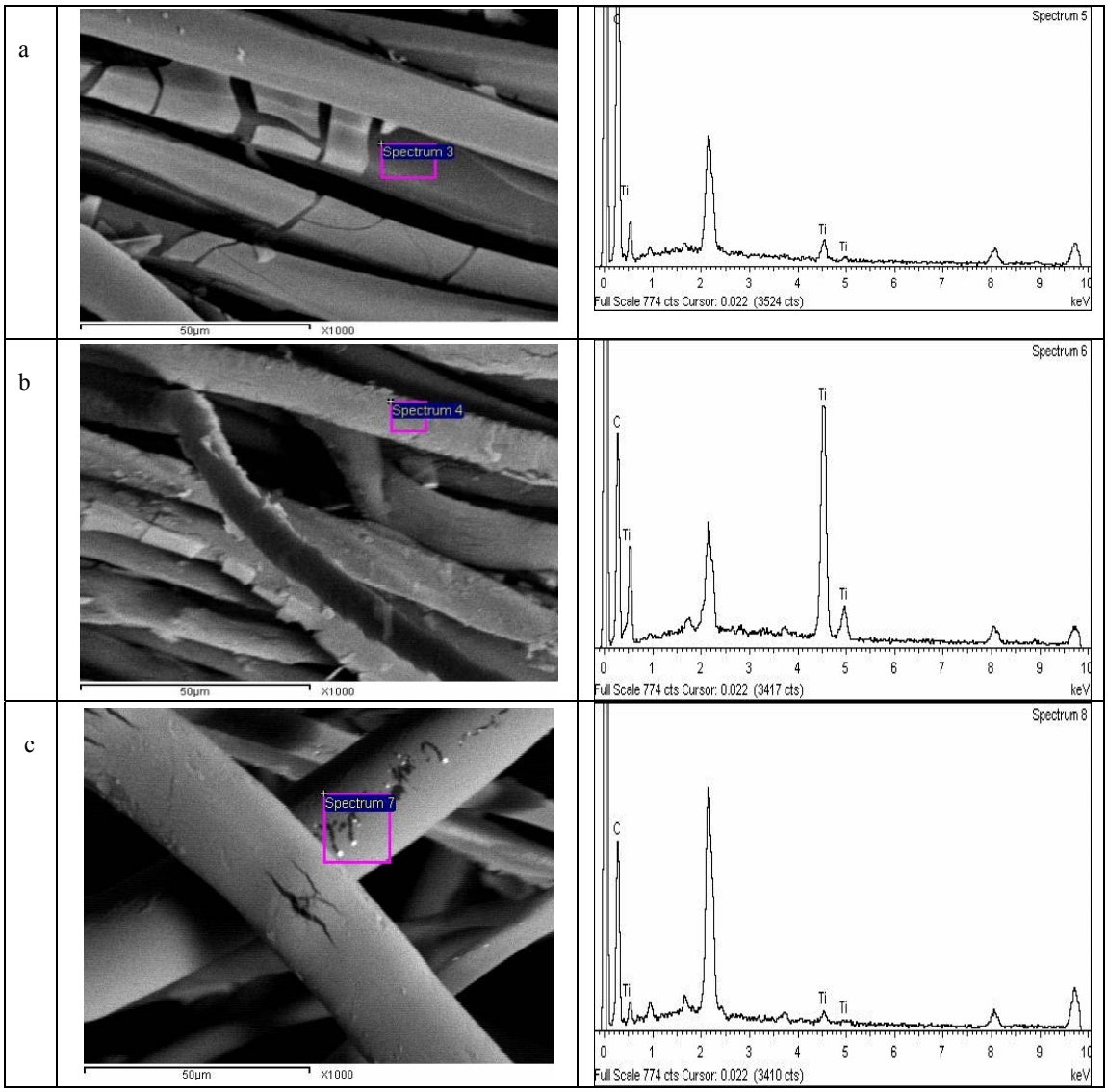

Fig. 1: EDX Spectra of PET Fabrics Activated wit Air Plasma and Loaded with TiO_2 Nanoparticles *
(a) PET Fabric+TiO_2
(b) PET/C Fabric + TiO_2
(c) PET Nonwoven Fabric + TiO_2
*After one Washing Cycle; AATCC Test Method (61-1989)

This once again is in good agreement with the residual Ti percentage on the surface of PET fabrics (Table 1).

(d) After 5 washing cycles (Figure 3-f); the fact which is in agreement with the residual Ti% on the fiber surface (Table 1).

(c) Treatment of PET nonwoven fabrics with TIP after activation with plasma in the presence of air is also accompanied with the formation of precipitates which disappear largely after 5 washing cycles [Figure 3 (g),(h)]. This is reflected on the amount of Ti percentage on the fiber's surface (Table 1).

3. PET and PET/C fabrics hydrolyzed with NaOH solutions before treatment with TIP are characterized with pits and grooves. The treatment with TIP leads to blocking these defects and formation of thin layer of active substrate on the fiber surface [Figure 3 (I), (j)].

The above mentioned changes which took place on the surface topography of PET fabrics loaded with TiO_2 nanoparticles are a direct indication that Ti nanoparticles are attached to the fabrics surfaces.

