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Functionalization of polyester fabrics with alginates and TiO_2 nanoparticles

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ABSTRACT

This study was aimed to investigate the possibility of engineering the multifunctional textile nanocomposite material based on the polyester fabric modified with natural polysaccharide alginate and colloidal TiO_2 nanoparticles. The multifunctionality of such nanocomposite material was evaluated by analyzing its UV protection efficiency, antibacterial and photocatalytic activity. The level of UV protection was verified by the UV protection factor (UPF) of polyester fabrics. Antibacterial activity of modified polyester fabrics was tested against Gram-negative bacterium *Escherichia coli*. The photocatalytic activity of TiO_2 nanoparticles deposited on the polyester fabrics was followed by degradation of methylene blue as a model compound in aqueous solution. Modified polyester fabrics exhibited outstanding antibacterial activity and UV protection efficiency even after five washing cycles, indicating the excellent laundering durability. The total photodegradation of methylene blue was reached after 24 h of UV illumination and this ability was preserved and even enhanced after two consecutive cycles.

1. Introduction

Global trends in textile industry are oriented towards development and manufacturing of high-added value products with multifunctional properties. In addition to fashion and comfort demands, the garments today must simultaneously provide self-cleaning properties, antimicrobial and UV protection (Wong, Yuen, Leung, Ku, & Lam, 2006). Developing technologies should offer desirable level of material functionality and its efficiency, but also they should meet environmental and economic demands.

Several recent studies reported the promising potentials of non-toxic and inexpensive TiO_2 nanoparticles (TiO_2 NPs) for imparting multifunctional properties to different textile materials (Bozzi, Yuranova, Guasaquillo, Laub, & Kiwi, 2005a; Daoud & Xin, 2004; Daoud, Xin, & Zhang, 2005; Daoud et al., 2008; Dong, Bai, Zhang, Liu, & Zhu, 2006; Fei, Deng, Zhang, & Pang, 2006; Liuxue, Xiulian, Peng, & Zhixing, 2007; Meilert, Laub, & Kiwi, 2005; Qi et al., 2006, 2007a; Uddin et al., 2007, 2008; Xin, Daoud, & Kong, 2004; Yuranova, Laub, & Kiwi, 2007; Yuranova, Mosteo, Bandara, Laub, & Kiwi, 2006). The compatibility of TiO_2 NPs surface with fiber surface chemical functionalities is one of the most important prerequisites for obtaining stable composite system and long-term durability effects. The tailoring of desirable fiber surface from the standpoint of its chemical functionality and improvement of TiO_2 NPs binding efficiency recently gained much scientific interest (Bozzi et al., 2005a; Meilert et al., 2005; Mihailović et al., 2008; Qi, Xin, Daoud, & Mak, 2007b). Keeping in mind that hydroxyl and particularly carboxylic groups are the potential sites for binding of TiO_2 NPs, both, chemical and physico-chemical treatments proposed so far, rely mainly on the introduction of these groups to the fiber surfaces. Latest studies indicated that treatments of hydrophobic fibers by low-pressure plasma and corona at atmospheric pressure can significantly enhance the binding efficiency of TiO_2 NPs (Bozzi, Yuranova, & Kiwi, 2005b; Mihailović et al., 2008; Qi et al., 2007b). Daoud et al. reported that acylation of wool fibers with non-toxic succinic acid anhydride led to an increase in reactivity toward anatase nanocrystals (Daoud et al., 2008). It was shown that the introduction of additional carboxylic groups to wool likely induced more efficient binding of TiO_2 NPs and more uniform coating of the fiber surface, which in turn resulted in enhanced self-cleaning efficiency. Meilert et al. used commercially available non-toxic and low cost saturated poly-carboxylic acids (succinic acid, 1,2,3-propanetriccarboxylic acid and 1,2,3,4-butanetetracarboxylic acid) as chemical spacers to attach TiO_2 NPs to cotton fibers (Meilert et al., 2005). ATR-IR spectroscopy revealed the formation of ester bonds between the spacer and cotton fiber surface while some free carboxylic groups remained available to bind TiO_2 NPs. The cotton textiles modified in such a manner performed stable self-cleaning properties.

