



Superhydrophobic fabrics from hybrid silica sol-gel coatings: Structural effect of precursors on wettability and washing durability

AUTHOR(S)

Hong Wang, J Ding, Y Xue, Xungai Wang, Tong Lin

PUBLICATION DATE

01-01-2010

HANDLE

[10536/DRO/DU:30032612](#)

Downloaded from Deakin University's Figshare repository

Deakin University CRICOS Provider Code: 00113B

DRO

Deakin University's Research Repository

This is the published version:

Wang, Hongxia, Ding, Jie, Xue, Yuhua, Wang, Xungai and Lin, Tong 2010, Superhydrophobic fabrics from hybrid silica sol-gel coatings: Structural effect of precursors on wettability and washing durability, *Journal of materials research*, vol. 25, no. 7, pp. 1336-1343.

Available from Deakin Research Online:

<http://hdl.handle.net/10536/DRO/DU:30032612>

Reproduced with the kind permission of the copyright owner.

Copyright : 2010, Cambridge University Press

INFO #: 19701993



CustID: 177439
The National Library of Australia
ARIEL: 128.184.60.201
Deakin University Library

Geelong , Australia 3217

Customer No: **177439 / 805320**
Date of Order: **10/08/2010**
Date of Shipping: **10/08/2010**
Orderer: **ARIEL: 128.184.60.201**
Department:
Bill Ref:
Order No: **104862**
Shipping method: **eMail**
lib-ill-glg@deakin.edu.au

Standard

Journal: Journal of Materials Research
Citations: vol. 25, issue 7():pp. 1336-1343 2010
Author: Wang, Hongxia; Ding, Jie; Xue, Yuhua; Wang, Xungai; Lin, Tong
Title: Superhydrophobic fabrics from hybrid silica sol-gel coatings: Structural ef
ISSN: 08842914

**This work was copied under licence from the Copyright Agency Limited (CAL).
A licence is required from CAL for the making of further copies by any means.**

Infotrieve Australia Pty
344 Ferntree Gully Road
Notting Hill VIC 3168
AUSTRALIA

Ph: +61-3-9544 4911
Fax: +61-3-9544 3277
Email: status@infotrieve.com.au
www.infotrieve.com

Superhydrophobic fabrics from hybrid silica sol-gel coatings: Structural effect of precursors on wettability and washing durability

Hongxia Wang

Centre for Material and Fibre Innovation, Deakin University, Geelong, VIC 3217 Australia

Jie Ding

Human Protection and Performance Division, Defence Science & Technology Organisation (DSTO), Melbourne, VIC 3207 Australia

Yuhua Xue, Xungai Wang, and Tong Lin^{a)}

Centre for Material and Fibre Innovation, Deakin University, Geelong, VIC 3217 Australia

(Received 8 March 2010; accepted 12 April 2010)

Particle-containing silica sol was synthesized by co-hydrolysis and co-condensation of two silane precursors, tetraethylorthosilicate (TEOS) and an organic silane composed of a non-hydrolyzable functional group (e.g., alkyl, fluorinated alkyl, and phenyl), and used to produce superhydrophobic coatings on fabrics. It has been revealed that the non-hydrolyzable functional groups in the organic silanes have a considerable influence on the fabric surface wettability. When the functional group was long chain alkyl (C16), phenyl, or fluorinated alkyl (C8), the treated surfaces were highly superhydrophobic with a water contact angle (CA) greater than 170°, and the CA value was little affected by the fabric type. The washing durability of the superhydrophobic coating was improved by introducing the third silane containing epoxide group, 3-glycidoxypyltrimethoxysilane (GPTMS), for synthesis. Although the presence of epoxide groups in the coating slightly reduced the fabrics' superhydrophobicity, the washing durability was considerably improved when polyester and cotton fabrics were used as substrates.

I. INTRODUCTION

Superhydrophobicity is typically used to describe surfaces with a water contact angle greater than 150°. ¹⁻⁴ Nature has provided many examples of superhydrophobic surfaces, such as lotus leaves, butterfly wings, and duck feathers, to show water repellent and self-cleaning functions. It is of practical importance to develop superhydrophobic surfaces on fabrics so that they can repel water/ice/snow and have anti-sticking, anti-contaminating, and/or self-cleaning characteristics, but are still permeable to air and moisture for comfort.

Extensive research has recently been conducted to understand the formation of superhydrophobicity on various substrates. It has been established that superhydrophobicity depends on not only the surface chemistry but also the surface topology. Two distinct theoretical models (Wenzel and Cassie-Baxter) ^{1,2} have been developed to guide the production of superhydrophobic surfaces by either roughening the surface or lowering the surface free energy, or both. For example, superhydrophobic surfaces were prepared by building a nano-structured surface on a substrate, ⁵⁻²¹ followed by treatment with fluoro-containing polymer or silane. ^{9,12} Most of the superhydrophobic tech-

niques, however, involve a tedious and multiple-step procedure, which is impractical for large-scale production. In this regard, coating solutions using a one-step preparation and a simple coating process are highly desirable because of the simplicity in both the process and the equipment involved. So far, several one-step superhydrophobic treatments have been reported, using micellar polymer solutions, ^{22,23} phase-separated polymers, ²⁴ nanofiller-added polymers, and sol-gel solutions. ^{25,26}

Fabric materials have micro-scaled rough surfaces arising from the fibrous structure which can increase the surface hydrophobicity if the fiber materials are hydrophobic. Despite that, the conventional fabrics are rarely superhydrophobic, and a finishing treatment is normally required to impart fabrics with surface superhydrophobicity. Many superhydrophobic techniques have been used to treat fabrics, including solution coatings of carbon nanotubes, ²⁷ ZnO nanorods, ²⁸ metal and silica particles, ^{29,30} chemical vapor deposition, and plasma or laser treatment. ^{31,32} However, the majority of the studies have focused on the static contact angle of the treated fabric. Little attention has been paid to contact angle hysteresis, which is another important factor influencing the self-cleaning behavior. In addition, durability is an issue of concern for most superhydrophobic fabrics that have to be repeatedly and rigorously washed as use demands.

