

Effect of Wettability and Silicone Surface Modification on the Self-Cleaning Functionalization of Wool

Wing Sze Tung, Walid A. Daoud

School of Applied Sciences and Engineering, Monash University, Churchill VIC 3842, Australia

Received 14 June 2008; accepted 29 September 2008

DOI 10.1002/app.29396

Published online 22 December 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Self-cleaning wool has been realized by treatment with a colloidal sol of anatase nanocrystals. However, the mechanical properties of wool have been significantly deteriorated following the self-cleaning functionalization treatment. To minimize the undesirable side-effects induced by the nanocoating, a silicone surface modification post-treatment has been introduced. The change in mechanical properties of TiO₂-coated wool after modification with silicone was examined, and the effect of this process on the photocatalytic activity and its stability was assessed by a degradation test of food stains. Moreover,

the wettability of wool has been modified using different nonionic wetting agents, in an attempt to shorten the wetting time during dip-coating and the absorption rate was compared. The effect of wetting agents on the functionalization process and the photocatalytic activity was examined. The synchronized effect of wettability and silicone surface modification on the self-cleaning functionalization of wool was also studied. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 235–243, 2009

Key words: nanotechnology; biopolymers; self-cleaning

INTRODUCTION

Since the discovery of photocatalytic water splitting on titanium dioxide (TiO₂) electrodes in late 1960s, intensive studies have been carried out on photoelectrochemistry.^{1,2} With the advancement of the bottom-up nanotechnology, photocatalysis function can now be imparted on materials to possess self-purification property and become capable of decomposing their contaminants such as dirt, stains, and harmful microorganisms via a powerful oxidation effect triggered by incident light.^{3,4} Owing to its fascinating potential in various applications, this novel concept has attracted great scientific interest universally in recent decades.^{5–8} Among all photosensitive semiconductors, titanium dioxide, particularly in the anatase nano-crystalline form, has been regarded as the most promising photocatalyst because of its special physical and chemical attributes, such as efficient photocatalytic activities, facilitated by its particle size to diffuse the excited electrons and holes toward the surface before recombination, high stability, high oxidizing ability, nontoxicity, and low-cost.^{2,9} Therefore, many research groups have

investigated the potential application of nano-crystalline anatase TiO₂, especially focusing on the functions of self-cleaning, environmental purification of air and water, sterilization, and deodorization.^{10–13}

TiO₂ nanoparticles have been applied in low thermal resistant fiber materials using a low temperature sol-gel method.^{4,14} These innovative self-cleaning fiber materials are currently in the stage of development and optimization.^{3,15,16} The self-cleaning coating technology has mostly been applied to cellulosic fibers in the concurrent research effort. However, transferring the application technology to protein fibers has been hindered because of the relatively low chemical and thermal resistance of protein materials.^{17–20} Nevertheless, there has been a breakthrough when self-cleaning keratin fibers have been successfully realized by our research group,²¹ where the natural protein fibers possess self-purification properties after imparting nano-crystalline anatase TiO₂ on their surface.^{22,23} Unfortunately, the intrinsic properties of wool fibers, such as mechanical and physical properties, have been deteriorated after the self-cleaning coating treatment, which hampered the practicability of self-cleaning wool fibers and limited their utilization. Moreover, the poor wettability of wool fibers in TiO₂ colloids causes a difficulty in the implementation of this technology in a large-scale industrial production. Therefore, it is necessary to modify the coating treatment to achieve maximum maintenance of the intrinsic properties of wool fibers and improving the industrial feasibility of the self-cleaning treatment. In this contribution, the

Correspondence to: W. A. Daoud (walid.daoud@sci.monash.edu.au).

Contract grant sponsors: Monash Research Graduate School, School of Applied Sciences and Engineering, Monash University; Australian Wool Innovations.

application process of self-cleaning coating treatment has been modified using wetting agents and silicone to overcome the aforementioned shortfalls. In this study, the post-treatment with amino-modified silicone has been introduced to investigate its effect on the recovery of the mechanical properties as well as on the purification performance. To improve the wettability of wool, different nonionic surfactants have been used as wetting agents and their effect on the self-cleaning properties has also been studied.

EXPERIMENTAL

Preparation of titanium dioxide colloid

The titanium dioxide sol was prepared by hydrolysis and condensation of 97% titanium tetraisopropoxide (Yizheng City Tianyang Chemical Plant, China) in acidic aqueous containing glacial acetic acid (Lab-Scan, Thailand) and 37% hydrochloric acid (Lab-Scan, Thailand). The concentration ratio of titanium tetraisopropoxide, acetic acid, and hydrochloric was 1 : 1 : 0.28 as previously reported.^{22,23} The mixed solution was then heated at 60°C under vigorous agitation for 16 h.

Self-cleaning surface coating

Pure commercial white worsted wool with twill weaving structure was used in this experiment. Samples were firstly precleaned by nonionic detergent (Kieralon OL) in a volume-to-weight ratio of 50 : 1 at 45°C for 30 min to remove all impurities prior to self-cleaning coating. The dried samples were then dipped in the titanium dioxide sol for 1 min and pressed with an automatic horizontal press (Rapid N. 413, Rapid Labortex Co., Taiwan) at a nip pressure of 2.75 kg cm⁻² with a roller rotation speed of 7.5 rpm. After drying in a preheated oven at 60°C for 5 min, the samples were cured in a curing oven (Mathis Labdryer, Werner Mathis AG Co., Switzerland) at 120°C for 3 min.

