

Article

Fabrication of an Organo-Fluoride-Free Hydrophobic Film Using the Sol-Gel Method by Factors Screening and Poly-Acrylic Acid Addition

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Abstract: Improving silica film's contact angle (CA) using tetraethoxysilane (TEOS) and iso-butyltrimethoxysilane (iso-BTMS) by the sol-gel method without adding organo-fluoride substances is of interest. Five factors, namely type of solvent, molar ratio and amounts of TEOS and iso-BTMS, mixing intensity, sol aging time, and presence and absence of poly-acrylic acid (PAA), were assessed to improve the static water CA of the film and its surface quality. Results revealed that when ethanol was used as the dissolving solvent and after adding initial iso-BTMS and TEOS concentrations of 0.0270 and 0.0194 mol/L (molar ratio = 1.39), respectively, without sonication and adding PAA/TEOS weight ratio of 0.029, then the maximum static CA of the film reached 147°, a nearly super-hydrophobic surface. Under given conditions, long-term film durability was observed, and the added PAA prevented the formation of nonhomogeneous film surfaces caused by the highly clustering aggregation of silanols under high pH conditions.

Keywords: tetraethoxysilane (TEOS); iso-butyltrimethoxysilane (iso-BTMS); sol-gel method; contact angle; film quality index (FQI); poly-acrylic acid (PAA)

1. Introduction

Mimicking the lotus effect to change the surface structure and functions has been a widely researched topic [1–7] and is used in many fields [8], including surface coating [9,10] and textile manufacturing [11–13]. Among these studies, sol-gel methods have been widely employed to fabricate various hydrophobic films [14–19] with detailed manufacturing processes [20]; however, although some individual influencing factors have been investigated separately [21,22], a detailed screening of the influencing factors was considered useful in improving the film quality and identifying the key affecting factors of a sol-gel preparing process. Furthermore, the use of organo-fluoride alkoxysilane as a hydrophobic agent to obtain a super-hydrophobic surface is helpful but is questioned due to its carcinogenicity [11,23]. Some nonhazardous substances like iso-butyltrimethoxysilane (iso-BTMS) and phenyltrimethoxysilane, etc. have been used to replace organo-fluoride reagents, yet the contact angle (CA) of the so-prepared film is often decreased [15,19]. Again, a detailed survey of the factors in these sol-gel processes free of the organic-fluoride substances to maintain a high film quality was desired.

To achieve this, factorial experiments for important factor screening during sol-gel film preparation and use of poly-acrylic acid (PAA, a blocking polymer) for improving film quality were considered important and were to be tested in this study. Factorial experiments were to be performed to determine crucial influencing factors and their operational conditions during hydrophobic film formation using

the sol-gel method. By comparing effects of all factors in one test, the factorial experiments are able to eliminate time blocks of the one-factor-at-a-time test [24]. A total of five factors, namely the type of solvent, amount and/or ratio of TEOS and iso-BTMS, mixing intensity, sol aging time, and presence and absence of PAA, were examined and adjusted to obtain an optimal hydrophobic film surface. PAA was used to minimize the formation of highly branched siloxane clusters under basic conditions. A phenomenon mentioned by Esposito [25], which might have caused the combination of the siloxane clusters and formed nonhomogeneous film surface areas with uneven hydrophobicity. Film quality index (FQI) was adopted to rate the film quality and is further introduced in the Material and Methods section. Finally, images of the obtained films were taken by a scanning electron microscope with a secondary electron detector (SEM-SE) and examined to reveal the effectiveness of PAA addition. In summary, seven solvents were tested, the ratio and amount of iso-BTMS/TEOS was determined, the mixing operation was optimized, sol aging time was set, and amount of PAA was revealed. Thus, an easy-to-prepare, nontoxic, and nearly super-hydrophobic film surface was obtained. Moreover, film durability and the formation mechanism caused by the presence of PAA were explained.

2. Materials and Methods

Figure 1 presents the procedure of sample processing by using the sol-gel method. A 35-mL Teflon tube containing a total working volume of 14.5 mL of the designated reagents including TEOS and iso-BTMS mixed in the solvent, ammonia, and distilled and deionized water (DDW) was used. A 30-min mixing at 100 rpm and up to 24 h of sol aging (no mixing) were mainly conducted using a shaking-type incubator at a constant temperature of 37 °C. Sonication of the sol mixture to enhance mixing intensity (especially during the PAA addition) might or might not be conducted depending on the experimental design. After the sol-gel reaction, 2-mL sol mixture liquid in the form of droplets was placed on a microscope glass substrate pretreated with isopropanol and DDW. The sample was loaded onto the glass substrate, spread evenly by gravity, and dried at 105 °C for 0.5 h to synthesize the hydrophobic film. The static CA and FQI of the film were examined using a CA meter (SEO, Phoenix series, Gyeonggi-do, Korea). All the key chemicals and reagents used were purchased from Sigma-Aldrich Inc. (St. Louis, MO, USA).

