

B. Vengadaesvaran^{1,*}, A. Syafiq¹, A. K. Pandey¹, Nasrudin Abd. Rahim^{1,2}

UM Power Energy Dedicated Advanced Centre (UMPEDAC), University of Malaya, Level 4, Jalan Pantai Baharu, 59990 Kuala Lumpur, Malaysia
Renewable Energy Research Group, King Abdulaziz University, Jeddah 21589, Saudi Arabia

ARTICLE INFO	ABSTRACT
Article history: Received 5 October 2018 Received in revised form 4 December 2018 Accepted 8 December 2018 Available online 1 January 2019	In general, hydrophobic coating is termed as the coating with water contact angle (CA) above 90°. The fabrication of hydrophobic coating on the glass substrate has high potential to induce self-cleaning property, anti-fog, and oil-repellent coating. In this study, transparent self-cleaning coating of modified Polydimethylsiloxane (PDMS) has been successfully developed for glass panel application. 3-aminopropyltriethoxyslane (APTES) provides a flexible amino group for reacting with the silica structure of Polydimethylsiloxane. The hydrophobic coating is applied onto glass plates through simple dip-coating method. The hydrophobicity of coating is achieved water contact angle as high as 103 and the transparency of the coating is above 80% in UV-Vis region. The prepared-coating also exhibit an excellent self-cleaning property which the coating completely expels the mud, dilute-ketchup solution, syrup favor, and methylene-blue dye. In addition, the coating shows great anti-fog behavior which the tiny droplets on the coating surface are completely disappears after 6 min at ambient temperature. The droplet impact testing has showed the hydrophobicity of coating is slightly decreases by 4.9° only after injecting with continuous droplet for 168h which indicated that the excellent surface durability of coating.
Anti-fog, hydrophobic, self-cleaning coating, transparent	Copyright © 2019 PENERBIT AKADEMIA BARU - All rights reserved

1. Introduction

Some undesirable plants such as gorse and common yard weeds were buildup of waxy leaf which causes the surface is very difficult to wet. Lotus plant also was buildup of paraffinic wax crystals which is containing $-CH_{2}$ - groups and results to high apparent WCA> 160° and nil sliding [1,2]. Researchers have utilized various raw materials to mimicking the superhydrophobic nature such as silanes and siloxanes for either structure construction typically sol-gel method of tetraethoxysilane or chemical modification typically CVD modification of fluorosilane [3-6]. Fujishima group [7] have fabricated a robust transparent superhydrophobic TiO₂ film through templating by employing the flame soot layer as a nanoimprint template. The hydrophobicity of the

* Corresponding author.

E-mail address: venga@um.edu.my (B. Vengadaesvaran)



film was introduced through surface modification with fluorosilane, however fluorinated polymers are limited solubility and cannot be used for direct linkage [8,9]. Besides, the fluorinated is expensive and have highest toxicity [10-12]. Liu *et al.*, [13] have prepared the superhydrophobic surfaces through the first ever self-modification approach by using PDMS and candle soot. However, the process requires multiple calcinations at 550° and 330° on the candle-soot coated PDMS film. PDMS is not only of low surface energy but also less reactive, less toxic and cheaper compared to low molecular weight of fluorosilanes and chlorosilanes [14-17]. In this study, attempts have been made to prepare transparent superhydrophobic surfaces by using inexpensive PDMS as raw materials which was served for both structure construction and surface modification.

Surface stability, transparency and wettability are closely related to the surface roughness which the nano-aggregation can improve the water CA but cost on the transparency and the mechanical strength. Weak adhesion between nanoparticles and substrates reduces the life-span of the coating as the nanoparticles get detached from substrates easily [18]. Therefore, we have developed the self-cleaning surfaces with the absence of hierarchical nano-structures. The coating surface exhibits non-wettable surfaces like a wax as we combined the silane coupling agent with PDMS. Silane coupling agents are being applied to the glass substrates in order to obtain maximum adhesion and form molecular bridges between organic polymer matrix and substrates surface [19,20]. Coupling agent not only improves the total adhesive strength but also the durability of the adhesive join. Hence, our self-cleaning surface is being driven by strong mechanical property. We expect the wide applications of our coating will emerge as excellent coating technology to develop multi-functional glass in all known glass hardware industries and PV panel.