Silicone surface modification

A commercial cationic surfactant, amino-modified silicone emulsion, [(aminoethylaminopropylmethyl-

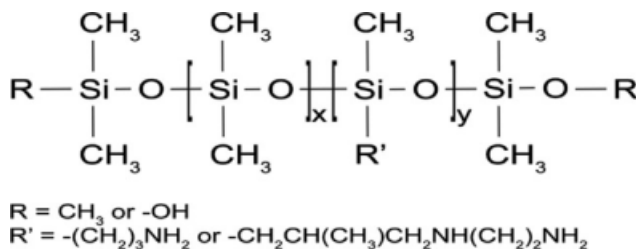
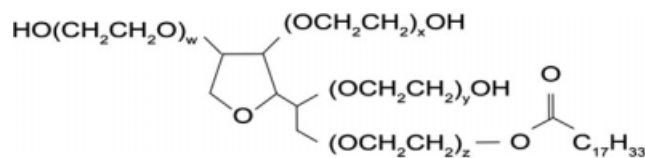


Figure 1 Molecular structure of amino-modified silicone polymer.



(Sum of w, x, y and z is 20)

Figure 2 Molecular structure of Tween[®] 80.

siloxane)-(dimethylsiloxane)] copolymer (BD-10076-80A, Bald Silicone Technology, China), was employed as a softening agent in the chemical post-treatment process for recovering the deteriorated mechanical properties after the anatase coating treatment. The chemical structure of the amino-modified silicone polymer is shown in Figure 1. The silicone polymer was diluted at concentrations 20 g/L (2%) and 40 g/L (4%) with 45°C warm water in different concentration ratios of 10 mL : 1 g and 30 mL : 1 g. The self-cleaning coated samples were subjected to the silicone solutions at 45°C for 30 min. After that, the samples were dried at room temperature prior to evaluation. The anatase coated sample without post-treatment is termed S0, coated and post-treated with 2 and 4% silicone in concentration ratio of 10 : 1 are termed S1 and S2; and coated and post-treated with 2 and 4% silicone in concentration ratio of 30 : 1 are termed S3 and S4, respectively.

Effect of surfactants on self-cleaning coating

Two commercial nonionic surfactants, Tween[®] 80 (T80) and Triton[®] X-100 (X100), were used as wetting agent to improve the wettability of the fibers. The chemical structures of T80 and X100 are shown in Figures 2 and 3. The wetting agent, in an appropriate concentration, was either mixed into the titanium dioxide sol prior to the dip-coating process or added *in situ* during the formulation preparation. The sols prepared with 0.1 and 0.4% T80 prior to dip-coating are termed T80A and T80B, respectively. The sol prepared with 0.1% X100 prior to dip-coating is termed X100A, and the sol prepared with 0.1% X100 *in situ* is termed X100S.

Mechanical properties

The mechanical properties were evaluated before and after the silicone surface modification. The tearing strength of the samples was measured using

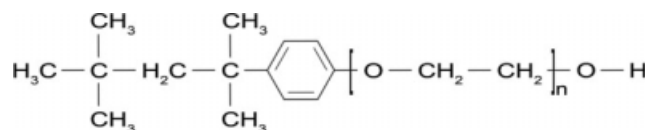


Figure 3 Molecular structure of Triton[®] X-100.

TABLE I
Tearing Strength of Pristine and Coated Wool with and Without Silicone Modification

	Pristine fibers	S0	S1	S2	S3	S4
Warp (gf)	2816	1728	2368	2187	2165	2112
Weft (gf)	1184	800	1067	1067	1056	1013
Average (gf)	2000	1264	1717	1627	1611	1563
Overall change (%)		-36.80	-14.13	-18.67	-19.47	-21.87

Elmendorf Tearing Tester (Thwing-Albert Instrument Co., USA) with a standard capacity of 6400 g in accordance with ASTM D 1242-96. The bending rigidity of the samples was obtained on Kawabata Pure Bending Tester—KES-FB2 (KATO Tech. Co., Japan) according to the Kawabata Evaluation System for Fabrics (KES-F).

Photocatalytic purification performance

The photocatalytic degradation of food stains, such as concentrated coffee and red wine stains, was evaluated using Suntest solar simulator—Xenotest[®] Alpha LM Light Exposure and Weathering Test Instrument (Atlas Material Testing Technology LLC, Germany) with the irradiance of 45–95 mWcm⁻² for 8, 20, and 40 h.

Reproducibility of photocatalytic purification performance

A stability test was performed to study the effect of different treatment processes on the reproducibility of the self-cleaning performance. The stain degradation activity of modified self-cleaning fibers were compared before and after repeated solvent washing according to ISO 105-D01 using petroleum ether as solvent.

Wettability and absorption rate

The samples absorption rate of sols prepared with and without wetting agents was observed. The wetting time required by a sample to thoroughly absorb the sol was recorded by stopwatch instantly after

soaking the sample into the titanium dioxide sol. The wetting time reported is the average of five measurements for each test sample.

RESULTS AND DISCUSSION

Silicone surface modification

Mechanical properties

From our previous work, it was found that the self-cleaning coating treatment causes damage to fibers, which is probably attributed to the acid content in the titanium dioxide sol and to the alteration of the fiber surface after the deposition of titanium dioxide nanoparticles. Hence, the tearing strength and bending rigidity of coated fibers were measured before and after a surface modification post-treatment with silicone. The tearing strength of pristine, coated and coated and silicone-modified wool fibers are shown in Table I. Compared with pristine wool fibers, S0 showed the greatest deterioration in tearing strength of 37% after self-cleaning coating treatment. On the other hand, the lost tearing strength was significantly recovered after the post-treatment. Of the four treated samples, S1 showed the least drop in tearing strength (14%) followed by S2, S3, and S4, indicating that S1 had the best recuperation of tearing strength. The recovery of the lost tearing strength is probably attributed to the change of frictions. Because surface friction of wool fibers can be altered by silicone treatments,²⁴ silicone-based polymers may act as lubricant to ease the interfiber and interyarn frictions leading to an improvement in tearing strength.