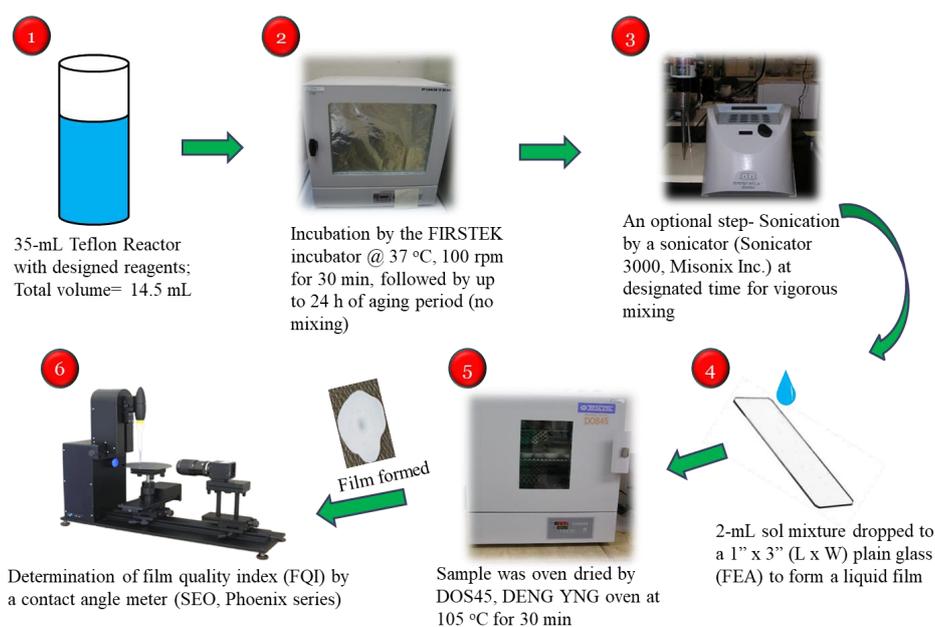


Figure 1. Sample handling and analyzing procedures used for preparing the sol-gel hydrophobic films.

For influencing factor examination, firstly, seven solvents (i.e., methanol, ethanol, propanol, iso-propanol, butanol, acetone, and hexane), some polar and some nonpolar, were employed to prepare sol-gel reagents to determine the most appropriate solvent to use in follow-up tests. Furthermore, the molar ratios (M) of iso-BTMS/TEOS in the range of 0.35–1.74 were assessed, at which the initial concentrations of iso-BTMS and TEOS equaled 0.0540 and 0.0387 mol/L, respectively, and the ratio is expressed as one time (1 \times) dilution. However, when the molar ratio was adjusted to ensure the highest CA, a nonhomogeneous film surface was observed if the sol aging time was >4 h, and the film quality worsened. Figure 2a illustrates an example nonhomogeneous film obtained by optical microscope, and the FQI ranging from 0 to 10 was adopted to quantify the film quality (Figure 2b), where 10 indicated a film surface with high homogeneity and without large empty holes and vice versa. The film nonhomogeneous problem was minimized using the blocking polymer PAA, which is an anionic polymer. Moreover, other polymers such as polydiacetylenes (cationic) and alkyl polyglycoside (surfactant) were also tested (data not shown); however, they could only slightly improve the quality of the film. The molecular size of PAA (ranging up to 1,250,000 Dalton) was tested and determined for evaluating its effectiveness in film performance. Second, two factorial experiments with four and three factors each were conducted in series to determine the necessity of sonication (Sonicator 3000, Misonix Inc., New York, NY, USA), the dilution of TEOS and iso-BTMS from original 1X dilution, the effect of PAA, and the time of reaction. The factors and their low/high levels (shown in the parenthesis) of the 2⁴ factorial run were sonication time (1, 2 min), dilution times (1 \times , 2 \times), PAA/TEOS ratio by wt. (0.03, 0.15), and sol aging time (4, 24 h). Similarly, for the 2³ factorial run the factors and their low/high levels were sonication time (0, 1 min), dilution times (1 \times , 5 \times), and sol aging time (4, 24 h). After the two factorial tests, two factors (i.e., time of sonication and weight ratio of PAA/TEOS ranging from 0 to 1 min and from 0 to 0.15, respectively) were further studied at several levels to assess film CA and FQI values. Furthermore, film performance in the presence and absence of PAA was tested and compared. Finally, the effect of temperature in sol-gel preservation (i.e., durability) was evaluated when the two solvents, ethanol and acetone, were used. The variation in film CA at 27 °C was studied for over 2 months to confirm the film durability. Images captured using an SEM-SE (TM-1000, HITACHI Inc., Tokyo, Japan) with and without PAA addition were compared. A postulated reaction was proposed to explain the phenomenon observed in SEM images.

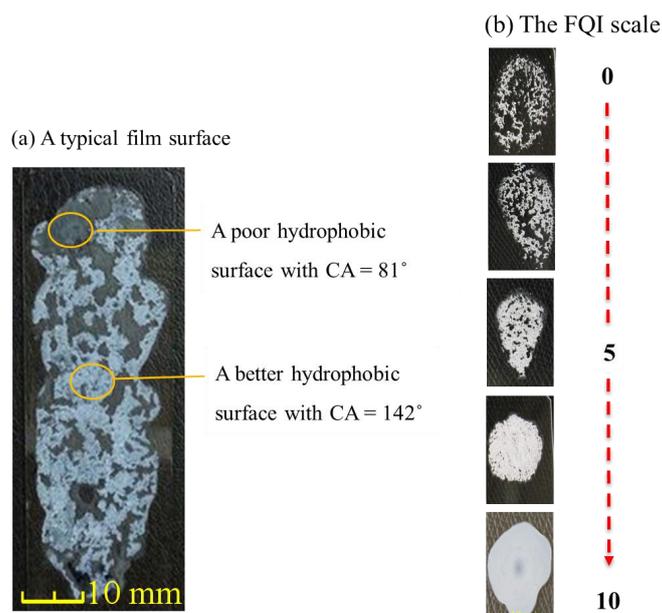


Figure 2. Film surface example, where (a) a typical film surface for sol aging time of >4 h, and (b) 0–10 scales of film quality index (FQI).

