## Influence of the Surface Hydrolysis on the Functionality of Poly(ethylene terephthalate) Fabric Treated with Nanotitanium Dioxide

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**ABSTRACT:** In this study, the polyester (PET) fabric was hydrolyzed with alkali to increase the surface activity and enhance the nano titanium dioxide (nano-TiO<sub>2</sub>) adsorption to produce higher functionality. The PET fabric was first treated with sodium hydroxide along with cetyl trimethyl ammonium bromide as a cationic surfactant and then dipped into an ultrasound bath containing nano-TiO<sub>2</sub> followed by curing at high temperature. The weight loss, vertical wicking, and water droplet adsorption time were evaluated and are reported. The photocatalytic activity of TiO<sub>2</sub> nanoparticles deposited on the PET fabric was examined by the degradation of methylene blue as a model stain under daylight irradiation. The residual TiO<sub>2</sub> on the fabric surface after 1 and 10 successive washings was

## INTRODUCTION

Polyester (PET) has a widespread range of use, and it has been the center of attention by many researchers all around the world to improve its properties.<sup>1</sup> This is especially important in functional properties for their added value.<sup>1</sup> The usual alkaline treatment hydrolysis of the PET fabric surface leads to create functional groups.<sup>1</sup> In addition to fashion and comfort demands, garments today must simultaneously provide self-cleaning properties and antimicrobial and UV protection properties.<sup>2,3</sup> Embedding particles on the fiber polymeric matrix is a high-performance method with noticeable advantages.<sup>4</sup> TiO<sub>2</sub> nanoparticles have created a new approach for remarkable applications as reasonable multifunctional materials.<sup>5,6</sup> These particles have been of great interest for environmental cleanup because they are stable, harmless, and inexpensive and can be potentially activated by solar energy.<sup>7-12</sup> In recent years, the use of nanotitanium dioxide photocatalysts to

determined to indicate the washing durability of the finished fabric. Also, the UV protection was assessed by UV reflectance spectroscopy. The scanning electron microscopy pictures and energy-dispersive X-ray spectra of some fabrics are also reported. The surface hydrolysis of the PET fabric with sodium hydroxide created some voids and hydrophilic groups on the fabric surface; this led to the higher adsorption of nano-TiO<sub>2</sub> particles and enhanced the wettability, vertical wicking, and higher durability against repeated washings of the nano-TiO<sub>2</sub> treated fabric. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1176–1184, 2012

**Key words:** adsorption; fibers; functionalization of polymers; modification; nanoparticle

cover textiles and improve their surface properties has expanded because of the ability to absorb UV irradiation.<sup>13–15</sup> In addition, the coating of nano titanium dioxide (nano-TiO<sub>2</sub>) particles on fabrics will not affect their breatheability or hand feel.<sup>16</sup> It is known that the stability of nano-TiO<sub>2</sub> on PET is low because of the lack of functional groups.<sup>17</sup> Then, it is necessary to create some functional groups on the polymer chain of PET. Several methods have been used to modify the PET surface, including low-pressure plasma and corona discharge at atmospheric pressure to enhance the binding efficiency of TiO<sub>2</sub> nanoparticles.<sup>18,19</sup> It has been also suggested that chemical surface modification, such as alkali hydrolysis, can increase the functionality of PET fibers by introducing hydroxyl and, particularly, carboxylic groups to bind TiO<sub>2</sub> nanoparticles.<sup>20–30</sup> On the other hand, the durability of these nanoparticles and their properties on the fabric surface is very important.<sup>4</sup> Depending on the type of nanoparticle and the fabric, a variety of methods and materials have been used to achieve durability.<sup>1,4,11</sup> Different techniques can be used<sup>7-13</sup> to improve the washing durability of the finishing materials on the fabrics, including the use of poly(carboxylic acids).<sup>31,32</sup> The use of thermal processes similar to thermosol conditions can be adapted as a new method for stabilizing imparted

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properties to the fabric.<sup>33,34</sup> In this method, high temperatures increase the vibrations of polymer chains and their distance as well. Then, the chance of penetrating materials such as nanoparticles into created free spaces increases considerably.<sup>35</sup>