The change of bending rigidity of coated fibers before and after post-treatment with silicone is shown in Table II. The pliability is directly affected

TABLE II
Bending Rigidity of Pristine and Coated Wool with and Without Silicone Modification

	Pristine fibers	S0	S1	S2	S3	S4
Warp (g cm ² /cm)	0.143	0.383	0.167	0.171	0.171	0.167
Weft (g cm ² /cm)	0.092	0.142	0.110	0.108	0.109	0.108
Average (g cm ² /cm)	0.118	0.263	0.139	0.140	0.140	0.138
Overall change (%)		123.40	17.87	18.72	19.15	17.02

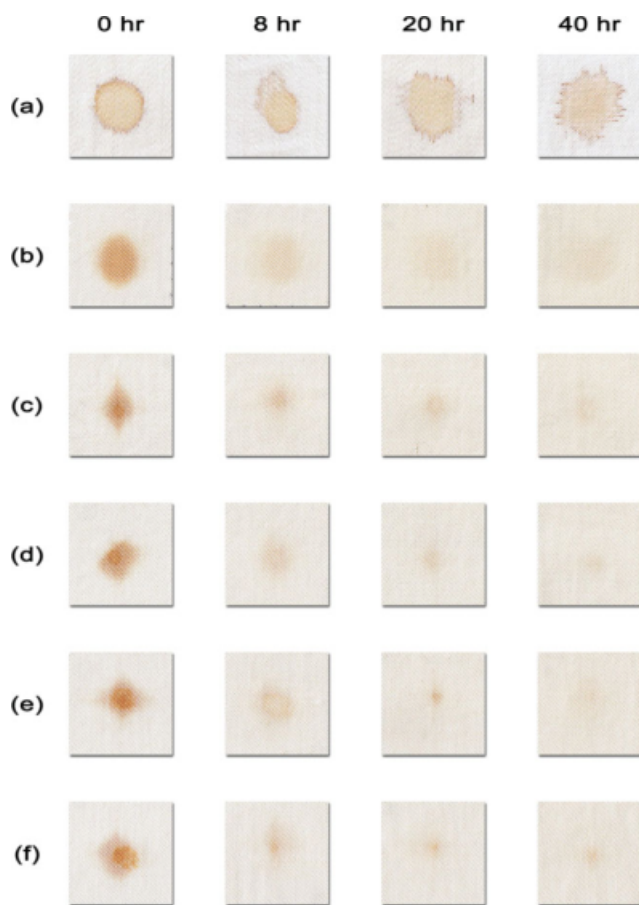


Figure 4 Stain degradation of concentrated coffee (a) pristine wool, (b) S0, (c) S1, (d) S2, (e) S3, and (f) S4. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

by the stiffness of the fibers, which corresponds to the bending rigidity. The higher the bending rigidity, the stiffer the fiber, and the less the pliancy. After the TiO_2 -coating treatment, the bending rigidity of S0 was significantly increased by 123.4%, whereas the bending rigidity of all post-treated TiO_2 -coated fibers was almost seven times lower when compared with S0. The bending rigidity of different post-treated fibers increased in the ascending order of S4 (17.02%), S1 (17.87%), S2 (18.72%), and S3 (19.15%), signifying that S4 possessed the greatest ability to restore the deteriorated pliability of wool, followed by S1, S2, and S3. In agreement with the observations from the tearing strength, it is believed that the modification of wool surface with silicone improved the bending rigidity as a result of friction diminution between fibers.

The above results confirm the ability of the silicone treatment to offset the drop of mechanical properties induced by the TiO_2 coating, where S1 showed the best performance among all post-treated TiO_2 -coated fibers.

Photocatalytic purification performance

Degradation of food stains was conducted to analyze the effect of silicone surface modification on the photocatalytic activity of self-cleaning functionalized wool fibers. Stain degradation of pristine, TiO_2 -coated, silicone-modified TiO_2 -coated wool fibers are illustrated in Figures 4 and 5, respectively. Consistent with our previous studies, stains on pristine fibers remained intact after solar-simulated irradiation, whereas the self-cleaning functionalized fibers (S0) were able to completely discolor both concentrated coffee and red wine stains upon irradiation. After the silicone post-treatment, all modified and TiO_2 -coated fibers were able to possess significant purification performance. However, when compared to S0, a slight change was observed on fibers treated with different silicone concentrations. S1 and S2 showed very similar degradation ability on both concentrated coffee and red wine stains, and they were able to completely discolor the stains within 40 h of solar-simulated irradiation; however, the photocatalytic ability of S3 and S4 was reduced

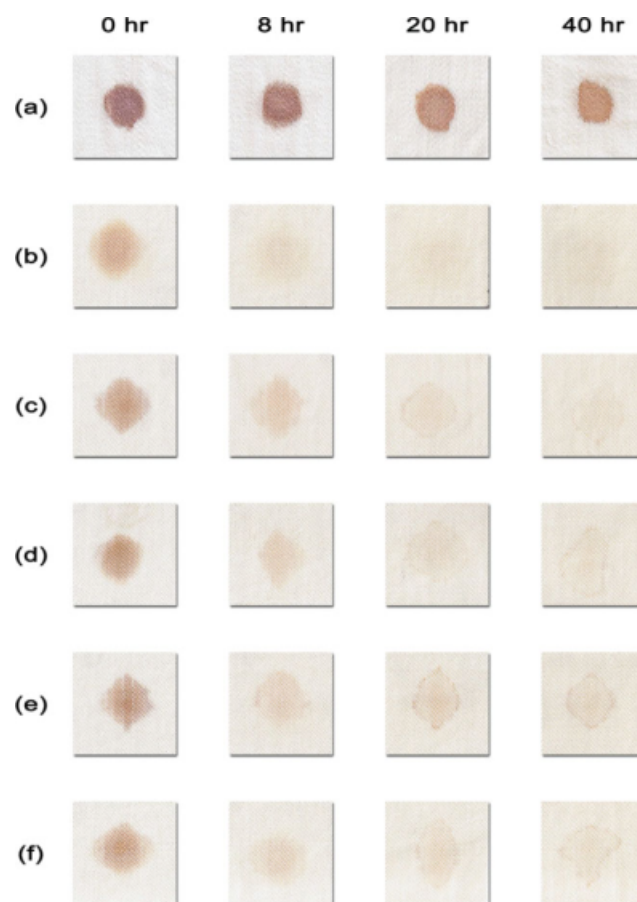


Figure 5 Stain degradation of red wine (a) pristine wool, (b) S0, (c) S1, (d) S2, (e) S3, and (f) S4. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