For quality assurance, all experiments were performed in triplicates, and their percentage error (%error) was calculated as the standard deviation divided by the mean of measurement outcomes. A 5% limit of the %error was adopted to ensure data consistency. Each experimental run was repeated for the samples, and average values were calculated and represented with the sample number *n*.

3. Results and Discussion

Table 1 presents the CAs of the seven solvents used to prepare sol-gel reagents. The results suggested that the more polar solvents such as ethanol and acetone exhibiting the higher CAs of 135° and 123°, respectively. Thus, the ethanol and acetone were used as dissolving solvents in some of the subsequent tests. By contrast, hexane, a hydrophobic solvent, formed no observable film after a specific reaction period. Polar solvents might dissolve more sol-gel reagents and silanols during the reaction, resulting a better polymer reactions and the film formation. Table 2 presents the effects of the molar ratio of iso-BTMS/TEOS (i.e., *M* value) on CAs during a 4-h reaction. The highest CA of 128° was obtained at an *M* value of 1.39. When *M* = 1.74, a greater CA was expected due to more reagents were presents, yet the CA value of the resulting film dropped, which implied that the higher the reagent contents, the poorer the film homogeneity. To proceed, the *M* value = 1.39 was adopted for the remaining the tests. Figure 3 reveals that after 4 h, the siloxane film prepared started to aggregate and formed a nonhomogeneous film surface. With an increase in the sol aging time, film non-homogeneity increased. The results revealed that in the homogeneous areas of the film, CAs remained normal; however, in its empty-hole areas, CA decreased drastically. Several kinds of polymers were tested to improve the film quality (data not shown), and PAA exhibited the most satisfactory results. The possible effect of the PAA size was verified, and the results indicated that when PAA with the molecular weight of 100,000 Dalton was added, the film exhibited the highest CA and FQI of 144.1° and 10, respectively (Table 3). Thus 100,000-Dalton PAA was chosen for subsequent experiments.

Table 1. Static water contact angle (CA) of the hydrophobic silica film fabricated with various solvents.

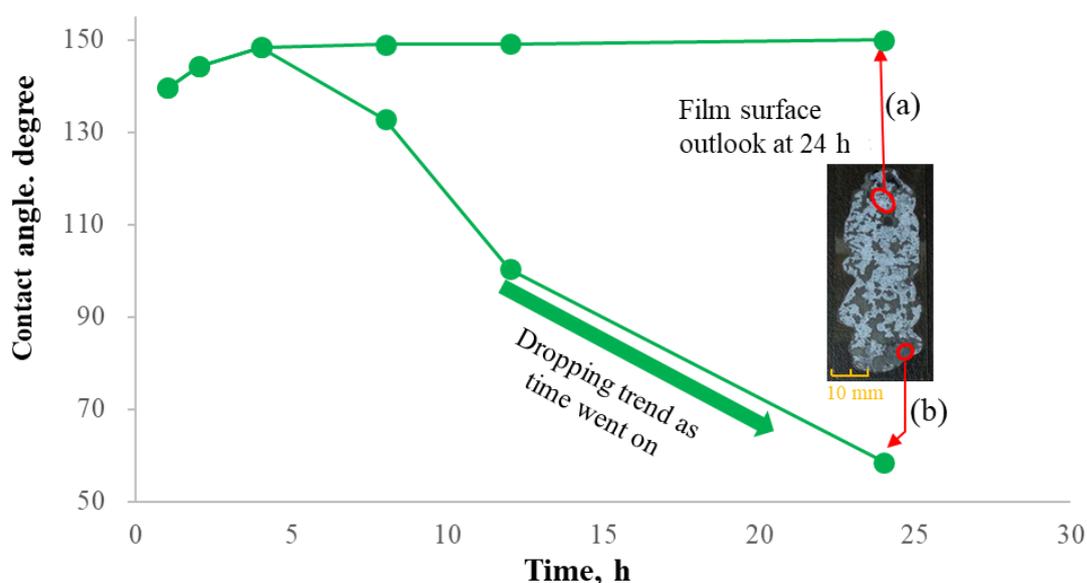
5-mL Solvent (Purity) Used	Contact Angle (Degree)	Images
Methanol (99.9%)	118	
Ethanol (95%)	135	
Propanol (95%)	80	
Iso-propanol	98	
Butanol	86	
Acetone	123	
Hexane	No film formed	NA

Note: Reaction time = 4 h; NA = not available.

Table 2. Static water CAs of the hydrophobic silica film at various molar ratios (M) of iso-butyltrimethoxysilane (BTMS)/tetraethoxysilane (TEOS).

