Multifunctionality of Poly(vinyl alcohol) Nanofiber Webs Containing Titanium Dioxide

Kyung Lee, Seungsin Lee

Department of Clothing and Textiles, Yonsei University, Seoul 120-749, Korea

Received 15 January 2011; accepted 17 May 2011
DOI 10.1002/app.34929

ABSTRACT: We prepared titanium dioxide/PVA nanocomposite fiber webs for application in multifunctional textiles by electrospinning. The morphological properties of the TiO_2/PVA nanocomposite fibers were characterized using scanning electron microscopy and transmission electron microscopy. Layered fabric systems with electrospun TiO_2 nanocomposite fiber webs were developed using various concentrations of TiO_2 and a range of web area densities, and then the UV-protective properties, antibacterial functions, formaldehyde decomposition ability, and ammonia deodorization efficiency of the fabric systems were assessed. Layered fabric systems with TiO_2 nanocomposite fiber webs containing 2 wt% TiO_2 nanoparticles at 3.0 g m^{-2} web area density exhibited an ultraviolet protection factor of greater than 50, indicating excellent UV protection. The same system showed a 99.3% reduction in *Staphylococcus aureus*. Layered fabric systems with TiO_2 nanocomposite fiber webs containing 3 wt % TiO_2 nanoparticles at 3.0 g m^{-2} web area density exhibited a 85.3% reduction in *Klebsiella pneumoniae*. Titanium dioxide nanocomposite fiber webs containing 3 wt % TiO_2 nanoparticles at 3.0 g m^{-2} web area density exhibited a formaldehyde decomposition efficiency of 40% after 2 h, 60% after 4 h, and 80% after 15 h under UV irradiation. The same system showed an ammonia deodorization efficiency of 32.2% under UV irradiation for 2 h. These results demonstrate that TiO_2 nanocomposite fibers can be used to produce advanced textile materials with multifunctional properties. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4038–4046, 2012

Key words: nanocomposite; titanium dioxide; nanoparticle; multifunctionality; electrospinning

INTRODUCTION

Increasing global competition in textiles has led to the development of high added-value products with multifunctional properties. Advanced textile materials that can provide multiple functionalities such as UV protection, disinfection, and pollutant decomposing properties are greatly in demand by a more discerning and demanding consumer market and have many potential applications in apparel fabrics, household textiles, and technical textiles.

Titanium dioxide (TiO_2), one of the most widely used photocatalysts, is a versatile semiconductor material that is used in various areas such as cosmetics, sensors, advanced coatings, and osseointegration in dental implants.[1,2] Titanium dioxide has diverse properties: it can block UV light, has antibacterial activity, can be used for environmental purification, and is self-cleaning under sunlight or fluorescent light. In a study on the mechanisms of titanium dioxide as a UV-blocking additive, Pan and coworkers[3] reported that TiO_2 composite films and fabrics treated with TiO_2 exhibited a significant decrease in transmittance of UV mainly due to the UV absorption of TiO_2. Yu et al.[4] prepared TiO_2 films coated on a stainless steel substrate by dip-coating and the films showed outstanding antibacterial activity against *Bacillus pumilus* under UV irradiation. Thin films of nanocrystalline TiO_2 on cotton fabrics were produced by a dip-pad-dry-cure process, and the self-cleaning property of the titania treatment was assessed by the degradation of organic dirt such as coffee, red wine and curry stains.[5] Significant discoloration of these stains on TiO_2 treated fabrics was observed under UV irradiation, which demonstrated self-cleaning performance of TiO_2. Titanium dioxide can inactivate bacteria and viruses and decompose common organic matters in the air such as odor molecules because of its ability to undergo photocatalytic oxidation. In addition, it is non-toxic, environmentally friendly, and harmless to humans. A study on use of nanotitania incorporation within a polymeric matrix to fabricate novel scaffolds for stem cells cultured *in vitro* demonstrated the harmless effect on human stem cells.[6] Because of these multifunctional properties, TiO_2 has been used in diverse fields.[7,8]

Electrospinning, which is a fiber-forming process based on electrostatic force, can yield polymer fibers

---

Correspondence to: S. Lee (SL158@yonsei.ac.kr).

Journal of Applied Polymer Science, Vol. 124, 4038–4046 (2012)

with diameters in the nanometer to micron range. Electrospinning is a relatively simple and convenient process that can be used to produce ultra-thin diameter fibers with a large surface area, which is attractive for various applications ranging from filters, sensors, scaffolds for tissue engineering, to high performance apparel.[9] In the field of textiles and clothing, electrospun polyurethane nanofibrous membranes were used to develop waterproof breathable materials that provide protection from environmental factors while allowing the diffusion of water vapor because of the small fiber/pore sizes.[10] Furthermore, the effect of laundering on the mechanical properties of mass-produced nanofiber web materials for use in clothing wear was examined,[11] and it was found that the mechanical properties of nanofiber webs were sufficient for use of these materials in outdoor clothing.

