

Fabrication and Characterization of TiO₂/Poly(dimethyl siloxane) Composite Fibers with Thermal and Mechanical Stability

Young Bum Kim,¹ Donghwan Cho,² Won Ho Park¹

¹Department of Advance Organic Materials and Textile System Engineering, and BK21 FTIT, Chungnam National University, Daejeon 305-764, Republic of Korea

²Department of Polymer Science and Engineering, Kumoh National Institute of Technology, Kumi, Kyungbuk 730-701, Republic of Korea

Received 30 June 2009; accepted 21 September 2009

DOI 10.1002/app.31480

Published online 1 December 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The mechanical stability of titania (TiO₂) nanofibers was improved by fabricating TiO₂/poly(dimethyl siloxane) (PDMS) composite fibers using a combination of hybrid electrospinning and sol-gel methods, followed by heat treatment at 250°C for 3 h. The compositions (90/10, 80/20, and 70/30, w/w) of the TiO₂/PDMS composite fibers were varied by adjusting the flow rate of the PDMS sol with the flow rate of TiO₂ sol fixed. There was no significant change in morphology and average diameter of the as-spun TiO₂/PDMS fibers after heat treatment. Both the tensile strength and modulus of the

TiO₂/PDMS composite fibers increased gradually with increasing PDMS content up to 30 wt %. In addition, from the photo-degradation reaction of methylene blue, the photocatalytic activity of TiO₂/PDMS composite fibers was strongly dependent on the TiO₂ content (%) in the composite fibers. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 449–454, 2010

Key words: titania (TiO₂); poly(dimethyl siloxane) (PDMS); electrospinning; composite fiber; mechanical stability; photocatalyst

INTRODUCTION

Titania (titanium oxide, TiO₂) is a promising material because of outstanding photocatalytic activity. To maximize its functional activity, TiO₂ has been fabricated into nanostructures including nanoparticles, nanotubes, and nanofibers. This nanostructured TiO₂ has been studied widely for optical and electrical applications, such as, photocatalysts, chemical sensors, dye-sensitized solar cells, and batteries.^{1–4} Among the many nanostructures produced, nanofibers have a distinctive advantage of being able to form the assembled structures (e.g., nonwoven) with a high surface area-to-volume ratio and porosity.

Electrospinning generally results in an assembled nonwoven structure composed of randomly oriented nanofibers. The electrospinning process, in combination with the sol-gel process, has been used to fabricate TiO₂ nanofibers from a TiO₂ precursor solution

mixed with an organic polymer (binder or gelator), such as, poly(vinyl pyrrolidone). The organic polymer is usually removed by a thermal treatment.^{5–10} Although this approach is advantageous, the polymer facilitates the formation of TiO₂ nanofibers by increasing the solution viscosity, the polymer additive needs to be removed from the resulting TiO₂/polymer blend fibers after electrospinning. This leaves pure TiO₂ fibers with inherent brittleness that can be broken easily, even under a low impact, which has restricted its practical use considerably.

In previous work,¹¹ ultrafine TiO₂ fibers were prepared from a titanium alkoxide precursor solution without an organic polymer by controlling the water content in the sol. Interestingly, the as-spun TiO₂ fibers could be converted to pure anatase by a heat treatment at lower temperatures (250°C, 3 h). However, the TiO₂ fibrous mat showed very poor mechanical stability. To improve the mechanical stability of the TiO₂ fibers, TiO₂/poly(dimethyl siloxane) (PDMS) composite fibers were fabricated by a hybrid electrospinning and sol-gel process. In the fabrication of the TiO₂/PDMS composite fibers, the use of PDMS has two important advantages. First, PDMS has high thermal stability that is capable of supporting the mechanical stability of TiO₂ fibers after heat treatment (250°C, 3 h). Second, the PDMS prepolymer also forms a network structure via a

Correspondence to: W. H. Park (parkwh@cnu.ac.kr).

Contract grant sponsor: Korea Science and Engineering Foundation [KOSEF] (Korea government [MOST]); contract grant number: 2005-00009.

