AJChE 2019, Vol. 19, No. 2, 91 – 99

Statistical Approaching for Superhydrophobic Coating Preparation using Silica Derived from Geothermal Solid Waste

***S. Silviana** *[1]*
***Adi Darmawan** [2]*
***Agus Subagio** [3]*
***Febio Dalanta** [4]*
[1] *Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Indonesia*
[2] *Department of Chemistry, Faculty of Science and Mathematics, Diponegoro University, Indonesia*
[3] *Department of Physics, Faculty of Science and Mathematics, Diponegoro University, Indonesia*
[4] *Master Program of Chemical Engineering, Faculty of Engineering, Diponegoro University, Indonesia*
[*] *e-mail:* silviana@che.undip.ac.id

Material quality can be affected by humidity resulting in short durability. Many observations have been conducted to endure the durability of material, such as coating methods. However, currently available methods are unaffordable. Therefore, this paper observes efficient and effective method to prepare superhydrophobic silica coatings derived from geothermal waste. The method was conducted by spraying. The objective of this paper is to observe optimum condition by using variables of silica concentration, TMCS (trimethylsilyl chloride) concentration, solvents and materials confirmed by contact angle of material based on statistical analysis. The study consisted of silica treatment for purification and preparation of superhydrophobic silica coatings. The study was carried out with factorial design of 81 experiments with one-time replication through Design Expert software (version 8.0.6). Based on previous research, the experiment was obtained optimum condition at 5.5 %w/v, 13 %v/v, isooctane, zinc coated for silica concentration, TMCS concentration, solvent and material, respectively, releasing contact angle by instrumentation of 180°. By ANOVA analysis, it was also complied the optimum condition of the superhydrophobic coating solution preparation achieved the same condition with experimental data releasing contact angle of 179.69°.

Keywords: ANOVA, geothermal silica, superhydrophobic coating, TMCS

INTRODUCTION

In Indonesia the high humidity affects in the nature and function of materials due to changing of material characteristics both in terms of physical and chemical properties (Yildirim et al. 2016). Materials quality can be affected by air humidity including quality of metals, glass and bamboo. The decrease in materials quality

DOI: 10.22146/ajche.51178

existing in an environment with high humidity can be found in the form of corrosion in metal materials, condensation on the surface of glass materials promoting growth of fungi and bacteria, and very fast weathering of bamboo materials (Glass 2007). Therefore, various ways have been carried out to maintain the properties and functions of those materials, such as coating.

Coating methods on materials depend on the type of material to be used. In metal materials prone to corrosion such as iron, coatings are carried out with Mg (magnesium) or Al (aluminum) with a relatively high thickness of 8 mm (Wang 2014). In addition, another method used is to make metal alloy materials that are corrosion resistant or stainless steel having an unaffordable (Wang 2014). In bamboo material, the coating method used is to coat the surface of bamboo with paint/varnish. However, the coating to minimize contact between moisture and bamboo material commonly used is normally easily peeled off (Sun 2014). Furthermore, the coatings used on glass are normally surfactants. The use of surfactants for glass coating must be carried out routinely. From the various material coating methods, it can be concluded that there are still many weaknesses such as high costs, chemical use, and time.

Development of material coating methods requires to be done to overcome these weaknesses. Superhydrophobic coating method is considered as one effective method in maintaining material quality. The working principle of this method is to create a superhydrophobic layer preventing contact between moisture and material. Moreover, the self-cleaning properties produced can resist water and carry dirt on the surface of the material. A lot of researches have been carried out on superhydrophobic coating such as the use of fluorocarbon compounds producing only contact angles of 110°, the addition of water glass requiring two stages of immersion, and the use of tetraethoxysilane compounds (TEOS) producing a contact angle of 150-180° but harmful to health (Xue et al. 2009). Other investigations, in single-step process using TEOS released 147° of contact angle (Kousaalya et al. 2013), and additional of perfluorooctyltriethoxysilane released 163° of contact angle (Liu et al. 2016). From the various studies that have been conducted, current research to find substitution of silica sources is further encouraged. The potential source of raw material that can be used to replace TEOS and other precursor as a source of silica in the superhydrophobic coatings preparation used in this study is geothermal solid waste from geothermal plant in Dieng.