^{a)}Address all correspondence to this author.

e-mail: tongl@deakin.edu.au

DOI: 10.1557/JMR.2010.0169

Silica coating using the sol-gel technology provides a simple and cost efficient approach to functionalize different surfaces.^{33,34} Depending on the chemical structure and fabrication condition, either viscous solution or nano-sized particles can be obtained from hydrolysis of a silane precursor, which can form a dense or porous film through a coating technique. Also, the film's mechanical properties and adhesion strength to the substrate can be enhanced by crosslinking the silica within the matrix and introducing chemical bonding between coating and substrate using functional silanes. In our previous study,³⁵ we developed a one-step method to produce coating solutions by cohydrolysis and cocondensation of tetraethylorthosilicate (TEOS) with a fluorinated alkyl silane (FAS) for superhydrophobic treatment. The treated surfaces have a high water contact angle with a small contact angle hysteresis.

In this study, we prepared coating solutions by cohydrolysis and cocondensation of TEOS with a series of organic silanes for superhydrophobic treatment of fabrics. The structural effect of the silane precursors on the superhydrophobicity was examined. The washing durability of the superhydrophobic coatings was improved by introducing epoxide groups to the coating layer through the addition of a third silane.

II. EXPERIMENTAL

A. Materials and measurements

Ethanol, tetraethylorthosilicate (TEOS), and ammonium hydroxide (28% in water) were obtained from Aldrich (St. Louis, MO). Tridecafluorooctyl triethoxysilane (FAS, Dynasylan F 8261), methyltriethoxysilane (MTES), phenyl triethoxysilane (PhTES), octyl triethoxysilane (OTES), hexadecyl trimethoxysilan (HDTMS) and 3-glycidoxypyltrimethoxysilane (GPTMS) were supplied by Degussa (Dusseldorf, Germany). Commercial polyester (plain weave, 168 g/m²), wool (plain weave, 196 g/m²), and cotton (plain weave, 160 g/m²) fabrics were used in this work.

Electron microscopic images were taken on scanning electron microscope (Leo 1530, Gemini/Zeiss, Oberkochen, Germany). A transmission electron microscope (TEM, JEM-200 CX JEOL, Seike Instruments, USA) was used to observe silica particles. Fourier Transform Infrared (FTIR) spectra were measured on an FTIR spectrophotometer (Bruker Optics, Ettlingen, Germany) in ATR mode. Water contact angles were measured using a contact angle meter (KSV CAM200 Instruments Ltd., Helsinki, Finland). Sliding angles were measured using a purpose-made device consisting of a sample holder and a digital angle meter. X-ray photoelectron spectra (XPS) were collected on a VG ESCALAB 220-iXL spectrometer with a monochromated Al $K\alpha$ source (1486.6 eV) using samples of approximately 3 mm² in size. The x-ray beam incidence angle was 0° with respect to the surface normal,

which corresponds to a sampling depth of ~10 nm. The obtained XPS spectra were analyzed by the XPSPEAK41 software (Shanghai, China).

The washing durability of the superhydrophobic coating was examined by washing the coated fabrics in a washing machine according to the method specified in Australian Standard (AS 2001.1.4). This standard wash procedure is equivalent to five cycles of home machine launderings. For convenience, we use the equivalent number of home machine launderings in this paper.

B. Synthesis of coating solution

The typical procedure to prepare the coating solutions is as follows: TEOS (5 mL), together with an appropriate amount of organic silane, was dissolved in 25 mL ethanol. The solution was mixed with ammonium hydroxide/ethanol solution (6 mL 28% NH₃·H₂O in 25 mL ethanol), and stirred intensively at room temperature for 12 h. The mixture solution was then ultrasonicated (VCX750 Sonics & Materials Inc., Newtown, CT) for 30 min to get a homogeneous suspension.