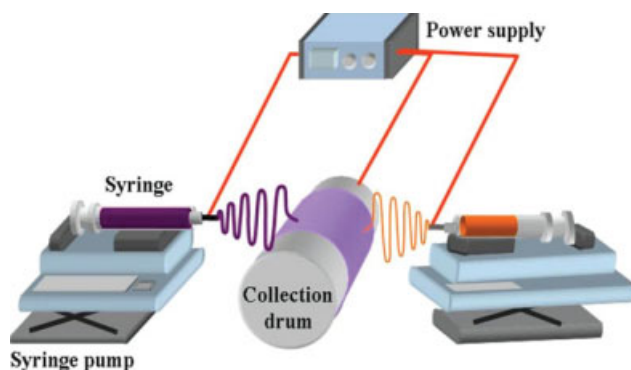


Figure 1 Schematic diagram of the hybrid electrospinning process. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

polycondensation and/or crosslinking reaction under the heat treatment conditions (250°C, 3 h), as reported elsewhere.¹²

The morphology and mechanical properties of the TiO₂/PDMS composite fibers with different PDMS contents were investigated after heat treatment. In addition, the photocatalytic activity of the heat-treated TiO₂/PDMS composite fibers was examined using the photo-degradation reaction of methylene blue (MB), and compared with that of pure TiO₂ fibers.

EXPERIMENTAL

Materials

Tetraisopropoxide titanium (TIPT, 98.0%) was purchased from Samchun Chemical Co. 2-methoxy ethanol was obtained from Kento Chemical Co. Nitric acid (HNO₃) (Duksan Pure Chemical) was used as an acid catalyst for the hydrolysis and polycondensation of TIPT. Hydroxyl terminated PDMS ($M_n = 46,000$) was supplied by Aldrich Co. Tetraethyl orthosilicate (TEOS, 95%) was purchased from Junsei Co. Tetrahydrofuran (THF, 98.5%), Samchun Chemical Co., and nitric acid (HNO₃) were used as the solvent and acid catalyst, respectively, for the hydrolysis of TEOS. The photocatalytic activity was measured using MB, Samchun Chemical Co., as a model pollutant dye. All chemical reagents were used without further purification.

Hybrid electrospinning

The titanium precursor solution was prepared using a titanium isopropoxide precursor and 2-methoxy ethanol as the solvent, based on the sol-gel procedure. Titanium isopropoxide (0.1M) was dissolved in 50 mL of 2-methoxy ethanol, which was followed by the addition of 0.01M nitric acid. The mixed solu-

tion was stirred and aged at 80°C for 70 min, resulting in a viscous transparent TiO₂ sol. To induce a slow hydrolysis reaction, the TiO₂ sol was placed in contact with moisture in the air (RH = 50, $T = 21^\circ\text{C}$) for aging. The viscosity of the sol increased with the hydrolysis reaction of the sol-gel precursor as a result of contact with moisture and solvent evaporation. The TiO₂ nanofibers were prepared by electrospinning a viscous TiO₂ sol.

The PDMS prepolymer solution was prepared using TEOS and THF, based on a sol-gel procedure. PDMS (0.13M) was dissolved in 30 mL of THF, and TEOS (2 mL) and nitric acid (200 μL) were then added. The mixed solution was stirred and aged at 80°C, resulting in a viscous transparent PDMS sol by a hydrolysis reaction and solvent evaporation. The viscosity of the sol was adjusted by adding THF (15 mL) for electrospinning. The PDMS fibers were prepared by electrospinning the viscous PDMS sol.

Figure 1 shows a schematic diagram of the hybrid electrospinning apparatus (Chungpa EMT) to fabricate TiO₂/PDMS composite fibers. In the hybrid electrospinning process, the TiO₂ and PDMS sols were electrospun simultaneously in opposite directions facing a single rotating target, which is herein called hybrid electrospinning. The compositions (90/10, 80/20, and 70/30, wt/wt) of the TiO₂/PDMS composite fibers were controlled by adjusting the flow rate of the PDMS solution from 5.0 to 15.0 mL/h at a fixed flow rate of the TiO₂ sol (3 mL/h). Table I lists the optimized conditions of the TiO₂ and PSF sols for hybrid electrospinning.