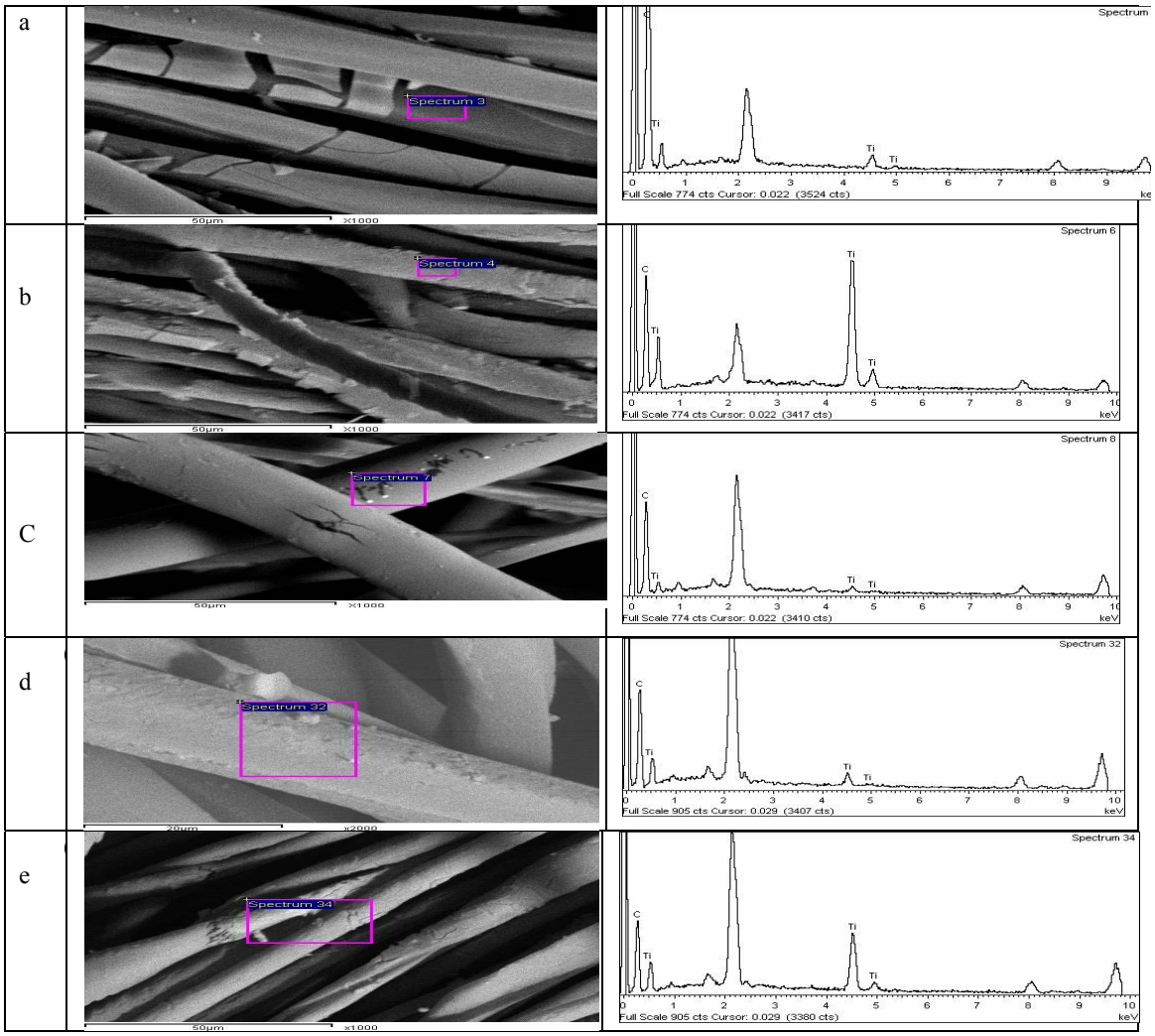

Fig. 2: EDX Spectra of PET Fabrics Activated with Air plasma and Alkali Hydrolysis and Loaded with TiO_2Nanoparticles*
(a) PET Fabric+TiO_2 (b) PET/C Fabric + TiO_2 (c) PET Nonwoven Fabric + TiO_2
(d) PET Fabric , Hydrolyzed (WL**28%) +TiO_2 (e) PET/C Fabric , Hydrolyzed (WL**19%) + TiO_2
*After Five Washing Cycles; AATCC Test Method (61-1989) ** WL= Weight Loss (%)

FT-IR:

Evidently, alkali hydrolysis and DBD plasma activation induced a significant change in the chemical composition of the polyester fabrics surfaces. The FTIR spectrum (Figure 4) of unmodified PET fabric shows absorptions at 1649-1712, 3408-3388, and 2317 cm^{-1}, which are typical to those of C=O, OH, and CH stretching respectively. New bands at 847 and 689 cm^{-1} respectively, are observed in the spectrum of PET and PET/C fabrics activated with alkali hydrolyzed which can correspond to Ti-O of the new bonds PET+ TiO_2 and PET/C blend + TiO_2. The presence of this band can support the ionic character of the new band formed due the addition of TiO_2NPs to alkali hydrolyzed fabrics. The FT-IR spectrum of activated PET, PET/C blend and PET nonwoven fabrics with DBD plasma and loaded by TiO_2NPs (Figure A5) shows that new characteristic peaks are appeared and located at around 558 cm^{-1} and 888 cm-^{1} , as well as 794 cm^{-1} , respectively. These peaks are corresponding to Ti-O bond. The similar finding was reported by *Qi, et al 2007*. During this study we found that only activated surfaces were able to fix TiO_2NPs from sol-gel solutions.