No. of Test	Iso-BTMS/TEOS Molar Ratio (M)	Contact Angle Degree \pm Std. Dev. ($n = 3$)
1	0.35	65 \pm 4
2	0.70	80 \pm 5
3	1.05	118 \pm 3
4	1.39	128 \pm 4
5	1.74	94 \pm 6

Note: Reaction time = 4 h.

**Figure 3.** Two distinct contact angles on the forming hydrophobic film within 24 h of sol aging time at the ratio of the iso-BTMS/TEOS = 1.39; where (a) film areas, and (b) hole area.**Table 3.** Static water CAs of the hydrophobic film with various molecular weights of poly-acrylic acid (PAA).

MW of PAA	CA (Degree)/FQI at Sonication Time = 0 min
Blank (no PAA)	138.4/6
5,000	140.0/5
100,000	133.1/10
1,250,000	134.1/7

Note: @PAA/TEOS weight ratio= 0.029.

Figure 4a presents the FQI effects of the first 2⁴ factorial experiment, where four factors, namely sonication time, iso-BTMS/TEOS dilution rate, PAA/TEOS molar ratio, and sol aging time, were screened and represented as factors A, B, C, and D, respectively; the results revealed that the effects of sonication and sol aging time were minimal, iso-BTMS/TEOS dilution led to a small but positive effect (i.e., higher film performance), and the increased PAA/TEOS ratio considerably enhanced film performance (Figure 4a). Moreover, a normal plot (Figure 4b) indicated similar conclusions, with most effects forming a straight line in the middle of the plot representing normal distribution of most data. The effects of C, ABC, and ABD were represented by three distinct values, which revealed

the importance of adding PAA (i.e., C) to the reaction mixture; film quality improvement caused by the combination of sonication, diluted iso-BTMS and TEOS, and PAA addition (i.e., ABC); and the film quality deteriorating in the absence of PAA (i.e., ABD and no C). Thus, the PAA/TEOS ratio was fixed to 0.15, and a 2^3 factorial experiment was then conducted with and without sonication, the range of the iso-BTMS/TEOS dilution ratio was increased, and sol aging time remained the same. The results showed that (1) with sonication the film quality aggravated, (2) compared to the previous factorial run, high dilution of the iso-BTMS/TEOS molar ratio led to the minimal improvement so that the dilution was fixed to two times ($2\times$) (i.e., the initial concentration of iso-BTMS and TEOS was 0.0270 and 0.0194 mol/L, respectively), and (3) the longer sol aging time enhanced film performance (Figure 5a). The combination of the three factors exhibited a positive effect that must be further clarified with more tests. The normal plot (Figure 5b) showed a normal distribution of the measured effects, except for A and ABC, which matched the effect data.

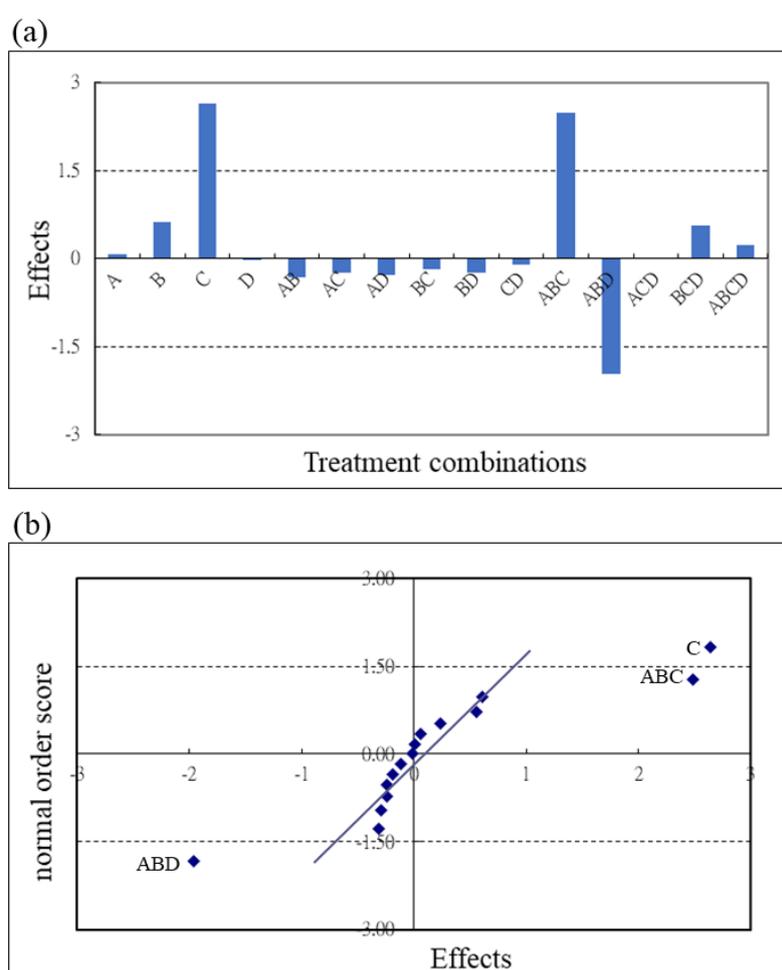


Figure 4. Results of the first factor screening (2^4 factorial run): (a) effects versus treatment combinations, and (b) normal plot.