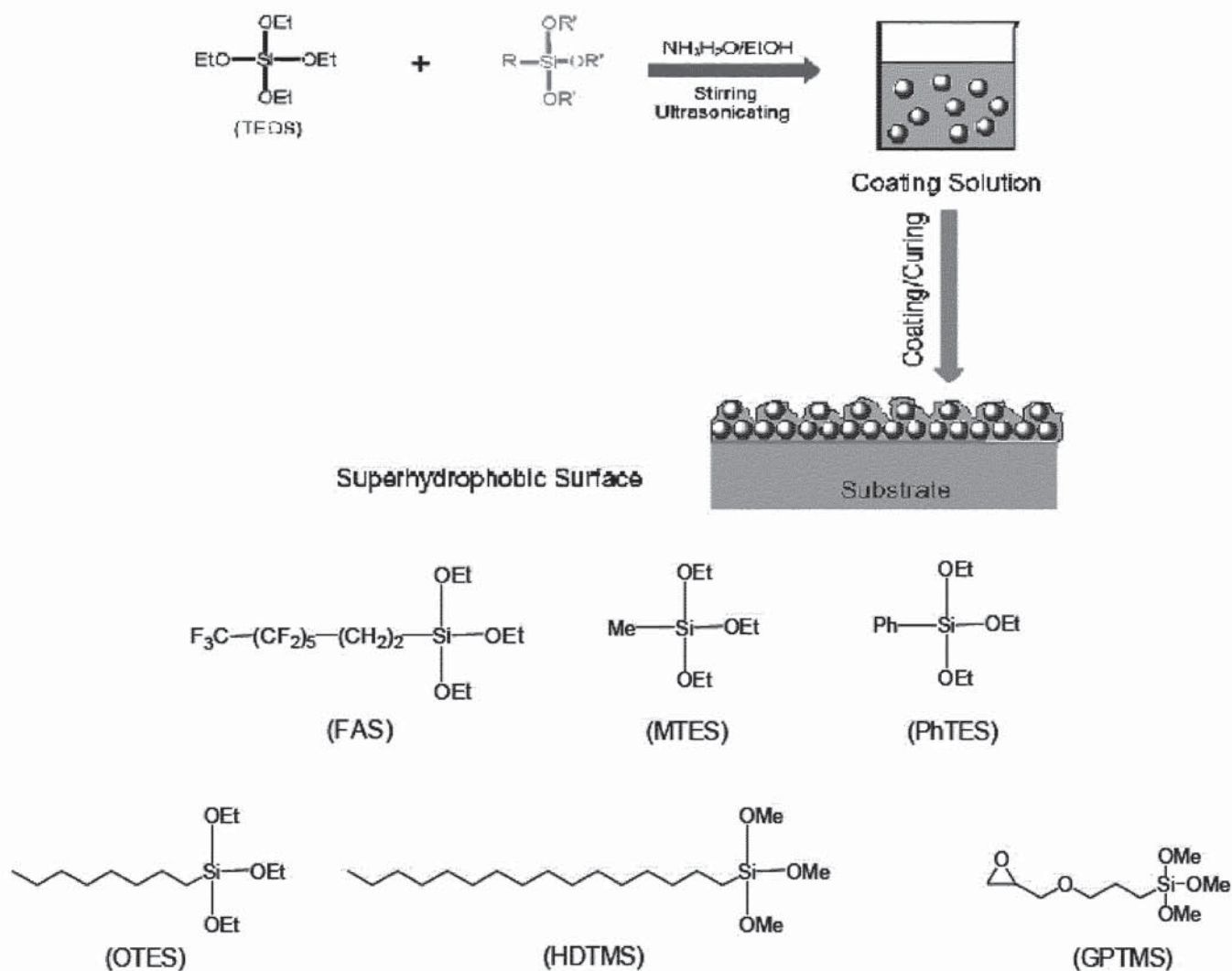
C. Coating procedure

The as-prepared solution was directly padded onto the fabric samples (dip-coating and then using squeeze rollers to remove extra coating liquid). Upon drying at room temperature, the treated substrate was further cured at 110 °C for 1 h.

III. RESULTS AND DISCUSSION

The coating solutions were prepared by cohydrolysis and cocondensation of tetraethyl silicate (TEOS) with an organic silane in NH₃·H₂O-ethanol solution. Without any purification, the as-hydrolyzed solution can be directly applied to fabrics by different coating techniques, such as padding, dip-coating, or spraying, to form a transparent coating on the fabrics. The procedure for preparation of the coating solutions and fabric coating procedure, as well as the chemical structures of the silane precursors used, are shown in Scheme 1. All the organic silanes are composed of a non-hydrolyzable functional group and three alkoxy groups. The difference between these organic silanes is mainly in the non-hydrolyzable group. When an organic silane was co-hydrolyzed with TEOS, hybrid silica was formed, and the non-hydrolyzable groups remained both in the silica matrix and on the surface. Therefore, the non-hydrolyzable group in the organic silane is expected to affect the physical, chemical, and surface properties of the hydrolysis products.

In this study, three types of fabrics, polyester, wool, and cotton, were used as the substrates and they were coated with different silica solutions synthesized under the same conditions. Figure 1 reveals a nearly sphere-like droplet



SCHEME 1. Reaction route to the coating solutions, coating procedure, and the chemical structures of the organic silanes used.

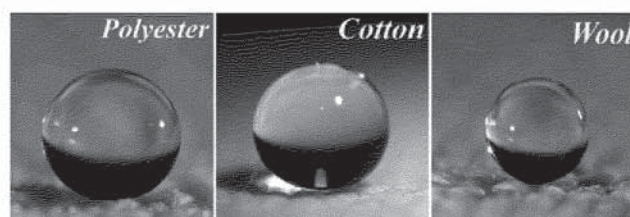


FIG. 1. Photos of water drops on the treated fabrics (silanes TEOS/HDTMS).

formed when water (4 μL) was placed on the fabrics treated with the TEOS/HDTMS coating solution, which can stay on the fabrics for a long period of time. The water contact angle (CA) for the coated polyester fabric was $170 \pm 2.7^\circ$, indicating a highly superhydrophobic surface. Here, the sliding angle (SA) was used to measure the contact angle hysteresis,³⁶ and the SA value for the treated polyester fabric was $6.4 \pm 0.1^\circ$. The CA and SA data of all the fabrics treated by different coating systems is given in Fig. 2. For comparison, the CA and SA values of the untreated pristine

fabrics (control) are also included in the figures. Although the coating loading varied in the range of 2.6–5.0 mg/cm^2 , and also the untreated pristine fabrics had different water contact angles, all the fabrics treated by the TEOS/HDTMS coating solution exhibited a similar CA value, while the SA was slightly lower when the CA of the control fabric was higher. This suggested that the sliding angle was more sensitive to the wettability of the substrate.

It was interesting to note that the silica treatments did not make all the fabrics superhydrophobic [Fig. 2(a)].