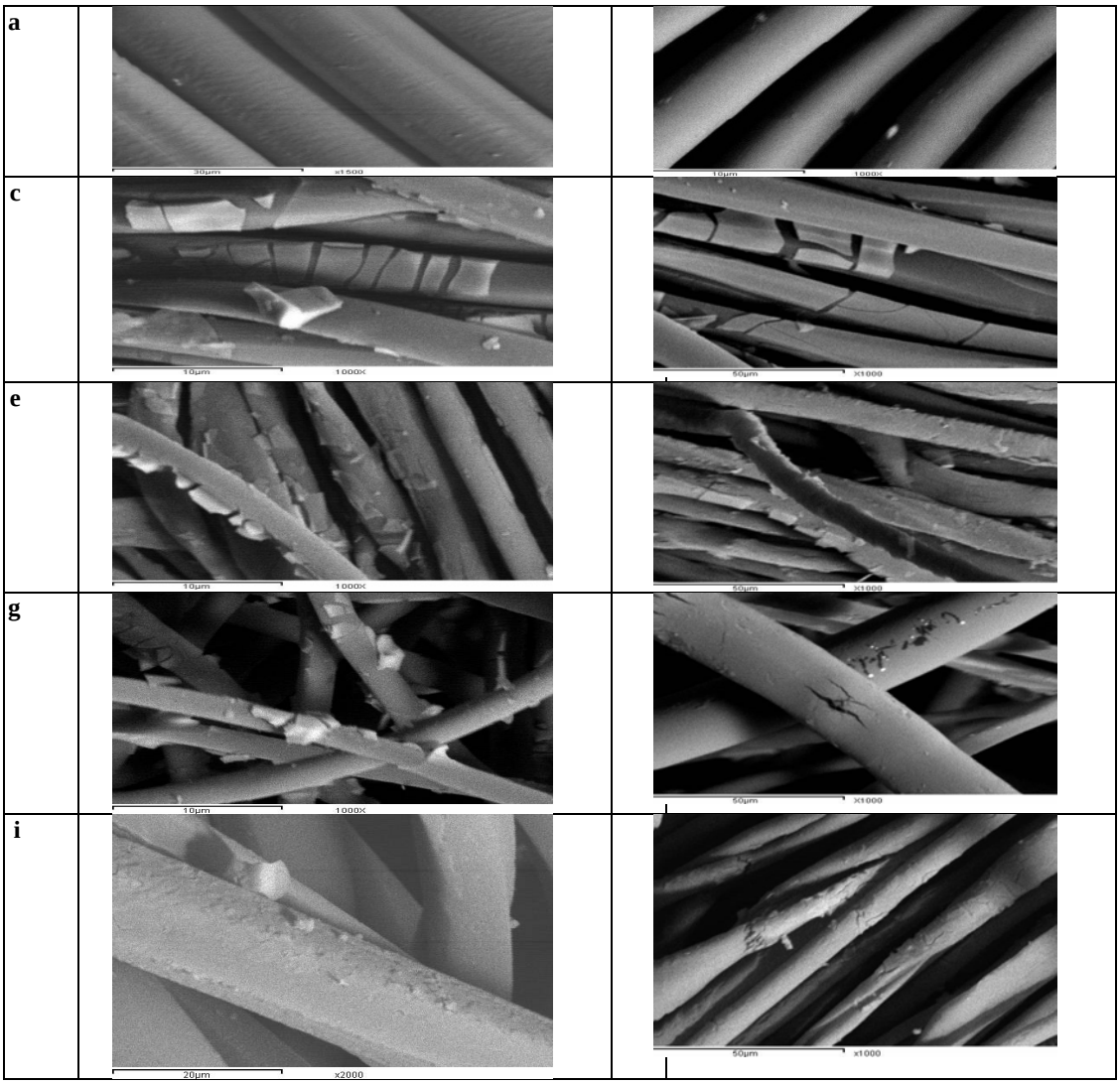

Fig. 3: SEM Micrographs of PET Fabrics Activated with Air Plasma and Alkali Hydrolysis and Loaded with TiO_2 Nanoparticle
(a) PET Fabric Untreated (b) PET/C Fabric Untreated (c) PET Fabric+TiO_2*(Pl)
(d) PET Fabric+TiO_2** (Pl) (e) PET/C Fabric + TiO_2*(Pl) (f) PET/C Fabric + TiO_2** (Pl)
(g) PET Nonwoven Fabric + TiO_2*(Pl) (h) PET Nonwoven Fabric + TiO_2** (Pl)
(i) PET Fabric (WL**28.0%) +TiO_2 Hydrolyzed (j) PET/C Fabric (WL**19.0%) + TiO_2 Hydrolyzed
(Pl) = plasma * and **after One and five Washing Cycles; AATCC Test Method (61-1989) WL= Weight Loss (%)