2. Experimental Procedure

The coating system was prepared through sol-gel method. 60 wt% of Polydimethylsiloxane resin (hydroxy terminated / viscosity of 3500cSt / Sigma-Aldrich (Malaysia)) was blended inside the 250ml of ethanol solution ((C_2H_6O) /Evergreen Engineering & Resources Malaysia) through vigorous stirring above the magnetic stirrer. 50 wt% of 3-Aminopropyltriethoxysilane resin (in liquid form / Shin-Etsu Chemical Co,Ltd. (US)) (and 70wt% of 3-Glycidoxypropyl trimethoxysilane (in liquid form / Shin-Etsu Chemical Co,Ltd. (US)) were then dripped into the PDMS resin and the mixture resin has been subjected to constant stirring for another 1h at 50°C. The mixture was subjected to sonicating process at 60°C for 25min to swell the organic resin within aqueous solution. The preparation of coating system was illustrated in Figure 1. The thin films were casted on the prepared glass slides through simple dip-coating fabrication and subjected to condensation process at room temperature for 20min.

3. Results

The incorporation of silicone coupling agents such as silane and siloxane groups in surface treated polymers have controlled a various interactions involving modified chains, surface molecules interactions among the coupling functional groups and the morphology of the polymer [21,22]. As a result, the employed silanes have improved the hydrophobicity of PDMS surface in which the water CA of the coating achieves as high as 103° as presented in Fig 1.



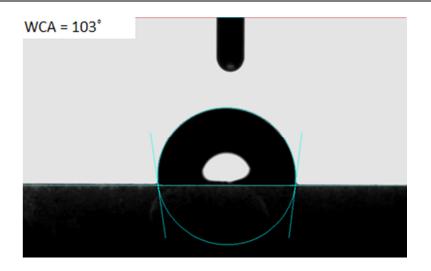


Fig. 1. The hydrophobicity of coating

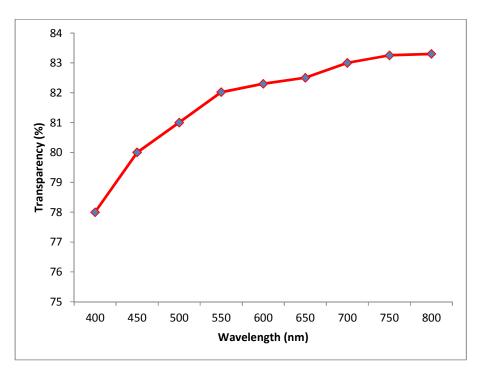


Fig. 2. Transparency of the coating

Anti-reflective properties of as-prepared coating are presented in Fig 2. The optical transmission of the coated glass is above than 82% in the wavelength range of 600-800 nm which have indicated the coating surface is transparent in the visible region. However, the transmission is reduced at short wavelength range less than 600nm which was attributed to wavelength dependent scattering losses in the previous report. The optical transmission is maintained at 78% in the wavelength range of 400-500nm. Fog occurs in cold environment and hot-vapor. Vapor from the fog condense into droplets on the glass surface and scatter the incident light. The surface then becomes translucent or foggy surface and poor optical performances [23-25]. Coating is suggested as one of the relevant and easy approach towards anti-fogging application. Fig 3 depicts the condensed



droplet formed on bare glass and modified PDMS coating glass. The obtained results have showed that the tiny droplets appear on the coated glass after condensation process where else the bare glass plate was covered by large droplets. The tiny fog droplets absolutely disappeared on the coated glass after 7 min for the first-test and about 10 min for the second-test under room temperature. The droplets remain on the bare glass after 20min and completely disappear after 30 min.

