Egypt. J. Chem. **Vol. 60**, No. 6, pp.1045 - 1057 (2017)

Effect of Wet Processing Operations on Functional Properties Imparted to PET Fabrics Loaded with Different Metal Oxides Nanoparticles
Part I: Effect of Finishing on Properties Imparted to Bleached PET Fabrics loaded with TiO_2, ZnO and SnO_2 NPs

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THE PRESENT article investigates the effect of finishing wet operations on functional properties imparted to bleached and partially hydrolyzed PET fabrics by loading with TiO_2, ZnO and SnO_2 nanoparticles. Different trials have been carried out to clarify the effect of the sequences of finishing wet process on the properties of loaded with nanoparticles PET fabrics. Characterization of the so finished fabrics was carried out through SEM, EDX and FT-IR. EDX and FT-IR have confirmed that, interaction has actually taken place between carboxylic groups created on PET fabrics and each of the applied nanoparticles. Moreover, the obtained data revealed that, the finishing wet operation has no effect on the abovementioned interaction. The effect of finishing wet operation on the functional performances of PET fabrics was evaluated by analyzing its antimicrobial activity and ultraviolet protection properties. The antimicrobial activity was tested against *B. mycoides*, *E. coli* and *C. albicans*. It has been found that, loading PET fabrics with TiO_2 and ZnO during or after carrying final finishing process using pad-dry-cure method paves the way for imparting outstanding antimicrobial activity even after five washing cycles. Also the obtained results revealed that, the sequence of loading the applied NPs before or during or after carrying finishing wet operation highly affect the UPF values.

Keywords: PET fabrics, Alkali hydrolysis, Finishing, TiO_2, ZnO, SnO_2 NPs, EDX, SEM, FT-IR, Antimicrobial, UPF.

1. Introduction

During the last decade the application of metallic oxides nanoparticles has been widely used for imparting different functional performances to textile fabrics [1-17]. Titanium dioxide (TiO_2), Zinc oxide (ZnO), Tin dioxide (SnO_2) and nano-Ag were used over the last few years for imparting antimicrobial [1,4,7,11,12,13,15,16], UV blocking [2,5,8,9], self- cleaning [3,14] and photo catalytic [6] activities to textile fibers.

Recently, we have treated polyester (PET) and Nylon -6 fabrics using TiO_2 and ZnO nanoparticles after surface activation by chemical and physical means [13, 16, 17]. The obtained results have revealed that, such modification has imparted to the abovementioned fabrics high antimicrobial and UV protection properties even after repeated washings.

Needless to say that, the properties were imparted on laboratory scale to bleached and partially hydrolyzed PET fabrics [13, 17]. But, the technological and economic factors necessitate the imparting of such properties on the wet processing operations line for bleached, dyed and finished fabrics. Therefore, studying the effect of this sequential pattern of wet processing operations on the gained functional properties is of great importance. This will help to select the most appropriate technological choice to design the complete modified technological line, before starting the production on industrial scale.

Stemming from the abovementioned, the present subject will cover the effect of the wet processing operations on the imparted properties to the PET fabrics. This will be demonstrated in three successive articles.

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DOI: 10.21608/ejchem.2017.1955.1160

The aim of the present article is to investigate the effect of finishing wet operation on functional performances imparted to bleached and partially hydrolyzed PET fabrics by loading with different metal oxides nanoparticles (TiO_2, ZnO and SnO_2).

Experimental

Materials

Fabrics

Bleached and partially hydrolyzed (carboxylic content 10.9 meq / 100gr. fabric) polyester woven fabric (PET→B→H) was used throughout this work. PET fabric was kindly supplied by local Egyptian textile companies. These fabrics were partially hydrolyzed using the method reported by Shalaby, etal [20].

Chemicals

TiO_2, ZnO nano - emulsions and SnO_2 nano - powder were purchased from Sigma -Aldrich. Sodium hydroxide, Sedco finish SMA and nonionic detergent (dispersant agent) were purchased from Fluka and have been used as received.

Microorganisms

Bacillus mycoides (Gram - positive bacterium), *Escherichia coli* (Gram - negative bacterium), and *Candida albicans* (nonfilamentous fungus) were used for estimation of antimicrobial potency of control and treated samples. Microorganisms were obtained from the culture collection of the Department of Microbial Chemistry, Division of Genetic Engineering and Biotechnology, National Research Centre of Egypt.

Modified nutrient agar medium was used and is composed of the following ingredients(g / l): peptone (10.0), beef extract (5.0), NaCl (5.0) and agar (20.0). The pH was adjusted to 6.8. This medium was sterilized for 20 min. at 121°C under pressure.

Methods

Preparation of metal oxides NPs

0.5 gr of metal oxides NPs were added in1liter of distilled water and subjected to sonication for 30 minutes at room temperature. Nonionic detergent was used as emulsifying agent to enhance the stability of the emulsion.

Loading of PET→B→H fabrics with metal oxides NPs

PET→B→H fabric samples were immersed in metal oxides NPs colloidal solutions, squeezed to the required pickup increase, dried at 100 °C for 60 minutes. and then cured at 150 °C for 10 minutes in case of loading with TiO_2 and ZnO and at130 °C for 5 minutes in case of SnO_2. The PET loaded samples were then washed with distilled water to remove NPs that did not attach to the fabrics surfaces. In order to evaluate NPs adhesion to PET textiles, the loaded fabrics were repeatedly washed for five cycles according to the standard AATCC test method (61-1989).

Finishing (softening)

PET→B→H fabrics have been immersed in finishing solution (Sedco Finish SMA) (20g/l), squeezed, dried at 100°C, and cured at 160°C for 3.0 minutes.

Analysis

Carboxylic content

Carboxylic content was determined according to the method described by Daul, et al [21].

Antimicrobial activity

Antimicrobial activity of PET→B→H fabrics loaded with metal oxides NPs was quantified using shake flask method. In this method the antimicrobial activity of immobilized antimicrobial agents is determined under dynamic contact conditions according to ASTM standard test method 2143 (2001).