X-ray Diffraction Measurements:

The internal structure of activated PET fabrics and loaded with TiO_2NPs was investigated by XRD technique. Based on the results obtained in Table (2), the following can be concluded:

1- All investigated samples have the same diffraction patterns with three peaks at 2Θ values 17.5, 22.50^o and 26.0^o, irrespective of the type of PET fabrics and the activation method used. There aren't any individual peaks characteristic to the pure TiO_2NPs phase in the range of 2Θ (25^o to 45^o) on the XRD patterns of any treated sample irrespective of the type of activation. This may be attributed to the formation of chemical bonds between Ti-O groups of TiO_2 and COOH groups formed on modified PET surfaces. This was confirmed by FT-IR analysis.

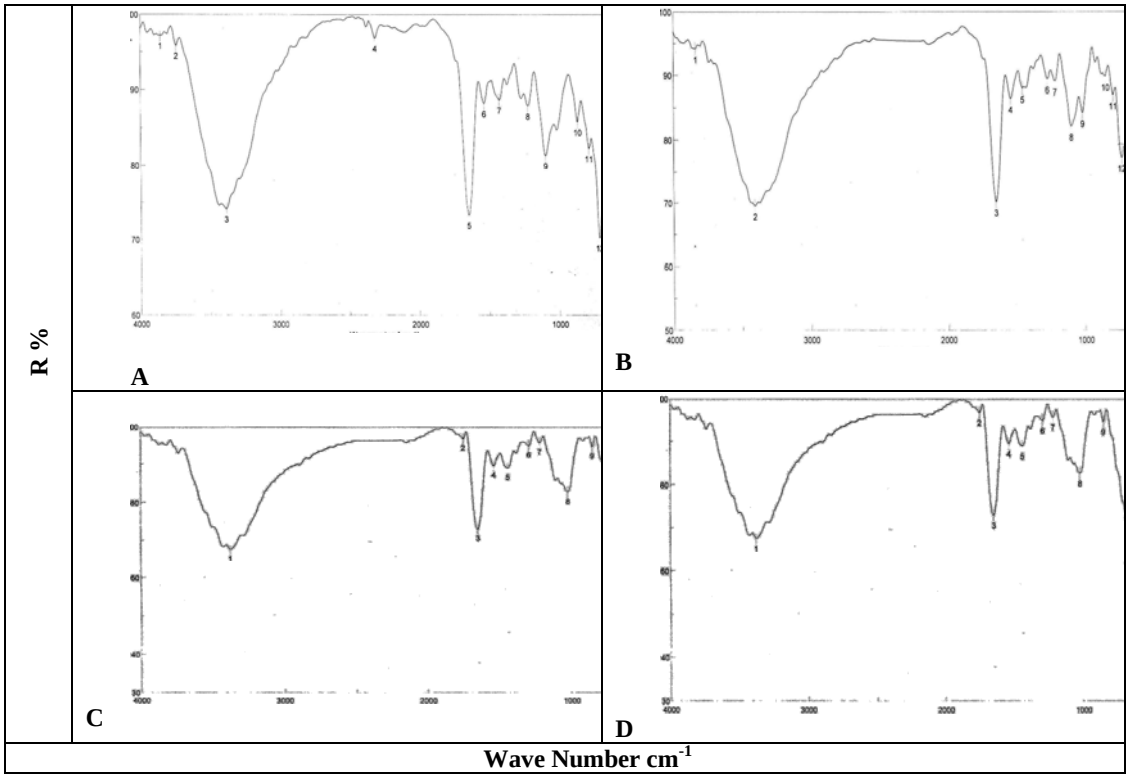

Fig. 4: FT-IR Spectra of PET Fabrics Activated with Alkali Hydrolysis and Treated With TIP* (1000x)
(A) PET Fabric-H (WL**28%) (B) PET Fabric -H (WL**28%)+TiO_2
(C) PET/C Fabric-H (WL**19%) (D) PET/C Fabric-H (WL**19%) + TiO_2
*After Five Washing Cycles; AATCC Test Method (61-1989) **WL= Weight Loss (%)

2- It can be seen from Table (2) that, the peak intensities of the modified PET fabrics and loaded by TiO_2NPs became weaker compared to those of the untreated PET fabrics. This may be attributed to the presence of TiO_2 NPs on PET surface which shields the X-ray beam, making the intensities of the peaks of PET treated with TiO_2NPs to appear weaker.

3- A minor change in the interplaner spacing (d-Spacing) and 2Θ values for all investigated samples are observed with no specific trend.

4- The full width at half maximum (FWHM) of the XRD peaks corresponds to activated PET fabrics and loaded by TiO_2NPs are broader than untreated samples. Similar finding was presented by Qi, *et al* 2007. This may be due to overlapping between TiO_2NPs peaks and PET fabrics. The remarkable width of these peaks is a direct indication that the particle size of TiO_2NPs is quite small.