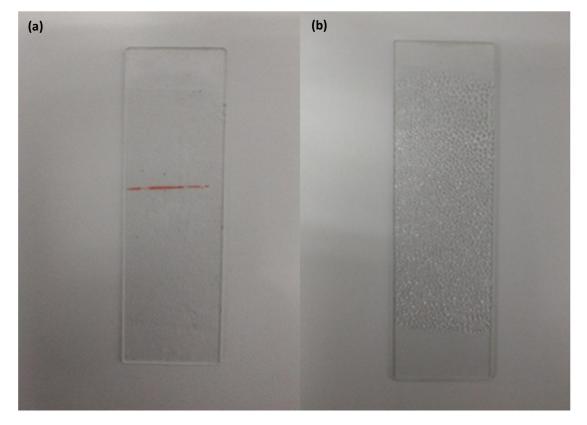


Fig. 3. Anti-fog property of (a) coated glass (b) uncoated glass

Self-cleaning of coating was analyzed for further specification of our hydrophobic glass. Fig 4 shows the mud layer do not adhere and was expelled from modified PDMS coating. It was suggested that the coating surface has relatively low surface tension than the adhered mud; as a result the mud is suspended above the surface. Mud is cannot be removed through simple water injection and mechanical vibration because their low force fail to remove the mud from the surface [26]. The obtained result shows the mud adhesion left the dirt streaks on the bare glass surface and resulting to transparency degradation. Our results have complete agreement with Quan and Zhang [27] which the promising anti-mud performances on treated-glass slides have been achieved. They have suggested that anti-soiling effect work well on both superhydrophobic surface and common hydrophobic surface.



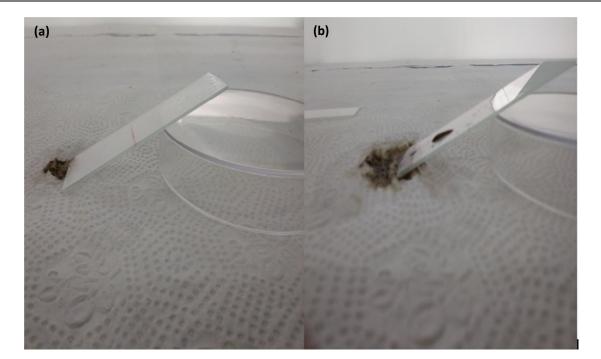


Fig. 4. Anti-mud behavior of (a) coated glass (b) uncoated glass

Figure 5 shows the self-cleaning property against dilute tomato ketchup solution, syrup favor solution, and methylene blue-dye solution. It was observed clearly that all the dirt solution do not adhered on the coated glass, however all the dirt solution was covering the entire bare glass surface as shown.

The results have a complete agreement with the self-cleaning property of non-hierarchical scales structures. It considers the low surface tension of coating is the main factors for our effective self-cleaning property. The wettability of applied liquids on the substrate surface can be tuned with various surface tension. Surface tension is the result from interaction between the surface molecules and surrounding molecules. The molecules of applied liquids are more strongly attracted to the molecules in the bare glass surface compared to the molecules of the gas at their interface which indicating the higher surface tension of the bare surface than applied liquids surface. As a result, the applied liquids spread spontaneously on the substrate surface.

Meanwhile, the molecules of applied liquids are weakly attracted to the molecules in the coating surface which indicating the lower surface tension of the coating surface than applied liquids surface. A drop of applied liquids stay as a drop on the surface and were easily removed through gentle vibration of glass.