The abundance of carboxylic groups existing in alginates makes this biopolymer a potential modifier of textile fiber surfaces, which

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may provide additional sites for binding of TiO_2 NPs. In addition to its traditional application as a thickening agent in textile printing, alginate has become one of the most valuable materials for wound management due to its high biocompatibility (Petrulyte, 2008). Alginates are natural polysaccharides extracted from brown seaweed (Da Silva, Bierhalz, & Kieckbusch, 2009). They comprise of 1,4-linked β-D-mannuronic (M) and α-L-guluronic (G) acid monomers. These monosaccharide units form the regions of M blocks (MM), G blocks (GG) and alternating structures (MG) (Da Silva et al., 2009; Kristiansen et al., 2009), the ratio of which affects the physical properties of biopolymer (Lawrie et al., 2007). Gorenšek and Bukošek reported that finishing of dyed cotton fabrics with zinc chloride and alginates provides satisfactory UV protection and antimicrobial properties (Gorenšek & Bukošek, 2006).

This study was aimed to engineer the multifunctional nanocomposite textile material based on the polyester (PES) fabric modified with alginates and TiO_2 NPs. The alginate was applied as a fiber surface modifier for improvement of binding efficiency between colloidal TiO_2 NPs and PES fabric. Antibacterial activity was tested against Gram-negative bacterium *Escherichia coli*. The UV blocking efficiency was examined by determining the UV protection factor (UPF) of PES fabrics. The photocatalytic activity of TiO_2 NPs deposited on the PES fabrics was evaluated by degradation of methylene blue as a model compound.

2. Experimental

2.1. Synthesis of colloidal TiO_2 NPs

All the chemicals used for the synthesis of TiO_2 colloid were analytical grade and used as received without further purification (Aldrich, Fluka). Milli-Q deionized water was used as a solvent. The colloid of TiO_2 NPs was prepared in a manner analogous to the procedure proposed by Rajh, Ostafin, Mićić, Tiede and Thurnauer (1996). The solution of $TiCl_4$ cooled up to −20 °C was added drop-wise to cooled water (at 4 °C) under vigorous stirring and then kept at this temperature for 30 min. The pH value of the solution was between 0 and 1, depending on $TiCl_4$ concentration. Slow growth of the particles was achieved by applying dialysis against water at 4 °C until the pH of the solution reached 3.5. The concentration of TiO_2 colloid was determined from the concentration of the peroxide complex obtained after dissolving the particles in concentrated H_2SO_4 (Thompson, 1984). Subsequently, the colloid was thermally treated in reflux at 60 °C for 16 h.

2.2. Substrate preparation

Desized and bleached polyester (PES, 115 g/m^2) fabric was chosen as a substrate in this study. The impurities from the fabric surface were removed in the bath containing 0.5% nonionic washing agent Felosan RG-N (Bezema) at liquor-to-fabric ratio of 50:1 (Radetić et al., 2008). After 15 min of washing at 50 °C, the fabrics were rinsed once with warm water (50 °C) for 3 min and three times (3 min) with cold water. Afterwards, the fabrics were dried at room temperature.

Low viscosity sodium alginate (CHT-alginat NVS, Bezema) was used for the preparation of 0.1% alginate solution. Sodium alginate was dissolved in deionized water and stirred for 30 min. One gram of PES fabric was dipped into 50 mL of freshly prepared 0.1% alginate solution for 10 min. After 10 min of curing at 100 °C, the fabrics were rinsed twice (5 min) with deionized water and dried at room temperature.

One gram of PES fabric was immersed in 20 mL of 0.1 M TiO_2 colloidal solution for 5 min and dried at room temperature. After 30 min long curing at 100 °C, the fabrics were rinsed twice (5 min) with deionized water and dried at room temperature.

2.3. Methods

The shape and size of TiO_2 nanocrystalls were characterized by conventional transmission electron microscopy (TEM, JEOL 100 CX at 100 kV) and high resolution electron microscopy (HREM, Phillips CM200 with a FEG at 200 kV).

Room-temperature micro-Raman spectra were collected in backscattering configuration using Jobin Yvon T64000 triple spectrometer equipped with a nitrogen cooled charge-coupled-device detector and confocal microscope. Argon ion laser line at 514.5 nm was used as an excitation source with an incident laser power less than 10 mW. Such low laser power was applied in order to avoid sample heating.

Fiber morphology was characterized by scanning electron microscopy (SEM, JEOL JSM 6460 LV). Energy dispersive X-ray (EDX) mode was applied for the elemental composition analysis. Gold layer was deposited on the samples before the analysis.

The total content of Ti in the PES fabrics was quantitatively determined using a Perkin-Elmer 403 atomic absorption spectrometer (AAS).