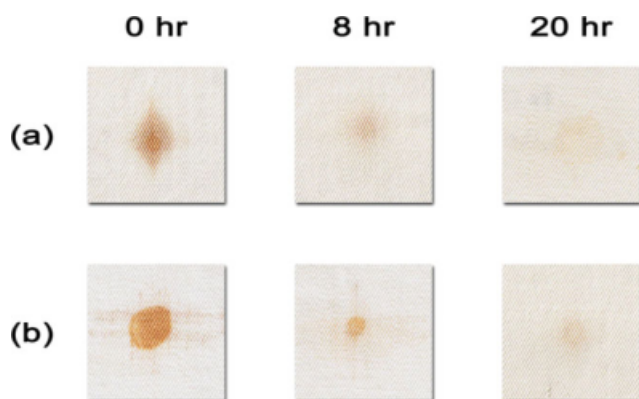


Figure 6 Stain degradation of concentrated coffee on S1 (a) before stability test and (b) after stability test. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

especially on red wine stain. This signifies that the photocatalytic efficiency is affected by the level of silicone concentration used in the post-treatment. It was found that a concentration ratio of 10 : 1 is more favorable for TiO₂-coated fibers. Of the two coated fibers treated with 10 : 1 ratio, both S1 and S2 possessed similar self-cleaning performance as S0 did; nevertheless, S1 is more favorable because of the lower silicone concentration applied. Moreover, the shape and size of the stains varied between TiO₂-coated and silicone-treated TiO₂-coated wool. Stains on S0 were spread in a circular shape over a large area on fibers surface, whereas the area and shape of stains in S1, S2, S3, and S4 were smaller and irregular. This implies that the silicone-treated TiO₂-coated wool is comparatively more hydrophobic than TiO₂-coated wool. This change in surface wettability after treatment with silicone is attributed to the hydrophobic nature of silicone. It is believed that the hydrophobic alkyl groups of silicone altered the chemical structure through H-bonding between

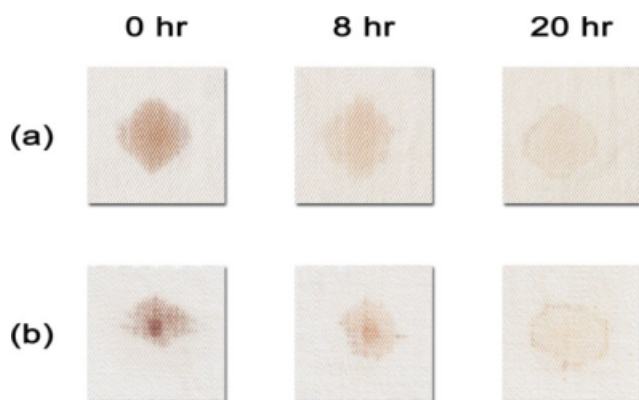


Figure 7 Stain degradation of red wine on S1 (a) before stability test and (b) after stability test. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Absorption Time of Pristine and Coated Wool with and Without Silicone Modification

	Pristine fibers	T80A	T80B	X100A	X100S
Time (sec)	60+	55–56	2–3	2–3	2–3

oxygen atoms of titanium dioxide and amino groups of silicone. These results showed that the photocatalytic purification performance was adversely affected if high concentration of silicone is used.

Reproducibility of photocatalytic purification performance

Considering the results discussed in sections Mechanical Properties and Photocatalytic Purification Performance, S1 showed the best improvement in mechanical properties with no significant adverse effect on the purification performance. Therefore, the stability testing was conducted on S1 only. The reproducibility of the photocatalytic ability of S1 is demonstrated in Figures 6 and 7. In contrast to S1 before washing, the shape of the stains on S1 after washing was unevenly spread on the fiber surface, and the stain area was smaller. This denotes that the hydrophilicity of the titanium dioxide coating

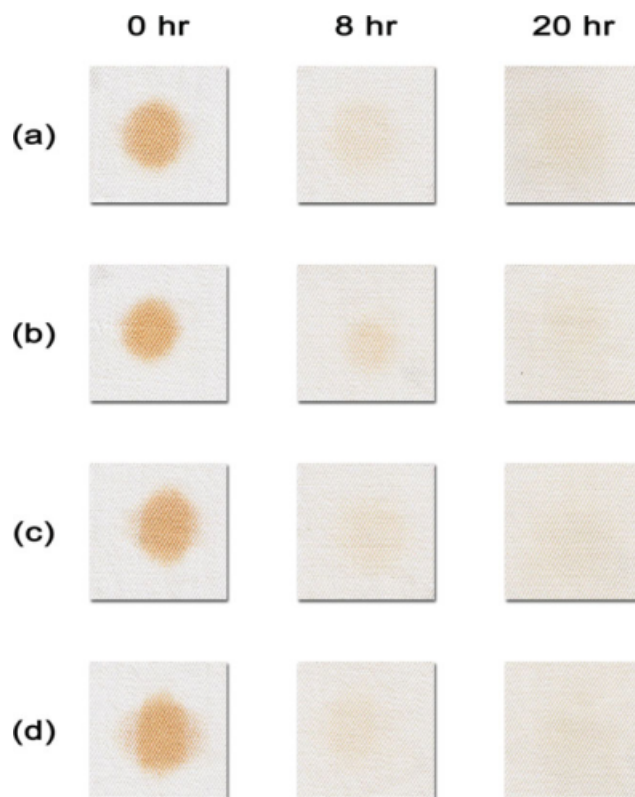


Figure 8 Stain degradation of concentrated coffee (a) T80A, (b) T80B, (c) X100A, and (d) X100S. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