A particular advantage of electrospinning is that various functionalities can be imparted to polymer nanofibers by simultaneous spinning of the polymer material with a functional material.[12] Because of the convenience of producing functional polymer nanofibers in a single step, interest in electrospinning polymers with functional nanoparticles has been increasing. Lee[13] electrospun a polyurethane polymer solution containing zinc oxide nanoparticles to obtain a material with UV blocking and antimicrobial properties. Hong[14] incorporated silver nanoparticles into PVA nanofibers through electrospinning and investigated the antimicrobial activities of the electrospun PVA/$AgNO_3$ fiber webs. The functionalities of electrospun nanofiber webs can be maximized because of their large surface areas; additionally, these nanofiber webs are ultrathin, porous, lightweight, and mechanically flexible,[15] making these fibers preferred materials for the development of high performance apparel.

Poly(vinyl alcohol) (PVA) is a non-toxic, water-soluble, and biodegradable synthetic polymer. It has excellent chemical resistance and physical properties, and good fiber-forming properties.[16] For these reasons, PVA has been electrospun into ultrafine fibers and used in various applications including drug delivery, wound dressing, and biodegradable mats, to mention a few.[17]

When electrospun PVA nanofiber webs are exposed to an aqueous environment, a change in the morphology of the PVA nanofiber webs occurs; the unique nanofibrous structure is lost. Thus, it is necessary to crosslink PVA polymers to stabilize the morphology of PVA nanofiber webs.[14] Although PVA can be chemically crosslinked with chemicals such as acetylaldehyde, glutaraldehyde, or formaldehyde,[18,19] crosslinking PVA nanofibers using such chemicals might not be appropriate for the production of clothing textiles because of the toxicity of these chemicals. Previous research[14] showed that heat treatment was an effective method to stabilize PVA nanofibers against dissolution in water without the requirement for toxic chemicals.

Developing innovative textiles with high value-added functional performances could create niche markets and further expand textile applications. Our aim in this study was to examine the feasibility of developing multifunctional textile nanocomposite materials by incorporating TiO_2 nanoparticles into PVA nanofibers using electrospinning. Titanium dioxide/PVA nanocomposite fiber webs were heat-treated to stabilize the electrospun PVA fibrous structure against dissolution in water. The morphologic properties of the TiO_2/PVA nanofiber webs were characterized and then their UV blocking properties, antimicrobial properties, formaldehyde decomposition, and ammonia deodorization properties were examined.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (>99% hydrolyzed, M_w = 89,000–98,000, Sigma Aldrich, USA) was used as a polymer system, and distilled water was used as a solvent. We performed preliminary experiments with TiO_2 nanopowders and nanosized colloidal TiO_2 to fabricate uniform nanocomposite fibers. When TiO_2 colloid was added to a PVA polymer solution and then electrospun, uniform nanocomposite fibers in which TiO_2 particles were evenly dispersed were produced, whereas when TiO_2 nanopowders were used, aggregation of the TiO_2 nanoparticles in the nanofibers was observed. Based on our preliminary experiments, we selected water-based nanosized colloidal TiO_2 (AERODISP® W 740 X, Evonik Degussa, Germany). According to the supplier, the TiO_2 particles contained in the suspension are an 80 : 20% anatase-to-rutile mixture and the average particle size is 21 nm. Electrospinning solutions were prepared by dissolving the PVA polymer powder in distilled water at 80°C and stirring with a magnetic stirrer for 6 h, followed by mixing with colloidal TiO_2 and stirring for an additional 2 h.

To provide durability, nanofibrous webs must be used in a layered structure, with some other substrate material as a support. To form a layered fabric system, 100% polypropylene nonwoven fabric was used as a substrate. The substrate was a light-weight and highly porous spunbonded nonwoven. The thickness of the nonwoven substrate was 0.24 mm and its weight was 26 g m^{-2}.

Electrospinning process

A vertical electrospinning set-up with a two-axis robot system (NNC-ESP200R2, NanoNC, Korea) was used. The system consisted of multiple syringes with needles, a high voltage power supply capable of delivering 0–30 kV, a syringe pump, and a grounded collector, in which a computer-aided system controls the nozzle system and the collector so that they run lengthwise and crosswise, respectively, facilitating the fabrication of uniform nanofiber webs.

Titanium dioxide/PVA solution was put into a plastic syringe and an electrode was clipped to the nozzle system. The syringe pump controlled a constant volumetric feed rate, which ranged from 0.2 to 1.5 mL h^{-1}. A high voltage of 18–26 kV was applied to the needle. The needle gauges used were 26, 27, and 30 (0.23, 0.20, and 0.15 mm *i.d.*, respectively). When a high voltage was applied, a droplet at the needle tip was drawn into a fiber. Fibers were laid down on the grounded collector, which was placed 10–15 cm from the tip, and a nonwoven web was formed. Titanium dioxide nanocomposite fibers were electrospun and deposited directly onto the polypropylene nonwoven substrate to produce layered fabric systems.

Fiber morphology

The morphology of electrospun TiO_2 nanocomposite fibers was examined by a field-emission scanning electron microscope (FE-SEM) (Hitachi Model S-4200, Nissei Sangyo, Japan) after sputter-coating with Pt/Pd.

To further characterize the morphology of TiO_2 nanocomposite fibers and examine the chemical composition of the fibers, a transmission electron microscope (TEM) (HR TEM 2100F, JEOL, Japan) equipped with an energy dispersive X-ray analysis system (EDX) was used. To prepare TEM samples, nanocomposite fibers were collected on a carbon-coated copper specimen grid.