In this research, the effect of alkaline surface modification of PET fabrics on the improved adsorption of TiO<sub>2</sub> nanoparticles was studied. It has already been reported that crosslinking agents can potentially increase the binding efficiency and durability of nanoparticles on the fiber surface.<sup>6,11</sup> Here, a high temperature, namely, a thermosol process, was used to obtain nanofinishing with desirable durability. The content of nano-TiO<sub>2</sub> particles on modified and unmodified fabrics were measured after various washing cycles. The photocatalytic activity of  $TiO_2$ nanoparticles deposited on the PET fabrics was evaluated by the degradation of methylene blue as a model stain. Also, the UV blocking properties of the nano-TiO<sub>2</sub> treated fabrics were investigated and compared. Scanning electron microscopy (SEM) was used to observe the fabric surfaces and distribution of the nanoparticles on the fibers surface. All of these were applied to investigate the improvement of the PET fabric treated with nano-TiO<sub>2</sub> functionality through high-temperature (thermosol) processing.

#### **EXPERIMENTAL**

## Materials

The characteristics of the PET fabric were as follows. Plain, white PET fabric was used with a weight of 83 g/m<sup>2</sup> and 150 Den filaments in the warp and weft (Hejab Textile Co., Shahrekord, Iran). Sodium hydroxide (Merck, Gernsheim, Germany), cetyl trimethyl ammonium bromide (Merck, Darmstadt, Germany), and nano-TiO<sub>2</sub> (21 nm, Degussa P25, Evonik, Germany) were used.

#### Experiments

The fabric was scoured with a nonionic detergent solution (1 g/L) at 60°C for 20 min and then rinsed with distilled water to remove any impurities, such as lubricant left on the PET surface in previous processes.

The fabric samples were finally cut into  $20 \times 10 \text{ cm}^2$ and were conditioned overnight under standard conditions at 20°C and 65% relative humidity before the treatment. Then, some samples were treated in a modification bath consisting of 10% w/v sodium hydroxide and 1% (w/w) cetyl trimethyl ammonium bromide and had a liquor-to-goods ratio of 50:1 while boiling on a heater for 3 min. Then, the weight loss percentage (WL%) of the samples due to alkaline hydrolysis was measured. The samples (alkali-modified and unmodified) were then treated with nano-TiO<sub>2</sub> for 30 min in an ultrasonic bath (Retsch, Haan, Germany) at 0.1, 0.2, 1, 5, and 10% w/v concentrations with an exhaustion method and padded with foulard with 100% wet pickup. The fabrics were then dried at 90°C for 4 min; this was followed by curing at 220°C for 2 min in an oven (Memmert, Mannheim, Germany).

## Methods

#### WL%

The alkali-treated PET samples were dried at  $70^{\circ}$ C for 30 min and then cooled in P<sub>2</sub>O<sub>5</sub> desiccators at room temperature. The dry weight of the sample was obtained accurately. WL% for each sample was determined according to Eq. (1):

$$WL\% = \frac{W_1 - W_2}{W_1} \times 100$$
 (1)

where  $W_1$  and  $W_2$  are the weights of the samples before and after alkali treatment, respectively.

Residual TiO<sub>2</sub> on the fabric surface after washing

A heat treatment of  $575^{\circ}$ C for 3 h was done in chamber furnaces (CARBOLITE, London, United Kingdom) to measure the residual TiO<sub>2</sub> in different samples after the first cycle of washing (1W) and ten cycles of washing (10W) according to ASTM 5630 D 2584.

# SEM and energy-dispersive X-ray (EDX) spectroscopy

SEM was used to observe the fabric surfaces (XL30, Philips, Eindhoven, Netherlands). EDX mode was applied for elemental composition analysis. A gold layer was deposited on the samples before the analysis.