The UV transmission spectra of PES fabrics were measured by UV/Vis spectrophotometer Cary 100 Scan (Varian). The UV protection factor (UPF) values were automatically calculated on the basis of the recorded data in accordance with Australia/New Zealand standard AS/NZS 4399:1996 using a Startek UV fabric protection application software version 3.0 (Startek Technology).

The antibacterial efficiency of PES fabrics was quantitatively evaluated using a Gram-negative bacterium *Escherichia coli* ATCC 25922. Bacterial inoculum was prepared in the tripton soy broth (Torlak, Serbia), which was used as the growth medium for bacteria while the potassium hydrogen phosphate buffer solution (pH 7.2) was used as the testing medium. Bacteria were cultivated in 3 mL of tripton soy broth at 37 °C and left overnight (late exponential stage of growth). Afterwards, 70 mL of sterile potassium hydrogen phosphate buffer solution was added to sterile Erlenmeyer flask (300 mL), which was then inoculated with 0.7 mL of the bacterial inoculum. The zero counts were made by removing 1 mL aliquots from the flask with inoculum, and making 1:10 and 1:100 dilutions in physiological saline solution. 0.1 mL of the 1:100 solution was placed onto a tripton soy agar (Torlak, Serbia) and after 24 h of incubation at 37 °C, the zero time counts (initial number of bacterial colonies) of viable bacteria were made.

One gram of sterile fabric cut into small pieces was put in the flask (70 mL of sterile potassium hydrogen phosphate buffer solution inoculated with 0.7 mL of the bacterial inoculum) and shaken for 1 h. One-hour counts were made in accordance with an above described procedure.

The percentage of bacteria reduction (R,%) was calculated using the Eq. (1):

$$R = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

where: C_0 (CFU – colony forming units) is the number of bacteria colonies on the control fabric (untreated fabric without TiO_2 NPs) and C (CFU) is the number of bacteria colonies on the fabric loaded with TiO_2 NPs (Ki, Kim, Kwon, & Jeong, 2007; Lee, Yeo, & Jeong, 2003).

Photocatalytic activity of TiO_2 NPs deposited on the PES fabrics was assessed by degradation of methylene blue (MB). PES fabric (0.5 g) was immersed in 25 mL of MB solution (10 $mg\,L^{-1}$, pH 5.81) and illuminated by ULTRA-VITALUX lamp, 300 W (Osram) for 2, 4, 6, 8 and 24 h. The MB concentration was determined by measuring absorption intensity at 664 nm using an UV/Vis spectrophotometer Cary 100 Scan (Varian).

3. Results and discussion

TEM image of TiO_2 NPs with average dimension of 6 nm is shown in Fig. 1a. The NPs tend to be single crystalline (Fig. 1b), although the multiple twinned particles having the haring-bone structure were also observed. The particles are irregularly shaped. The ring electron diffraction pattern is characteristic of the anatase crystal structure (Fig. 1c). This result is in agreement with Raman spectroscopy measurements of powdered TiO_2 NPs. Raman peaks (Fig. 1d) correspond well to characteristic Raman signals of anatase at wavenumbers of 154, 406, 515 and 637 cm^{-1} (Uddin et al., 2007).

In order to determine the total TiO_2 content in the PES fabrics, elemental analysis using atomic absorption spectroscopy was carried out. The total TiO_2 content in the PES fabrics was calculated on the basis of measured Ti content. It was found that PES fabric loaded with TiO_2 NPs (PES + TiO_2) and PES fabric pretreated with alginate and loaded with TiO_2 NPs (PES + ALG + TiO_2) contains 1.5 and 2.1 wt.% of TiO_2, respectively. The 38% higher TiO_2 content in the PES + ALG + TiO_2 fabrics is the consequence of better binding efficiency of TiO_2 NPs to the carboxylic groups of alginates. Namely, when diameter of nanocrystalline anatase TiO_2 particles becomes smaller than 20 nm, the surface Ti atoms adjust their coordination environment from octahedral to more reactive penta-coordinated (square pyramidal) (Chen, Rajh, Jäger, Nedeljković, & Thurnauer, 1999; Rajh et al., 2002). These undercoordinated defect sites are likely the sources of enhanced binding between alginate functionalities and Ti atoms. Previous study indicated that surface complex formation involving Fe carboxylate is likely to be the mechanism for trivalent ion cross-linking of the alginate network (Fernandez, Dhananjeyan, Kiwi, Senuma, & Hilborn, 2000).