Heat treatment

Electrospun TiO_2/PVA nanocomposite fiber webs were heat-treated at 160°C for 3 min. To confirm that the heat treatment stabilized the PVA nanofibers against dissolution in water, both heat-treated and untreated nanofiber webs were immersed in water at 18°C for 1 h, and then the morphology of the electrospun fiber webs was examined using a field-emission scanning electron microscope (FE-SEM) (Hitachi Model S-4200, Nissei Sangyo, Japan). In addition, in order to test the effectiveness of the fiber stabilizing heat treatment under shear action in water, heat-treated nanofiber webs were laundered at 18°C for 10 min at 75 rpm in a Terg-O-Tometer (Model HS-277A, Hanwon, Korea). Then, the morphology of the electrospun nanofiber webs was examined.

UV transmission properties

Transmission of UV rays through our layered fabric systems and a control fabric was measured in accordance with the American Association of Textile Chemists and Colorists (AATCC) Test Method 183-2004 (Transmittance or Blocking of Erythemally Weighted Ultraviolet Radiation through Fabrics). Measurements were performed in the wavelength range from 280 to 400 nm in 2 nm steps using a UV/VIS/NIR spectrophotometer (Perkin-Elmer Lambda 950, PerkinElmer, USA) equipped with an integrating sphere. Transmission was measured four times for each sample. The results are the mean values of these measurements.

The UV transmission data were used to calculate the ultraviolet protection factor (UPF), which indicates how much a material reduces UV exposure. The UPF values were calculated as follows:

$$\mathrm{UPF} = \frac{\sum_{\lambda=280}^{400} E_\lambda S_\lambda \Delta\lambda}{\sum_{\lambda=280}^{400} E_\lambda S_\lambda T_\lambda \Delta\lambda}, \tag{1}$$

where E_λ is the relative erythemal spectral effectiveness, S_λ is the solar spectral irradiance (W cm^{-2} nm^{-1}), T_λ is the mean measured transmittance of the specimen (%), and $\Delta\lambda$ is the measured wavelength interval (nm).

Antimicrobial properties

The antimicrobial activities of the layered fabric systems were evaluated quantitatively in accordance with ASTM E 2149-01 (Standard Test Method for Determining the Antimicrobial Activity of Immobilized Antimicrobial Agents Under Dynamic Contact Conditions). The percent reduction of test organisms after a specified contact time with the specimen was measured using the following formula:

$$R(\%) = \frac{B - A}{B} \times 100 \tag{2}$$

where R is the reduction rate in the number of colonies, A is the number of bacterial colonies in the flask containing the treated fabric after a specified contact time, and B is the number of bacterial colonies in the flask before the addition of the treated fabric.

For the antimicrobial assessment, *Staphylococcus aureus* (ATCC 6538, Gram-positive bacterium) and *Klebsiella pneumoniae* (ATCC 4532, Gram-negative bacterium) were used as representative microorganisms to determine the antimicrobial properties of the electrospun TiO_2 nanocomposite fiber webs. Because TiO_2 is activated by UV irradiation, the surfaces of the TiO_2 nanocomposite fiber webs were

UV-irradiated for 3 h before antimicrobial assessment was conducted.

Formaldehyde decomposition properties

The formaldehyde decomposition properties of the fabric systems were evaluated using a gas detector tube, based on the Japanese Industrial Standard (JIS) K 0804: 1998 (Gas Detector Tube Measurement System). A definite amount of formaldehyde gas was inserted into two tedlar bags, one containing treated fabric and one containing no fabric, and then the bags were sealed. UV irradiation was applied to the surface of the TiO_2 nanocomposite fiber webs during the assessment. The experiments were conducted in a controlled atmosphere at an air temperature of 20 ± 2°C, a relative humidity of 65 ± 20%, and an atmospheric pressure between 86 and 106 kPa. After a specified time, the concentration of formaldehyde gas in the two tedlar bags was measured using the gas detector tube attached to each tedlar bag. The formaldehyde decomposition efficiency was calculated using the following formula:

$$D\ (\%) = \frac{C_b - C_s}{C_b} \times 100 \tag{3}$$

where D is the decomposition efficiency, C_b is the concentration of formaldehyde gas in the blank bag after a specified time, and C_s is the concentration of formaldehyde gas in the tedlar bag with the treated fabric after a specified time.

Ammonia deodorization properties

The ammonia deodorization properties of the fabric systems were measured using the gas detector tube method suggested by the Japan Textile Evaluation Technology Council (JTETC). A definite amount of ammonia gas was inserted into two tedlar bags attached to gas detector tubes, one containing treated fabric and the other not containing fabric. The two bags were then sealed. UV irradiation was applied to the surface of the TiO_2 nanocomposite fiber webs during the assessment. After 2 h, the concentration of ammonia gas in the two tedlar bags was measured. The ammonia deodorization efficiency was calculated using the following formula:

$$\mathrm{DE}(\%) = \frac{C_b - C_s}{C_b} \times 100 \tag{4}$$

where DE is the deodorization efficiency, C_b is the concentration of ammonia gas in the blank bag after 2 h, and C_s is the concentration of ammonia gas in the tedlar bag with the treated fabric after 2 h.