#### Self-cleaning

The degradation activity of  $15-\mu$ L methylene blue (0.02% w/v) was evaluated by daylight irradiation of the washed samples for 4, 8, and 12 h. The color changes were studied on the basis of reflectance data with a Color Eye 7000A spectrophotometer (X-Rite, Las Vegas, Mexico, USA), and the color difference ( $\Delta E$ ) was calculated by Eq. (2):

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \tag{2}$$

where  $L^*$ ,  $a^*$ , and  $b^*$  are the values of lightness, redness–greenness, and yellowness–blueness, respectively.

#### Self-cleaning durability

The durability of TiO<sub>2</sub> particles on the PET fabric surface was evaluated by repeated washing. The washing was carried out at 60°C for 20 min. This was repeated on the samples for 10 cycles. The self-cleaning performance of the washed samples was examined with the same method as described previously.

#### Ultraviolet-visible (UV-vis) spectroscopy

A Varian Cary 300 spectrophotometer (Sandiego, California, USA) was used for the characterization of the UV–vis absorption spectra of washing effluents in the wavelength of 324 nm (related to nano-TiO<sub>2</sub> absorption) after 1W and 10W.

#### Water droplet adsorption

The hydrophilicity of the samples was studied by the measurement of the time required for the water droplet to adsorb and spread on the fabric surfaces. The test was done based on AATCC Test Method 79-2000. To this end, water was dropped from 1 cm on the fabric surface by a small syringe. The time of the complete adsorption of water droplets on the fabric surfaces was measured for 10 replicates, and the average value is reported.<sup>36</sup>

#### UV protection (reflectance spectrum)

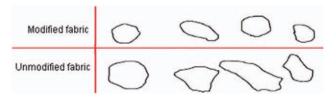
A Varian Cary 500 UV–vis–near infrared spectrophotometer instrument (Melbourne, Australia) was used to measure the diffuse UV reflectance of the fabrics at wavelengths ranging from 200 to 400 nm.

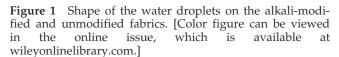
## Vertical wicking

Vertical wicking was examined with fabrics with dimensions of  $1 \times 5 \text{ cm}^2$  kept in vertical direction as 1 cm of their height was dipped in the distilled water, and the time of water movement in a defined height was recorded.

## **RESULTS AND DISCUSSION**

The treatment of PET fabric with alkali solution (sodium hydroxide) is a versatile method for imparting certain desirable properties because this topochemical degradation causes scission of the surface PET chains through hydrolysis and introducing hydrophilic groups such as OH and COOH on the surface of the fabric.<sup>29</sup> This treatment causes a weight loss of about 10–12% on each fabric sample because of surface hydrolysis and the cracks and voids created on the fiber surface. The handle and drape of surface-modified samples improves considerably.<sup>23</sup>





#### Hydrophilicity

The hydrophilicity of the fabrics was studied by measurement of the time required for the water droplet to adsorb and spread on the fabric surfaces. The average values of the droplet adsorption time showed a change from 6 s for the unmodified fabric to 12 s for the alkali-modified fabric. This could have been due to different reasons, including (1) decreasing fiber fineness, which led to increasing interfibers and intervarn capillary spaces and caused a slower rate of water flow; (2) increasing unevenness of the fabric surfaces, which led to a prolonged time for water movement on the fabric surface; and (3) a longer time required for interaction of the water molecules with the hydrophilic groups created on the alkali-modified fabric surface as a result of hydrogen bonding. The shape and area of water droplets on the alkali-modified and unmodified samples (Fig. 1) proved higher horizontal wicking for the unmodified fabrics, as the droplet spread rapidly on these fabric surfaces. This made larger random shapes compared to that of the alkali-modified fabrics with the smaller circular shapes (spreading; Fig. 1).

#### Vertical wicking

The vertical wicking test of the alkali-modified and unmodified fabrics showed an increase in the vertical wicking time for the alkali-modified fabrics (from 10 s for the unmodified fabric to 63 s for the alkali-modified fabric) could have been due to the (1) time required for hydrogen bonding of the water molecules and the hydroxyl groups of alkalinehydrolyzed PET fabric, (2) bigger capillary spaces, and (3) increased fiber surface roughness.