Scan Electron Microscope (SEM)

Fabrics morphology was characterized by scanning electron microscope (SEM) (JEOL-Model TSM T20).

Electron Dispersion Emission X-ray (EDX)

Electron Dispersion Emission X-Ray (EDX) mode was applied for the elemental composition analysis. Gold layer was deposited on the samples before analysis.

Fourier Transformation Infrared (FT-IR)

The chemical structure was determined using the Fourier transformation infrared (FT-IR) spectrometer, model NEXUS 670, NICOLET USA. The measurements were carried in the spectral range from 4000 cm^{-1} to 500 cm^{-1}. Reflection percentage measurement technique was applied (R%). All investigated samples have the same area and weight.

Ultraviolet Protection Factor (UPF)

Ultraviolet Protection Factor (UPF) was determined using UV- Shimadzu 3101 P C spectrophotometer. It is a double beam direct ratio measuring system. It consists of the photometer unit and a PC computer. UPF factor was determined according to the method described in Australian/New Zealand standard AS/NZS 4399: 1996. UPF values were calculated automatically and classified according to Table A.

TABLE (A). Protection and classification according to AS/NZS 4399:1966.

UVP	UPF
Excellent	40,45,50,50+
Very good	25,30,35
Good	15,20
Non-Rateable	0,5,10

Results and Discussion

Different trials have been carried out to clarify the effect of the sequences of finishing wet process operation on the properties of bleached and partially hydrolyzed PET fabrics loaded with NPs, as follows:

1. hydrolyzed fabrics (PET→B→H) were separately immersed in TiO_2, ZnO, and SnO_2 emulsions, squeezed to 75% pick up increase, dried at 100°C for 60 min and cured at 150°C for 10 minutes. The loaded fabrics were then washed with distilled water to remove the metal oxide NPs that did not attach to the fabric surface, and were finally evaluated.

PET→ B→H→TiO_2 PET→B→H→ZnO PET→B→H→SnO_2

2. PET→B→H fabrics have been immersed in finishing solution, squeezed to constant pick up increase in weight, dried at 100oC and finally cured at 160°C for 3 minutes. The obtained fabrics were then washed and evaluated. (PET→B→H→F)

3. The PET fabrics which have been prepared in trail (2) were separately treated in water emulsions of each of TiO_2, ZnO and SnO_2 NPs according to the conditions and sequences listed in trial (1). The obtained fabrics were washed and evaluated.

PET→B→ H→F→TiO_2 PET→B→H→F→ZnO PET→B→H→F→SnO_2

4. Each of PET→B→H fabrics was treated in a bath containing at the same time the finishing agent and each of TiO_2, ZnO and SnO_2 emulsions. The fabrics were then treated according to the same sequences and conditions used in trial (1).

PET→B→ H→ (F+TiO_2) PET→B→H→(F+ ZnO) PET→B→ H→ (F+SnO_2)

5. PETBH Fabrics were loaded, separately, with each of TiO_2, ZnO, SnO_2 emulsions according to sequences and conditions used in trail (1). Then these fabrics were finally finished as listed in trial (2), washed, and evaluated.

PET→ B→H→ TiO_2→F PET→B→ H→ZnO→F PET→B→H→SnO_2→F

Characterization of PET→B→H fabrics loaded with TiO_2, ZnO and SnO_2 NPs at different conditions

We have mentioned before that, the present work aims to clarify the effect of finishing wet operation on the functional properties imparted to bleached, partially hydrolyzed and loaded with different NPs polyester fabrics. Therefore, characterization of the so finished fabrics seems to be of great importance to confirm that interaction has actually taken place between carboxylic groups created on PET fabrics and each of the used NPs. This was carried out through Electron Dispersion Emission X-ray (EDX), Scanning Electron Microscope (SEM) and FT-IR measurements.

Electron Dispersion Emission X-ray (EDX)

SEM analysis performed in EDX mode was used to confirm the presence of the applied NPs on the PET fabrics, loaded with TiO_2, ZnO and SnO_2 NPs, following the washing step, are shown in Fig. (1-3).The obtained results confirm the existence of metallic Ti, Zn and Sn, irrespective of the mode and sequences of carrying out loading and finishing operations. It was found that the fabrics still contain Ti, Zn and Sn even after five standard washing cycles (Table1). Data listed in Table 1 also reveal higher Zn and Sn contents on PET→B→H fabrics. Based on the abovementioned, one can conclude that the finishing wet operation has no effect on the interaction between the carboxylic groups and the metal oxides NPs.

Scan Electron Microscope (SEM)

The surface topography of PET→B→H fabrics loaded with metal oxides NPs and finished was investigated using SEM technique. The obtained results (Fig. 1, 2, 3) reveal the following:

1- PET→B→H fabrics are characterized by rough surfaces with pits [Fig. 1, 2, 3 (a)]