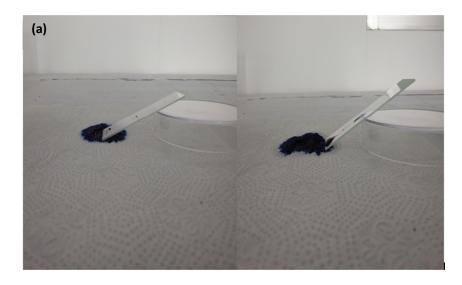






Fig. 5. Self-cleaning ability of coating against (a) methylene blue-dye (b) syrup favor (c) dilute-ketchup solution



4. Conclusions

Transparent self-cleaning coating of modified Polydimethylsiloxane (PDMS) on the glass substrate have been developed with the silicone coupling agents of 3-aminopropyltriethoxysilane (APTES) which provides a flexible amino group for reacting with the silica structure of Polydimethylsiloxane and 3-Glycidoxypropyl trimethoxysilane (GLYMO) which provides methyl group for silica reactive site. The modified PDMS coating has achieved water contact angle as high as 103° with the transparency is above 80% in UV-Vis region. In terms of self-cleaning property, the coating completely expels the mud, dilute-ketchup solution, syrup favor, methylene-blue dye. Great anti-fog behavior of modified PDMS coating have presented that tiny droplets on the coating surface are completely disappears after 7 min at ambient temperature.

Acknowledgements

The authors thank the technical and financial assistance of UM Power Energy Dedicated Advanced Centre (UMPEDAC) and the Higher Institution Centre of Excellence (HICOE) Program Research Grant, UMPEDAC - 2016 (MOHE HICOE - UMPEDAC).

References

- [1] Ma, Minglin, and Randal M. Hill. "Superhydrophobic surfaces." *Current opinion in colloid & interface science* 11, no. 4 (2006): 193-202.
- [2] Hill, Randal M. "Superspreading." Current opinion in colloid & interface science 3, no. 3 (1998): 247-254.
- [3] Kim, M. C., and C-P. Klages. "One-step process to deposit a soft super-hydrophobic film by filamentary dielectric barrier discharge-assisted CVD using HMCTSO as a precursor." *Surface and Coatings Technology* 204, no. 4 (2009): 428-432.
- [4] Boscher, Nicolas D., David Duday, Stéphane Verdier, and Patrick Choquet. "Single-step process for the deposition of high water contact angle and high water sliding angle surfaces by atmospheric pressure dielectric barrier discharge." *ACS applied materials & interfaces* 5, no. 3 (2013): 1053-1060.
- [5] Boscher, Nicolas D., Véronique Vaché, Paul Carminati, Patrick Grysan, and Patrick Choquet. "A simple and scalable approach towards the preparation of superhydrophobic surfaces–importance of the surface roughness skewness." *Journal of Materials Chemistry A* 2, no. 16 (2014): 5744-5750.
- [6] Crick, Colin R., James A. Gibbins, and Ivan P. Parkin. "Superhydrophobic polymer-coated copper-mesh; membranes for highly efficient oil–water separation." *Journal of Materials Chemistry A* 1, no. 19 (2013): 5943-5948.
- [7] Liu, Shanhu, Munetoshi Sakai, Baoshun Liu, Chiaki Terashima, Kazuya Nakata, and Akira Fujishima. "Facile synthesis of transparent superhydrophobic titania coating by using soot as a nanoimprint template." *Rsc Advances* 3, no. 45 (2013): 22825-22829.
- [8] Yabu, Hiroshi, and Masatsugu Shimomura. "Single-step fabrication of transparent superhydrophobic porous polymer films." *Chemistry of materials* 17, no. 21 (2005): 5231-5234.
- [9] Xu, Lianbin, Wilfred Chen, Ashok Mulchandani, and Yushan Yan. "Reversible conversion of conducting polymer films from superhydrophobic to superhydrophilic." *Angewandte Chemie International Edition* 44, no. 37 (2005): 6009-6012.
- [10] Lu, Yao, Sanjayan Sathasivam, Jinlong Song, Colin R. Crick, Claire J. Carmalt, and Ivan P. Parkin. "Robust selfcleaning surfaces that function when exposed to either air or oil." *Science* 347, no. 6226 (2015): 1132-1135.
- [11] Chen, Kunlin, Shuxue Zhou, Shu Yang, and Limin Wu. "Fabrication of All-Water-Based Self-Repairing Superhydrophobic Coatings Based on UV-Responsive Microcapsules." *Advanced Functional Materials* 25, no. 7 (2015): 1035-1041.
- [12] Zhou, Hua, Hongxia Wang, Haitao Niu, Adrian Gestos, Xungai Wang, and Tong Lin. "Fluoroalkyl silane modified silicone rubber/nanoparticle composite: a super durable, robust superhydrophobic fabric coating." Advanced materials 24, no. 18 (2012): 2409-2412.
- [13] Liu, Xiaojiang, Yan Wang, Zao Chen, Keyang Ben, and Zisheng Guan. "A self-modification approach toward transparent superhydrophobic glass for rainproofing and superhydrophobic fiberglass mesh for oil water separation." *Applied Surface Science* 360 (2016): 789-797.