## TiO<sub>2</sub> content

The total  $TiO_2$  content in the PET fabrics surface was calculated on the basis of measured residual  $TiO_2$  for the fabrics after 1W and 10W. Figure 2 shows the amount of residual  $TiO_2$  after different washing cycles.

The modified PET fabric loaded with nano- $TiO_2$  contained the higher nano- $TiO_2$  content even after 10W (Fig. 2). The higher nano- $TiO_2$  content in the

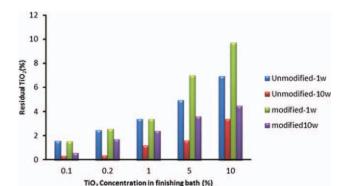
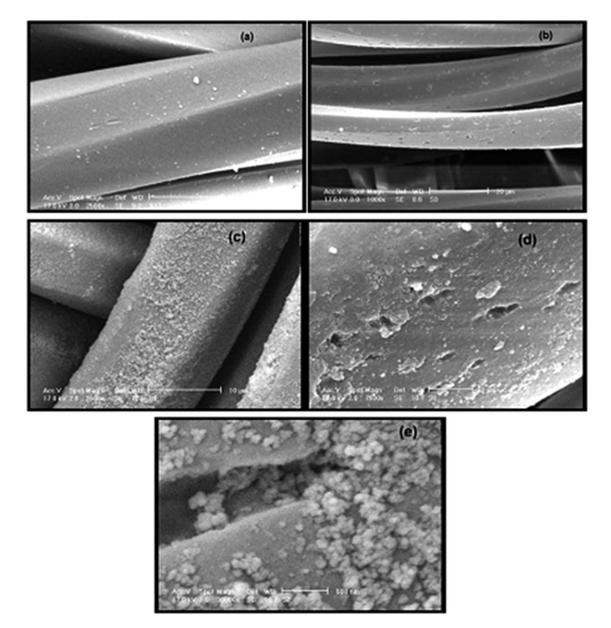


Figure 2 Residual  $TiO_2$  after 1W and 10W on the alkalimodified and unmodified fabric. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

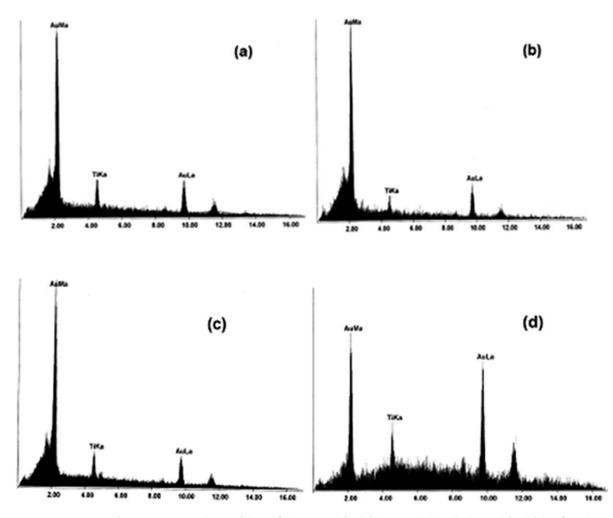
modified fabrics was the consequence of the more efficient binding of nano-TiO<sub>2</sub> to the carboxylates groups created by the alkaline hydrolysis.<sup>37–39</sup> Also, the agglomerations of nano-TiO<sub>2</sub> entrapped in the created voids and cracks on the alkali-treated PET could be considered for this phenomenon, as shown in Figure 3(e).

#### SEM images

The surfaces of the fabrics were observed with SEM. The effect of alkaline hydrolysis on the surface of fabric was completely clear in SEM. Figure 3 reveals the unevenly distributed aggregates of nano-TiO<sub>2</sub> with dimensions of less than 100 nm on the surface



**Figure 3** SEM picture of the different PET surfaces: (a) raw, (b) alkali-modified, and (c) TiO<sub>2</sub>-coated unmodified fabric; (d) TiO<sub>2</sub>-coated, alkali-modified fabric; and (e) TiO<sub>2</sub>-coated, alkali-modified fabric with higher resolution.