To further clarify the effects of sonication with respect to the amount of PAA used, the CAs and FQIs of each film were determined at various sonication times versus the PAA/TEOS ratio (Figure 6). Two high film performance areas were concluded and circled: the first with high PAA dosage and medium sonication and the second with low PAA and low to medium sonication. To minimize the PAA use and avoid energy costs, the addition conditions of PAA/TEOS ratio (by wt.) at 0.029 with no sonication were adopted for subsequent film manufacturing. Figure 7 presents the results of CAs for the sol-gel process conducted with and without PAA. Without PAA, some film surface remained

normal, and its averaged CA approached $149.4^\circ \pm 0.64^\circ$ (std. dev.) ($n = 4$), and some film surface formed empty holes with its CAs decreasing to approximately 60° . However, with PAA, homogeneous film surface was observed, and its average CA of the last four measurements conducted within 24 h was $147.4^\circ \pm 0.72^\circ$ (std. dev.) ($n = 4$). PAA addition to the film evidently improved the film quality.

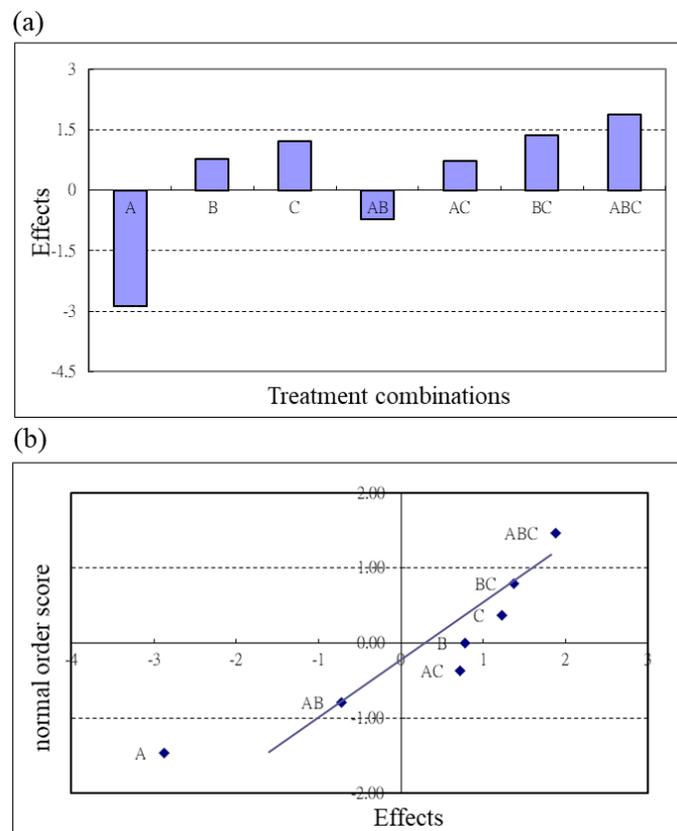


Figure 5. Results of the second factor screening (2^3 factorial run): (a) effects versus treatment combinations, and (b) normal plot.

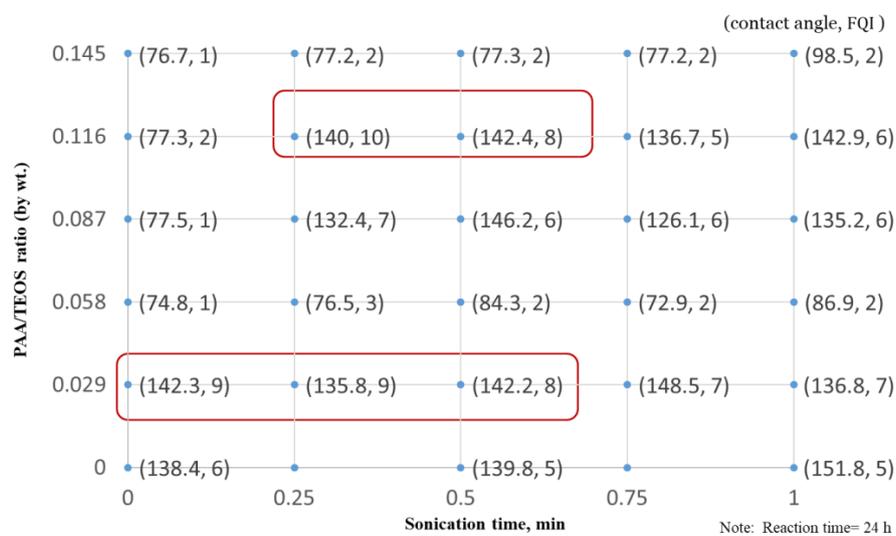


Figure 6. Results of CA and FQI scores obtained for various PAA/TEOS ratios (by wt.) versus the sonication time.