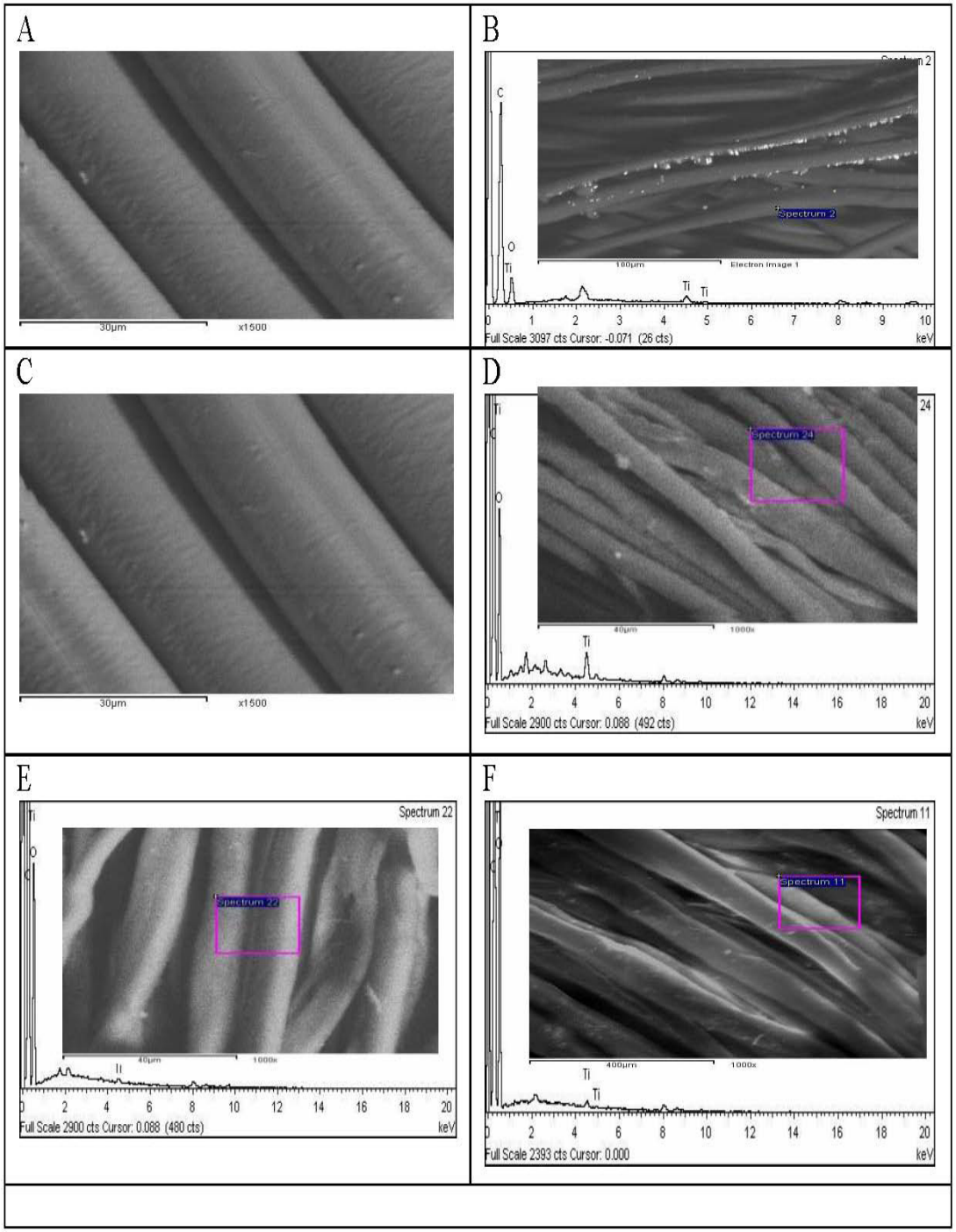

Fig. 1. SEM and EDX micrographs of bleached and partially hydrolyzed PET fabrics loaded with TiO_2 NPs* (X2000).
[A] PET→B→H (Blank) [B] PET→B→H→ TiO_2 [C] PET →B→H→ F (Blank)
[D] PET→B→H→F→TiO_2 [E] PET→B→H→(F+TiO_2) [F] PET→B→H→TiO_2→F
***After five Washing Cycle; AATCC Test Method (61-1989).**