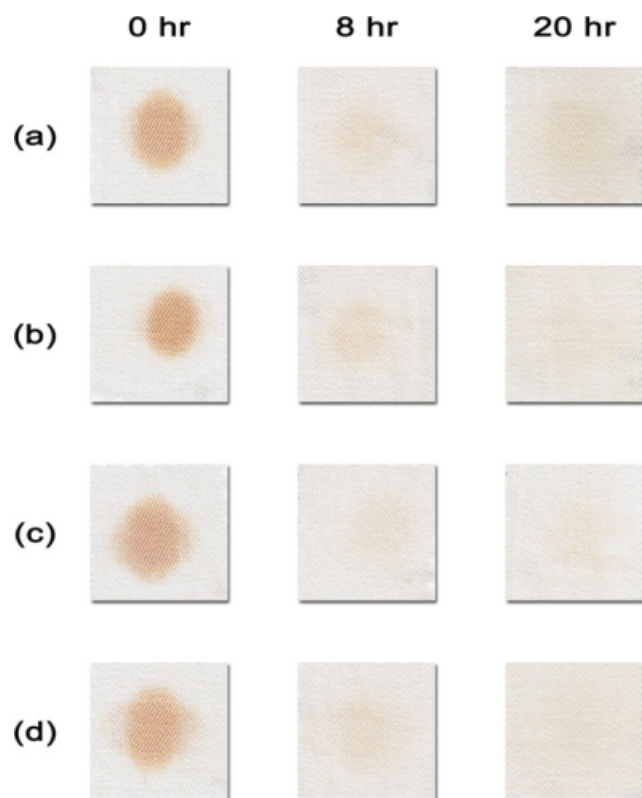


Figure 9 Stain degradation of red wine (a) T80A, (b) T80B, (c) X100A, and (d) X100S. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

surface decreases after repeated washing. Although the hydrophilicity changed, there was no significant change observed in the discoloration of concentrated coffee and red wine stains of silicone-modified TiO₂-coated fibers (S1) before and after the stability test, which could possibly be attributed to the silicone bonding with the titanium dioxide which acts as a protective shield, thus preventing titanium dioxide from being washed off during the stability test. From these results, it can be concluded that S1 possessed remarkably reproducible photocatalytic ability even after severe stability testing and that the surface modification of TiO₂-coated wool with 2% silicone in a 10 : 1 concentration ratio can offset the loss of wool mechanical properties while not adversely affecting the photocatalytic performance or its reproducibility.

Effect of surfactants on self-cleaning coating

Wettability and absorption rate

The time required for wool fibers to thoroughly absorb the titanium dioxide nano-sol colloid during dip-coating was recorded with and without two common wetting agents, Tween[®] 80 (T80) and Triton[®] X-100 (X100). In the industry, the contact

time permitted is generally less than 5 s; however, pristine fibers could not get thoroughly wetted even after 60 s of dipping. To facilitate the industrial implementation of the self-cleaning coating treatment, it is necessary to shorten the time required for a thorough wetting. In this experiment, T80B, X100A, and X100S revealed close absorption rates, which were almost 20 times faster than that of pristine fibers and T80A. It is believed that the improvement in wettability is attributed to the hydrophilic oxyethylene groups in T80 and X100. The introduction of extra hydrophilic groups onto the nonpolar surface of wool fiber increased the absorption rate of fibers. From Table III, a thorough wetting was obtained after 3 s of dipping for T80B, X100A, and X100S, whereas T80A required 55–56 s. The results denote that T80B, X100A, and X100S effectively dispersed the titanium dioxide nanoparticles in the sol and shortened the absorption time during TiO₂ coating. The effectiveness of a wetting agent depends highly on the nature of functional groups of substrate, polarity of substrate surface, conditions of the aqueous solution (e.g., temperature, solution composition, and duration), and molecular structure of the wetting agent.²⁵ In this view, owing to the fact that the fiber substrate and solution conditions are fixed,

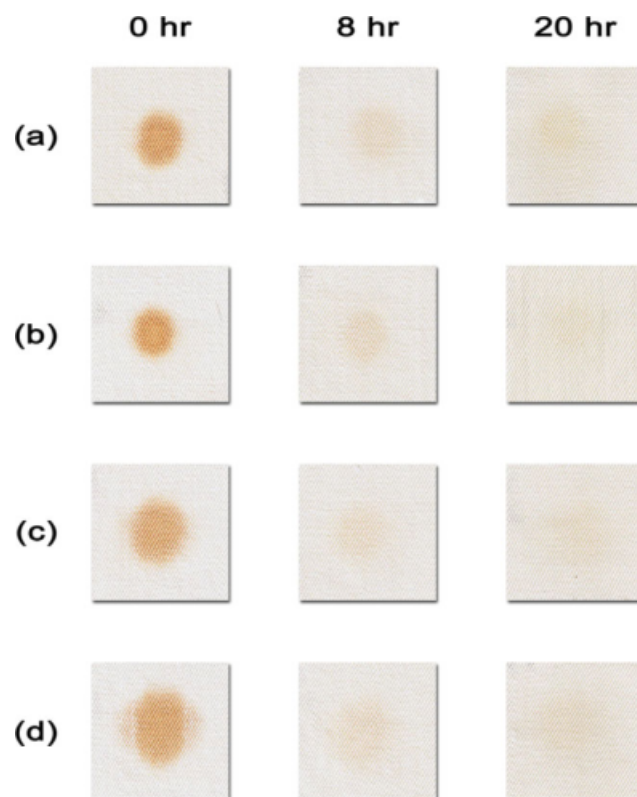


Figure 10 Stain degradation of concentrated coffee after stability test (a) T80A, (b) T80B, (c) X100A, and (d) X100S. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