Photocatalytic activity measurement

The photocatalytic activity of the heat-treated pure TiO₂ and TiO₂/PDMS composite fibers was evaluated by observing the degradation of a model pollutant dye, MB. Fifty milligrams of fiber was immersed into an aqueous 0.025M MB solution (3 mL), and irradiated with UV light at 254 nm for up to 8 h using a 500 W high-pressure Hg lamp system (StabiLight, NT-LS-HG50-SR). At fixed time intervals (2, 4, 6, and 8 h), the absorbance of

TABLE I
Optimized Processing Conditions for Hybrid Electrospinning

	TiO ₂	PDMS
Prepolymer conc. (wt %)	–	38
Needle size (mm)	0.838	0.838
Applied voltage (kV)	25	10.5
Flow rate (mL/h)	3	5–15
Spinning distance (cm)	10	10
Humidity (%)	<40	<40
Temperature (°C)	21	21

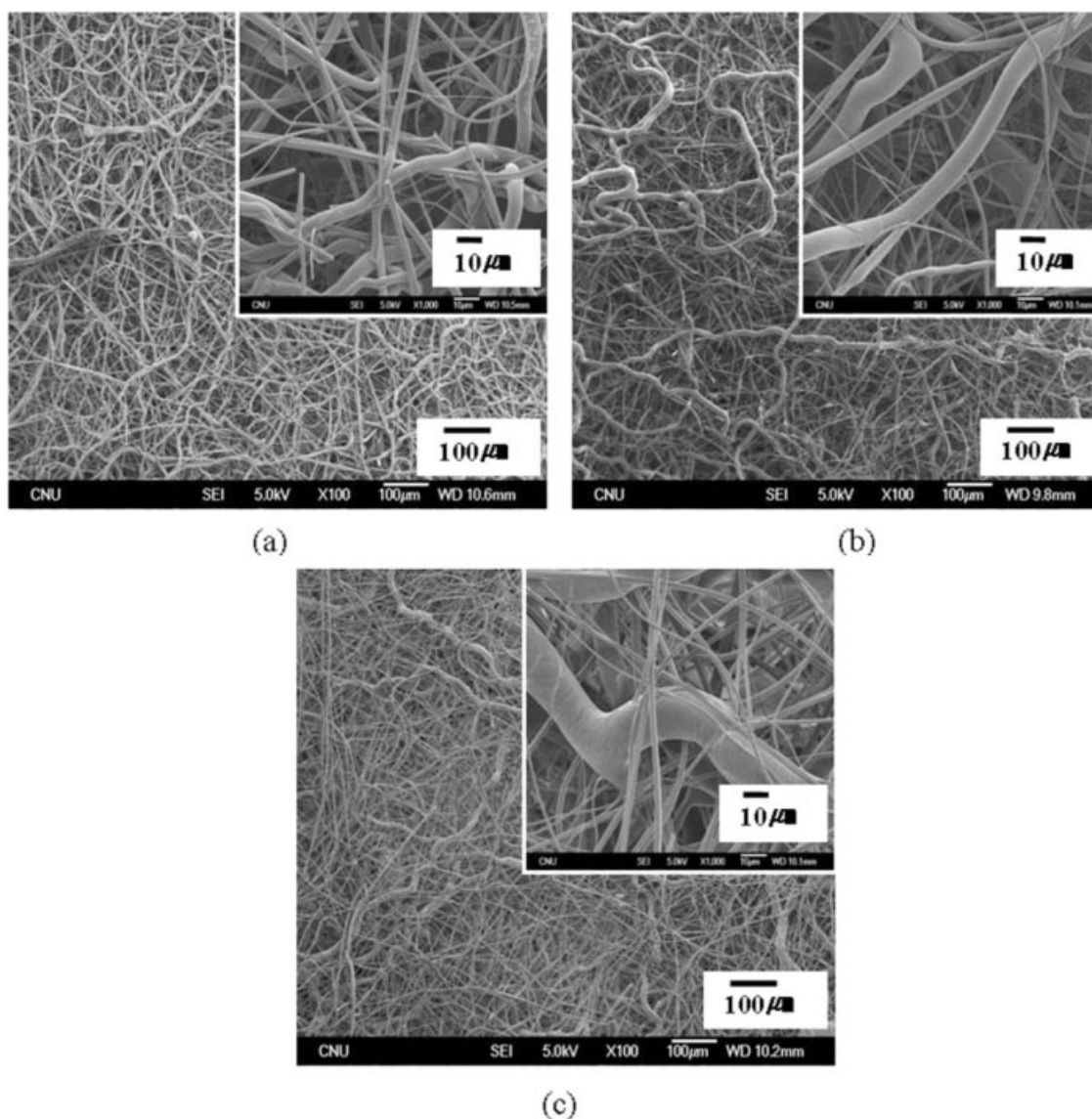


Figure 2 SEM images of the as-spun TiO₂/PDMS composite fibers: (a) 90/10, (b) 80/20, and (c) 70/30.