Additionally, the presence of TiO_2 NPs on the surface of PES fabrics was proved by SEM analysis performed in EDX mode. EDX spectra of the PES + TiO_2 fabric and PES + ALG + TiO_2 fabric are shown in Fig. 2. EDX measurements also reveal higher Ti content on the PES + ALG + TiO_2 fiber surface.

The presence of alginates was confirmed by SEM analysis. Approximately 330 nm thick layer of biopolymer on the surface of PES fiber can be observed in Fig. 3a. Fig. 3b reveals unevenly distributed aggregates of TiO_2 NPs with dimensions less than 100 nm on the surface of the PES + ALG + TiO_2 fiber.

To examine the antibacterial activity of PES fabrics loaded with TiO_2 NPs the test against Gram-negative bacterium *E. coli* was accomplished. The values of bacterial reduction of differently modified PES fabrics are given in Table 1. The PES + TiO_2 fabric showed poor antibacterial activity. The contribution of alginates to antibacterial efficiency of PES fabric (PES + ALG) is negligible (R = 9.6%). However, the impregnation of PES fabrics with alginates and sub-

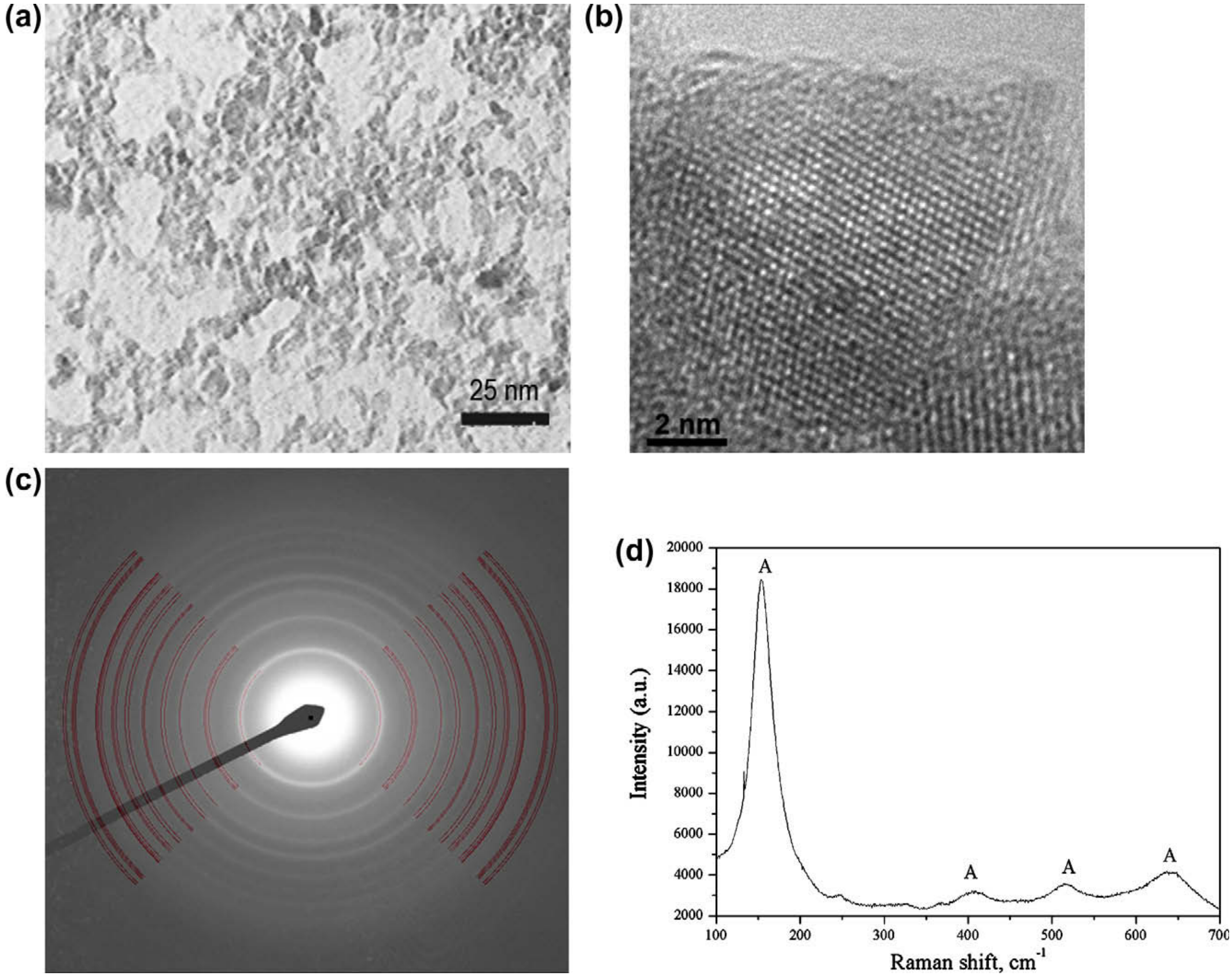

Fig. 1. Characterization of TiO_2 NPs: TEM image (a), HREM image (b), SAED pattern (c) and Raman spectrum (d).