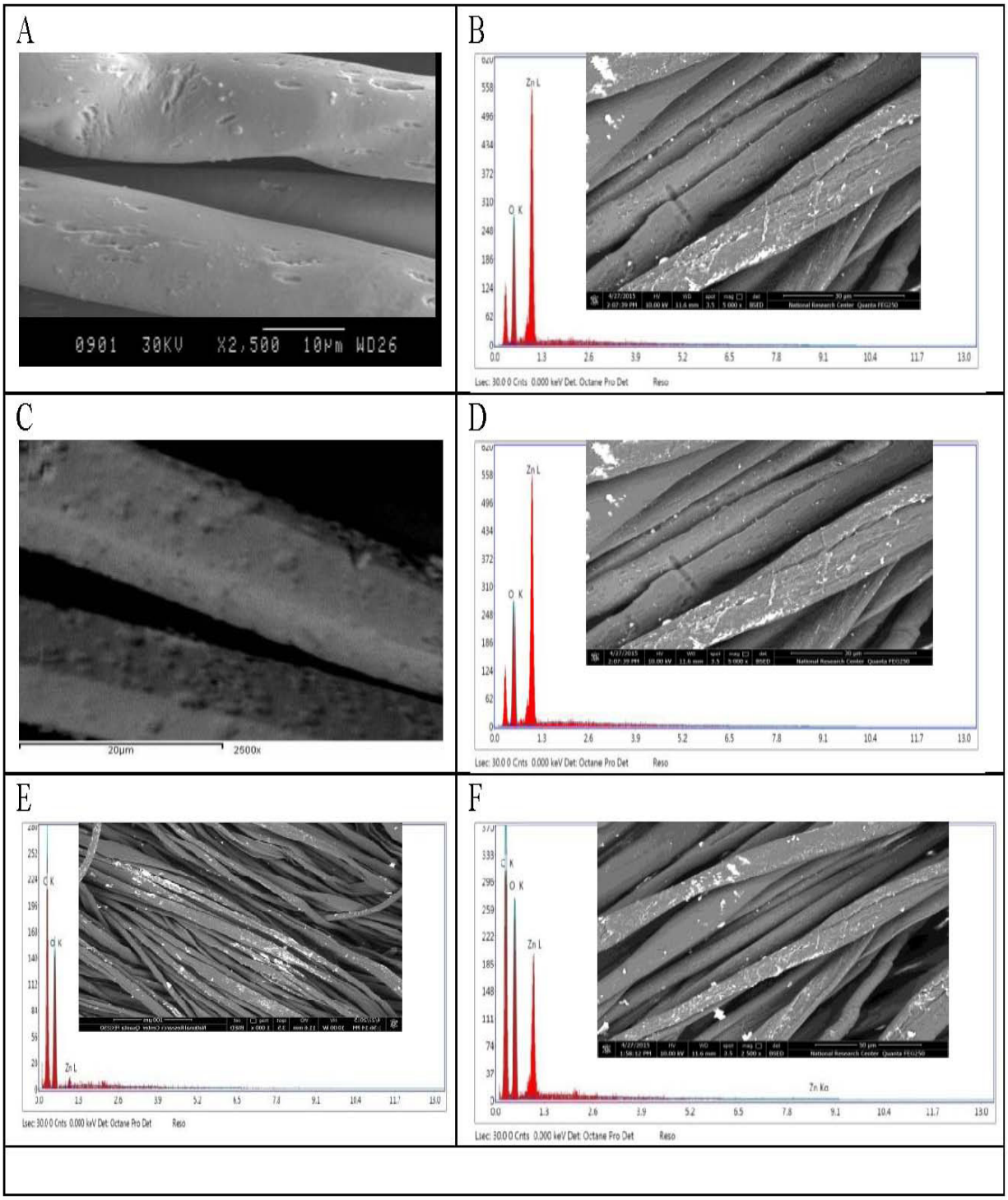

Fig. 2. SEM and EDX micrographs of bleached and partially hydrolyzed PET fabrics loaded with ZnO NPs* (X2000).
[A] PET→B→H (Blank) [B] PET→B→H→ZnO [C] PET→B→H→F (Blank)
[D] PET→B→H→F→ZnO [E] PET→B→H→ (F+ZnO) [F] PET→B→H→ZnO→F
***After Five Washing Cycles; AATCC Test Method (61-1989).**

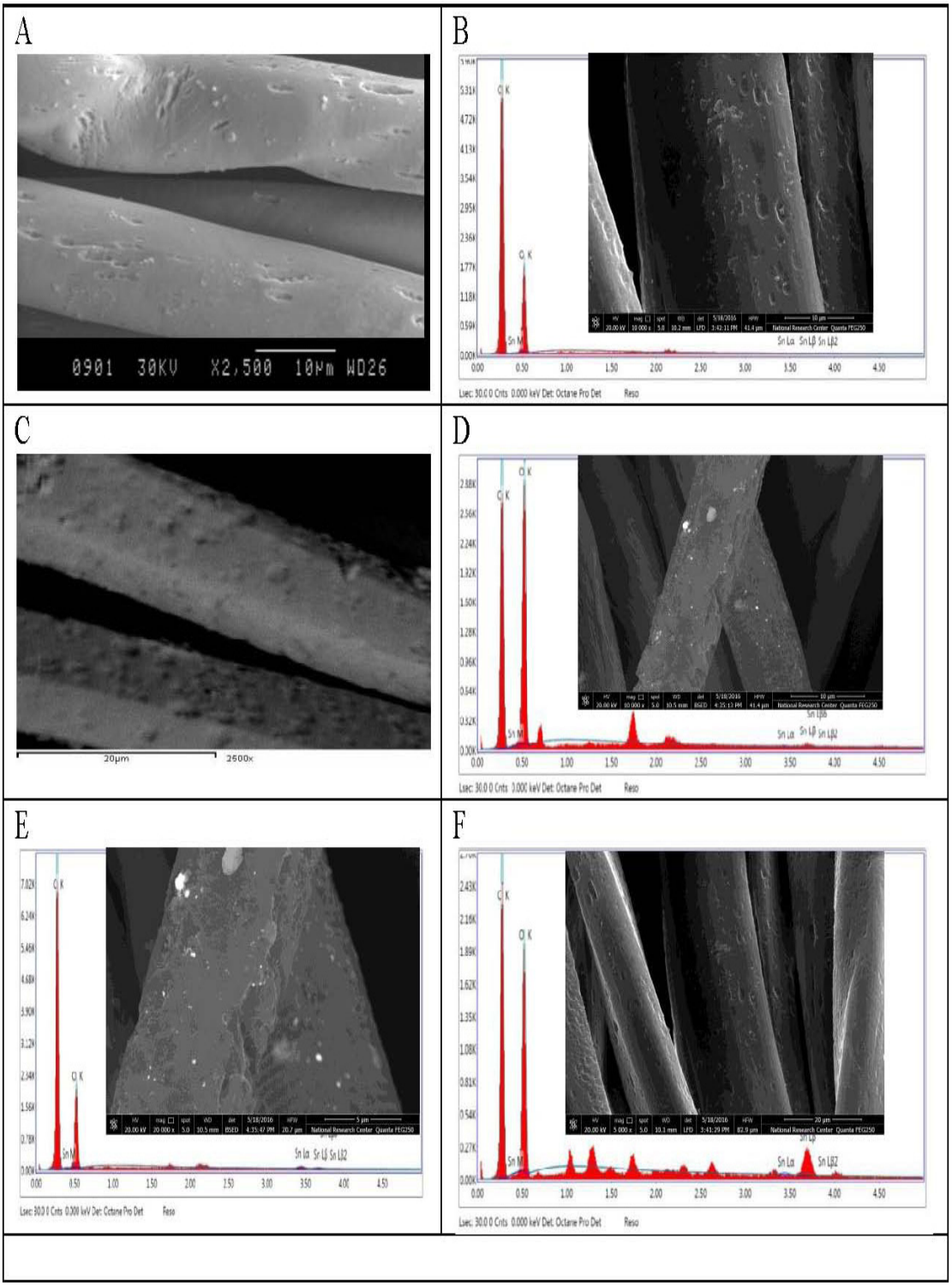

Fig. 3. SEM and EDX micrographs of bleached and partially hydrolyzed PET fabrics loaded with SnO_2 NPs* (X2000).
[A] PET→B→H (Blank) [B] PET→B→H→ SnO_2 [C] PET→B→H→F (Blank)
[D] PET→B→H→ F→SnO_2 [E] PET→B→H→ (F+SnO_2) [F] PET→B→H→SnO_2→F
***After Five Washing Cycles; AATCC Test Method (61-1989).**