**Figure 4** EDX spectra of 5%  $TiO_2$ -coated PET fabrics [(a) unmodified fabric and (b) alkali-modified fabric] and 1%  $TiO_2$ -coated PET fabrics [(c) unmodified fabric and (d) alkali-modified fabric].

of the modified PET fabric. In Figure 3(a,b), SEM micrographs show the surface of the unmodified and alkali-modified PET fabrics, and Figure 3(c,d) shows the nano-TiO<sub>2</sub> coated surface of the unmodified and alkali-modified fabrics, respectively. Figure 3(e) shows the nano-TiO<sub>2</sub> coated surface of the modified fabric at higher resolution. We observed an even distribution of nano-TiO<sub>2</sub> particles on the surface of the unmodified fabric compared to the modified fabric, which had some uneven cracks and voids produced on its surface during the alkaline hydrolysis. These cracks contained more nano-TiO<sub>2</sub> entrapped inside them. The large particles could be easily removed from the fiber surface, whereas the small particles could penetrate the fabric matrix and adhere more strongly to the fabric surface.<sup>40</sup>

#### EDX

Additionally, the presence of nano-TiO<sub>2</sub> on the PET fabric surfaces was proven by SEM performed in EDX mode. The EDX spectra of the unmodified and alkali-modified fabrics coated with the same concen-

tration of TiO<sub>2</sub> (5% w/v) after 10W are shown in Figure 4(a,b), respectively. A higher peak for Ti content can be seen in Figure 4(a) and was related to the higher nano-TiO<sub>2</sub> adsorbed on the unmodified fabric surface (3.51%) compared to that of the modified fabric, shown in Figure 4(b), with about 1.48% TiO<sub>2</sub> on the fabric surface. The same results could be seen for the fabric treated with 1% TiO<sub>2</sub> as the amount of adsorbed titania for the unmodified sample [Fig. 4(c)] was 3.18%; it was about 1.12% for the modified fabric. Considering the higher residual TiO<sub>2</sub> on the modified fabric surface proven by the heat-treatment test and SEM, to this could be a result of the agglomeration of nanoparticles in the cracks of the hydrolyzed PET.

#### Self-cleaning

The degradation of methylene blue was evaluated on the blank sample and alkali-modified and unmodified PET coated with TiO<sub>2</sub>. The  $\Delta E$  values are shown in Tables I and II for both the unmodified and alkali-modified PET before daylight irradiation

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TiO <sub>2</sub> (%)	<i>L</i> * (AF)	<i>L</i> * (BF)	a* (AF)	<i>a</i> * (BF)	<i>b</i> * (AF)	<i>b</i> * (BF)	$\Delta E$
Blank sample	71.151	68.464	-3.411	-1.702	-10.614	-14.463	4.4966
0.1	69.831	60.519	-1.363	4.738	-11.893	-25.552	17.6211
0.2	71.72	59.14	-2.538	3.395	-8.912	-27.121	22.9134
1	77.261	61.296	-2.123	0.691	-5.447	-26.755	26.7736
5	78.375	59.658	-1.408	4.041	-4.744	-28.428	30.6749
10	78.752	59.887	-1.85	2.39	-4.54	-29.368	31.4689

 TABLE I

 Spectrophotometric Characterization of the Unmodified PET Treated with Various Amounts of Nano-TiO2

(BF) and after daylight irradiation (AF). It can be clearly seen that  $\Delta E$  significantly increased with increasing TiO<sub>2</sub> concentration; this confirmed the photocatalytic activity of TiO<sub>2</sub>, in that the greater increase in TiO<sub>2</sub> caused the higher color change. This means that more discoloration occurred on the TiO<sub>2</sub>-treated PET than in the blank sample (Fig. 5). It could also be seen that the *L*\* values increased AF for all of the nano-TiO<sub>2</sub> treated fabrics. However, the *L*\* value was higher for the fabrics with the higher nano-TiO<sub>2</sub>. This confirmed the enhanced photoactivity of the fabrics.