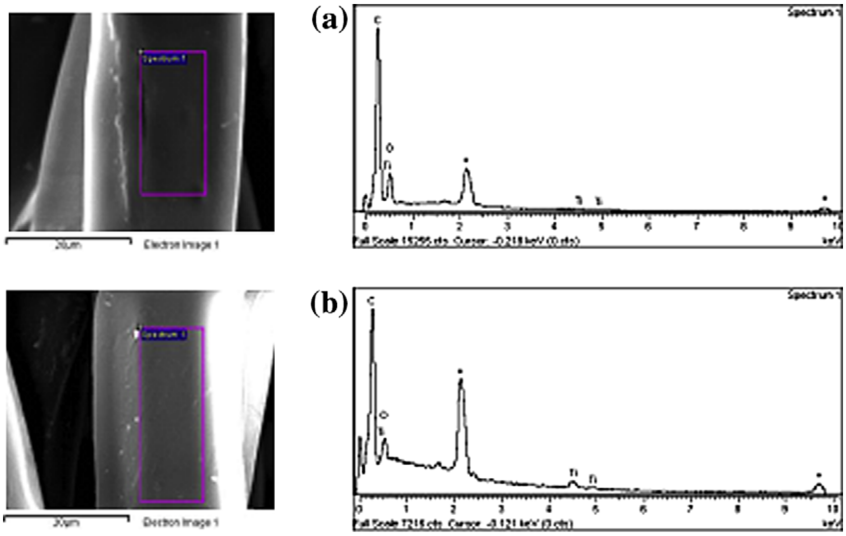

Fig. 2. EDX spectra of (a) PES + TiO_2 fiber and (b) PES + ALG + TiO_2 fiber ($*$ in spectra corresponds to Au peaks).