Geothermal solid waste has the potential as a sustainable source of silica because the waste is not empowered yet. The Indonesian Institute of Sciences (LIPI) stated that geothermal plant has a solid waste capacity of one ton/day for brine solution of 10 tons/day (Silviana et al. 2017). In this study, an assessment has been carried out in the form of superhydrophobic layer preparation using geothermal solid waste with the addition of TMCS (trimethylsilyl chloride) through a single stage mixing process by means of spray coating method. This paper is expected to produce a more effective, efficient and environmentally friendly material coating method for material with statistical studies using expert design.

This paper determines the optimum conditions on superhydrophobic coating solution preparation with variables of silica concentration, TMCS concentration, solvents and materials confirmed with the contact angle response produced using statistical analysis.

EXPERIMENTAL SECTION

Materials and Equipment

The equipment used in this study included High Energy Milling (HEM), spray gun, and ultrasonic bath homogenizer. While the materials used were silica waste as raw material, trimethylsilyl chloride (TMCS) (99%, Merck), HCl (37%, Merck), solvents i.e. isooctane (≤ 100 %, Merck), n-hexane (≤ 100 %, Merck), and xylene (≥12.5% - <20%, Merck) and demineralized water. The material tested were bamboo, glass, and metal in the form of zinc roof.

Determination of Variables

The control variables were the temperature of 50 °C and the solvent volume of 20 mL. The independent variables were material type (bamboo, glass, and zinc), TMCS concentration (3; 8; 13 %v/v), silica concentration (0.5; 3; 5.5 %v/v) and solvent type (n-hexane, isooctane and xylene). The dependent variable observed was the contact angle acquired by Contact Angle Meter equipment (FACE 90-2-1) at Center for Isotope and Radiation Application, National Nuclear Energy Agency of Indonesia.

Research Procedures

Experiment procedure referred to previous research (Purnomo et al. 2018). First, 50 grams of geothermal solid silica waste collected from geothermal plant in Dieng was reduced moisture content at 105 °C for 24 hours and reduce particle size to 400 nm using high energy milling (HEM). Inorganic impurities were removed by immersion in 200 mL of hydrochloric acid 6 M, then mixed and heated at 90 °C for leaching in 3 hours. After aging for 24 hours, it allowed to wash with demineralized water to obtain neutral filtrate. The silica was then filtered and evaporated the water at 110 °C for 3 hours (Purnomo et al. 2018). The solution was prepared by dissolving nanometer-sized silica at various concentrations in 20 mL of each solvent. Then, TMCS was added at various concentrations slowly into silica solution at 50 ºC for 2 hours (Rao et al. 2009). Then the solution was introduced to the material using a spray gun. All steps were referred to previous experimental procedure (Purnomo et al. 2018).

RESULTS AND DISCUSSION

This study used statistical methods to determine the significant variables effect on the quality of the resulting superhydrophobic solution. The concentration of TMCS (A), concentration of silica (B), type of solvent (C) and type of material (D) act as independent variables, while the response is the contact angle produced. Statistical designs resulted in 81 experiments with 4 variables. The statistical method applied in this study uses a factorial design 3^4 with one-time replication. Replication in the experimental design is used to maintain the consistency of the response generated so as to reduce estimates of errors or errors in research conducted with a minimum accuracy of 80% (Montgomery 2001). This statistical method produces an equation model using Analysis of Variance (ANOVA) to determine the effect of each independent variable and the interaction between the independent variables on the response and test the adequacy of the model. In ANOVA, as known p value is used to determine the significance of the influence of independent variables and the value of F which is the ratio of noise to response. The equation model is confirmed to be significant if the value of p > F is less than 0.05 and the value of F is greater than one (Montgomery 2001). While the feasibility of the equation model is assessed from the value of R^2, adjusted-R^2, predicted-R^2 and adequate precision where the difference is small (<0.2) from each R^2 value with adjusted-R^2 and predicted-R^2, and adequate precision values of more than four shows the model meets the eligibility requirements. The results of ANOVA for the contact angle response tested with Race Contact Angle Measurement as shown in Table 1 confirming the model is significant (p > F less than 0.05). Table 1 informs the contact angle is significantly influenced by the four variables, namely the concentration of TMCS (A), concentration of silica (B), type of solvent (C), and type of material (D), as well as a combination of AC, AD, CD, ABC, ABD, ACD also has a significant influence.