2- Treatment of PET→B→H fabrics with TiO_2, ZnO, SnO_2 NPs emulsions using pad- dry -cure method leads to the formation of some precipitation on the surfaces [Fig. 1,2,3- (b)]

3- Finishing of PET→B→ H leads to obtain fabric surfaces characterized by less roughness and pits compared with unfinished ones [Fig.1, 2, 3- (c)]

4- Carrying out treatment with the applied metal oxides NPs emulsions after finishing wet operation leads to increase the density of the thin layer formed on the surface of fabrics [Fig. 1, 2, 3- (d)]

5- Carrying out the loading and finishing operations at the same time leads to an increase of the thin layer formed on the surface. In addition to this, such treatment paves the way for filling the pits formed after partial hydrolysis with alkali [Fig.1, 2, 3- (e)]. The same holds true in case of carrying out the finishing wet operation after loading with metal oxides NPs [Fig. 1 2, 3- (f)].

6- It is worth mentioning that, carrying out finishing wet operation followed by loading with metal oxide NPs with pad- dry- cure method leads to get fabrics with more homogeneous and smooth fabric surfaces compared with that obtained after loading with NPs followed by finishing wet operation.

The abovementioned changes which took place on the surface topography of PET→B→H fabrics loaded with TiO_2, ZnO, and SnO_2 NPs and finished are a direct indication that these NPs are attached to the fabric surfaces.

Fourier Transformation Infrared (FT-IR)

Data in Table 2 show the effect of finishing wet operation on FT-IR absorption bands of functional groups in bleached and partially hydrolyzed PET fabrics loaded with different metal oxides NPs. Based on these data one can conclude the following:

In the case of loading with TiO_2 NPs

The finishing of PET→B→H fabrics did not affect the absorption bands of >C=O groups, but caused a slight decrease in its intensities (from 87.7% -Table 3 to 85.6% - Table 2).

TABLE 1. Ti, Zn and Sn content on the surfaces of bleached and partially hydrolyzed PET fabrics loaded with TiO_2, ZnO and SnO_2 NPs.

No.	Fabrics	Contents (Atomic %) on the Surfaces of Fabrics of:					
		Ti		Zn		Sn	
		Number of Washing Cycles:					
		1*	5*	1*	5*	1*	5*
1	PET→B→H (Blank)	0.00		0.00		0.00	
2	PET→B→H→ TiO_2	0.29	0.24				
3	PET→B→H→ ZnO			0.06	0.04		
4	PET→B→H→ SnO_2					0.11	0.04
5	PET→B→H→F (Blank)	0.00		0.00		0.00	
6	PET→B→H→F→ TiO_2	0.03	0.03				
7	PET→B→H→F→ ZnO			0.12	0.08		
8	PET→B→H→F→ SnO_2					0.08	0.07
9	PET→B→H→ (F+ TiO_2)	0.03	0.03				
10	PET→B→H→ (F+ ZnO)			0.14	0.11		
11	PET→B→H→ (F+ SnO_2)					0.14	0.11
12	PET→B→H→ TiO_2→F	0.04	0.03				
13	PET→B→H→ ZnO →F			0.11	0.08		
14	PET→B→H→ SnO_2 →F					0.11	0.08

B = Bleached H = Partially Hydrolyzed F = Finished

Treatment Conditions: Pad−dry −cure Method

[TiO_2] and [ZnO], 0.5%; Curing Temperature, 150˚C; Curing Time, 10 min.,

[SnO_2], 0.5%; Curing Temperature, 130˚C; Curing Time, 5 min.,

Finishing Conditions:

[Sedco Finish], 20.0 g/l; Curing Temperature, 160˚C; Curing Time, 3.0 min.,

* After 1 and 5 washing Cycles; AATCC Test Method (61-1989).

The loading of finished fabrics (PET→B→H→F) with TiO_2 NPs did not affect the absorption bands position of the carbonyl group, irrespective of the loading position with the above mentioned NPs before or during or after the finishing wet operation. However, the loading of such fabrics caused only a little drop in the intensity of the absorption band to 85.6% (Table 2) compared with 89% for the unfinished loaded with the same NPs (Table 3). The data listed in Table 2 point to that , the loading PET→B→H fabrics during or before carrying out the finishing wet operation results in increasing the intensity of >C=O group.

TABLE 2. Effect of finishing on ft-ir absorption bands of functional groups in bleached and partially hydrolyzed PET fabrics loaded with metal oxides NPs.

No.	Fabrics	Absorption Bands and Intensities of >C=O and OH groups after finishing PET→B→H fabrics loaded with metal oxides NPs				New Absorption Bands Appeared	
		>C=O		—OH			
		Position (Cm^{-1})	Intensity (%)	Position (Cm^{-1})	Intensity (%)	Position (Cm^{-1})	Intensity (%)
1	PET→B→H→F	1713.9	85.6	3488.2	98.9	-	-
2	PET→B→H→F→TiO_2	1714.9	85.9	3749.8	85.9	783.3	92.7
3	PET→B→H→(F+TiO_2)	1713.0	87.6	3502.6	99.7	802.2	92.1
4	PET→B→H→TiO_2→F	1713.1	90.1	3676.0	99.8	809.8	96.0
5	PET→B→H→F	1743.3	49.0	3431.7	46.3	-	-
6	PET→B→H→F→ZnO	1739.5	47.0	3431.7	48.4	633.5	85.6
7	PET→B→H→(F+ ZnO)	1742.4	56.0	3431.7	52.1	631.8	86.2
8	PET→B→H→ZnO→F	1738.5	56.0	3432.7	52.8	635.1	84.3
9	PET→B→H→F	1710.6	46.2	3554.2	92.7	-	-
10	PET→B→H→F→SnO_2	1710.6	46.2	3426.9	91.9	435.8	95.5
11	PET→B→H→(F+SnO_2)	1710.6	39.6	3426.9	88.9	436.9	92.5
12	PET→B→H→SnO_2→F	1711.5	39.3	3430.7	67.9	433.0	90.6