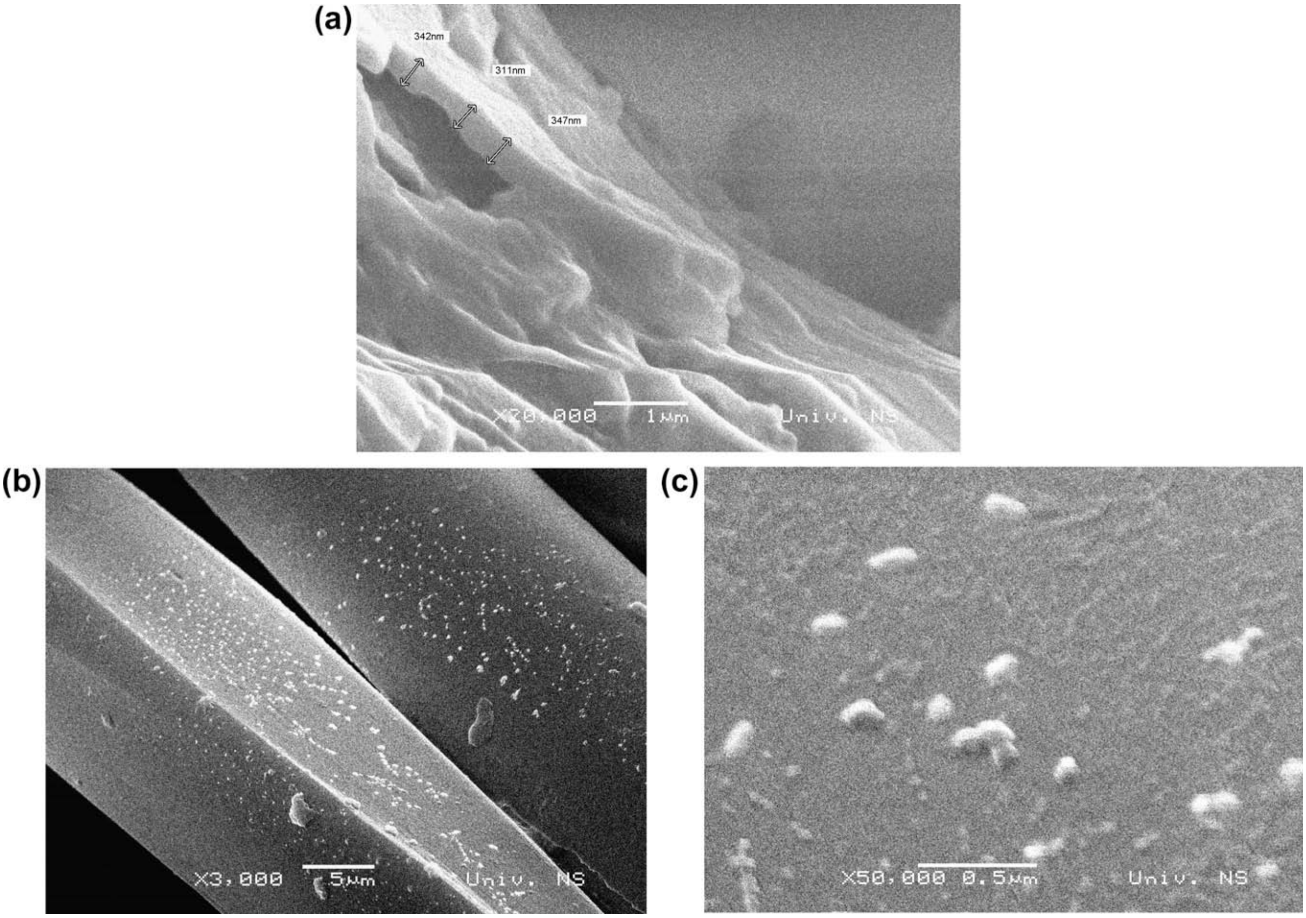

Fig. 3. SEM images of (a) alginate biopolymer on the PES fiber surface and (b) TiO_2 NPS on the PES + ALG + TiO_2 fibers scanned at different magnifications.

sequent loading with TiO_2 NPs (PES + ALG + TiO_2) provided maximum bacteria reduction. Excellent antibacterial efficiency of this nanocomposite textile material was preserved (R = 99.8%) after five washing cycles, indicating the good laundering durability.

The exact mechanism of bacterial destruction by TiO_2 is not yet fully understood (Robertson, Bahnemann, Robertson, & Wood, 2005). It is suggested that outer membrane of *E. coli* bacteria cells is destroyed by degradation of endotoxin, an integral component of cell membrane (Sunada, Kikuchi, Hashimoto, & Fijishima, 1998). Another proposed mechanism relies on the "lipid peroxidation" (Maness et al., 1999; Sunada, Watanabe, & Hashimoto, 2003). It is supposed that extremely reactive species such as superoxide ions and hydroxyl radicals, generated on the UV irradiated TiO_2 surface, attack the polyunsaturated phospholipids in the bacterial

Table 1
Antibacterial efficiency of PES fabrics loaded with TiO_2 NPs.

Sample	Initial number of bacterial colonies (CFU)	Number of bacterial colonies (CFU)	R,%
Before washing			
Control PES	3.7×10^5	1.5×10^5	
PES + TiO_2		1.3×10^4	91.3
Control PES	4.1×10^5	1.7×10^5	
PES + ALG		1.5×10^5	9.6
Control PES	5.7×10^5	1.3×10^5	
PES + ALG + TiO_2		165	99.9
After washing			
Control PES	7.5×10^5	1.1×10^5	
PES + ALG + TiO_2		195	99.8

Table 2
UPF values of PES fabrics loaded of with TiO_2 NPs.

Sample	UPF value	UPF rating
PES	43.0	40
PES + ALG	42.0	40
PES + TiO_2	91.6	50+
PES + TiO_2 (after washing)	66.2	50
PES + ALG + TiO_2	119.8	50+
PES + ALG + TiO_2 (after washing)	111.6	50+

cell membrane and destroy it. In this way, the interior of the cell and intracellular components become more accessible to TiO_2 particles and killing of bacteria can be completed due to the loss of essential functions such as respiratory activity (Huang et al., 2000; Maness et al., 1999).