solution at 660 nm was measured to determine the concentration of MB using an UV-vis spectrophotometer (UV-2450, Shimadzu) over the wavelength range, 200–800 nm.

Characterization

The morphology of the as-spun and heat-treated TiO₂/PDMS composite fibers was observed by field emission scanning electron microscopy (FE-SEM, JSM-7000F, JEOL). The average fiber diameter was determined by analyzing the FE-SEM images using a custom-code image analysis program (Scope Eye II). The tensile properties of the heat-treated TiO₂/PDMS composite fibers mat were measured 10 times on an Instron tensile tester (Instron 4467) according to the ASTM D-638.

RESULTS AND DISCUSSION

The morphology of TiO₂/PDMS composite fibers

It was previously reported that TiO₂ nanofibers could be fabricated using only a titanium precursor sol solution by electrospinning in combination with a sol-gel method.¹¹ However, the TiO₂ nanofibrous mats were easily broken, even under a low impact, indicating very weak mechanical strength. In this study, PDMS was chosen as a reinforcing fiber for pure TiO₂ ultrafine fibers because it has high thermal and chemical stability. Figure 2 shows SEM images of the TiO₂/PDMS composite fibers with different PDMS contents electrospun under the optimized processing conditions in Table I. The composition of the TiO₂/PDMS composite fibers (90/10, 80/20, and 70/30, w/w) was varied by adjusting the flow rate of the PDMS solution at a fixed flow rate