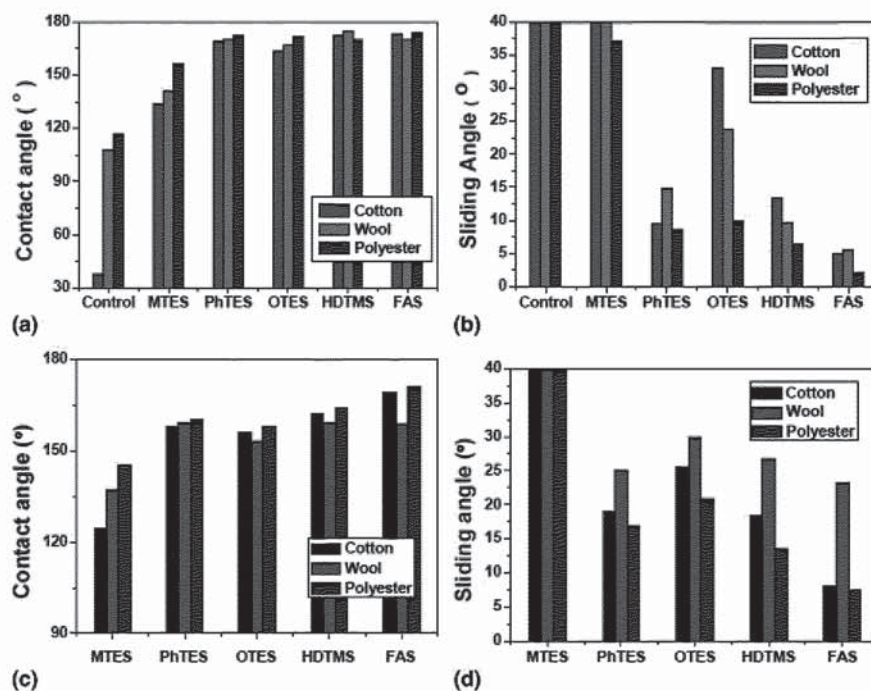


FIG. 2. (a, b) Water contact and sliding angles of the fabrics treated by TEOS/organic silica coating systems (TEOS: organic silane = 1:1 mol/mol), (c, d) Water contact and sliding angles of the fabrics treated with TEOS/GPTMS/organic silane silica systems (TEOS: [organic silane + GPTMS] = 1:1; organic silane: GPTMS = 2:1, mol/mol).

The treatment from MTES/TEOS coating solution only made the polyester fabric superhydrophobic. Although the treated cotton and wool fabrics showed considerably increased CA, the values were below 150° . Most treated cotton fabrics had a lower CA compared to the wool and polyester fabrics treated with the same coating system, confirming that the fiber type influenced the fabric hydrophobicity.

The main difference among MTES, OTES, and HDTMS is the chain length of non-hydrolyzable alkyl, which is C1, C8, and C16 for MTES, OTES, and HDTMS, respectively. By associating the length of the alkyl chain with the water contact angle value, it was clear that increasing the alkyl chain length led to increase in the CA value. With the precursor FAS, the fluorinated alkyl is composed of six fully fluorinated carbons and two non-fluorinated carbons. However, the fabrics treated by the TEOS/FAS coating showed similar contact angle values to those treated by TEOS/HDTMS, even though the alkyl in HDTMS is twice as long as that in FAS. In addition, the TEOS/PhTES silica also led to a similar CA value compared to the TEOS/FAS, and the CA value was little affected by the fabric types.

Besides the water contact angle, the sliding angle was also affected by the silane and fabric types. As shown in Fig. 2(b), the sliding angle of all the MTES/TEOS coated fabrics is greater than 35° . Due to instrument limitation, sliding angles greater than 40° were not obtainable. The sliding angles for the fabrics treated by TEOS/FAS,

TEOS/HDTMS, and TEOS/PhTES coating systems were lower than those treated by TEOS/OTES solution. For MTES, OTES, and HDTMS, with the increase in the alkyl chain length, the coated fabric showed a reduced sliding angle, which has a reverse trend to the contact angles. In addition, the fluorinated alkyl group in FAS led to the lowest sliding angle value.

In order to improve the coating adhesion, glycidoxypolytrimethoxysilane (GPTMS), an organic silane containing an epoxide in the non-hydrolyzable functional group, was also used for synthesis. Cofunctionalization of GPTMS with TEOS resulted in a homogeneous viscous solution. Although applying this solution to fabrics led to increased water contact angle, the contact angle value was still below 150° , at approximately 140° , 130° , and 110° for the treated polyester, wool, and cotton fabrics, respectively. In order to achieve a superhydrophobic coating, TEOS and GPTMS were cofunctionalized with another organic silane, and the CA and SA values of the coated fabrics showed a dependence on the ratio between GPTMS and the organic silane used. The molar ratio of TEOS/(GPTMS + organic silane) was kept at 1:1; the influence of the GPTMS/organic silane ratio on the water contact angle of the coated fabrics for two coating systems, TEOS/GPTMS/FAS and TEOS/GPTMS/HDTMS, is depicted in Fig. 3.

It was interesting to note that the dependency of CA on the GPTMS/organic silane ratio showed slightly different trends for the two coating systems. When the ratio of

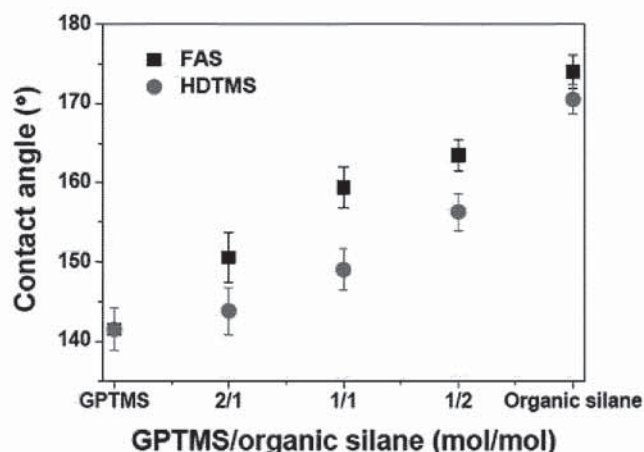


FIG. 3. Influence of GPTMS/organic silane ratio in the hydrolysis reaction on the resulting water contact angles of the coated fabrics (TEOS: [organic silane + GPTMS] = 1:1, mol/mol).