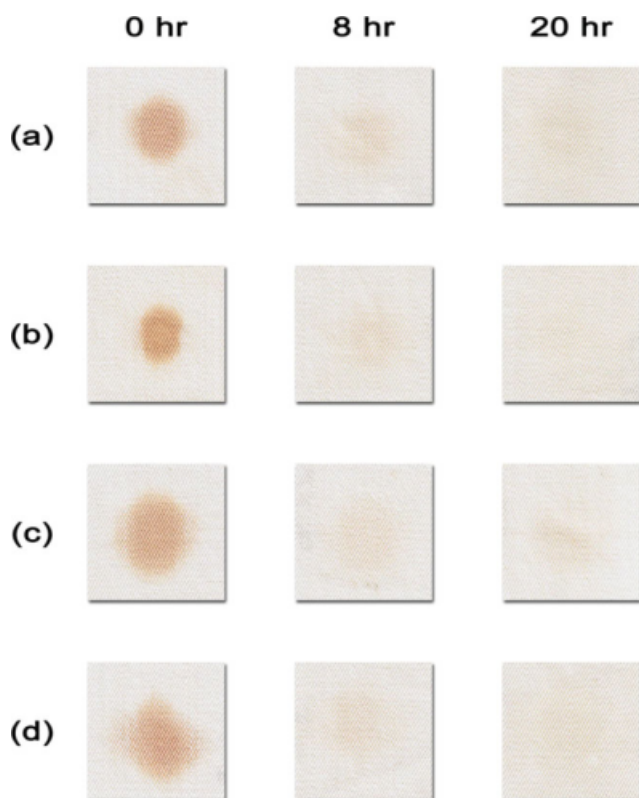


Figure 11 Stain degradation of red wine after stability test (a) T80A, (b) T80B, (c) X100A, and (d) X100S. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the molecular structure of the wetting agent becomes the major factor in affecting the wettability performance. Compared to X100, T80 appeared less efficient in improving the fiber wettability because of its long-chain molecular structure, and hence its inability to efficiently disperse titanium dioxide nanoparticles. However, the absorption rate can be facilitated by increasing the concentration of the surfactant,²⁵ which explained why T80B led to shorter wetting time than T80A.

Photocatalytic purification performance and reproducibility

The stain degradation on fibers coated with and without wetting agents is illustrated in Figures 8 and 9. Fibers coated with TiO₂ in presence of T80A, T80B, X100A, and X100S possessed excellent stain degradation ability. Both concentrated coffee and red wine stains were almost completely discolored within 8 h and totally removed within 20 h of solar-simulated irradiation. The photocatalytic activity was substantially enhanced, where the time required to completely degrade the stains decreased from 40 to 20 h of irradiation when compared with S0. Besides, all wettability-modified TiO₂-coated fibers

exhibited outstanding stability, where the stain degradation ability was retained after repeated washing (Figs. 10 and 11). It is believed that T80 and X100 assisted the dispersion and stabilization of TiO₂ particles on fibers during the dip-coating due to the fact that they consist of both hydrophilic and hydrophobic groups.^{25,26} Hence, both types of nonionic wetting agents led to improvement of the photocatalytic activity of TiO₂-coated wool.

The synchronized effect of wettability control and silicone surface modification on the self-cleaning properties of wool fibers was also studied by means of stain degradation and stability test. After the silicone treatment, the discoloration of stains was slightly reduced. Figures 12 and 13 show that both concentrated coffee and red wine stains were notably degraded after 8 h of solar-simulated irradiation; however, an insignificant amount of stain can still be observed after 20 h of irradiation. From the shape of the stains, all wettability-modified and silicone-modified TiO₂-coated fibers became more hydrophobic, which is in agreement with the results shown in section Photocatalytic Purification Performance. Although wettability-modified TiO₂-coated fibers displayed similar purification property after the stability test (Figs. 10 and 11) and silicone treatment

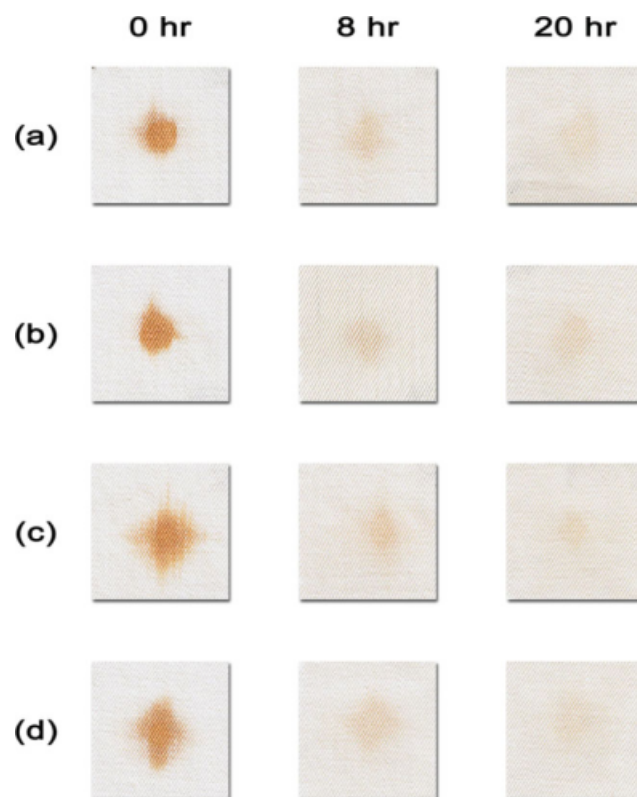


Figure 12 Stain degradation of concentrated coffee after silicone modification (a) T80A, (b) T80B, (c) X100A, and (d) X100S. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