RESULTS AND DISCUSSION

Fiber morphology

To fabricate uniform nanocomposite fibers using electrospinning, an appropriate set of parameters for the polymer solution and processing conditions need to be selected. Based on previous research,[20] the PVA polymer solution concentration was set to 11 wt %, and then PVA nanofibers were electrospun under various processing conditions to determine the optimum spinning conditions for our electrospinning set-up. Electrospun nanofibers obtained from 11 wt % PVA solution with a 25-gauge needle at a feed rate of 0.2 mL h^{-1}, a voltage of 18 kV, and a collecting distance of 13 cm are shown in Figure 1(a). These conditions yielded cylindrical fibers with diameters ranging from 300 to 400 nm.

TiO_2 nanoparticles were added to PVA solutions to impart multifunctionality to the resulting materials such as UV blocking, antimicrobial activity, and the decomposition of organic contaminants in the air. Nanocomposite fibers obtained from a 11 wt % PVA solution containing 3 wt % TiO_2 nanoparticles are shown in Figure 1(b). The fibers were fabricated with a 30-gauge needle at a feed rate of 0.2 mL h^{-1}, a voltage of 20 kV, and a collecting distance of

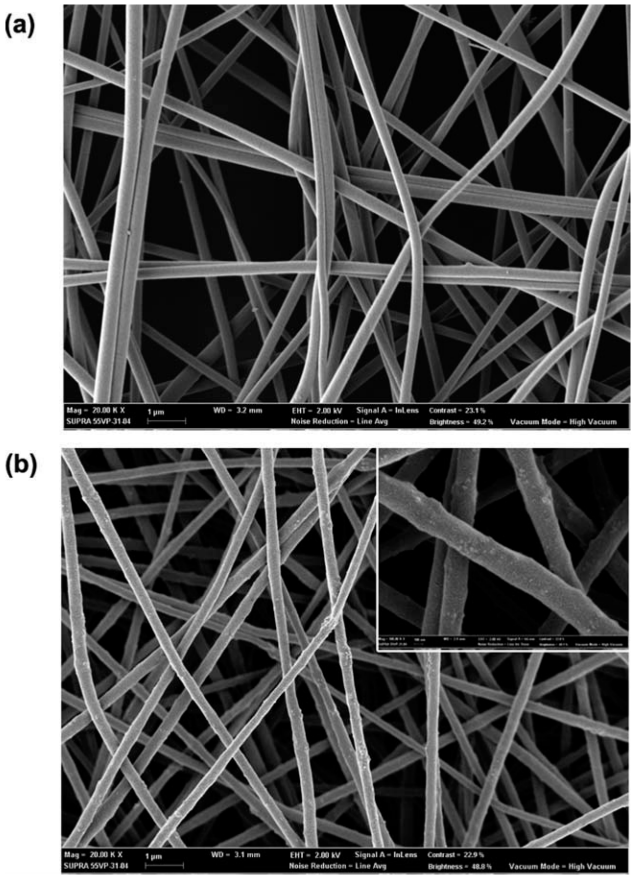

Figure 1 SEM images of (a) electrospun PVA nanofibers, (b) TiO_2/PVA nanocomposite fibers.

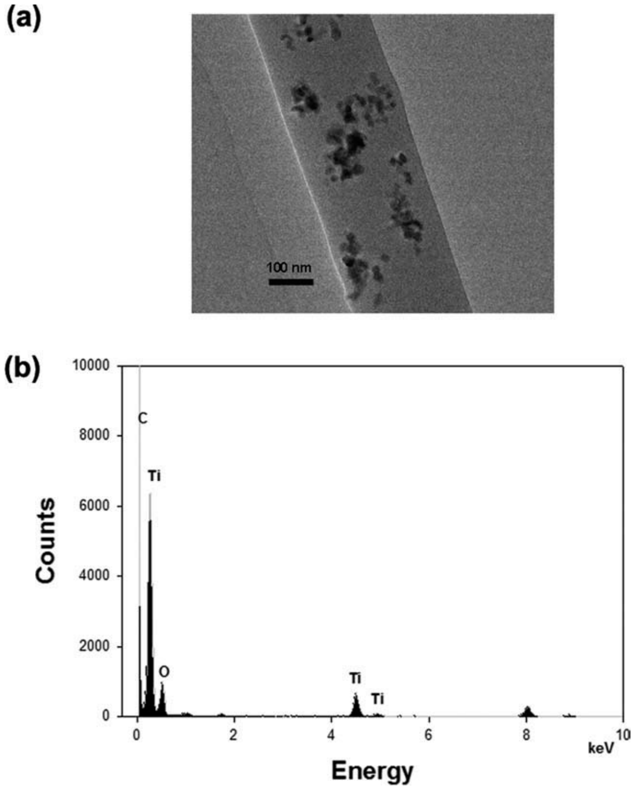

Figure 2 (a) TEM image of an electrospun TiO_2/PVA nanocomposite fiber, (b) EDX spectrum of an electrospun TiO_2/PVA nanocomposite fiber.

13 cm. TiO_2 nanoparticles were evenly dispersed in the nanocomposite fibers, as shown in the figure inset. The diameter of the nanocomposite fibers ranged from 300 to 400 nm.