The effect of TiO_2 NPs onto UV protection efficiency of PES fabrics was evaluated by measuring the transmission spectra. The transmission spectra were recorded across the UVB (280–315 nm) and UVA (315–380 nm) spectral regions as presented in Fig. 4. The treatment of PES fabrics with alginates insignificantly affected the UV transmission. The loading of PES fabrics with TiO_2 NPs resulted in an overall decrease in UV transmission intensity. The PES + TiO_2 and PES + ALG + TiO_2 fabrics showed comparable transmission curves in the region between 360 and 380 nm, but they differ in the region between 310 and 360 nm. UV transmission decrease is more prominent on the PES + ALG + TiO_2 fabric, indicating its stronger absorption ability likely due to higher amount of deposited TiO_2 NPs. The UV transmission intensities of the PES + ALG + TiO_2 fabric exposed to five washing cycles slightly increased compared to the same sample before washing. In contrast, the PES + TiO_2 fabric showed poor laundering durability and UV transmission intensities significantly increased after washing.

The rate of UV protection was quantified and expressed via UPF values that are given in Table 2. It is suggested that UPF of garments should be at least 40 to 50+. UPF value of 43 and corresponding UPF rating of 40 categorize the PES fabric to fabrics with an excellent UV protection. The TiO_2 NPs deposition onto PES fabrics led to a rise of UPF values to the level corresponding to UPF rating of 50+, which assigns the maximum UV protection. UPF value of the PES + TiO_2 fabric decreased by 27.7% after five washing cycles and consequently UPF rating dropped from 50+ to 50. The washing of PES + ALG + TiO_2 fabric induced slight decrease in UV transmission intensity, but still its UPF value is by 7% higher compared to PES + TiO_2 fabric that was not washed. These results imply good laundering durability of the PES + ALG + TiO_2 fabric. Good laundering durability can be attributed to enhanced binding efficiency of TiO_2 NPs to the PES fabric modified by alginate.

The photocatalytic activity of TiO_2 NPs deposited on the PES fabrics was evaluated by degradation of methylene blue (MB) under UV light illuminnation. The photodegradation of MB on the TiO_2 NPs surface deposited on the PES and PES + ALG fabrics was followed by MB concentration changes (C/C_0) as a function of UV illumination time (Fig. 5).

The adsorption of MB on the PES fabric got saturated after 6 h of UV illumination. The extension of UV illumination time caused no further decrease in MB concentration. In fact, the PES fabric became blue-colored and adsorbed dye was not completely decomposed under the UV illumination, indicating that PES fabric itself does not posses any photocatalytic activity.

The degradation of MB on the PES + TiO_2 fabric was much slower compared to the PES + ALG + TiO_2 fabric as can be seen in Fig. 5. The PES + TiO_2 fabric removed about 72% of MB from solution after 24 h of UV illumination. After repeated rinsing in water, the PES + TiO_2 fabric was still pale blue, demonstrating that TiO_2 NPs could not complete the degradation of MB neither in solution nor on the fabric. On the contrary, the PES + ALG + TiO_2 fabric provided complete removal of MB from the solution after 24 h of UV illumination. The PES + ALG + TiO_2 fabric remained white after performed experiments confirming the total degradation of MB.

The PES + ALG + TiO_2 fabric showed excellent photocatalytic activity due to the presence of TiO_2 NPs. The exact mechanism of MB photodegradation is still not established. For example, Tatsuma

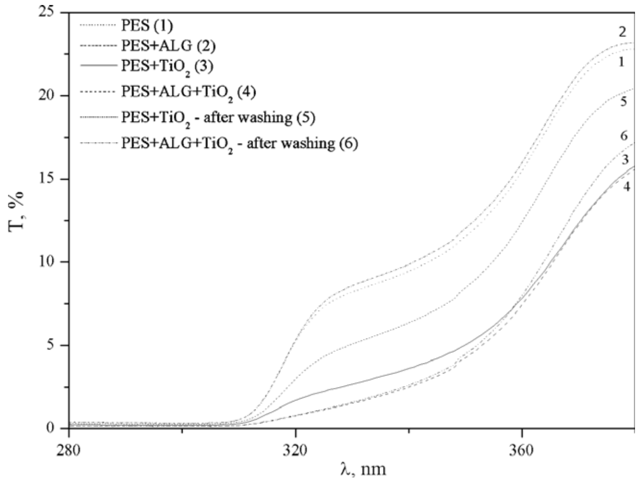

Fig. 4. Transmission spectra of PES fabrics loaded of with TiO_2 NPs.