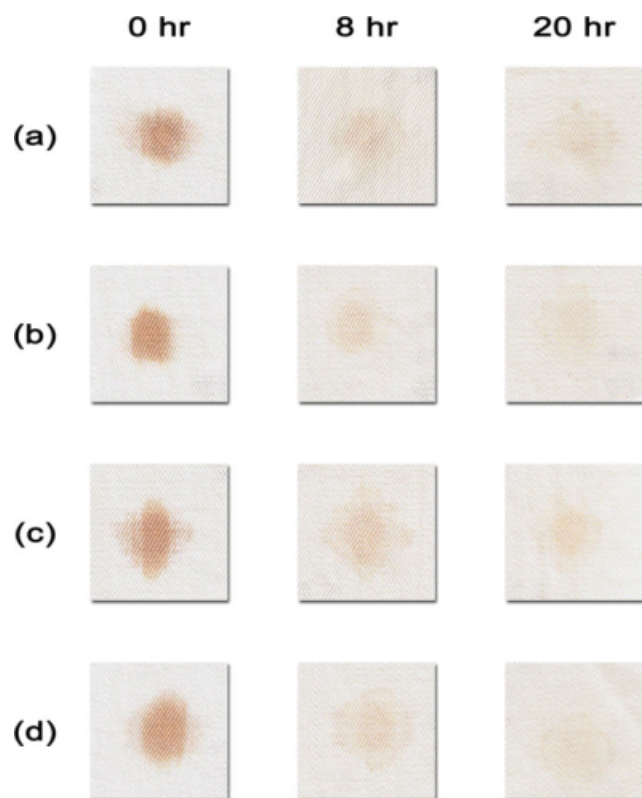


Figure 13 Stain degradation of red wine after silicone modification (a) T80A, (b) T80B, (c) X100A, and (d) X100S. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

(Figs. 12 and 13), they were significantly different in their self-cleaning ability after having undergone both silicone treatment and stability test. For concentrated coffee stain in Figure 14, all wettability-modified TiO_2 -coated and silicone-modified fibers showed similar photocatalytic activity before and after stability test. On the other hand, they reacted very differently on red wine stain (Fig. 15). Silicone-treated T80A no longer possessed photocatalytic properties after stability test; where red wine stain remained intact on the fiber surface after solar-simulated irradiation. The photocatalytic ability of silicone-treated T80B was significantly reduced after stability test, where the red wine stain was observable even after 20 h of solar-simulated irradiation. On the other hand, fibers treated with X100 displayed better photocatalytic reproducibility after washing. The photocatalytic activity of both silicone-treated X100A and X100S was completely reproducible after the stability test, where red wine stains were almost completely discolored after 20 h of irradiation. When comparing TiO_2 -coated X100, silicone-modified X100S demonstrated comparatively better reproducibility than silicone-modified X100A. The results imply that, although Tween[®] 80 successfully dispersed titanium dioxide nanoparticles in the sol,

it was unable to promote a strong binding between the nanoparticles and wool to be able to withstand the silicone treatment and stability test. Whereas Triton[®] X-100 was able to expedite the absorption rate effectively and promoted good binding between titanium dioxide and wool, and thus reproducible photocatalytic properties could be obtained after the silicone post-treatment and stability test. Moreover, the results further verify that X100S TiO_2 -coated fibers prepared with Triton[®] X-100 *in situ* possessed significant self-cleaning property with good stability.

CONCLUSIONS

The self-cleaning functionalization of wool via titanium dioxide coating has been modified by wettability promotion using nonionic surfactants and surface modification with silicone. The TiO_2 -coating-induced drop of wool mechanical properties can be substantially recovered with minimal adverse effect on the self-cleaning performance. The initial deterioration on tearing strength and bending rigidity caused by TiO_2 -coating has notably been offset, particularly when 2% amino-modified silicone emulsion was used in a concentration ratio of 10 : 1. Although the

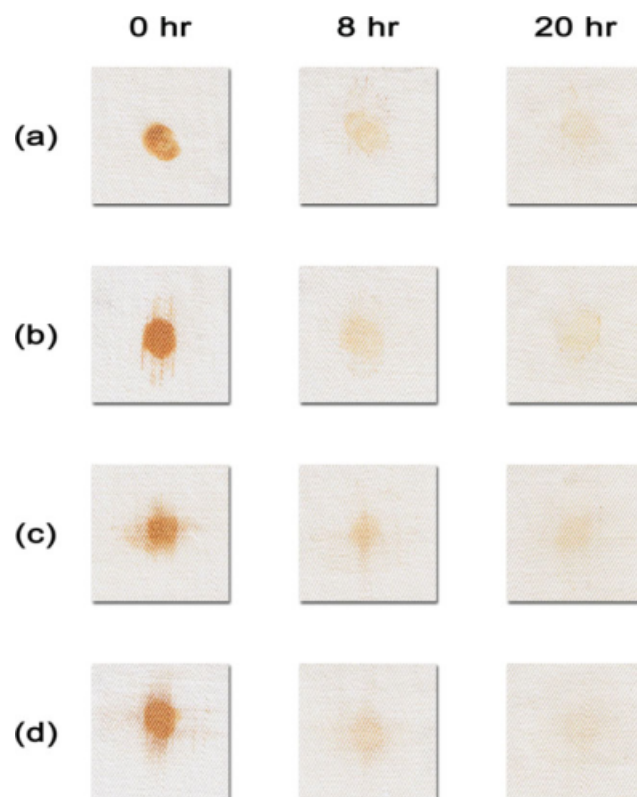


Figure 14 Stain degradation of concentrated coffee after silicone modification and stability test (a) T80A, (b) T80B, (c) X100A, and (d) X100S. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