Figure 2 shows a TEM image and the EDX spectrum of the electrospun TiO_2/PVA nanocomposite fibers. Nanoscale TiO_2 particles were observed inside the nanocomposite fibers as well as on the surfaces of the fibers, as illustrated in Figure 2(a). EDX analysis of the nanocomposite fibers confirmed the presence of TiO_2 in these fibers, as shown in Figure 2(b).

Effect of heat treatment

When electrospun PVA nanofiber webs are immersed in water, the unique nanofibrous structure is lost. Hong[14] reported that heat treatment was an effective method to stabilize PVA fibrous structures against dissolution in water. Thus, we heat-treated the electrospun TiO_2/PVA nanocomposite webs containing 3 wt % TiO_2 nanoparticles at 160°C for 3 min.

Figure 3 shows the changes in the morphology of electrospun nanofiber webs after immersion in water at 18°C for 1 h and after laundering in a Terg-O-Tometer at 75 rpm at 18°C for 10 min. As shown in Figure 3(a), an untreated TiO_2/PVA nanocomposite web lost its fibrous structure after exposure to an aqueous environment. In contrast, the fibrous structure of the heat-treated TiO_2/PVA nanocomposite web containing 3 wt % TiO_2 nanoparticles was maintained after immersion in water, as shown in Figure 3(b). The heat-treated nanocomposite webs were laundered to confirm the effectiveness of the heat treatment under shear action in water. The SEM image of the heat-treated nanocomposite fibers

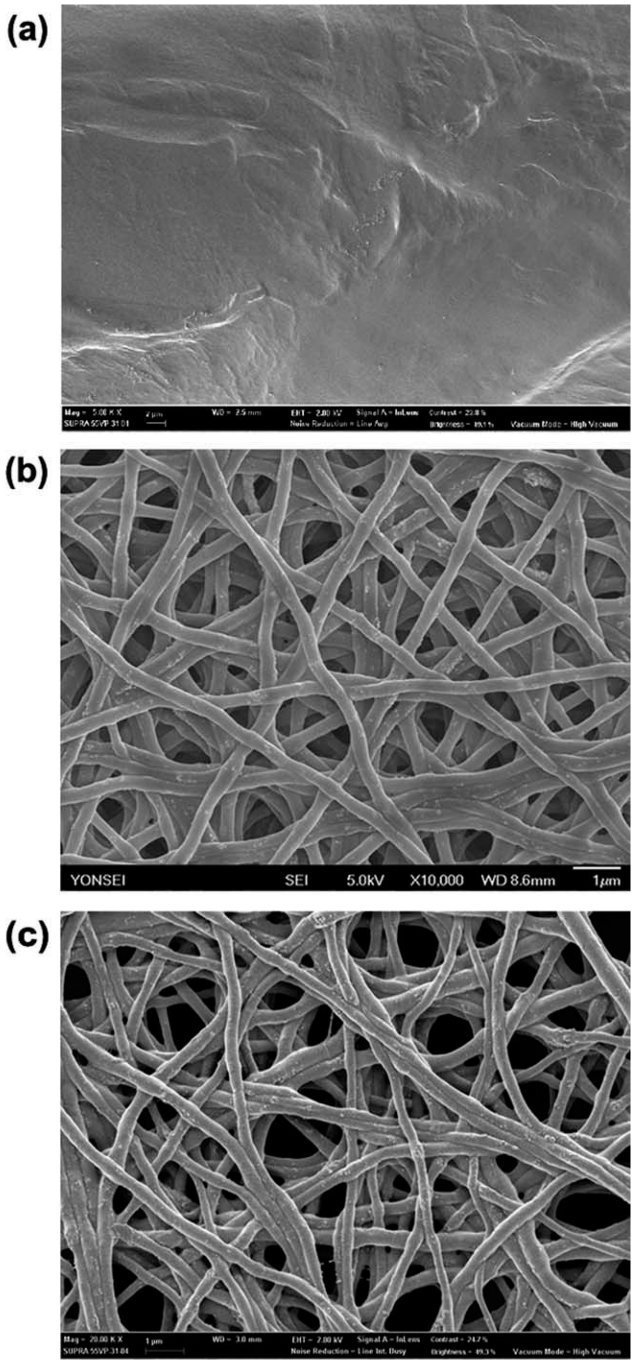

Figure 3 Surface views of electrospun TiO_2/PVA nanofiber webs (a) untreated TiO_2/PVA nanocomposite fibers after immersion in water (b) heat-treated TiO_2/PVA nanocomposite fibers after immersion in water (c) heat-treated TiO_2/PVA nanocomposite fibers after agitation in water.

TABLE I

UV-A and UV-B Transmittances of Layered Fabric Systems and of a Control Fabric, and the UPF Values of the Fabrics

Sample code	TiO_2 concentration (wt %)	Web area density (g m^{-2})	Average UV-A transmittance (%)	Average UV-B transmittance (%)	UPF[a]
T0	0	0	67.9	71.7	1
T1	1	1.5	47.3	43.4	2
T2	1	3.0	27.3	17.1	5
T3	2	1.5	22.2	6.9	13
T4	2	3.0	8.8	0.3	50+

[a] UPF (ultraviolet protection factor).

after laundering shows that the fibrous structure was maintained after agitation in water [Fig. 3(c)].