Comparison of the  $\Delta E$  values of the alkali-modified and the unmodified fabrics showed a higher  $\Delta E$ for the unmodified fabrics. This means that the rate of discoloration decreased for the alkali-modified samples as a result of the interaction between the cationic methylene blue with the anionic hydrophilic groups OH and COOH of the alkali-modified PET. This made discoloration more difficult.

## Washing durability

Because  $TiO_2$  has some particular absorption peak detectable in the UV–vis spectrum, shown in Figure 6, this can be used for identification of  $TiO_2$  in washing effluent.<sup>36</sup> As the UV–vis spectrum method is a direct method, it can provide the most exact method for evaluating durability against washing.<sup>6</sup> For this goal, the  $TiO_2$  concentration in the effluent was considered as the washing durability. Ten repeated washing cycles for determining the durability of the  $TiO_2$ particles on the PET fabric surface showed that the concentration of  $TiO_2$  in the effluents was increasing.

Increasing the TiO<sub>2</sub> concentration in the washing effluent shows a lower permanent property on the fabric. Consequently washing effluents with the suit-

able ratio were evaluated by UV–vis absorption. Figure 7 shows that the TiO<sub>2</sub> concentration in the effluent increased by increasing nano-TiO<sub>2</sub> on the fabrics in the both alkali-modified and unmodified fabrics. However, the alkaline pretreatment had a major effect on decreasing the nano-TiO<sub>2</sub> content in the effluent even after 1W. Consequently, a major improvement of stability could be obtained with surface modification.<sup>40,41</sup> This was due to the increasing tendency of the nano-TiO<sub>2</sub> particles to the created anionic hydrophilic groups on the fabric surface. This made the treatment more durable and the physical entrapment of nanoparticles in the cracks and voids a result of alkaline hydrolysis.

### Water droplet adsorption time

Increasing the TiO<sub>2</sub> concentration from 0.1 to 10% w/v after each washing cycle expectedly caused a decline in the time required for the water droplet to adsorb on the fabric surfaces (Table III). This confirmed the improved wettability with nano-TiO<sub>2</sub>. Increasing the adsorption time for 1W and the last washing cycles of various fabrics with different TiO<sub>2</sub> contents confirmed that frequent washing decreased the nano-TiO<sub>2</sub> on the fabric surface.<sup>40</sup>

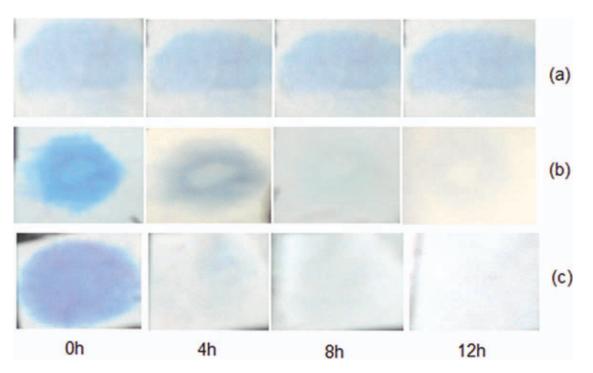
The alkali-treated samples after 10W shown in Figure 8 indicate the shorter time of the water droplet adsorption compared to that of the untreated fabrics. This verified the higher residual nano-TiO<sub>2</sub> on the pretreated fabrics surface and the greater hydrophilic properties.

The area and time of water droplet adsorption on the alkali-modified fabrics are shown in Figures 8 and 9. A decrease in the time and an increase in the area of water spreading by increasing nano-TiO<sub>2</sub> concentration could be seen. This means that increasing

TABLE II Spectrophotometric Characterization of the Alkali-Modified PET Treated with Various Amounts of Nano-TiO<sub>2</sub>