On the basis of the above mentioned results, it can be suggested with a high probability that, the attachment of TiO_2NPs to the PET activated surfaces is electrostatic in nature. This is, mainly, due to the interaction between the positively charged TiO_2 nanoparticles and negatively charged PET fabrics surfaces. The negative charge is due to the $CO\bar{O}$ and C-$\bar{O}$ groups induced on the textile surface by the atomic and ionized O_2 generated in the cavity of the plasma during pretreatment and alkali hydrolysis.

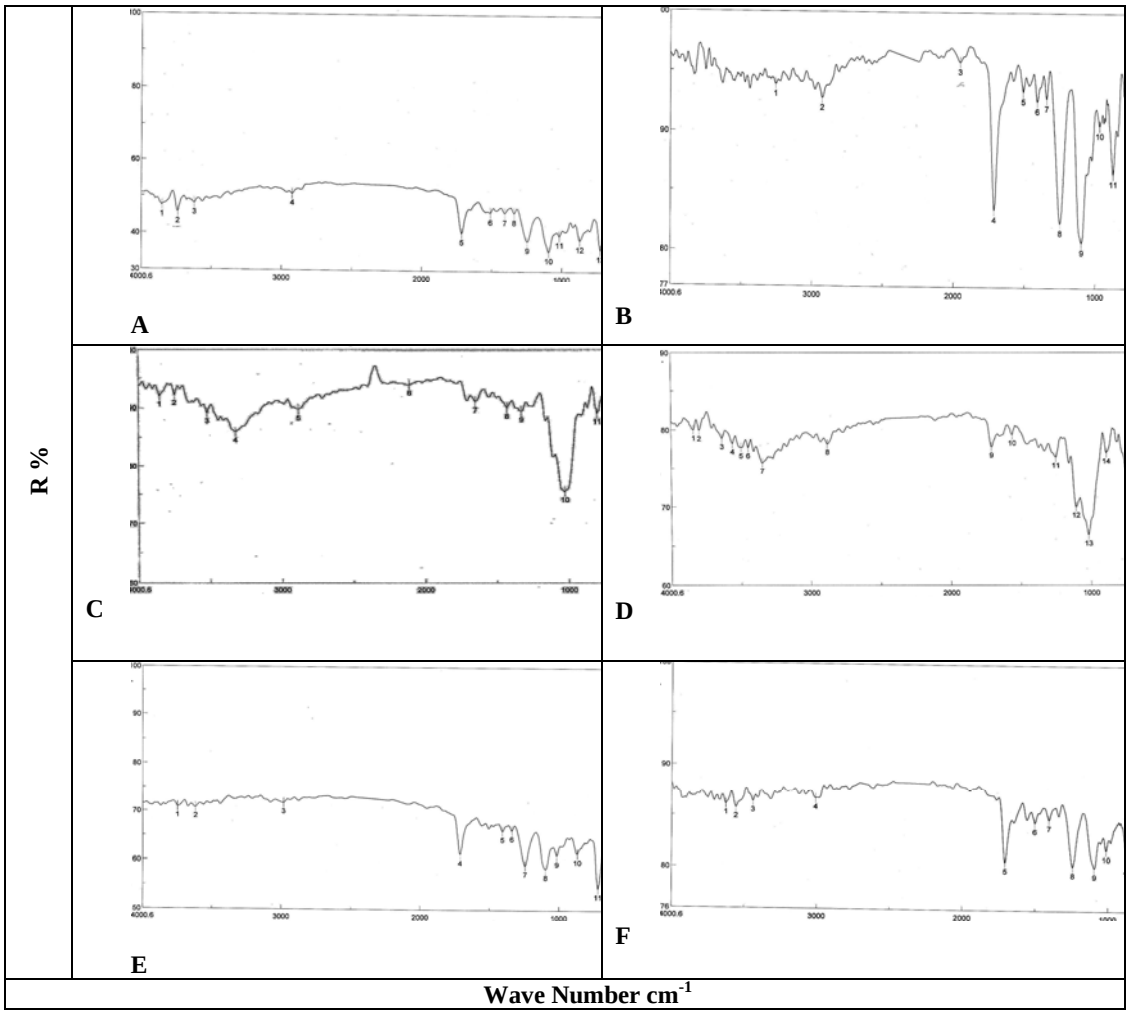

Fig. 5: FT-IR Spectra of PET Fabrics Activated with Oxygen Plasma and Treated With TIP*
(E) PET Nonwoven Fabric (F) PET Nonwoven Fabric + TiO_2
*After One Washing Cycle; AATCC Test Method (61-1989)

Table 2: 2θ, d-Spacing, Relative Intensity, and FWHM for PET Fabrics Activated With Oxygen Plasma* and Alkali hydrolysis **and loaded with TiO_2 nanoparticles