PET= Polyester Fabric B= Bleached H = Partially Hydrolyzed F = Finished
Treatment Conditions: Pad−Dry–Cure Method
[TiO_2] and [ZnO], 0.5%; Curing Temperature, 150˚C; Curing Time, 10 min., [SnO_2], 0.5%; Curing Temperature, 130˚C; Curing Time, 5min.,
Finishing Conditions:
[Sedco Finish], 20g/l; Curing Temperature, 160˚C; Curing Time, 3min.
* After 1Washing Cycle; AATCC Test Method (61-1989).

TABLE 3. FT-IR absorption bands of functional groups in bleached and partially hydrolyzed PET fabrics loaded with metal oxide NPs.

No.	Fabrics	Absorption Bands and intensities of >C=O and OH groups after loading PET→B→H fabrics with metal oxides NPs				New Absorption Bands Appeared	
		>C=O		—OH			
		Position (Cm^{-1})	Intensity (%)	Position (Cm^{-1})	Intensity (%)	Position (Cm^{-1})	Intensity
1	PET→B→H	1712.0	87.7	3354.3	99.7	-	-
2	PET→B→H→ TiO_2	1713.2	89.0	3549.9	92.0	769.0	96.0
3	PET→B→H	1741.4	62.0	3432.7	42.6	-	-
4	PET→B→H→ZnO	1740.7	58.0	3431.7	50.8	632.5	91.2
5	PET→B→H	1711.5	28.1	3558.0	98.3	-	-
6	PET→B→H→ SnO_2	1711.5	39.5	3558.0	81.5	428.1	82.6

PET= Polyester Fabric B = Bleached H = Partially Hydrolyzed F = Finished
Treatment Conditions:Pad−Dry –Cure Method
[TiO_2] and [ZnO], 0.5%; Curing Temperature, 150˚C; Curing Time, 10 min. [SnO_2], 0.5%; Curing Temperature, 130˚C; Curing Time, 5min.,
* After 1Washing Cycle; AATCC Test Method (61-1989).

The finishing of PET→B→H fabrics leads to a noticeable shift towards higher frequencies of the OH group (Table 2) in comparison with the unfinished fabrics (Table 3). The maximum shift of frequencies of this group reached its top value after finishing and loading with TiO_2 NPs (PET→B→H→F→TiO_2). The frequencies shifted from 3549.9 cm^{-1} (Table 3) in case of PET→B→H→TiO_2 to 3749.8 cm^{-1} in case of finished and loaded with TiO_2 NPs fabrics (Table 2). At the same time, this was accompanied with a decrease in the intensity of –OH group from 92% (Table 3) to 85.9% (Table 2). Data listed in Table 2, also indicate that, loading PET→B→H→F with TiO_2 NPs, before or during carrying out the finishing operation leads to an increase in the intensity of this group, compared with that in case of loading with the same NPs after the finishing operation.

The FT-IR spectra of all fabrics finished and loaded with TiO_2 NPs show the appearance of new absorption bands in the range of 783.3 cm^{-1} to 809.8 cm^{-1} which characterizes the formation of bonding (Ti-O-C) irrespective of the loading position of NPs (Table 2).

In the case of loading with ZnO NPs

Results shown in Table 2 reveal that, the absorption bands of carbonyl group in all fabrics loaded with ZnO NPs did not change its position. Contrary to this, the intensity of such group has increased especially in the case of fabrics loaded with ZnO NPs before or during finishing operation (Table 2). The same holds true in case of the position and the intensity of the OH-group.

The FT-IR spectra of all fabrics loaded with ZnO NPs and finished show the appearance of new absorption bands in the range of 631.8 cm^{-1} to 635.1cm^{-1} which characterizes the formation of new bonding (Zn-O-C) irrespective of the position of loading NPs (Table 2).

In the case of loading with SnO_2 NPs

It was found (Table 2) that, the wave length of carbonyl group in all fabrics loaded with SnO_2 NPs did not change its position. On the contrary, this was accompanied with a decrease in the intensity of this group reaching its maximum in the case of loading the fabrics before or during carrying out the finishing operation. The same holds true in case of the position and the intensity of the OH^- group. Moreover, it was found that the maximum decrease in OH^- group intensity takes place in case of loading fabrics with SnO_2 before carrying out the finishing operation.

The FT- IR spectra of all fabrics loaded with SnO_2 NPs and finished confirm the appearance of new absorption bands in the range of 433.0 cm^{-1} to 436.9 cm^{-1} which characterizes the formation of bonding (Sn-O-C) irrespective of the loading position of SnO_2NPs [22].

Stemming from the abovementioned one can conclude that, the C=O and OH^- groups are affected as a result of loading PET→B→H→F with metal oxides (TiO_2, ZnO and SnO_2 NPs). This happens irrespective of the nature of loaded NPs and the sequences of the loading process: after alkali treatment, or during or after or before carrying out finishing operation. In addition to this, the carboxylate groups, created on the fabrics surface after alkali treatment reacted with NPs forming a new chemical bond with such NPs. Similar findings have been reported [23].