GPTMS and organic silane was at 1:2 (mol/mol), the coated surfaces all became superhydrophobic regardless the fabric type for the five coating systems. Therefore, the ratio 1:2 was chosen to synthesize other coating systems. The CA and SA values of the fabrics treated by different TEOS/GPTMS/organic silane coating systems are shown in Figs. 2(c) and 2(d). It was clear that all the treated fabrics had lower CA but higher SA values compared to those that were treated by the coating solution prepared from the same TEOS/organic silane but without GPTMS involved in the hydrolysis reaction [Figs. 2(a) and 2(b)].

Figure 4(a) shows a typical surface morphology of the TEOS/FAS silica coating on wool fiber. Particulate structures were observed on the fiber surface, immobilized by the resin hydrolyzed from the organic silane. The inset TEM image of the particles reveals that the particles look irregular in shape. They aggregated randomly over the coated area, and were stuck together due to the presence of the thin resin layer. These particles with resin shell have an average size of ~150–300 nm. The coatings on other fabrics showed a similar surface morphology and the particulate/resin structures were also formed in other silane coating systems.

In order to understand the particle formation in the cohydrolysis reaction, TEOS and organic silane were hydrolyzed separately under the same condition. It was observed that TEOS in $\text{NH}_3\cdot\text{H}_2\text{O}$ -ethanol solution was hydrolyzed quickly into silica particles that turned the solution milky, while the organic silane typically formed a thick and clear resin that phase-separated out from the solution. The hydrolysis of organic silane was slower than that of TEOS. When the two silane precursors were cohydrolyzed, the quickly formed silica particles were covered with the slowly-hydrolyzed organic silane resin.

The sizes of the particles from all coating systems are given in Fig. 5. The sizes of particles for the TEOS/

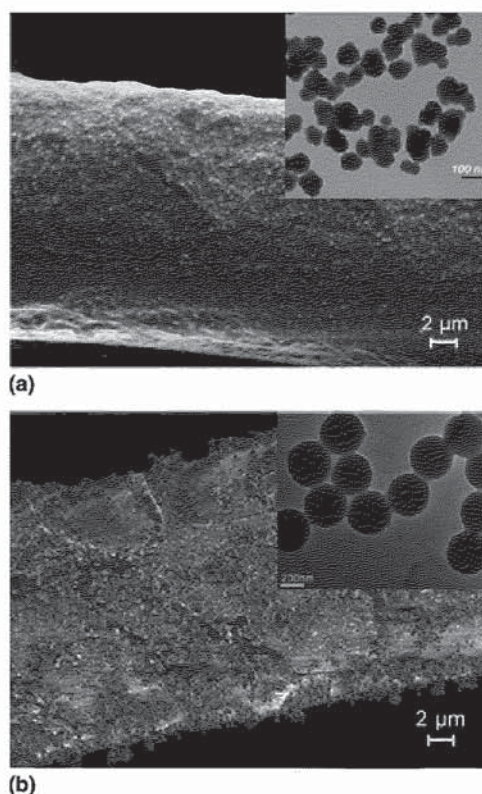


FIG. 4. SEM of the silica coated wool fibers, and TEM image of the silica particles (inset images). Coating system: (a) TEOS/FAS, (b) TEOS/GPTMS/FAS.

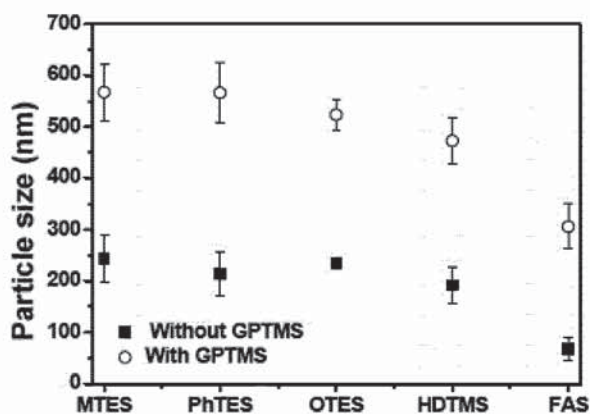


FIG. 5. Sizes of silica particles from different coating systems.

MTES, TEOS/OTES, and TEOS/HDTMS coating systems were 240 ± 12 nm, 230 ± 46 nm, and 190 ± 36 nm, respectively. This suggests that organic silane had a slight influence on particle size. From MTES to OTES and to HDTMS, with an increase in the length of alkyl chain, the particle size decreased (Fig. 5). This can be explained due to the organic silane having a short nonhydrolyzable alkyl chain, which tends to hydrolyze slightly faster than one having a longer chain. As a result, an intermediate layer could be formed from

cocondensation of hydrolyzed TEOS and alkyl silane yielding larger particles. On the other hand, an organic silane having a long nonhydrolyzable alkyl chain tends to have better shielding effect when it is adsorbed by particles, which prevents the particle from growing in size. It should also be noted that the resin-like hydrolysis product from the organic silane is not necessarily fully adsorbed by the silica particles. The resin dispersing in the solution could deposit directly on the fabric during the coating treatment.

The presence of GPTMS in the hydrolysis reaction influenced the particle size considerably. As also shown in Fig. 5, the GPTMS involved hydrolysis reaction leads to particle size increasing for approximately 250 nm for the TEOS/FAS system, and the particles look more regular in shape [Fig. 4(b)]. A similar increase in the particle size due to the presence of GPTMS was also found in other coating systems. Such an apparent increase in the particle size can be attributed to the faster hydrolysis rate for GPTMS compared to the organic silanes. As a result of the increased particle size, the roughness of the coating surface also changed, which could be a reason for the reduction of the surface hydrophobicity.