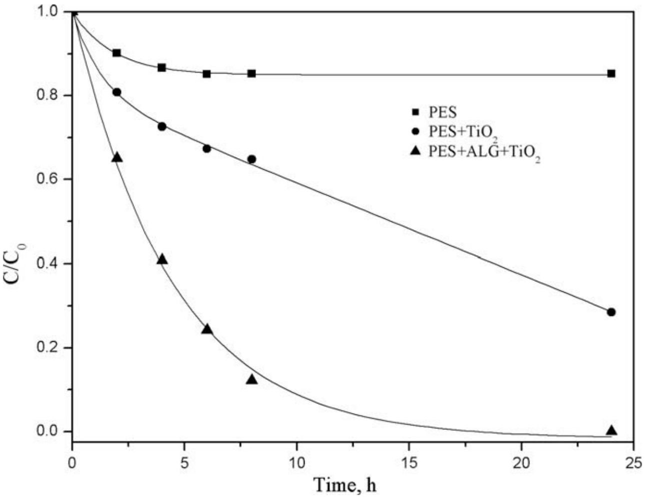

Fig. 5. The dependence of C/C_0 versus time of UV illumination for the PES, PES + TiO_2 and PES + ALG + TiO_2 fabrics.

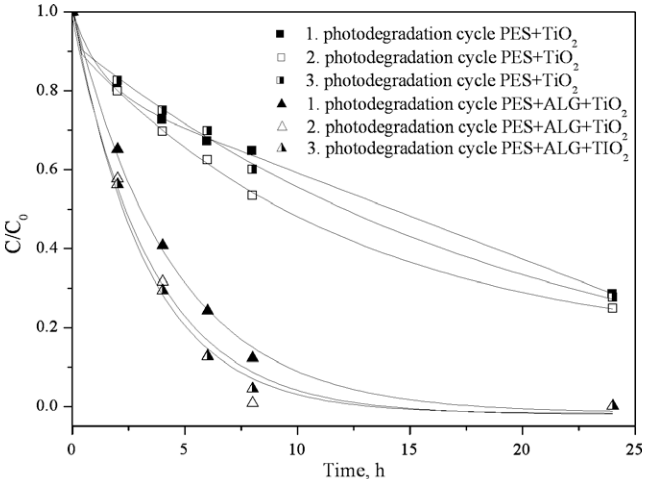

Fig. 6. Changes in relative concentration of MB after repeated photodegradation processes under the UV illumination for the PES + TiO_2 and PES + ALG + TiO_2 fabrics.

et al. proposed two possible mechanisms for the bleaching of MB: reversible reduction of MB to the leuco form and irreversible oxygenation or decomposition of MB (Tatsuma, Tachibana, Miwa, Tryk, & Fujishima, 1999).

In order to elucidate the durability of photocatalytic activity of TiO_2 NPs deposited on the PES + TiO_2 and PES + ALG + TiO_2 fabrics, the photodegradation process under the UV illumination was repeated two more times as presented in Fig. 6. It can be noticed that the second repeated cycle of photodegradation led to a slight improvement of photodegradation activity of the PES + TiO_2 fabric. However, the photodegradation activity of the PES + ALG + TiO_2 fabric continually increased. It should be underlined that after the second cycle, the MB completely degraded already after 8 h of the UV illumination on the PES + ALG + TiO_2 fabric. Additionally, the curves corresponding to the second and the third cycle of photodegradation overlapped almost in the whole range of analyzed UV illumination times. Similar trend was reported by other researchers (Uddin et al., 2007). Higher photocatalytic activity of TiO_2 nanoparticles in repeated cycles appears as a consequence of surface particles cleaning from impurity compounds during the first cycle.

4. Conclusion

The results indicated that multifunctional nanocomposite textile material can be tailored by modification of polyester fabric with biopolymer alginate and TiO_2 nanoparticles. The presence of alginates and TiO_2 nanoparticles on the surface of polyester fibers was confirmed by SEM analysis. Atomic absorption spectroscopy revealed that pretreatment of polyester fabrics with alginates positively affected the loading of TiO_2 nanoparticles. This nanocomposite textile material exhibited excellent antibacterial properties against Gram-negative bacterium *E. coli*, which were preserved after five washing cycles. The TiO_2 nanoparticles deposition onto polyester fabrics induced the rise of UPF values to the level corresponding to UPF rating of 50+, which designates the maximum UV protection. In addition to excellent UV blocking, deposited TiO_2 nanoparticles provided total photodegradation of methylene blue after 24 h of UV illumination and this ability was even enhanced after two repeated cycles.

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