The effect of finishing on functional performances imparted to bleached PET fabrics loaded with different NPs

Antimicrobial activity

The antimicrobial activity of bleached and partially hydrolysed (PET→B→ H) fabrics loaded with TiO_2, ZnO and SnO_2 NPs was evaluated by deterring the reduction percentage of Gram-positive (*Bacillus mycoides*) Gram negative (*Escherichia Coli*), and nonfilamentous fungs (*Candida albicans*) bacteria using the shake flask method. Data given in Table 4 illustrate the effect of finishing wet operation, the sequences used for loading the fabrics with NPs and the repeating washing on the percentages of colony forming units (% CFU) reduction on the above mentioned fabrics. Based on the data given in Table 4, one can conclude the following:

1- In general, the loading of TiO_2, ZnO and SnO_2 NPs on (PET→B→H) fabrics, led to the reduction of microbes on the surface of fabrics. This reduction depends on the nature of NPs, the sequences of loading, and the resistance towards repeated washings.

2- It was found that the sequence of loading with the above mentioned NPs during wet processing operations for PET fabrics plays a pivotal role. This conclusion is based on the following:

a) The obtained results revealed that, CFU of the fabrics loaded with TiO_2 after alkali treatment has reached after five repeated standard washing cycles 36%, 52%, 36% in case of B.

mycod, *E. Coli* and *C. albicans* respectively.

This is in contrast with 68%, 38%, 63%, respectively, in case of ZnO loading. At the same time, the loading with SnO_2 NPs exhibits much lower effect than in case of TiO_2 and ZnO NPs.

b) The loading of TiO_2 and ZnO NPs using pad-dry- cure method after or during finishing operation, led to obtaining PET fabrics with 100 % CFU reduction after one standard washing cycle with respect to the above mentioned three types of bacteria. It is worth mentioning that, the repeated washings of such fabrics did not cause a noticeable decrease in its ability for reduction of microbes. The data listed in Table 4 illustrate that after 5 washing cycles, the fabrics still acquire excellent CFU reduction towards *B.m* and *E.C*. On the contrary, the application of SnO_2 NPs did not cause any noticeable improvement in the antimicrobial activity of such fabrics in comparison with those obtained after loading with such NPs directly after alkali treatment.

c) The loading of TiO_2 and ZnO NPs on PET fabrics before carrying out the finishing operation also leads to imparting antimicrobial properties to a lesser extent compared with those obtained after loading during or after finishing operation (Table 4). It was found that, the antimicrobial activity of PET fabrics loaded with SnO_2 NPs before finishing process continues to decrease.

Based on the above mentioned, we can conclude that, the best method for loading bleached and partially hydrolyzed PET fabrics with TiO_2 and ZnO NPs for imparting high antimicrobial activity even after repeated washings should follow the sequence:

1- Bleaching PET fabrics using standard method;

2- Partial hydrolysis of fabrics using NaOH water solutions;

3- Loading bleached and partially hydrolyzed PET fabrics with TiO_2 and ZnO during or after

TABLE 4. Antimicrobial activity of bleached and partially hydrolyzed PET fabrics loaded with TiO_2, ZnO and SnO_2NPs, determined by shake flask method.

No.	Fabrics	% CFU Reduction					
		B.m		*E. c*		*C.a*	
		Number of washing Cycles:					
		1*	5*	1*	5*	1*	5*
1	PET→B→H (Blank)	0.0		0.0		0.0	
2	PET→B→H→TiO_2	-	36.0	-	52.0	-	36.0
3	PET →B→H→ZnO	68.0	68.0	55.0	38.0	77.0	63.0
4	PET→B→H→ SnO_2	59.0	-	16.0	-	33.0	-
5	PET→B→H→F (Blank)	0.0		0.0		0.0	
6	PET→B→H→F→TiO_2	100	100	100	84.0	100	84.0
7	PET →B→H→F→ZnO	100	100	100	100	100	95.0
8	PET →B→H→F→SnO_2	43.0	-	13.0	-	47.0	-
9	PET →B→H→ (F+TiO_2)	100	94.0	99.0	84.0	99.0	82.0
10	PET →B→H→(F+ZnO)	100	100	100	100	100	100
11	PET→B→H→ (F+ SnO_2)	67.0	-	24.0	-	75.0	-
12	PET→B→H→TiO_2→F	-	20.0	-	36.0	-	36.0
13	PET→B→H→ZnO→F	100	93.0	89.0	62.0	100	54.0
14	PET→B→H→SnO_2→F	26.0	-	16.0	-	41.0	-

B = Bleached H = Partially Hydrolyzed F = Finished

Treatment Conditions: Pad–Dry –Cure Method

[TiO_2], and [ZnO], 0.5%; Curing Temperature, 150˚C; Curing Time, 10 min.,

[SnO_2], 0.5%; Curing Temperature, 130˚C; Curing Time, 5 min.,

Finishing Conditions:

[Sedco Finish], 20.0 g/l; Curing Temperature, 160˚C; Curing Time, 3.0 min.,

* After 1 and 5 washing Cycles; AATCC Test Method (61-1989).

carrying final finishing process using pad-dry-cure method.

Ultraviolet protection properties

The effect of the sequences of finishing wet operation on UV protection properties of bleached and partially hydrolysed PET fabrics loaded with TiO_2, ZnO and SnO_2 NPs was investigated. The obtained data listed in Table 5 indicate the following:

1- In general TiO_2 and ZnO NPs are able to impart bleached and partially hydrolyzed PET fabrics UV protection properties compared to unloaded ones. On the contrary, the loading with SnO_2 NPs did not cause any noticeable improvement in such properties.

2- It was found that, the finishing of (PET→B→H) fabrics was not accompanied with changing UPF rating after 5 washing cycles in comparison to the unfinished fabrics.

3- The data in Table 5 indicate that, the sequence of loading the applied NPs after, during or before carrying out the finishing wet operation highly affect the UPF values of such fabrics as follows:

a- Loading the fabrics with TiO_2 NPs before, during or after finishing wet operation leads to imparting PET fabrics good UV protection properties even after 5 standard washing cycles. The best result (UPF= 22.5) was obtained after loading TiO_2 simultaneously during the finishing wet operation.

b- Loading PET→B→H fabrics with ZnO NPs after, or during finishing operation causes a substantial increase in UPF (50+, 47) even after 5 washing cycles.

c- Based on the listed data in Table 5, one can conclude that loading ZnO NPs after carrying the final finishing seems to be the ideal method

TABLE 5. Ultraviolet Protection Factor (UPF) of bleached and partially hydrolyzed PET fabrics loaded with TiO_2, ZnO and SnO_2NPs.