Table 1. ANOVA result for the response of contact angle

Source	F-value	Prod > F	Significance
Model	15.01	<0.0001	Significant
Atmcs	21.66	<0.0001	Significant
Bsilica	156.82	<0.0001	Significant
Csolvent	93.24	<0.0001	Significant
Dmaterial	64.51	<0.0001	Significant
AB	2.07	0.1327	
AC	15.58	<0.0001	Significant
AD	6.92	0.0020	Significant
BC	0.73	0.5854	
BD	0.88	0.4991	
CD	16.91	<0.0001	Significant
ABC	4.44	0.0054	Significant
ACD	5.25	0.0024	Significant
BCD	1.91	0.1279	
Lack of Fit	16	16	
R^2	0.9836		
Adj R^2	0.9181		
Pred R^2	0.5801		
Adeq R^2	14.817		
ACD	5.25	0.0024	Significant

R^2 value obtained from this model was 0.9836 resulting a small difference compared to the adjusted-R^2 and predicted-R^2 values with adequate precision value of 14.817 indicated the feasibility of the model. Lack of Fit (LOF) is a criterion for assessing the feasibility of a model in experimental results. The insignificant LOF value (p > F greater than 0.1) shows that a model is suitable for experimental results (Montgomery 2001). Table 1 shows the LOF value for the equation model above is 16 thus the model is suitable for the contact angle response. Residual analysis is used to confirm that the equation model of ANOVA meets the eligibility requirements.

Graphs that draw residual analysis with diagnostic plots include the normal plot of residuals shown in Fig. 1 and the box-cox plot shown in Fig. 2 for the resulting contact angle response. The plot that forms linear line shown in Fig. 1 indicates the model that is suitable for experimental results (Montgomery 2001).

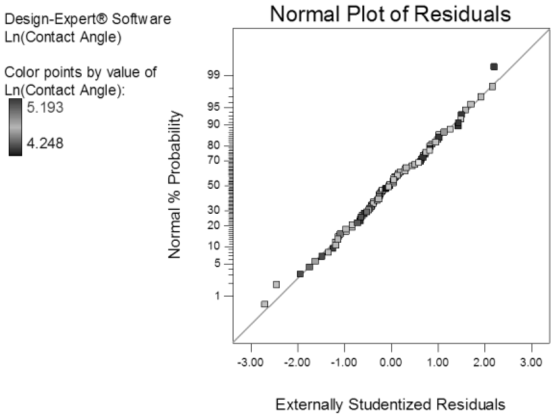

Fig. 1: Normal plot of residuals for contact angle response

The graph of Box-Cox plot for Power Transforms is used to determine the strength of a transformation that matches the experimental data. The blue line in the graph indicates the transformation of the model and the green line indicates the best lambda value. The red line indicates 95% confidence interval which is associated with the best lambda value. A model is said to be eligible if the blue transformation line is located between the red and green lines on the transformation curve shaped like a log curve. In Fig. 2, it is shown that the transformation line located between the green line and the red line indicating the model is complied for the experimental results.

Fig. 3 shows the interaction between independent variables, i.e. the concentration of TMCS and silica on the wettability response. The wettability response is quantified by contact angle. The effect of the surface modifying agent in term of wettability properties was analyzed by varying the concentration of TMCS. The assessment used isooctane solvent and bamboo as a control variable. This result indicated the success exchange of silanol groups with alkyl on the surface of silica (Eakins 1968).