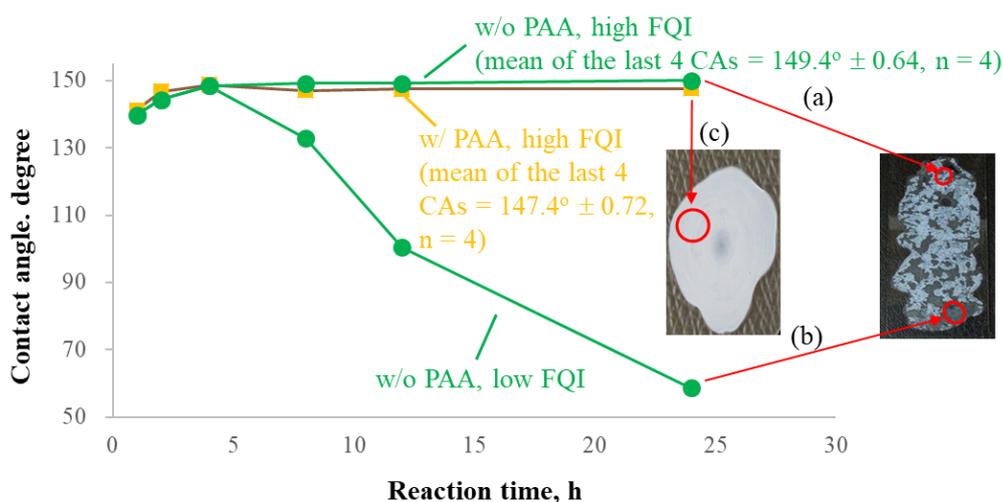


Figure 7. CAs at various film surface after 24 h of sol aging time: (a) film area without PAA; (b) hole area without PAA; (c) film area with PAA.

Table 4 presents the averaged results of film performance obtained within 28 days under various temperature conditions for film durability assessment. The effect of the temperature variation (i.e., 4–45 °C) on film performance was minimal, and the use of ethanol as the solvent led to a more satisfactory CA value performance. Figure 8 shows the results of long-term monitoring of CAs obtained using both ethanol and acetone at 27 °C conducted for >2 months. The variation in CAs with respect to the mean value was within $\pm 3.5\%$ for both ethanol and acetone during the testing period. SEM images (Figure 9) revealed that when PAA was added, small cracks appeared during the early stage of film formation, and the final film surface exhibited larger cracks similar to the surface obtained without PAA. The film surface that exhibited cracks provided more satisfactory film performance irrespective of the presence and absence of PAA after 24 h of the reaction. Thus, we postulated a possible reaction mechanism as follows: during esterification, when water is present, the PAA might serve as a dispersive agent to prevent the clustering of silanols. Once the water evaporated, some silanol molecules might have reacted with PAA and formed a Si–O–COR structure, resulting in the formation of the finer cracks in the early stage of the reaction (Figure 10), and thus preventing the aggregation of siloxane clusters under basic conditions, as described by Esposito [25].

The sol-gel method is considered a simple and easy technique for fabricating highly hydrophobic films; however, further improvements in terms of film CA and FQI values were achieved through screening and testing of factors. Hydrophobic films were prepared based on the process and reagents used by Dhere [15]; the CA value increased from 140° reported by Dhere et al. to 147° in the current study, which is close to the margin value of a super-hydrophobic film. To the best of our knowledge, this is the highest CA value realized using the sol-gel method without addition of organo-fluoride substances as a hydrophobic reagent. Moreover, this study suggested that through factor examination, including a factorial design technique, the performance of hydrophobic films fabricated through sol-gel or other methods can be improved.

Table 4. Temperature effect on the film contact angles using ethanol or acetone within 28 days.

Temperature (°C)	Contact Angle (Degree) \pm Std. Dev. (Solvent = Ethanol)	Contact Angle (Degree) \pm Std. Dev. (Solvent = Acetone)
4	142 \pm 1 (n = 5)	136 \pm 1 (n = 5)
27	142 \pm 2 (n = 5)	138 \pm 1 (n = 5)
45	142 \pm 1 (n = 5)	138 \pm 2 (n = 5)

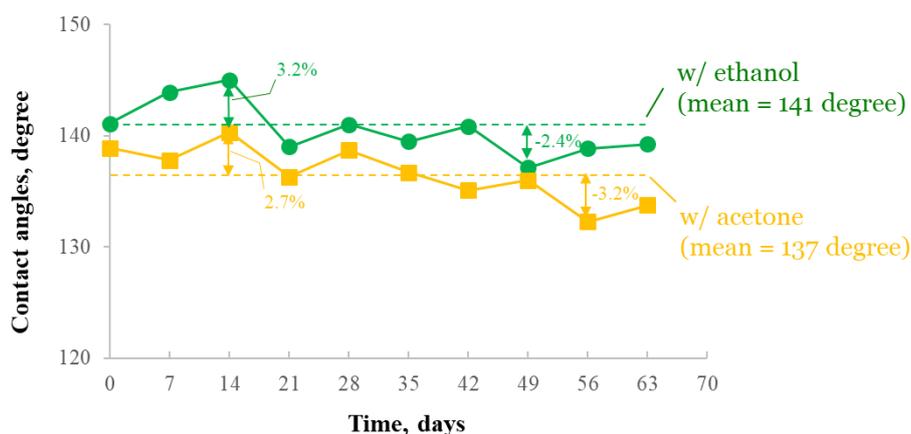


Figure 8. CAs with ethanol or acetone versus time at a temperature of 27 °C.

Solvent	1 h	4 h	24 h
Ethanol only			
CA	132°	133°	142°
Ethanol + PAA			
CA	78°	126°	147°

Figure 9. SEM images of the formed hydrophobic films with and without PAA.