As already demonstrated by the energy-dispersive x-ray analysis in our previous paper,³⁵ the TEOS/FAS silica coating showed an even coverage on the fiber surface. The uniform coverage of coating was also found for other coating systems for all the fabric substrates, owing to the fluidic nature of the coating solution containing a viscous resin. For the GPTMS involved coating system, the coating coverage was slightly different due to the larger particle size. However, the TEM image [Fig. 4(b)] clearly indicated that an inter-bonded particle network structure formed in the coating layer.

The chemical components of the silica coatings with and without GPTMS were studied by Fourier transform infrared (FTIR) and x-ray photoelectron spectroscopy (XPS). For the GPTMS involved coating, vibration bands at 960 and 1730 cm^{-1} , corresponding to the characteristic vibrations of oxirane and C-O,³⁷ occurred in the FTIR spectrum [Fig. 6(a)]. The occurrence of plain bands at 3379 and 1640 cm^{-1} was respectively assigned to the O-H stretching and bending vibrations. Also, the peaks at 2970 and 2900 cm^{-1} are characteristic of C-H vibrations from alkyl groups. The high resolution XPS C1s showed binding energies of 294, 292, 289, and 285 eV for the TEOS/FAS silica coated surface, which are typical characteristics of $-\text{CF}_3$, $-\text{CF}_2$, $-\text{CSi}$, and C-C moieties, respectively.³⁵ The addition of GPTMS to the coating system led to one more peak at 286 eV, which is assigned to the C-O moiety of epoxide.³⁸ In addition, all the coatings showed silica characteristic with a binding energy of Si2p at 104.6 eV.

Durability is an important criterion for the practical applications of superhydrophobic coatings on textile fab-

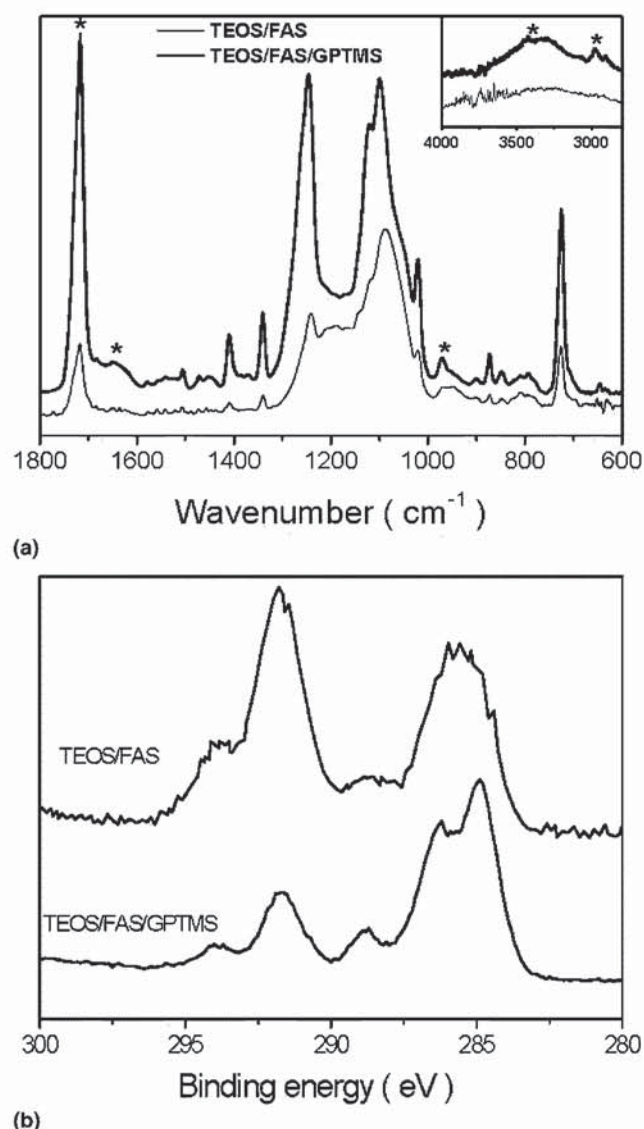


FIG. 6. (a) FTIR spectra and (b) XPS high resolution C1s spectra of the coated polyester fabrics.

rics. The washing durability of the superhydrophobic coatings was evaluated based on a standard washing procedure for testing the washing durability of fabrics. When the fabrics were treated with a silica coating not containing GPTMS, within 10 laundering cycles, the contact angle returned to the uncoated level. When the GPTMS was involved in the coating system, the washing durability was improved considerably. As shown in Fig. 7, polyester and cotton fabrics retained their superhydrophobicity even after 50 laundering cycles, when the fabrics were coated with either TEOS/FAS/GPTMS or TEOS/HDTMS/GPTMS silica. However, the superhydrophobicity for the coated wool fabrics deteriorated within 10 laundering cycles when they were treated with the same coating solutions.