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TiO <sub>2</sub> (%)	L* (AF)	L* (BF)	a* (AF)	<i>a</i> * (BF)	<i>b</i> * (AF)	<i>b</i> * (BF)	$\Delta E$
Blank sample	71.151	68.464	-3.411	-1.702	-10.614	-14.463	4.4966
0.1	67.885	60.151	-5.827	-1.936	-13.704	-26.314	15.2959
0.2	61.182	56.172	-1.969	1.223	-18.484	-32.451	15.17781
1	62.47	55.562	-3.475	1.993	-16.56	-32.184	17.134
5	72.564	62.134	-3.918	-7.6	-8.15	-27.525	22.4838

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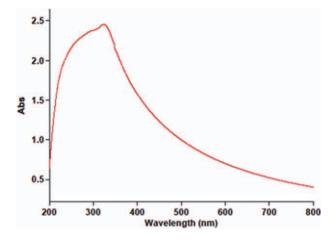
**Figure 5** Discoloration of methylene blue (0.02%) on the various PETs with different exposure times under daylight: (a) blank, (b) alkali-modified, and (c) unmodified. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the TiO<sub>2</sub> concentration led to the rapid water droplet spreading on the fabric surface, and the presence of the hydrophilic nano-TiO<sub>2</sub> accelerated the wicking.

Comparison of the alkali-modified and unmodified fabrics perfectly confirmed the hydrophilic efficiency of the alkali-modified fabrics, as it took less time for the water droplets to spread on their surfaces.

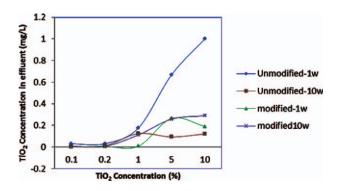
## Vertical wicking

Vertical wicking results of the alkali-modified and unmodified fabrics loaded with TiO<sub>2</sub> nanoparticles



**Figure 6** TiO<sub>2</sub> absorption peak detected by the UV–vis spectrum. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

showed a decrease in the time required for the water to move upward for the alkali-modified samples, as shown in Table IV. The results in the vertical test were in accord with the results of the water droplet spreading on the fabric surface as the wettability increased. The lower wetted surface area or the smaller water spreading on the alkali-modified fabrics was a result of the higher wettability and water adsorption by the hydrophilic groups and an increase in the capillary spaces for the water transport through the fabric; this prevented water spreading. However, in the case of the vertical wicking of the nano-TiO<sub>2</sub> treated fabrics, the hydrophilic nano-TiO<sub>2</sub> particles helped to adsorb water and



**Figure 7**  $\text{TiO}_2$  concentrations in the washing effluent bath for the alkali-modified and unmodified fabrics treated with different nano-TiO<sub>2</sub>'s after 1W and 10W. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

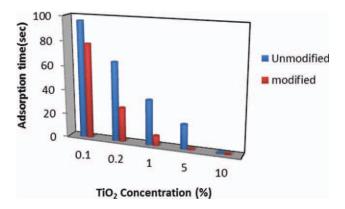
	Water Droplet Adsorpti Unmodified fabric		Alkali-modified fabric		
TiO <sub>2</sub> (%)	1W	10W	1W	10W	
0.1	80	96.2	4.57	78	
0.2	50	65	0.65	28.01	
1	23.8	36.8	2.69	8.06	
5	6.5	20.28	0.52	0.86	
10	0.76	0.85	0.42	0.53	

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transferred them to the other hydrophilic groups and/or particles and also decreased the interfiber and intervarn capillary spaces and filled the voids and cracks by nano-TiO<sub>2</sub>. This led to the rapid vertical wicking of water molecules. Thus, the presence of nano-TiO<sub>2</sub> led to improvements in vertical wicking and wettability.