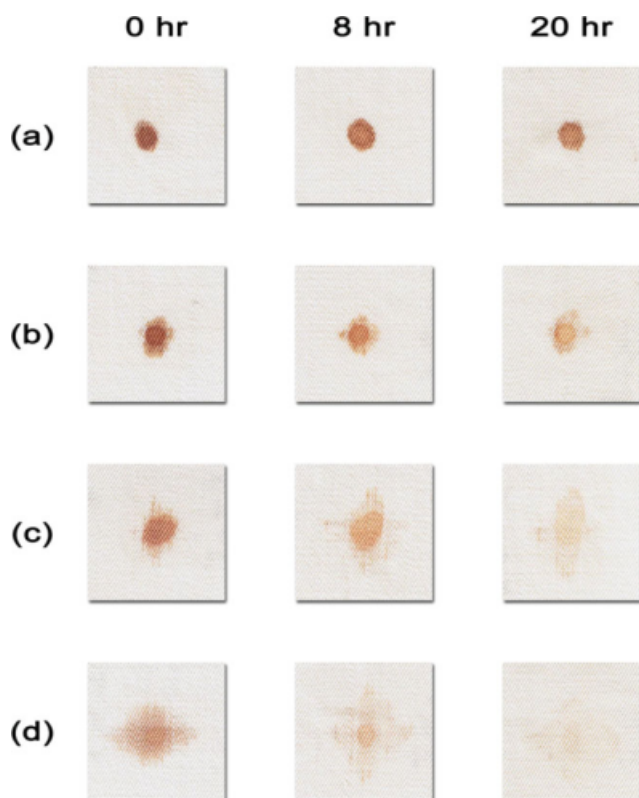


Figure 15 Stain degradation of red wine after silicone modification and stability test (a) T80A, (b) T80B, (c) X100A, and (d) X100S. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

self-cleaning ability toward both concentrated coffee and red wine stains remained unchanged, its reproducibility after stability test was slightly impaired. Moreover, the absorption rate of TiO_2 sol by fibers was greatly increased with good photocatalytic self-cleaning activity by using different wetting agents. However, only Triton[®]X-100 modified TiO_2 -coated possesses good and reproducible photocatalytic activity. This study demonstrates that improving fibers wettability during TiO_2 coating and the ability to recover fibers mechanical properties following TiO_2 -coating using a surface modification treatment with

amino-modified silicone show great potential in the practical self-cleaning functionalization of wool materials.

The authors are grateful to Dr. S. K. Leung for her experimental assistance and fruitful discussions and to Mr. X. Wang for his help with the silicone modification study.

References

1. Fujishima, A.; Honda, K. *Nature* 1972, 238, 37.
2. Fujishima, A.; Zhang, X. *C R Chim* 2006, 9, 750.
3. Daoud, W. A.; Xin, J. H. *J Am Ceram Soc* 2004, 87, 953.
4. Daoud, W. A.; Xin, J. H. *Chem Commun* 2005, 2110.
5. Fujishima, A.; Rao, T. N.; Tryk, D. A. *J Photochem Photobiol C-Photochem Rev* 2000, 1, 1.
6. Mills, A.; Lee, S. K. *J Photochem Photobiol A-Chem* 2002, 152, 233.
7. Yang, H.; Zhu, S.; Pan, N. *J Appl Polym Sci* 2004, 92, 3201.
8. Daoud, W. A.; Xin, J. H.; Zhang, Y. H. *Surf Sci* 2005, 599, 69.
9. Anpo, M.; Shima, T.; Kodama, S.; Kubokawa, Y. *J Phys Chem* 1987, 91, 4305.
10. Oppenländer, T. *Photochemical Purification of Water and Air*; Wiley-VCH: Germany, 2003.
11. Kaneko, M.; Okura, I. *Photocatalysis: Science and Technology*; Kodasha-Springer: Tokyo, 2002.
12. Rincón, A. G.; Pulgarin, C. *Appl Catal B-Environ* 2004, 49, 99.
13. Daoud, W. A.; Xin, J. H.; Zhang, Y. H.; Qi, K. H. *J Non-Cryst Solids* 2005, 351, 1486.
14. Daoud, W. A.; Xin, J. H. *J Sol-Gel Sci Technol* 2004, 29, 25.
15. Kaneko, M.; Yuranova, T.; Guasaquillo, I.; Laub, D.; Kiwi, J. *J Photochem Photobiol A-Chem* 2005, 174, 156.
16. Langlet, M.; Kim, A.; Audier, M.; Herrmann, J. M. *J Sol-Gel Sci Technol* 2002, 25, 223.
17. Meilert, K. T.; Laub, D.; Kiwi, J. *J Mol Catal A-Chem* 2005, 237, 101.
18. Yuranova, T.; Mosteo, R.; Bandara, J.; Laub, D.; Kiwi, J. *J Mol Catal A-Chem* 2006, 244, 160.
19. Bozzi, A.; Yuranova, T.; Kiwi, J. *J Photochem Photobiol A-Chem* 2005, 172, 27.
20. Qi, K. H.; Daoud, W. A.; Xin, J. H.; Mak, C. L.; Tang, W. S.; Cheung, W. P. *J Mater Chem* 2006, 16, 4567.
21. Daoud, W. A.; Leung, S. K.; Tung, W. S.; Xin, J. H.; Cheuk, K.; Qi, K. *Chem Mater* 2008, 20, 1242.
22. Tung, W. S.; Daoud, W. A. *J Colloid Interface Sci* 2008, 326, 283.
23. Tung, W. S.; Daoud, W. A. *Acta Biomater* 2009, 5, 50.
24. Kim, M. S.; Kang, T. *J Textile Res J* 2002, 72, 113.
25. Simončič, B.; Rozman, V. *Colloid Surf A* 2007, 292, 236.
26. Alexeev, V. L.; Ilekto, P.; Persello, J.; Lambard, J.; Gulik, T.; Cabane, B. *Langmuir* 1996, 12, 2392.