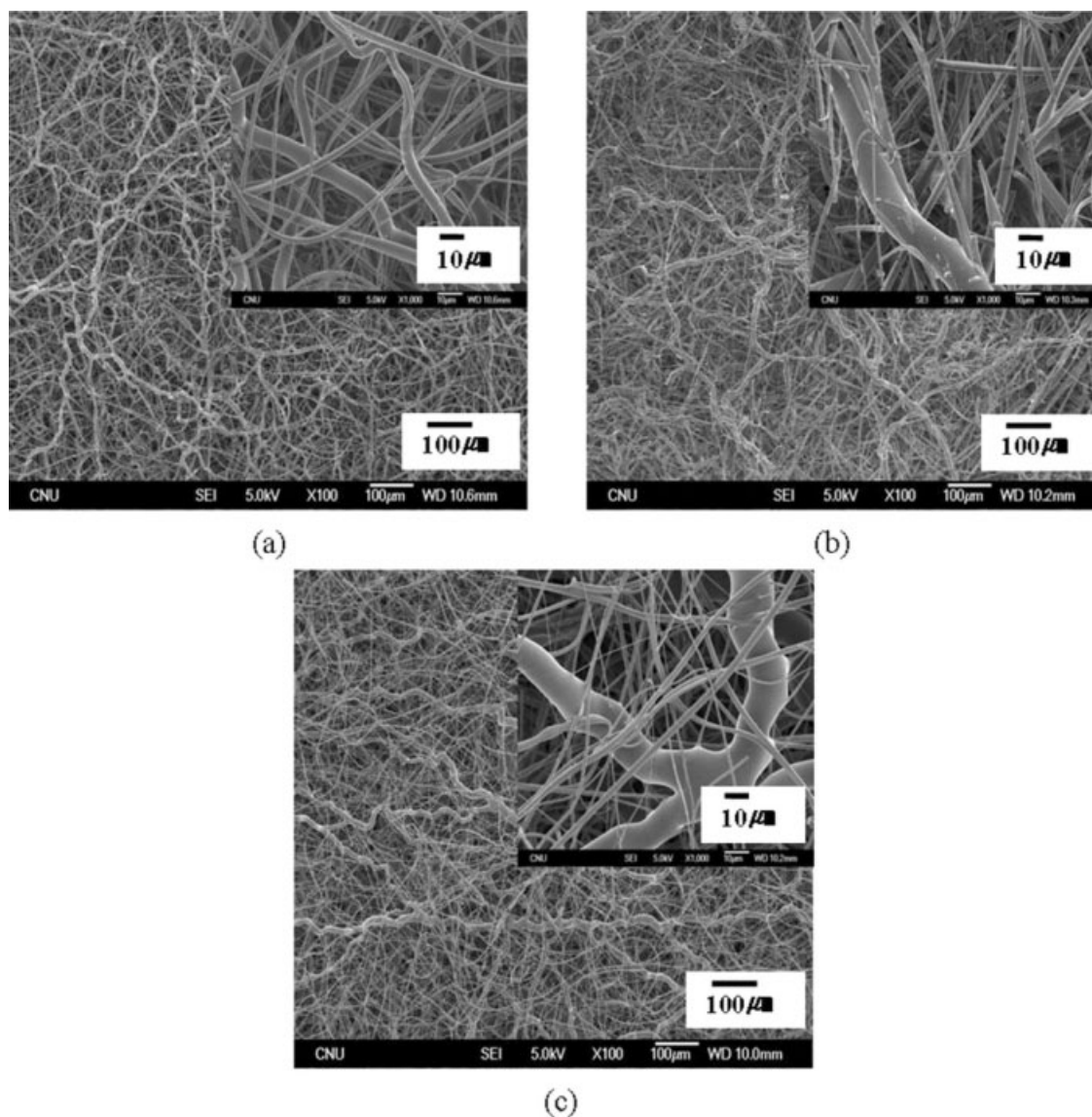


Figure 3 SEM images of the heat-treated TiO_2 /PDMS composite fibers: (a) 90/10, (b) 80/20, and (c) 70/30.

of the TiO_2 sol. As shown in Figure 3, the average diameter (AFD, $11.4 \mu\text{m}$) of the PDMS fibers was much higher than that ($1.11 \mu\text{m}$) of the TiO_2 fibers. The well mixed TiO_2 /PDMS composite fibers could be fabricated by hybrid electrospinning.

As-spun TiO_2 /PDMS composite fibers with different PDMS contents were subsequently heat-treated at 250°C for 3 h, to produce both the anatase crystalline phase of TiO_2 fibers and the polycondensation reaction of PDMS fibers. Figure 3 shows SEM images of the heat-treated TiO_2 /PDMS composite fibers with different PDMS contents. In particular, there was no significant change in fiber morphology and AFD of the TiO_2 /PDMS composite fibers after heat treatment (The AFD of TiO_2 decreased slightly from $1.11 \mu\text{m}$ to $0.94 \mu\text{m}$, whereas that of PDMS increased slightly from 11.4 to $12.7 \mu\text{m}$.). This suggests that the PDMS fibers have high thermal stability, which is

different from the organic polymers. The thermal stability of PDMS originated from the nature of the Si–O bonds, which have higher bond strength than the C–C bonds.¹³

TABLE II
Tensile Properties of the Electrospun TiO_2 and TiO_2 /PDMS Composite Fibers Mats

	Tensile strength (MPa)	Breaking elongation (%)	Modulus (MPa)
TiO_2	–	–	–
TiO_2 /PDMS (90/10)	0.013 ± 0.002	2.7 ± 0.3	0.81 ± 0.07
TiO_2 /PDMS (80/20)	0.015 ± 0.002	3.0 ± 0.5	0.90 ± 0.18
TiO_2 /PDMS (70/30)	0.023 ± 0.005	2.6 ± 0.2	1.18 ± 0.34
PDMS	0.019 ± 0.001	97.8 ± 6.2	0.027 ± 0.002

Mechanical stability of heat-treated TiO₂/PDMS composite fibers

Table II lists the tensile properties of the heat-treated TiO₂, PDMS, and TiO₂/PDMS composite fibers. As described previously, the pure TiO₂ fibrous mat did not have sufficient mechanical strength to be measured. The PDMS fibers provided the mechanical stability to the TiO₂ fibrous mat. Both the tensile strength and the modulus of the TiO₂/PDMS composite fibers increased gradually with increasing PDMS content up to 30 wt %, whereas the breaking elongation remained unchanged. However, the breaking elongation (~ 3%) of the TiO₂/PDMS composite fibers was much lower than that (~ 98%) of the pure PDMS fibers, because the PDMS content in the composite fibers was only 30 wt % at most.