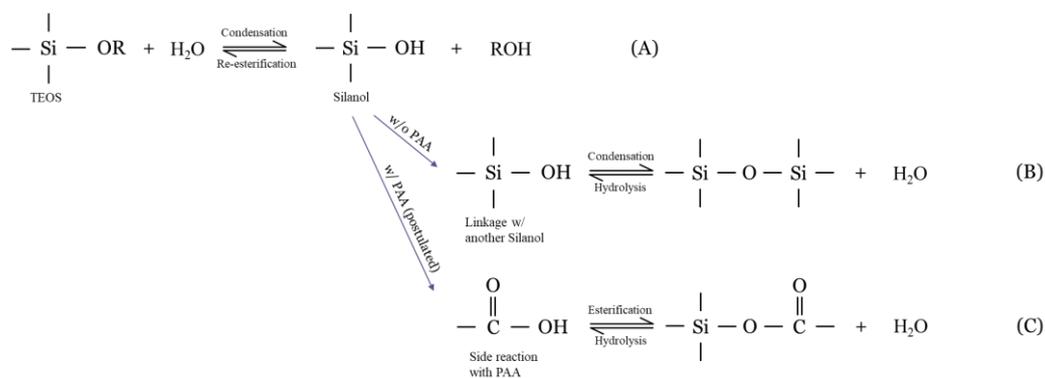


Figure 10. Reaction mechanisms of forming hydrophobic films at with and without PAA: (A) silanol-forming reactions; (B) formation of Si-O-Si structure at no PAA addition; (C) formation of Si-O-CO structure at the presence of PAA (postulated).

4. Conclusions

Through factor screening, the sol-gel method was successfully used to prepare a highly hydrophobic and homogeneous (i.e., both with high CA and FQI values) film surface with TEOS and iso-BTMS. The operational conditions are as follows: (1) Ethanol was used as the dissolving solvent, (2) the molar ratio of iso-BTMS and TEOS was set to 1.39 at the initial iso-BTMS and TEOS concentrations of 0.0270 and 0.0194 mol/L, respectively, (3) sonication was not used for mixing, and (4) a PAA/TEOS weight ratio at 0.029 was added to prevent formation of a nonhomogeneous film with empty holes. By using these conditions, the averaged CA of the film obtained during the sol aging time of 4–24 h was $147.4^\circ \pm 0.72^\circ$ ($n = 4$) with a nice homogeneous surface.

In terms of the durability of the manufactured film, the effect of temperature ranging from 4 to 45 °C was minimal. At 27 °C, the film exhibited high CA and FQI values for a minimum of 2 months. Finally, addition of PAA with a molecular size of 100,000 Dalton improved film performance, especially in minimizing film nonhomogeneous conditions. The SEM images revealed an early appearance of cracks during film formation. Crack formation is postulated to prevent large aggregation of clustered siloxanes, resulting in the high-FQI films observed.

Author Contributions: M.-W.S. and S.-T.C. worked through the original idea and experimental scheme together. M.-W.S. conducted the experimental tests and presented the draft results. S.-T.C. wrote and revised the draft manuscript. All authors discussed and responded the questions if any and contributed their perspectives to the final manuscript. All authors have read and agreed to the published version of the manuscript.

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References

1. Kim, J.; Choi, S.O.; Williams, J. Superhydrophobicity. In *Waterproof and Water Repellent Textiles and Clothing*; Woodhead Publishing: Elsevier: New York, NY, USA, 2018; Volume 11, p. 267.
2. Lakshmi, R.V.; Bharathidasan, T.; Bera, P.; Bharathibai, J.B. Fabrication of superhydrophobic and oleophobic sol-gel nanocomposite coating. *Surf. Coat. Technol.* **2012**, *206*, 3888. [[CrossRef](#)]
3. Grozea, C.M.; Rabnawaz, M.; Liu, G.; Zhang, G. Coating of silica particles by fluorinated diblock copolymers and use of the resultant silica for superamphiphobic surfaces. *Polymer* **2015**, *64*, 153. [[CrossRef](#)]
4. Minehan, W.T.; Messing, G.L.; Pantano, C.G. Titania-silica glasses prepared by sintering alkoxide derived spherical colloids. *J. Non-Cryst. Solids* **1989**, *108*, 163. [[CrossRef](#)]
5. Dos Santos, C.G.; Geraldo, M.d.L. Tin and organotin coordination polymers and covalently bonded supramolecular materials—The last 15 years of research. *Coord. Chem. Rev.* **2020**, *410*, 213236. [[CrossRef](#)]
6. Catauro, M.; Barrino, F.; Poggetto, G.D.; Crescente, G.; Piccolella, S.; Pacifico, S. New SiO₂/caffeic acid hybrid materials: Synthesis, spectroscopic characterization, and bioactivity. *Materials* **2020**, *13*, 394. [[CrossRef](#)]
7. Catauro, M.; Barrino, F.; Blanco, I.; Piccolella, S.; Pacifico, S. Use of the sol-gel method for the preparation of coatings of titanium substrates with hydroxyapatite for biomedical application. *Coatings* **2020**, *10*, 203. [[CrossRef](#)]
8. Yang, S.; Jia, Z.; Ouyang, X.; Wang, S. Inhibition of algae growth on HVDC polymeric insulators using antibiotic-loaded silica aerogel nanocomposites. *Polym. Degrad. Stab.* **2018**, *155*, 262. [[CrossRef](#)]
9. Eduok, U.; Suleiman, R.; Khaled, M.; Akid, R. Enhancing water repellency and anticorrosion properties of a hybrid silica coating on mild steel. *Prog. Org. Coat.* **2016**, *93*, 97. [[CrossRef](#)]
10. Mozumder, M.S.; Abdel-Hamid, I.; Mourad, H.P.; Surkatti, R. Recent developments in multifunctional coatings for solar panel applications: A review. *Solar Energy Mater. Solar Cells* **2019**, *189*, 75. [[CrossRef](#)]
11. Shen, K.; Yu, M.; Li, Q.; Sun, W.; Zhang, X.; Quan, M.; Liu, Z.; Shi, S.; Gong, Y. Synthesis of a fluorine-free polymeric water-repellent agent for creation of superhydrophobic fabrics. *Appl. Surf. Sci.* **2017**, *426*, 694. [[CrossRef](#)]
12. Textor, T.; Mahltig, B. A sol-gel based surface treatment for preparation of water repellent antistatic textiles. *Appl. Surf. Sci.* **2010**, *256*, 1668. [[CrossRef](#)]