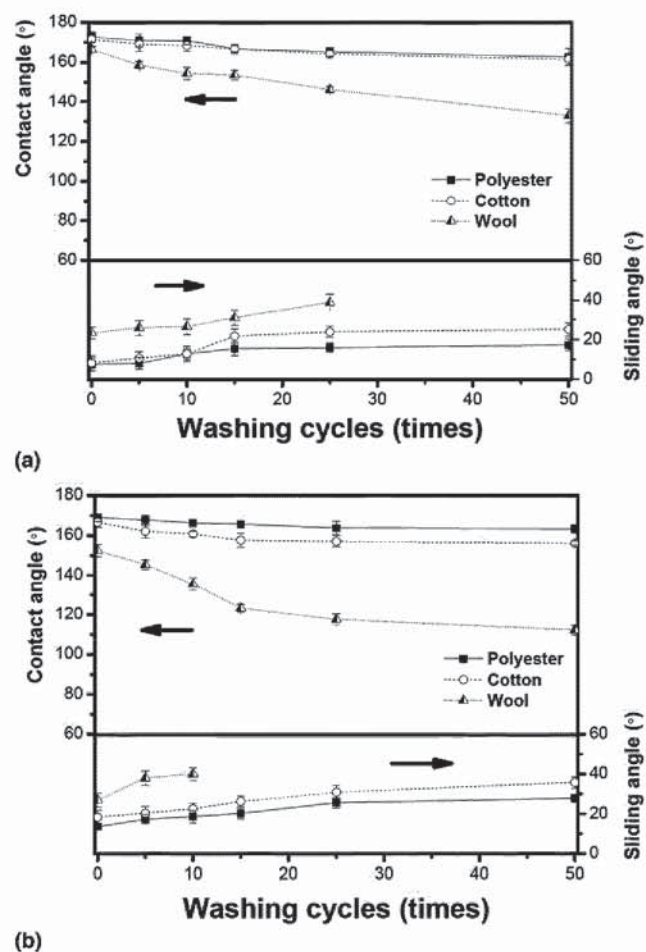


FIG. 7. Washing durability of the superhydrophobic coatings on different fabrics. Coating system: (a) TEOS/FAS/GPTMS, (b) TEOS/HDTMS/GPTMS.

The sliding angle of the treated fabrics changed with the laundering cycles. With the increase in the laundering cycles, the increase in the sliding angle was observed for all the treated fabrics. The SA increase rate for the coated wool fabrics was larger than that for other types of fabrics. Also, the SA values for the coatings from TEOS/FAS/GPTMS system showed a smaller increase compared to those from the TEOS/FAS/HDTMS system. In comparison with the contact angle, the sliding angle was more sensitive to the washing process.

The driving force for the formation of the superhydrophobic surface comes from a rough surface formed from the silica nanoparticles immobilized by a resin hydrolyzed from organic silane. The superhydrophobicity is highly influenced by the surface free energy of silica particles, which is associated with the functional group of the organic silane. The lower the surface energy is, the higher the superhydrophobicity. That was why the alkyl with longer alkyl chain could lead to higher water contact angles and lower sliding angles.

Possible effect(s) of the substrate nature on the superhydrophobic durability could come from the adhesion of silica coating on the substrate. Chemical bonds between the substrate and coating layer play an important role in determining the adhesion strength. Under acidic or basic conditions, epoxy rings can open to react with many reactive groups (e.g., amino, carboxyl, and hydroxyl groups) through a nucleophilic addition mechanism. For amino or carboxyl groups, the reactions are easy to perform. However, for hydroxyl groups, the ring opening reaction needs to be catalyzed by a strong base. It has been reported that some epoxy-containing chemicals have been used for functionalization of cotton fibers, and the chemical bonding between epoxy and the hydroxyl groups of cotton has been proven.³⁹ In our case, the coatings are formed by directly applying the alkaline hydrolyzed silica solution. The ammonium hydroxide in the coating solution served as a catalyst, especially when the solvent ethanol is evaporated off during the curing of the coating material. The concentrated ammonium hydroxide in the coating layer assists the reaction between epoxy and hydroxyl groups. This could be the main reason for the improvement of coating adhesion on cotton fibers. Polyester contains either hydroxyl and/or carboxyl groups at the polymer ends. The existence of these groups on the polyester fiber surface facilitates the formation of chemical bonds between the coating layer and the fibers, either through hydroxyl or carboxyl groups. The wool surface typically contains amino and carboxyl groups. The coating on the wool fiber surface should have improved durability. However, the presence of ammonium hydroxide could also lead to the hydrolysis of the wool keratin. The degradation of the wool keratin in the surface layer reduced the washing durability even if the chemical bonds were present between the coating and the wool substrate.

IV. CONCLUSION

We have demonstrated that coating solutions prepared by one-step cohydrolysis/cocondensation of TEOS with an organic silane under alkaline condition can effectively generate superhydrophobic surfaces on different fabrics (e.g., polyester, wool, and cotton). The nonhydrolyzable functional groups brought by the organic silane played an important role in determining the superhydrophobicity of the coated fabrics. For some silane systems, such as the ones containing fluorinated alkyl, long chain alkyl (C16), and phenyl groups, the resultant surface superhydrophobicity was little influenced by the intrinsic feature of the fabric substrate, and the treatment led to a high water contact angle ($>170^\circ$) and a low sliding angle ($<15^\circ$). The introduction of epoxide groups into the coating due to addition of a silane having epoxide group for synthesis can significantly improve the washing durability of the

superhydrophobic coating, although it leads to a slight reduction in the superhydrophobicity. This work may provide a simple, universal, and cost-efficient method to produce superhydrophobic surfaces on various fabric media.

ACKNOWLEDGMENT

Funding support from DSTO and Deakin University under the Central Research Grant Scheme (CRGS) is acknowledged.