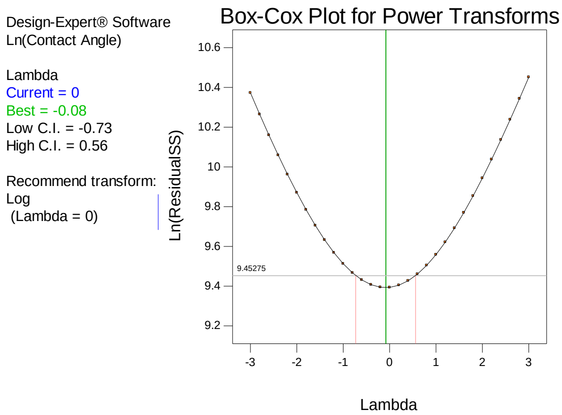

Fig. 2: Box-cox plot for power transforms for the contact angle response

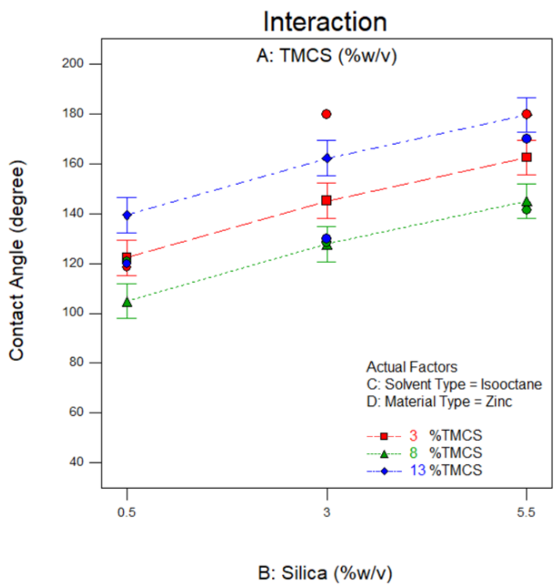

Fig. 3: Model interaction of TMCS-silica concentration for the resulting contact angle response

Determination of the best solvent was carried out with various types of solvents based on differences in chemical structure, namely n-hexane, isooctane and xylene. This assessment used 13 %v/v TMCS and glass as control variables. The appropriate solvent found with a contact angle of 180° referred to isooctane. The result was obtained regard with FTIR spectra (Fig. 4).

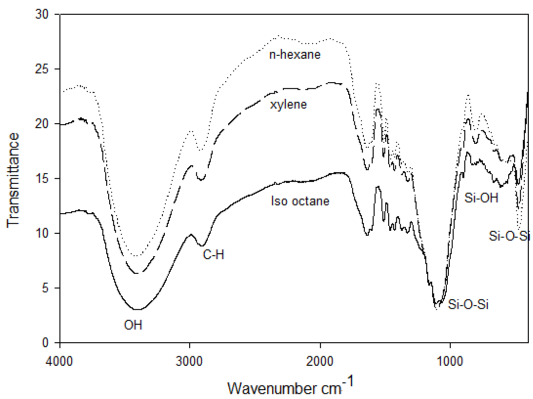

Fig. 4: Spectra of FTIR analysis with different solvents

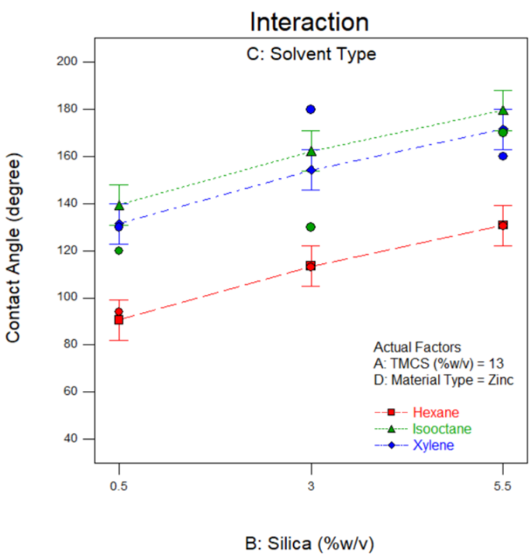

Fig. 5: Model interaction of Solvent type-silica concentration to the response

The isooctane solvent has a higher intensity of non-polar groups (Si-O-Si, C-H, and silicate) so that the isooctane polarity is the lowest compared to other solvents. With a low polarity, the reactivity of exchange between the alkyl groups in isooctane to the silanol group in silica is greatest (Fig. 5) (Hwang et al. 2008).

The effect of material on the wettability response showed that the material produced good wettability using 5.5 %w/v silica solid (Fig. 6). With the use of silica at 0.5 %w/v, glass and zinc materials produced high wettability due to the fact the structure of glass and zinc than that of bamboo. In order to shift its hydrophilicity into superhydrophobic, an interfacial bonding between inorganic (-OH) group and organic silane agent (R-Si) is formed by applying silica superhydrophobic coating (Kumundinje 2001). Since glass itself already contains high content of silica in its amorphous structure (Hasanuzzaman 2015), high amount of hydroxyl groups also presents in its surface, and thus requires less silica in the coating composition. Meanwhile, the application of superhydrophobic coating introduces organic silane solvent which may lower zinc surface energy, thus creating superhydrophobic surface. Even the direct immersion of zinc in FAS (Ferrous ammonium sulfate) and ethanol solution, may decrease zinc surface energy considerably (Ali 2018). Therefore, less silica is required in the superhydrophobic solution due to the ability of organic silanes directly reducing zinc surface energy. In addition, the product solution able to alter bamboo behavior with a contact angle of 70° into a material with a contact angle of up to 180° or superhydrophobic property (Glass 2007). Therefore, coating product was created in this research can produce high roughness with low surface energy in various materials.