13. Yu, M.; Li, P.; Feng, Y.; Li, Q.; Sun, W.; Quan, M.; Liu, Z.; Sun, J.; Shi, S.; Gong, Y. Positive effect of polymeric silane-based water repellent agents on the durability of superhydrophobic fabrics. *Appl. Surf. Sci.* **2018**, *450*, 492. [[CrossRef](#)]
14. Bhagat, S.D.; Kim, Y.; Ahn, Y. Room temperature synthesis of water repellent silica coatings by the dip coat technique. *Appl. Surf. Sci.* **2006**, *253*, 2217. [[CrossRef](#)]
15. Dhere, S.L.; Latthe, S.S.; Kappenstein, C.; Pajonk, G.M.; Ganesan, V.; Rao, A.V.; Wagh, P.B.; Gupta, S.C. Transparent water repellent silica films by sol-gel process. *Appl. Surf. Sci.* **2010**, *256*, 3624. [[CrossRef](#)]
16. Nakagawa, T.; Soga, M. A new method for fabricating water repellent silica films having high heat-resistance using the sol-gel method. *J. Non-Cryst. Solids.* **1999**, *260*, 167. [[CrossRef](#)]
17. Rao, A.; Venkateswara, A.B.; Gurav, S.S.; Latthe, R.S.; Vhatkar, H.I.; Charles Kappenstein, P.B.W.; Satish, C.G. Water repellent porous silica films by sol-gel dip coating method. *J. Colloid Interface Sci.* **2010**, *352*, 30. [[CrossRef](#)] [[PubMed](#)]
18. Tao, C.; Yan, H.; Yuan, X.; Yin, Q.; Zhu, J.; Ni, W.; Yan, L.; Zhang, L. Sol-gel based antireflective coatings with superhydrophobicity and exceptionally low refractive indices built from trimethylsilanized hollow silica nanoparticles. *Colloids Surf. A: Physicochem. Eng. Asp.* **2016**, *509*, 307. [[CrossRef](#)]
19. Rao, A.; Venkateswara, S.S.; Latthe, D.Y.; Nadargi, H.H.; Ganesan, V. Preparation of MTMS based transparent superhydrophobic silica films by sol-gel method. *J. Colloid Interface Sci.* **2009**, *332*, 484.
20. Ramezani, M.; Vaezi, M.R.; Kazemzadeh, A. Preparation of silane-functionalized silica films via two-step dip coating sol-gel and evaluation of their superhydrophobic properties. *Appl. Surf. Sci.* **2014**, *317*, 147. [[CrossRef](#)]
21. Lakshmi, R.V.; Parthasarathi Bera, C.; Anandan, B.; Basu, J. Effect of the size of silica nanoparticles on wettability and surface chemistry of sol-gel superhydrophobic and oleophobic nanocomposite coatings. *Appl. Surf. Sci.* **2014**, *320*, 780. [[CrossRef](#)]
22. Ramezani, M.; Vaezi, M.R.; Kazemzadeh, A. The influence of the hydrophobic agent, catalyst, solvent and water content on the wetting properties of the silica films prepared by one-step sol-gel method. *Appl. Surf. Sci.* **2015**, *326*, 99. [[CrossRef](#)]
23. Parale, V.G.; Mahadik, D.B.; Mahadik, S.A.; Kavale, M.S.; Wagh, P.B.; Satish, C.G.; Rao, A.V. OTES modified transparent dip coated silica coatings. *Ceram. Int.* **2013**, *39*, 835. [[CrossRef](#)]
24. Berthouex, P.M.; Linfield, C.B. *Statistics for Environmental Engineers*; Lewis Publishers: Ann Arbor, MI, USA, 2002; p. 335.
25. Esposito, S. "Traditional" sol-gel chemistry as a powerful tool for the preparation of supported metal and metal oxide catalysts. *Materials* **2019**, *12*, 668. [[CrossRef](#)] [[PubMed](#)]

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