No.	Sample	2θ			d-Spacing			Relative Intensity (%)			FWHM		
		1St	2nd	3rd	1St	2nd	3rd	1St	2nd	3rd	1St	2nd	3rd
1	PET*	17.6	22.4	26.0	5.1	3.97	3.429	29.83	48.24	100	2.80	3.00	5.20
2	PET*+TiO_2	18.0	22.10	26.00	5.057	4.024	3.426	17.78	41.92	100	3.00	3.70	6.50
3	PET/C*	14.92	16.38	22.73	5.934	5.262	3.908	17.33	36.46	100	0.95	2.51	1.79
4	PET/C*+TiO_2	14.66	16.57	22.64	6.038	5.345	3.924	17.37	24.30	100	1.04	2.17	1.36
5	PET Nonwoven*	17.47	22.55	25.88	5.072	3.940	3.440	57.29	72.90	100	2.51	4.00	2.88
6	PET Nonwoven*+ TiO_2	17.57	22.53	25.81	5440	3.940	3.450	58.20	67.59	100	2.28	3.60	3.26
7	PET-H (WL =22%)	17.40	22.40	26.17	5.084	3.971	3.403	46.52	60.62	100	3.00	4.00	5.00
8	PET-H (WL =22%)+TiO_2	16.24	17.40	22.60	5.455	5.088	3.924	17.46	75.36	100	0.80	2.90	4.40
9	PET/C-H (WL =19%)	14.85	16.68	22.80	5.960	5.310	3.293	23.01	34.22	100	1.31	2.91	1.90
10	PET/C-H (WL =22%)+TiO_2	14.64	16.45	22.61	6.045	5.383	3.930	13.52	24.01	100	1.19	2.40	1.52

PL=plasma, H = hydrolyzed, * after one and ** five washing cycle AATCC Test Method (61-1989)

Antimicrobial Activity:

The antimicrobial activity of PET fabrics activated with plasma on one hand, and with alkali hydrolysis, on the other hand, and loaded with TiO_2NPs, was investigated against Gram-positive *B. mycoides*, Gram-negative, *E. coli* and non-filamentous fungus *C. albicans*. The activity by diffusion is quantified by the measurement in

millimeters of the width of the zone of inhibition around the sample. Table 3 indicates the antimicrobial activity of PET, PET/C, and nonwoven PET fabrics loaded with TiO_2NPs after activation with different methods. It is seen from the data listed is this table that , all PET fabrics showed, after one washing cycle, high antimicrobial activity against the previously mentioned three microorganisms. In fact, the inhibition zones for all tested PET fabrics samples are significant, whereas it is null for all the unactivated ones. The role of activation of PET fabrics with alkali hydrolysis before loading with TiO_2NPs on the antimicrobial activity seems to be more significant as the samples were laundered repeatedly in launder-Ometer. It was found that, the bioactivity of the substrates activated either by plasma or by alkali hydrolysis became significantly different (Table 4). The decrease in antimicrobial activity of PET and PET/C fabrics activated by plasma occurred progressively as the number of washes increased. Under these activation conditions both PET and PET/C fabrics has lost about 50% and 20%, respectively, its antimicrobial activity against Gram-positive bacteria *B. mycoides* after 5 Launder-Ometer washes. In contrast in case of hydrolyzed samples, the antimicrobial functions were slightly reduced to certain level. After 5 washing cycles the hydrolyzed PET and PET/C fabrics could still provide 86.3% and 88.1% microbial reduction against *B. mycoides*. This verities the feasibility of the alkali activation of PET fabrics before its antimicrobial finishing with TiO_2NPs.

Table 3: Effect of Surface Activation Method of PET Fabrics on Its Antimicrobial Activity Determined by Disk Diffusion Method

Surface Activation Method		Inhibition Zone Diameter * {mm} In Case of Loaded PET Fabrics with TiO_2 Nanoparticles								
		B .mycoides			*E.Coli*			*C.albicans*		
		PET	PET/C	PET nonwoven	PET	PET/C	PET nonwoven	PET	PET/C	PET nonwoven
Without		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Plasma	Air	12	11	13	17	13	14	16	14	13
	O_2	13	13	13	14	14	14	14	14	13
	Ar	13	13	14	13	14	13	13	13	13
Alkali Hydrolysis		13** (a),(b)	15** (c),(d)	-	13** (a),(b)	13** (c),(d)	-	11** (a),(b)	12** (c),(d)	-

Plasma Treatment Condition:

Electrode Gap Distance, 3 mm; Treatment Time, 10 min.; power, 3 w.; frequency, 50Hz; I,1.5 mA

Alkali Hydrolysis Treatment Conditions:

[NaOH],1.5 mol/L; Time,60 min.; Temperature ,100 ^oC ; M:L ,1.50

Sol-gel Treatment Conditions:

[Titanium isopropoxid], 3.3×10^{-1} mol/L; curing time, 15 min; curing Temperature, 130 ^oC, Carboxylic Content (meq/100g fabric) (a) ,10.9;(c),22.4 ,Ti content (atomic %): (b) ,2.88; (d),6.76,

After one and ** five washing cycles According to AATCC Test Method (61-1989)

Table 4: Effect of Launder-Ometer Washings of PET Fabrics Loaded with TiO_2 Nanoparticles on Its Antimicrobial Activity, Determined By Shake Flask Method