REFERENCES

1. R.N. Wenzel: Resistance of solid surfaces to wetting by water.
2. A.B.D. Cassie and T.S. Baxter: Wettability of porous surfaces.
3. R.E. Johnson and R.H. Dettre: *Contact Angle, Wettability, and Adhesion* (American Chemical Society, Washington, DC, 1964).
4. A. Marmur: The lotus effect: Superhydrophobicity and metastability.
5. D. Oener and T.J. McCarthy: Ultrahydrophobic surfaces; Effects of topography length scales on wettability. (2000)
6. J.C. Love, B.D. Gates, D.B. Wolfe, K.E. Paul, and G.M. Whitesides: Fabrication and wetting properties of metallic half-shells with submicron diameters.
7. L. Feng, Y. Song, J. Zhai, B. Liu, J. Xu, L. Jiang, and D. Zhu: Creation of a superhydrophobic surface from an amphiphilic polymer.
8. M. Morra, E. Occhiello, and F. Garbassi: Contact angle hysteresis in oxygen plasma treated poly(tetrafluoroethylene).
9. W. Chen, A.Y. Fadeev, M.C. Hsieh, D. Oener, J. Youngblood, and T.J. McCarthy: Ultrahydrophobic and ultralyophobic surfaces: Some comments and examples.
10. F. Burmeister, C. Kohn, R. Kuebler, G. Kleer, B. Blaesi, and A. Gombert: Applications for TiAlN- and TiO₂-coatings with nanoscale surface topographies.
11. M.T. Khorasani, H. Mirzadeh, and Z. Kermani: Wettability of porous polydimethylsiloxane surface: Morphology study. *Appl.*
12. J.D. Samuel, S. Jayaprakash, and J. Ruehe: A facile photochemical surface modification technique for the generation of microstructured fluorinated surfaces.
13. S. Ren, S. Yang, Y. Zhao, T. Yu, and X. Xiao: Preparation and characterization of an ultrahydrophobic surface based on a stearic acid self-assembled monolayer over polyethyleneimine thin films.
14. M. Li, J. Zhai, H. Liu, Y. Song, L. Jiang, and D. Zhu: Electrochemical deposition of conductive superhydrophobic zinc oxide thin films.
15. J. Genzer and K. Efimenko: Creating long-lived superhydrophobic polymer surfaces through mechanically assembled monolayers.
16. Z.-Z. Gu, H. Uetsuka, K. Takahashi, R. Nakajima, H. Onishi, A. Fujishima, and O. Sato: Structural color and the lotus effect.
17. Y. Li, W. Cai, G. Duan, B. Cao, F. Sun, and F. Lu: Superhydrophobicity of 2D ZnO ordered pore arrays formed by the solution-dipping template method. *J. Colloid Interface Sci.* **287**, 634 (2005).
18. G. Zhang, D. Wang, Z.-Z. Gu, and H. Mohwald: Fabrication of superhydrophobic surfaces from binary colloidal assembly. *Langmuir*.
19. K. Tadanaga, N. Katata, and T. Minami: Formation process of super-water-repellent Al₂O₃ coating films with high transparency by the sol-gel method.
20. A. Nakajima, C. Saiki, K. Hashimoto, and T. Watanabe: Processing of roughened silica film by coagulated colloidal silica for superhydrophobic coating. *J. Mater. Sci. Lett.* **20**, 1975 (2001).
21. A. Roig, E. Molins, E. Rodriguez, S. Martinez, M. Moreno-Manas, and A. Vallibera: Superhydrophobic silica aerogels by fluorination at the gel stage.
22. Q. Xie, G. Fan, N. Zhao, X. Guo, J. Xu, J. Dong, L. Zhang, Y. Zhang, and C.C. Han: Facile creation of a bionic superhydrophobic block copolymer surface.
23. N. Zhao, Q. Xie, L. Weng, S. Wang, X. Zhang, and J. Xu: Superhydrophobic surface from vapor-induced phase separation of copolymer micellar solution.
24. H. Yabu and M. Shimomura: Single-step fabrication of transparent superhydrophobic porous polymer films.
25. M. Hikita, K. Tanaka, T. Nakamura, T. Kajiyama, and A. Takahara: Super-liquid-repellent surfaces prepared by colloidal silica nanoparticles covered with fluoroalkyl groups. (2005).
26. S. Wang, L. Feng, and L. Jiang: One-step solution-immersion process for the fabrication of stable bionic superhydrophobic surfaces.
27. C.-T. Hsieh, W.-Y. Chen, and F.-L. Wu: Fabrication and superhydrophobicity of fluorinated carbon fabrics with micro/nanoscaled two-tier roughness.
28. B. Xu and Z.S. Cai: Fabrication of a superhydrophobic ZnO nanorod array film on cotton fabrics via a wet chemical route and hydrophobic modification.
29. T. Wang, X. Hu, and S. Dong: A general route to transform normal hydrophilic cloths into superhydrophobic surfaces. *Chem.*
30. K. Ramaratnam, V. Tsyalkovsky, V. Klep, and I. Luzinov: Ultrahydrophobic textile surface via decorating fibers with a monolayer of reactive nanoparticles and non-fluorinated polymer.
31. S. Li, H. Xie, S. Zhang, and X. Wang: Facile transformation of hydrophilic cellulose into super hydrophobic cellulose. *Chem.*
32. B. Balu, V. Breedveld, and W. Hess Dennis: Fabrication of "roll-off" and "sticky" superhydrophobic cellulose surfaces via plasma processing.
33. J.D. Wright and N.A.J. Sommerdijk: *Sol-Gel Materials Chemistry and Applications* (CRC Press, Boca Raton, FL, 2001).
34. C. Sanchez, B. Julián, P. Belleville, and M. Popall: Applications of hybrid organic-inorganic nanocomposites.
35. H. Wang, J. Fang, T. Cheng, J. Ding, L. Qu, L. Dai, X. Wang, and T. Lin: One-step coating of fluoro-containing silica nanoparticles for universal generation of surface superhydrophobicity. *Chem.*
36. L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang, and D. Zhu: Super-hydrophobic surfaces: From natural to artificial.
37. E.K. Kim, J. Won, J.-y. Do, S.D. Kim, and Y.S. Kang: Effects of silica nanoparticle and GPTMS addition on TEOS-based stone consolidants.
38. D. Briggs and M.P. Seah: *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy* (John Wiley & Sons, New York, 1983), p. 533.
39. J.B. McKelvey, B.G. Webre, and E. Klein: Reaction of epoxides with cotton cellulose in the presence of sodium hydroxide. *Text.*