## **UV** protection

The UV reflectance spectrum of the nano-TiO<sub>2</sub> treated PET fabrics revealed that increases in nano-TiO<sub>2</sub> for all of the alkali-modified and unmodified fabrics caused a decrease in the reflectance percentage of irradiated UV rays; this meant that the nano-TiO<sub>2</sub> particles blocked the UV rays, and it proved the UV protection property of the nano-TiO<sub>2</sub> treated fabrics.<sup>14</sup> It could also be seen that the alkali modification improved some of the properties of the fabrics, such as providing a higher nano-TiO<sub>2</sub> adsorption, but it did not affect the UV protection properties of the fabric. As for both the unmodified and the alkali-modified fabrics with 1% w/v TiO<sub>2</sub> after 10W, almost the same reflectance curves were obtained. The UV reflectance of the alkali-modified fabric was almost similar to the unmodified fabric at the same concentration of nano-TiO2. This means that the alkali surface modification improved the nano-TiO<sub>2</sub> adsorption to the fabric but could not



**Figure 8** Water droplet adsorption time on the alkali-modified and unmodified PET fabrics treated with different amounts of nano-TiO<sub>2</sub>. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

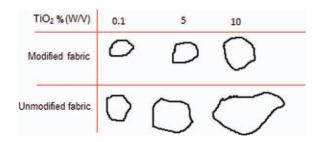


Figure 9 Area and shape of the water droplets on the alkali-modified and unmodified PET treated with various amounts of nano-TiO<sub>2</sub>. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

change the UV protection property of the alkalimodified fabrics. This could have been due to the agglomeration of nano- $TiO_2$  particles in the cracks and voids produced on the fabric surface after alkaline hydrolysis. Therefore, the outer layer of nanoparticles blocked the irradiated UV rays and then entrapped nanoparticles on the alkali-modified fabric surface did not affect the reflectance. This means that the alkali modification did not affect the UV protection properties.

It can be observed from Figure 10 that the lowest amount of UV reflectance belonged to the unmodified PET fabric treated with 1% w/v nano-TiO<sub>2</sub> with no modification pretreatment after 1W. This could be explained by the evenly distributed TiO<sub>2</sub> nanoparticles on the fabric surface compared to the alkali-modified sample, as the UV reflectance in the unmodified fabric was greater than that of the sample after 10W.

This means that the use of 1% nano-TiO<sub>2</sub> on the unmodified fabric was enough to obtain the high UV protection properties after just 1W. However, as the number of washing cycle increased to 10, there was a significant decrease in UV protection for the unmodified fabric. For the alkali-modified fabrics, there was no significant difference between the UV reflectance percentage of the 1W and 10W samples. This proved the effect of surface modification through alkali hydrolysis on the durability of the nano-TiO<sub>2</sub> deposited particles and UV protection properties.

All of these showed the influence of alkali hydrolysis on various properties of the PET fabrics. In one

TABLE IV Vertical Wicking Time for the Alkali-Modified and Unmodified Samples Treated with Various Amounts of Nano-TiO<sub>2</sub>

TiO <sub>2</sub> (%)	Unmodified PET	Alkali-modified PET		
0.1	310	150		
0.2	240	183		
1	180	124		
5	30	10		
10	14	3		

60

**Figure 10** UV reflectance percentages of the modified and unmodified fabrics. H shows the hydrolyzed samples, and W shows the number of washing cycles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

way, the alkali hydrolysis improved the hydrophilicity of the PET fabrics with increasing fiber surface roughness and interfiber/interyarn capillary spaces. By this, the wettability and wicking rate decreased. PET surface hydrolysis helped to increase the nano- $TiO_2$  adsorption but caused the agglomeration of nanoparticles in the voids.

#### CONCLUSIONS

The modification of PET fabric is an important process for increasing its applications. This research has shown that alkaline hydrolysis is a compatible method for introducing hydrophilic groups onto the surface of PET fabric to impart new specifications to the fabric, such as better binding to nano-TiO<sub>2</sub> particles. Also, the use of high temperature as a curing process can produce good stability for TiO<sub>2</sub> nanoparticles on the PET fabric surface, even after 10W. The alkali-modified PET fabric had a higher TiO<sub>2</sub> content compared to the unmodified one at the same concentration. Furthermore, the binding efficiency of the alkali-modified PET fabric was much higher than that of the unmodified one, as the lower amounts of nano-TiO2 were removed from the treated fabrics through the washing process. It was confirmed that increasing the nano-TiO<sub>2</sub> concentration led to improved self-cleaning properties of the fabrics because of the photocatalytic activity of the  $TiO_2$  nanoparticles.

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