Fabrics	*Number of Washing Cycle*	
	*1**	*5**
	Antimicrobial Activity (as % Microbial Reduction)	
	B.mycoides	
PET +TiO_2	100	49
PET /C+TiO_2	95.9	79
PET Nonwoven +TiO_2	98.7	84
PET – Hydrolyzed +TiO_2(a, b)	95.1	86.3
PET/C +TiO_2 Hydrolyzed(c,d)	96.2	88.1

Plasma Treatment Conditions:

Electrode Gap Distance, 3 mm; Treatment Time, 10 min.; power, 3 w.; Frequency, 50Hz; I, 1.5mA;Environmental gas, oxygen

Alkali Hydrolysis Treatment Conditions:

[NaOH],1.5 mol/L; Time,60 min.; Temperature ,100 ^oC ; M:L ,1.50

Sol-gel Treatment Conditions:

[Titanium isopropoxid], 3.3×10^{-1} mol/L; curing time, 15 min; curing Temperature, 130^oC, Carboxylic Content (meq/100g fabric) :(a) ,10.9;(c),22.4 Ti content (atomic %): (b) ,2.88; (d),6.76, (*) Number of washing cycles According to AATCC Test Method (61-1989)

Ultraviolet Protection Properties:

The effect of activation of PET fabrics either with air plasma or by alkali hydrolysis, before loading with TiO_2NPs, on UV protection efficiency was investigated. The rate of UV protection was quantified and expressed

via UPF values that are given in Table 5. It was found that the UPF factors for unactivated PET, PET/C, and nonwoven PET fabrics are equal to 13.5, 8.7 and 46.7 respectively. Activation with air plasma followed by the TiO_2NPs deposition onto the above mentioned PET fabrics led to a significant increase in UPF factor to the level corresponding to UPF rating of 50+, which assigns the maximum UV protection. After five washing cycles the UPF values for PET, PET/C and nonwoven PET fabrics were decreased to 22.3, 80.4, and 45.6 respectively. These results imply good laundering durability of PET fabrics and excellent laundering durability of PET/C and nonwoven PET fabrics activated with air plasma and loaded with TiO_2NPs.

It was found that, PET and PET/C blended fabrics activated with alkali hydrolysis and loaded with TiO_2NPs showed better UV protection efficiency compared to plasma activated ones. The advantage of alkali treated fabrics became even more prominent after washing test. The UV protection efficiency of these fabrics is by 13.9 % higher even after five washing cycles, indicating the excellent laundering durability.

Table 5: Effect of Surface Activation Method and Launder-Ometer washing of PET Fabrics loaded with TiO_2 Nanoparticles, on Its Ultraviolet Protection Factor (UPF)

No.	Surface Activation Method	Fabrics	UPF values After Washing for			
			1 Cycle (b)		5Cycles (b)	
			UPF Values	UPF Rating	UPF Values	UPF Rating
1	Air Plasma	PET+TiO_2	47.8	Excel	22.3	Good
2		PET/ C+TiO_2	183.5	Excel	80.4	Excel.
3		PET Nonwoven+TiO_2	83.5	Excel	45.6	Excel.
4	Alkali hydrolysis	PET Hydrolyzed (WL 22%)+TiO_2			25.4	V.Good
5		PET/C Hydrolyzed (WL 19%) +TiO_2			91.6	Excel

Plasma Treatment Conditions:

Electrode Gap Distance, 3 mm; Treatment Time, 10 min.; power, 3 w.; frequency, 50Hz; I, 1.5m

Alkali Hydrolysis Treatment Conditions:

[NaOH],1.5 mol/L; Time,60 min.; Temperature ,100 ^oC ; M:L ,1.50

Sol-gel Treatment Conditions:

[Titanium isopropoxid], 3.3×10^{-1} mol/L; curing time, 15 min; curing Temperature, 130^o

Carboxylic Content (meq/100g fabric) :(a) ,10.9;(c),22.4, Ti content (atomic %): (b), 2.88; (d),6.76, (*) After one and (**)five washing cycles According to AATCC Test Method (61-1989)

Conclusions:

The present study illustrates a simple and economic method for enhancing binding efficiency of TiO_2 nanoparticles to PET fabrics. This method is based on applying the chemical activation method as a practical alternative to the plasma treatment before loading PET fabrics with TiO_2 nanoparticles by sol-gel method. These loaded fabrics were characterized by SEM, EDX, FT-IR and XRD. SEM shows a more uniform distribution of TiO_2NPs on the PET fabrics activated with alkali hydrolysis. EDX and FT-IR spectroscopy confirmed that TiO_2 is chemically bonded to PET fabrics. The effect of surface activation method on antimicrobial activity and UV protection efficiency of PET fabrics was evaluated. It was found that PET fabrics activated with alkali hydrolysis loaded with TiO_2 nanoparticles showed better antimicrobial and UV protection properties compared to the plasma activated fabrics. The advantage of these fabrics became even more prominent after washing test. They exhibited outstanding antimicrobial activity and UV protection efficiency even after five washing cycles, indicating the excellent laundering durability. In general, the received data in the present work indicate the possibility of applying chemical surface activation methods to bind the TiO_2NPs to PET fabrics.