Photocatalytic activity of heat-treated TiO₂/PDMS composite fibers

The mechanism of the photocatalytic reaction in the presence of TiO₂ involves a free-radical reaction that is initiated by UV light.¹⁴ The photocatalytic activity of TiO₂ strongly depends on the crystalline phase and surface area.^{15,16} As reported elsewhere,¹² the TiO₂ and TiO₂/PDMS composite fibers, after heat treatment at 250°C for 3 h, were composed of a pure anatase crystalline phase. These TiO₂ and TiO₂/PDMS composite fibers with the anatase phase were used to examine the effect of the TiO₂ content in the composite fibers on the photocatalytic activity. The photocatalytic degradation of a MB solution was used as a model photoreaction, and was measured from the UV absorbance at ~ 660 nm, which is the

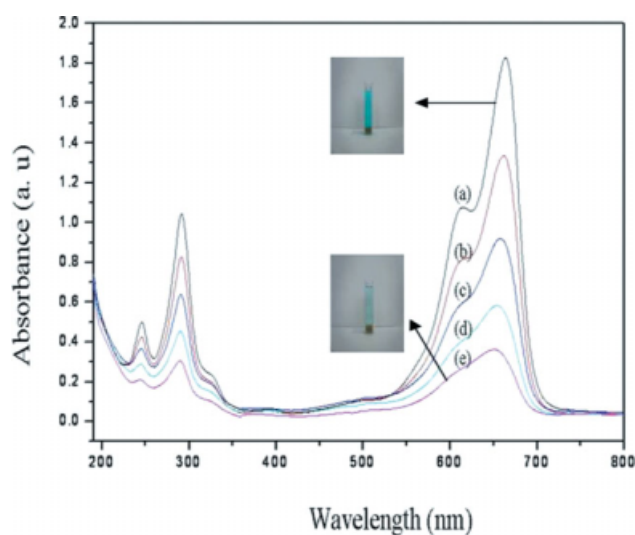


Figure 4 UV absorbance of MB solution containing TiO₂/PDMS (80/20) composite fibers as a function of the irradiation time: (a) 0, (b) 2, (c) 4, (d) 6, and (e) 8 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

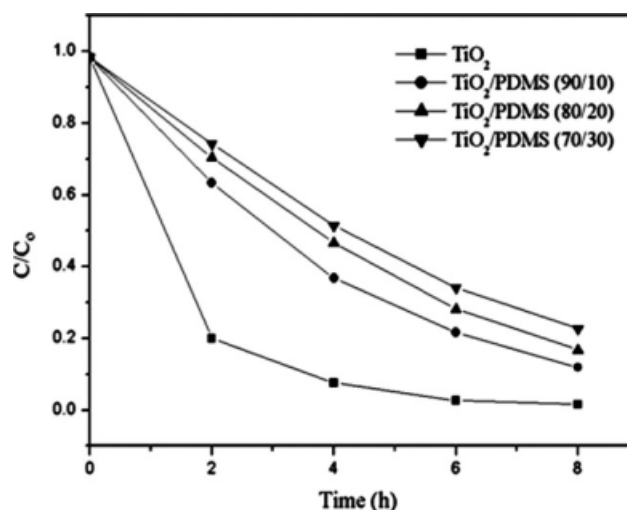


Figure 5 Degradation rate (C/C_0) of MB solution containing TiO₂/PDMS composite fibers: (—■—) TiO₂, (—●—) TiO₂/PDMS (90/10), (—▲—) TiO₂/PDMS (80/20), and (—▼—) TiO₂/PDMS (70/30).

maximum absorbance peak of MB in solution.^{17–19} Figure 4 shows the change in the absorbance on the UV-vis spectrum of the MB solution containing TiO₂/PDMS (80/20) composite fibers as a function of the UV irradiation time up to 8 h. As the photo-degradation of MB proceeded, the absorbance on the UV-vis spectrum decreased gradually, with the vanishing blue color of the MB solution. The decrease in absorbance is probably due to degradation of the MB chromophore.²⁰ The intensity of the absorbance at 660 nm is proportional to the concentration of MB in the solution. Therefore, the rate of degradation reaction can be determined by measuring the intensity of the absorbance of the MB solution at 660 nm.