UV blocking ability of the layered fabric systems

Layered fabric systems with electrospun TiO_2/PVA nanocomposite fiber webs were fabricated at various concentrations of TiO_2 and a range of web area densities to determine the optimal conditions to achieve sufficient UV protective properties. Titanium dioxide nanoparticles of 1 and 2 wt % were added to a 11 wt % PVA solution, respectively. Layered fabric systems with TiO_2/PVA nanofiber webs with web area densities of 1.5 and 3.0 g m^{-2} were fabricated for each concentration of titanium dioxide. The UV-protective properties of the layered fabric systems were then examined.

The transmissions of UV rays through layered fabric systems and through a control fabric were determined for UV-A in the range of 315–400 nm, and for UV-B in the range of 280–315 nm. Exposure to UV-A decreases the immunological response of skin cells and produces signs of aging, whereas exposure to UV-B causes erythema and is believed to cause skin cancer.[21] Table I shows the UPF values of the layered fabric systems and the control fabric, as well as the average UV-A and UV-B transmittances of the fabrics. The UPF value indicates the ability of a fabric to block ultraviolet radiation (UVR), and has been widely adopted by the textile and clothing industry.[21] The control fabric (T0 in Table I) showed a percent UV transmission of greater than 60% in both UV-A and UV-B regions and a UPF value of 1, which indicates that it offers little protection against UV radiation. The Australian/New Zealand (AS/NZ) standard classifies fabrics according to their sun-protective properties.[22] Fabrics with UPF values of 40–50 and above transmit less than 2.5% of UVR and are classified in the “Excellent” UV protection category. Fabrics with UPF values greater than 25 but less than 40 transmit from 2.6 to 4.1% of UVR and are classified in the “Very Good” UV protection category. Finally, fabrics with UPF values higher than 15 but less than 25 transmit from 4.2 to 6.7% of UVR and are classified in the “Good” UV protection category. The data (shown in Table I) indicate that the percent UV transmission was decreased significantly via the addition of a very thin layer of electrospun TiO_2 nanocomposite fiber webs in both UV-A and UV-B regions. The UV blocking ability of layered fabric systems in both UV-A and UV-B regions increased as the electrospun web area density of the TiO_2 nanocomposite fiber web increased, and as the concentration of TiO_2 nanoparticles increased.

Layered fabric systems with nanofiber webs containing 2 wt % TiO_2 nanoparticles at 3.0 g m^{-2} web area density transmitted 8.8% of UV-A and 0.3% of UV-B. According to the AS/NZ 4399 rating standard,[22] this system provides excellent UV protection, with an UPF of greater than 50. Thus, the use of 2 wt % TiO_2 nanoparticles at 3.0 g m^{-2} web area density is sufficient to impart excellent UV blocking properties to layered fabric systems.

Antimicrobial properties of the layered fabric systems

To determine the optimum conditions for antimicrobial function as well as UV-protection, layered

TABLE II

Antibacterial Activity of Layered Fabric Systems with TiO_2/PVA Nanocomposite Fiber Webs

			Reduction rate of bacteria (%)	
Sample code	TiO_2 concentration (wt %)	Web area density (g m^{-2})	*Staphylococcus aureus*	*Klebsiella pneumoniae*
T0	0	0	NR[a]	NR[a]
T4	2	3.0	99.3	6.3
T5	3	3.0	–	85.4

[a] NR (no reduction).

TABLE III
Decomposition of Formaldehyde Gas by Layered Fabric Systems with TiO_2 Nanocomposite Fiber Webs According to UV Light Irradiation Time

Gas	UV light irradiation (h)	Gas concentration (ppm) Blank	Gas concentration (ppm) TiO_2 nanocomposite fiber web	Decomposition efficiency (%)
Formaldehyde (HCHO)	0	25	25	–
	2	25	15	40
	4	25	10	60
	15	25	5	80

fabric systems with TiO_2 nanocomposite fibers containing 2 wt % TiO_2 nanoparticles at 3.0 g m^{-2} web area density, which we showed had outstanding UV-blocking ability, were fabricated, and the antimicrobial properties of these fabric systems were evaluated. Because TiO_2 is activated by UV irradiation, layered fabric systems with TiO_2/PVA nanocomposite fiber webs were exposed to UV irradiation for 3 h before conducting the antimicrobial assessment. Antimicrobial activity was assessed quantitatively using two microorganisms, *Staphylococcus aureus* as a representative Gram-positive organism, and *Klebsiella pneumoniae* as a representative Gram-negative organism.

The antibacterial activities of layered fabric systems are shown in Table II as the percentage reduction of *Staphylococcus aureus* and *Klebsiella pneumoniae*. Layered fabric systems with nanocomposite fiber webs containing 2 wt % TiO_2 nanoparticles at 3.0 g m^{-2} web area density exhibited a 99.3% reduction in *Staphylococcus aureus*. However, the same system exhibited only a 6.3% reduction in *Klebsiella pneumoniae*. Thus, we increased the TiO_2 concentration to 3 wt % and examined the antimicrobial activity of the system against *Klebsiella pneumonia*. The number of *Klebsiella pneumoniae* was reduced by 85.4% when a TiO_2 concentration of 3 wt % was used to produce TiO_2/PVA nanocomposite fibers for the layered fabric systems.