References

Becheri, A., M. Durr, P. LoNostro, 2002. Synthesis and characterization of zinc oxide Nanoparticles: application to textiles as UV-absorbers. J Nanopart Res., 10: 679-685.

Bozzi, A., T. Yuranova, J. Kiwi, 2005. Self-Cleaning of Wool-Polyamide and Polyester Textile by TiO_2- Rutile Modification under Daylight Irradiation at Ambient Temperature. J Photochem and Photobiology A: Chemistry, 172: 27-43.

Daoud, W.A., S.K. Leung, W.S. Tung, J.H. Xin, K. Cheuk, K. Qi, 2008. Self - Cleaning Keratins. Chemistry of Materials, 20: 1242-1244.

Daul, G., R.M. Rinhandt, J.D. Reid, 1993. Preparation of soluble yarns by the carboxymethyltion of cotton. Textile Res J. 23: 719.

Fu, G., P. Vary, C.T. Lin, 2005. Anatase TiO_2 Nanocomposities for Antimicrobial Coatings. J Phys Chem., B109(18): 8889-8898.

Gambichler, T., A. Avermaete, A. Bader, P. Altmeyer, K. Hoffman, 2001. Ultraviolet Protection by Summer Textiles. Ultraviolet Transmission verified by Determination of the minimal Erythematic Dose with Solar-Simulated Radiation. Br J Dermatol., 144: 484-489.

Han, K., M. Yu, 2006. Study of the Preparation and Properties of UV- Blocking Fabrics of PET/ TiO_2 Nanocomposite Prepared by In Situ Polycondensation. J Appl Polym Sci., 100: 1588-1983..

Ilic, V., P. Jovancic, M. Radetic, Z. Saponjic, V. Vodnik, J. Nedeljkovic, R. Molina, S. Dimitrijevic, 2009. Antifungal Efficiency of Crona Pretreated Polyester and Polyamide Fabrics Loaded with Ag Nanoparticles. J.Mater Sci, 44: 3983-3990.

Koneman, E.W., S.D. Allen, V.R. Dowell, W.M. Janda, M.M.W.C.J.Sommers, 1997. Color Atlas Textbook of Diagnostic Microbiology, 3rd ed.; Printed in UASJB Lippincott Company, East Washington Square, Philadelphia, PA, P334.

Lee, H.J., S.Y. Yeo, S.H. Jeong, 2003 Antibacterial effect of nanosized silver colloidal solution on textile fabrics. J.Mater Sci., 38: 2199-2204.

Meilert, K.T., D. Laubb, J. Kiwi, 2005. Photocatalytic Self-cleaning of Modified Cotton Textiles by TiO_2 Clusters Attached by Chemical Spacers. J Molec Catalysis A: Chemical, 237: 101-108.

Mejia, M.I., J.M. Marin, G. Restrepo, C. Pulgarin, J. Kiwi, 2011. Photocatalylic Evaluation of TiO_2/Nylon Systems Prepared at Different Impregnation Times. Catalysis Today, 161: 10-22.

Mihailovic, D., M. Radetic, V. Ilic, S. Stanlovic, P. Jovancie, B. Poylonjak, 2008. Modification of Corona Pretreated Polyester Fabrics with Colloidal TiO_2 Nanoparticles for Imparting Specific Properties. Proceedings of Achen Dresden International Textile Conference, Dresden, Germany, CD-ROM.

Mihailovic, D., Z. Saponjic, M. Radoicic, T. Radetic, P. Jovancic, J. Nedeljkovic, Radetic, 2010. M. Functionalization of Polyester Fabrics with Alginates and TiO_2 Nanoparticles. Carbohydrate Polymers., 97: 526-532.

Onsuratoom, S., R. Rujiravanit, I. Sreethawong, S. Tokura, 2010. Silver Loading on DBD plasma – modified woven PET Surface for Antimicrobial Property Improvement. Plasma Chem Plasma Process, 30: 191-206.

Qi, K., J.H. Xin, W.A. Daoud, C.L. Mak, 2007. Functionalizing of Polyester Fiber with a Self-cleaning Property Using Anatase TiO_2 and low-temperature Plasma Treatment. International Journal of Applied Ceramic Technology, 4: 554-563.

Shalaby, S.E., N.G. El-Balakosy, S.M. Abo El-Ola, 2007 Alkali Treatment of Polyethylene Glycol Modified polyethylene terepftalate Fabrics. J of Textile Association, May-June, pp: 31-38.

Stamate, M., G. Lazar, 2007. Application of TiO_2 Photocatalysis to Create Self-cleaning Materials. Romanian Technical Sciences Academy, pp: 280-285.

Wang, R.H., J.H. Xin, X.M. Tao, 2005. UV- blocking property of dumbbell- shaped ZnO crystallites on cotton fabrics. Inorg Chem., 44: 3926-3930.

Xin, J.H., W.A. Daoud, Y.Y. Kong, 2004. A new approach to UV-blocking treatment for cotton fabrics. Tex Res J 74: 97-100.