Figure 5 shows the rate (C/C_0) of MB degradation in a solution containing TiO₂ fibers or TiO₂/PDMS composite fibers under UV irradiation. C_0 and C denote the concentration of MB at a UV irradiation time of 0 and t , respectively. The rate of MB degradation increased with increasing TiO₂ content. Therefore, the rate of MB degradation is strongly dependent on the TiO₂ content in the TiO₂/PDMS composite fibers. The complete degradation of MB did not occur with TiO₂/PDMS composite fibers after 8 h irradiation. On the other hand, degradation was completed within 6 h using the pure TiO₂ nanofibers.

CONCLUSIONS

The TiO₂/PDMS composite fibers were fabricated by a combination of hybrid electrospinning and sol-gel methods to impart mechanical stability to the TiO₂ fibers. In addition, the compositions could be varied by adjusting the flow rate of the PSF solution at a

fixed flow rate of the TiO₂ sol. There was no significant change in the fiber morphology and fiber diameter of the TiO₂/PDMS composite fibers after heat treatment. Both the tensile strength and the modulus of the TiO₂/PDMS composite fibers increased gradually with increasing PDMS content. From the photodegradation reaction of MB, the TiO₂/PDMS composite fibers exhibited photocatalytic activity corresponding to the TiO₂ content (%). Overall, it is believed that the TiO₂/PDMS composite fiber has great potential for photocatalytic fibrous membranes with mechanical stability.

References

1. Hoffmann, M. R.; Martin, S. T.; Choi, W. Y.; Bahnemann, D. W. *Chem Rev* 1995, 95, 69.
2. Bach, U.; Lupo, D.; Comte, P.; Moser, J. E.; Weissortel, F.; Salbeck, J.; Spreitzer, H.; Gratzel, M. *Nature* 1998, 395, 583.
3. Wold, A. *Chem Mater* 1993, 5, 280.
4. Hayakawa, I.; Iwamoto, Y.; Kikuta, K.; Hirano, S. *Sens Actuators B* 2000, 62, 55.
5. Li, D.; Xia Y. *Nano Lett* 2003, 3, 555.
6. Tekmen, C.; Suslu, A.; Cocen, U. *Mater Lett* 2008, 62, 4470.
7. Chen, J. Y.; Chen, H. C.; Lin, J. N.; Kuo, C. *Mater Chem Phys* 2008, 107, 480.
8. Nuansing, W.; Ninmuang, S.; Jarernboon, W.; Maensiri, S.; Seraphin, S. *Mater Sci Eng B* 2006, 131, 147.
9. Hong, Y.; Li, D.; Zheng, J.; Zou, G. *Nanotechnology* 2006, 17, 1986.
10. Lee, S.; Tekmen, C.; Sigmund, W. M. *Mater Sci Eng A* 2005, 398, 77.
11. Son, W. K.; Cho, D.; Park, W. H. *Nanotechnology* 2006, 17, 439.
12. Kim, Y. B.; Cho, D.; Park, W. H. *J Appl Polym Sci* 2009, 114, 3870.
13. Urayama, K.; Kawamura, T.; Kohjiya, S. *Polymer* 2009, 50, 347.
14. Baran, W.; Makowski, A.; Wardas, W. *Dyes Pigm* 2008, 76, 226.
15. Zhan, S.; Chen, D.; Jiao, X.; Tao, C. H. *J Phys Chem B* 2006, 110, 11199.
16. Lee, K. M.; Suryanarayanan, V.; Ho, K. C. *Sol Energy Mater Sol Cells* 2007, 91, 1416.
17. Zhan, S.; Chen, D.; Jiao, X.; Song, Y. *Chem Commun* 2007, 2043.
18. Alves, A. K.; Berutti, F. A.; Clemens, F. J.; Graule, T.; Bergmann, C. P. *Mater Res Bull* 2009, 44, 312.
19. Zhang, T.; Ge, L.; Wang, X.; Gu, Z. *Polymer* 2008, 49, 2898.
20. Rizzo, L.; Koch, J.; Belgiorno, V.; Anderson, M. A. *Desalination* 2007, 211, 1.