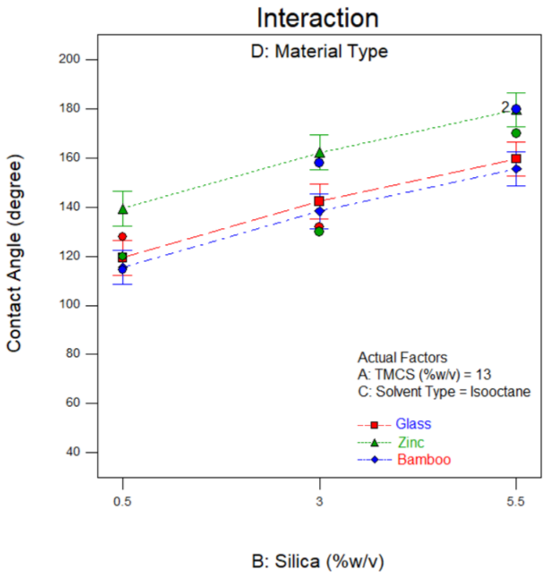

Fig. 6: Model interaction of Material type-silica concentration for the resulting contact angle response

Based on Fig. 3 and Figs. 5-6, higher contact angle as wettability response can be revealed by increasing silica concentration releasing better surface roughness. The surface will form higher needles at certain intervals so that it can trap enough air to produce a higher contact angle. At a 5.5 %w/v of silica, a contact angle of 180° was obtained thus each material falls into superhydrophobic and self-cleaning criteria. In addition, the high concentration of silica resulted high density of silica on the material surface, therefore water cannot be able to seep into the material due to the silica concentration (Latthe et al. 2014). The optimum condition of the superhydrophobic solution product in this study was determined using numerical statistical analysis of a Design Expert 8.0.6 software. The optimum superhydrophobic solution was expected to have 180° by statistical analysis as well as experimental data. The coated zinc released contact angle of 179.66° by statistical analysis with a desirability value of 0.997. It was confirmed by previous experimental data (Purnomo et al. 2018). Fig. 6 shows the ramp report from TMCS concentration, silica concentration, type of solvent and type of material at optimum conditions and the contact angle.

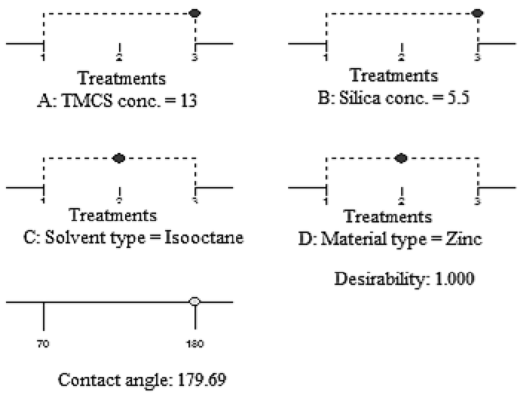

Fig. 7: Ramp report for the optimum conditions

CONCLUSIONS

By use of Design Expert 8.0.6 revealed the optimum condition of the superhydrophobic solution preparation, too. It was complied with previous research by experiment that by statistical analysis with contact angle of 179.69° on coated zinc.

ACKNOWLEDGEMENTS

Thank you for Institute of Research and Community Service (LPPM) of Diponegoro University to the first-year funding of this research with grant number of 474-44/UN7.P4.3/PP/2018.