The most commonly accepted photocatalytic inactivation of microorganisms by TiO_2 is as follows:[23,24] (1) the photoexcited TiO_2 nanoparticles produce electron-hole pairs when exposed to UV light; (2) photogenerated holes and electrons in the TiO_2 surfaces can react with adsorbed substances and produce reactive oxygen radicals; (3) these oxygen species attack and disrupt the bacterial cell wall, resulting in cell death. Our results showed that *Klebsiella pneumoniae* were more resistant to the photocatalytic process than *Staphylococcus aureus*. The lower reduction of Gram-negative *Klebsiella pneumoniae* than Gram-positive *Staphylococcus aureus* might be due to the more complex cell wall structure of Gram-negative bacteria; Gram-negative bacteria have an additional outer membrane containing two lipid bilayers that provide them a higher complexity,[24] which may protect these organisms. Our findings indicate that the use of no less than 3 wt % TiO_2 nanoparticles at a web area density of 3.0 g m^{-2} should be used to impart antimicrobial properties against both *Staphylococcus aureus* and *Klebsiella pneumonia*.

Formaldehyde gas decomposition and ammonia gas deodorization properties of the layered fabric systems

Increasing concerns about allergy-causing substances such as volatile organic compounds (VOCs) and other hazardous organic substances in living and working spaces have resulted in increased interest in the photocatalytic activity of titanium dioxide that allows it to oxidize organic pollutants. Photocatalytic oxidation refers to activation of a photocatalyst using UV light, resulting in the production of reactive oxygen radicals that oxidize VOCs to carbon dioxide and water.[25] Formaldehyde (HCHO), a VOC, is classified as a typical toxic gas species, but is commonly used in the workplace in the manufacture of resins, plastics, coatings, and fabrics, to name a few.[26] Formaldehyde emitted off furniture, carpeting, and wall coverings damages eyes, the nose, and respiratory organs,[27] and is thus becoming a major

TABLE IV
Deodorization Efficiency of Layered Fabric Systems with TiO_2 Nanocomposite Fiber Webs for Ammonia Gas

Gas	UV light irradiation (h)	Gas concentration (ppm) Blank	Gas concentration (ppm) TiO_2 nanocomposite fiber web	Deodorization efficiency (%)
Ammonia	0	100	100	–
	2	98.4	66.7	32.2

issue in indoor environments. Ammonia gas is another air pollutant with a pungent odor, and repeated exposure can cause eye irritation, skin diseases, and adversely affect the respiratory systems.[28] In this study, we examined the feasibility of developing textiles that can decompose formaldehyde and gaseous ammonia because of the presence of TiO_2 nanoparticles in PVA nanofibers.

Layered fabric systems with 3 wt % TiO_2 nanocomposite fibers and a web area density of 3.0 g m^{-2} were fabricated, and the formaldehyde decomposition properties of these systems were examined. The formaldehyde gas concentration and decomposition efficiency of the layered fabric systems for various UV light irradiation times are shown in Table III. For the blank tedlar bag, no change in the formaldehyde gas concentration occurred according to UV light irradiation time. In contrast, there was a gradual decrease in the formaldehyde gas concentration in the tedlar bag containing the treated fabric system with a TiO_2 nanocomposite fiber web. Under UV irradiation, the TiO_2 nanocomposite fiber web showed a formaldehyde decomposition efficiency of 40% after 2 h, 60% after 4 h, and 80% after 15 h.

We fabricated layered fabric systems with 3 wt % TiO_2 nanocomposite fibers and a 3.0 g m^{-2} web area density to assess the ammonia deodorization properties of the systems. The ammonia gas concentration and deodorization efficiency of the layered fabric systems containing TiO_2 nanocomposite fiber webs are shown in Table IV. After UV irradiation for 2 h, there was no apparent change in the ammonia gas concentration in the blank tedlar bag. However, the ammonia gas concentration in the tedlar bag containing the layered fabric system decreased from 100 to 66.7 ppm after 2 h. The TiO_2 nanocomposite fiber materials therefore have an ammonia deodorization efficiency of 32.2%.

With regard to air-pollutant degradation, the layered fabric systems containing 3 wt % TiO_2 nanocomposite fiber webs at a web area density of 3.0 g m^{-2} exhibited a 40% reduction in the formaldehyde gas concentration and a 32.2% reduction in the ammonia gas concentration after 2 h under UV irradiation. These results demonstrate that nanoscale TiO_2 contained in PVA nanofibers can decompose organic contaminants in the air, implying that TiO_2 nanocomposite fiber webs can potentially be used to produce functional textiles that can purify air pollutants. This finding could also inform the development of personal protective equipment such as face masks for workers and personnel exposed to such occupational toxins.

CONCLUSIONS

Our objective in this study was to develop multifunctional textile nanocomposite materials by incorporating nanoscale titanium dioxide particles into PVA nanofibrous structures via electrospinning. Layered fabric systems with electrospun TiO_2/PVA nanocomposite fiber webs containing various concentrations of TiO_2 and a range of web area densities were fabricated, and then the UV-protective properties, antibacterial functions, formaldehyde decomposition, and ammonia deodorization efficiency of the resulting fabric systems were examined. Water-soluble PVA nanofiber webs were heat-treated to stabilize the electrospun PVA fibrous structure against dissolution in water.