No.	Fabrics	Number of Washing Cycles:			
		1*		5*	
		UPF	UPF Rating	UPF	UPF Rating
1	PET→B→H (Blank)	12.1	Poor	11.5	Poor
2	PET→B→H→TiO_2	25.3	V. Good	22.7	Good
3	PET→B→H→ZnO	35.0	V. Good	26.0	V. Good
4	PET→B→H→ SnO_2	13.2	Poor	-	-
5	PET→B→H→F (Blank)	17.6	Good	13.4	Poor
6	PET→B→H→F→TiO_2	28.2	V. Good	21.8	Good
7	PET→B→H→F→ZnO	50+	Ex.	50+	Ex.
8	PET →B→H→F→SnO_2	15.2	Good	-	-
9	PET →B→H→ (F+TiO_2)	35.8	V. Good	22.5	Good
10	PET →B→H→ (F+ ZnO)	50+	Ex.	47.0	Ex.
11	PET→B→H→ (F+SnO_2)	13.2	Poor	-	-
12	PET→B→H→ TiO_2→F	28.2	V. Good	22.0	Good
13	PET→B→H→ ZnO→F	33.0	V. Good	23.0	Good
14	PET→B→H→ SnO_2→F	14.6	Poor	-	-

B = Bleached H = Partially Hydrolyzed F = Finished

Treatment Conditions: Pad–Dry –Cure Method

[TiO_2], and [ZnO], 0.5%; Curing Temperature, 150˚C; Curing Time, 10 min.,

[SnO_2], 0.5%; Curing Temperature, 130˚C; Curing Time, 5 min.,

Finishing Conditions:

[Sedco Finish], 20.0 g/l; Curing Temperature, 160˚C; Curing Time, 3.0 min.,

* After 1 and 5 washing Cycles; AATCC Test Method (61-1989).

for obtaining PET fabrics with excellent UPF, even after 5 standard washing cycles.

Conclusion

The present subject covers the effect of wet processing operations (bleaching, dyeing, finishing) on functional properties imparted to PET fabrics loaded with different metal oxides NPs. This will be demonstrated in three successive articles. The aim of the present article is to investigate the effect of finishing wet operation and its sequences on functional performances imparted to bleached and partially hydrolyzed fabrics by loading with TiO_2, ZnO and SnO_2 NPs. Characterization of the finished fabrics was carried out through SEM, EDX and FT-IR. The obtained results reveal that, TiO_2, ZnO and SnO_2 are chemically bonded to PET fabrics, and that, the finishing wet operation has no effect on this interaction. The antimicrobial activity of loaded and finished PET fabrics was tested. It has been found that, loading PET fabrics with TiO_2 and ZnO during or after carrying final finishing process paves the way for imparting outstanding antimicrobial activity even after five washing cycles, indicating excellent laundering durability. It was also found that the sequence of loading NPs after or during or before finishing wet operation highly affect the UPF values. Based on the abovementioned, one can conclude the feasibility of carrying out such modification on the wet processing line for PET fabrics.

Acknowledgment

The authors are grateful to the National Research Centre (NRC) for financial support in the Research Project No 10160001.

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(*Received* 30/10/2017;
(accepted 26/11/2017)

تأثير خط العمليات الرطبة على الخصائص الوظيفية المكتسبة لأقمشة البولى استر المحملة بجسيمات مختلفة لاكاسيد المعادن النانومترية
الجزء الأول: تأثير التجهيز على الخصائص المكتسبة لأقمشة البولى استر المبيضة والمحملة بالجسيمات النانومترية TiO_2و ZnO و SnO_2

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هذا البحث يهدف الي دراسه تأثير تحميل الاكاسيد النانومتريه "ثاني أكسيد التيتانيوم(TiO_2)، أكسيد الزنك (ZnO) وثاني أكسيد القصدير (SnO_2)" أثناء المراحل المتتاليه لخط العمليات الرطبة على الخصائص الوظيفية المكتسبة لاقمشة البولى استر المبيضة والمحررة بالقلوى. تم توصيف الأقمشة المعالجة بالأكاسيد النانومترية سالفة الذكر باستخدام الميكروسكوب الالكترونى الماسح (SEM)، وطيف الأشعة السينية المشتتة (EDX)، وطيف الأشعة تحت الحمراء (FT-IR). وقد اثبتت النتائج التى تم الحصول عليها أن التفاعل قد حدث بالفعل بين المجموعات الكربوكسيلية التي تم إنشاؤها على سطح الأقمشة المحررة بالقلوى والجسيمات النانومتريه. علاوة على ذلك، كشفت النتائج أن عملية التجهيز الرطب ليس لها تأثير على التفاعل المذكور. تم تقييم تأثير التجهيز الرطب على الأداء الوظيفي للأقمشة من خلال تقييم نشاطها المضاد للميكروبات وقدرتها علي الحماية من الأشعة فوق البنفسجية. تم اختبار النشاط المضاد للميكروبات لكل من الميكروبات موجبة و سالبة الجرام وكذلك الفطر اللاخيطى. وقد تبين أن تحميل الأقمشة بجسيمات اكاسيد التيتانيوم والزنك النانومترية أثناء أو بعد الانتهاء من عملية التجهيز النهائي باستخدام طريقة الغمر- العصر - التحميص يمهد الطريق لاكساب أقمشه البولي استر المبيضه والمحرره بالقلوى نشاط مضاد للميكروبات وكذلك قدره علي الحمايه من الاشعه فوق البنفسيجيه حتى بعد خمس دورات غسيل بالطريقة القياسية.