REFERENCES

1. Ali, H. M., Qasim, M. A., Malik, S., and M. Ghulam. (2018). *Techniques for the Fabrication of Super-Hydrophobic Surfaces and Their Heat Transfer Applications*. InTechOpen. (http://doi.org/10.5772/intechopen.72820).
2. Eakins, W. J. (1968). "Silanol Groups on Silica and Their Reactions with Trimethyl Chlorosilane and Trimethysilanol", *I&EC Prod. Res. Dev.*, 7 (1), 39-43. (https://doi.org/10.1021/i360025a009).
3. Glass, S. V., and TenWolde, A. (2007). *A. Review of In-Service Moisture and Temperature Cosditions in Wood-Frame Buildings*, United States Department of Agriculture: Quilcene, WA, USA, 25-30. (https://doi.org/10.2737/FPL-GTR-174).
4. Hasanuzzaman, M., Rafferty, A., Sajjia, M., and Olabi, A.-G. (2015). Reference Module in Materials Science and Materials Engineering, Elsevier. (https://doi.org/10.1016/B978-0-12-803581-8.03998-9).
5. Hwang, S.-W., Kim, T.-Y., and Hyun, S.-H. (2008). "Optimization of instantaneous solvent exchange/surface modification process for ambient synthesis of monolithic silica aerogels", *J. Colloid Interfaces Sci.*, 322 (1), 224-230. (https://doi.org/10.1016/j.jcis.2008.02.060).
6. Kumudinie, C. (2001). *Encyclopedia of Materials: Science and Technology (Second Edition)*, Elsevier. (https://doi.org/10.1016/B0-08-043152-6/01356-5).
7. Kousaalya, A.B, Garg, N., and Kumar, R. (2013). "Silica-based superhydrophobic coating by a single-step process", Surface Innovations, 1 (3), 173-180. (https://doi.org/10.1680/si.12.00014)
8. Latthe, S. S., Terashima, C., Nakata, K., Sakai, M., and Fujishima, A. (2014). "Development of sol–gel processed semi-transparent and self-cleaning superhydrophobic coatings", *J. Mater. Chem. A*, 2 (15), 5548-5553. (https://doi.org/10.1039/C3TA15017H
9. Liu, J., Janjua, Z.A., Roe, M., Xu, F., Turnbull, B., Choi, K., Hou, X. (2016). "Super-Hydrophobic/Icephobic Coatings Based on Silica Nanoparticles Modified by Self-Assembled Monolayers", Nanomaterials, 232 (6), 1-10. (https:// doi:10.3390/nano6120232)
10. Montgomery, D. C. (2001). *Design and Analysis of Experiments*, John Wiley & Sons, Inc., New York.
11. Purnomo, A., Dalanta, F., Oktaviani, A. D., and Silviana, S. (2018). "Superhydrophobic coatings and self-cleaning through the use of geothermal scaling silica in improvement of material resistance", *AIP Conf. Proc.*, 2026 (1), 020077. (https://doi.org/10.1063/1.5065037).
12. Rao, A. V., Latthe, S. S., Nadargi, D. Y., and Ganesan, V. (2009). "Preparation of MTMS based transparent superhydrophobic silica films by sol–gel method", *J. Colloid Interf.*, 332 (2), 484-490. (https://doi.org/10.1016/j.jcis.2009.01.012).

13. Silviana, S. Hasbi, R. M., Sagita, C. P., Nurhayati, O. D., Fauzan, A., Suhartana, Hatmoko, J. U. D. (2017). "Silika alam dari limbah padatan pengeboran geothermal di Dieng sebagai silika gel melalui proses ramah lingkungan", Prosiding Seminar Nasional Teknologi Industri Hijau 2 2017, 341-346. (http://sntih.kemenperin.go.id/prosiding/?hal=prosiding)
14. Sun, T., Hao, H., Hao W.-T., Yi, S.-M., Li, X.-P., and Li, J.-R. (2014). "Preparation and antibacterial properties of titanium-doped ZnO from different zinc salts", *Nanoscale Res. Lett.*, 9 (98). (https://www.doi.org/10.1186/1556-276X-9-98).
15. Wang, N., and Xiong, D. (2014). "Influence of trimethylethoxysilane on the wetting behavior, humidity resistance and transparency of tetraethylorthosilicate based films", *Appl. Surf. Sci.,* 292 (1), 68-73. (https://doi.org/10.1016/j.apsusc.2013.11.070).
16. Xue, L., Li, J., Fu, J., and Han, Y. (2009). "Super-hydrophobicity of silica nanoparticles modified with vinyl groups", *Colloid Surf.*, 338 (3), 15-19. (https://doi.org/10.1016/j.colsurfa.2008.12.016).
17. Yildirim, A., Khudiyev, T., Daglar, B., Budunoglu, H., Okyay, A. K., and Bayindir, M. (2016). "Superhydrophobic and Omnidirectional Antireflective Surfaces from Nanostructured Ormosil Colloid", *ACS Appl. Mater. Interf.*, 5 (3), 853-860. (https://doi.org/10.1021/am3024417).