Antibacterial and UV-protection functions were successfully imparted to the layered fabric systems by electrospinning the polymer material with TiO_2 nanoparticles. Layered fabric systems with TiO_2 nanocomposite fiber webs containing 2 wt % TiO_2 nanoparticles at a web area density of 3.0 g m^{-2} exhibited a UPF of greater than 50, indicating excellent UV protection and showed a 99.3% reduction in *Staphylococcus aureus*. Layered fabric systems containing 3 wt % TiO_2 nanoparticles at 3.0 g m^{-2} web area density exhibited a 85.3% reduction in *Klebsiella pneumoniae*.

The formaldehyde decomposition efficiency of layered fabric systems with TiO_2 nanocomposite fiber webs containing 3 wt % TiO_2 nanoparticles at a web area density of 3.0 g m^{-2} was evaluated for various UV light irradiation times. The longer the exposure to UV radiation, the greater the formaldehyde decomposition efficiency: 40% after 2 h, 60% after 4 h, and 80% after 15 h. The same system also exhibited an ammonia deodorization efficiency of 32.2% after UV irradiation for 2 h.

Our findings indicate that electrospinning of mixtures of polymers and functional materials imparted multiple functions to the resulting textiles, including UV protection, antimicrobial properties, formaldehyde decomposition, and ammonia deodorization. Titanium dioxide/PVA nanocomposite fiber materials with multiple functionalities have high potential for use in sports/outdoor textiles and technical textiles, and may potentially even have medical applications.

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (No. 2011-0004737).

References

1. Doh, S. J.; Kim, C.; Lee, S. G.; Lee, S. J.; Kim, H. J Hazard Mater 2008, 154, 118.
2. Park, J.; Moon, J.; Lee, S.; Kim, S. H.; Zyung, T.; Chu, H. Y. Thin Solid Films 2010, 518, 6642.
3. Yang, H.; Zhu, S.; Pan, N. J Appl Polym Sci 2004, 92, 3201.
4. Yu, J. C.; Ho, W.; Lin, J.; Yip, H.; Wong, P. K. Environ Sci Technol 2003, 37, 2296.

5. Qi, K.; Wang, X.; Xin, J. H. Text Res J 2011, 81, 101.
6. Mandoli, C.; Pagliari, F.; Pagliari, S.; Forte, G.; Nardo, P. D.; Licoccia, S.; Traversa, E. Adv Funct Mater 2010, 20, 1617.
7. Liu, R.; Huang, Y.; Xiao, A.; Liu, H. J Alloy Compd 2010, 503, 103.
8. Costa, R. G. F.; Ribeiro, C.; Mattoso, L. H. C. J Nanosci Nanotechnol 2010, 10, 5144.
9. Bedford, N. M.; Steckl, A. J. ACS Appl Mater Interfaces 2010, 2, 2448.
10. Yoon, B.; Lee, S. Fibers Polym 2011, 12, 57.
11. Lee, S.; Kimura, D.; Yokoyama, A.; Lee, K.; Park, J. C.; Kim, I. Text Res J 2009, 79, 1085.
12. Lee, S. Fibers Polym 2009, 10, 295.
13. Lee, S. J Appl Polym Sci 2009, 114, 3652.
14. Hong, K. H. Polym Eng Sci 2007, 47, 43.
15. Greiner, A.; Wendorff, J. H. Angew Int Chem Ed 2007, 46, 5670.
16. Zheng, H.; Du, Y.; Yu, J.; Huang, R.; Zhang, L. J Appl Polym Sci 2001, 80, 2558.
17. Charernsriwilaiwat, N.; Opanasopit, P.; Rojanarata, T.; Ngawhirunpat, T.; Supaphol, P. Carbohydr Polym 2010, 81, 675.
18. Kurihara, S.; Sakamaki, S.; Mogi, S.; Ogata, T.; Nonaka, T. Polymer 1996, 37, 1123.
19. Gao, L.; Seliskar, C. J. Chem Mater 1998, 10, 2481.
20. Wong, K. K. H.; Hutter, J. L.; Zinke-Allmang, M.; Wan, W. Eur Polym J 2009, 45, 1349.
21. Sarkar, A. K. In Textiles for Protection; Scott, R. A., Ed.; Woodhead Publishing Limited: Cambridge, 2005.
22. Australian/New Zealand Standard AS/NZS 4399. Sun Protective Clothing—Evaluation and Classification, 1996.
23. Page, K.; Wilson, M.; Parkin, I. P. J Mater Chem 2009, 19, 3819.
24. Fu, G.; Vary, P. S.; Lin, C. J Phys Chem B 2005, 109, 8889.
25. Fernandez-Ibanez, P.; Blanco, J.; Malato, S.; Nienes, F. J. Water Res 2003, 37, 3180.
26. Pickrell, J. A.; Mokler, B. V.; Griffs, L. C.; Hobbs, C. H. Environ Sci Technol 1983, 17, 753.
27. Suzuki, Y.; Nakano, N.; Suzuki, K. Environ Sci Technol 2003, 37, 5695.
28. Geng, Q.; Guo, Q.; Cao, C.; Zhang, Y.; Wang, L. Ind Eng Chem Res 2008, 47, 4363.