- [14] Zhang, Xin-Xiang, Shuang Cai, Dan You, Liang-Hong Yan, Hai-Bing Lv, Xiao-Dong Yuan, and Bo Jiang. "Templatefree sol-gel preparation of superhydrophobic ORMOSIL films for double-wavelength broadband antireflective coatings." *Advanced Functional Materials* 23, no. 35 (2013): 4361-436.
- [15] Park, Eun Ji, Jong Ki Sim, Myung-Geun Jeong, Hyun Ook Seo, and Young Dok Kim. "Transparent and superhydrophobic films prepared with polydimethylsiloxane-coated silica nanoparticles." *RSC Advances* 3, no. 31 (2013): 12571-12576.
- [16] Ye, Hui, Liqun Zhu, Weiping Li, Huicong Liu, and Haining Chen. "Constructing fluorine-free and cost-effective superhydrophobic surface with normal-alcohol-modified hydrophobic SiO2 nanoparticles." *ACS applied materials & interfaces* 9, no. 1 (2016): 858-867.
- [17] Liu, Hui, Jianying Huang, Zhong Chen, Guoqiang Chen, Ke-Qin Zhang, Salem S. Al-Deyab, and Yuekun Lai. "Robust translucent superhydrophobic PDMS/PMMA film by facile one-step spray for self-cleaning and efficient emulsion separation." *Chemical Engineering Journal* 330 (2017): 26-35.
- [18] Li, Chunling, Yangchao Sun, Meng Cheng, Shuangqing Sun, and Songqing Hu. "Fabrication and characterization of a TiO2/polysiloxane resin composite coating with full-thickness super-hydrophobicity." *Chemical Engineering Journal* 333 (2018): 361-369.
- [19] Li, Bucheng, Junping Zhang, Ziqian Gao, and Qingyun Wei. "Semitransparent superoleophobic coatings with low sliding angles for hot liquids based on silica nanotubes." *Journal of Materials Chemistry A* 4, no. 3 (2016): 953-960.
- [20] Deng, Zheng-Yan, Wei Wang, Li-Hua Mao, Cai-Feng Wang, and Su Chen. "Versatile superhydrophobic and photocatalytic films generated from TiO 2–SiO 2@ PDMS and their applications on fabrics." *Journal of materials chemistry A* 2, no. 12 (2014): 4178-4184.
- [21] Plueddemann, Edwin P. "Chemistry of silane coupling agents." In *Silane coupling agents*, pp. 31-54. Springer, Boston, MA, 1991.
- [22] Sabzi, M., S. M. Mirabedini, J. Zohuriaan-Mehr, and M. Atai. "Surface modification of TiO2 nano-particles with silane coupling agent and investigation of its effect on the properties of polyurethane composite coating." *Progress in Organic Coatings* 65, no. 2 (2009): 222-228.
- [23] Grosu, G., L. Andrzejewski, G. Veilleux, and G. G. Ross. "Relation between the size of fog droplets and their contact angles with CR39 surfaces." *Journal of Physics D: Applied Physics* 37, no. 23 (2004): 3350.
- [24] Kim, Philseok, Tak-Sing Wong, Jack Alvarenga, Michael J. Kreder, Wilmer E. Adorno-Martinez, and Joanna Aizenberg. "Liquid-infused nanostructured surfaces with extreme anti-ice and anti-frost performance." ACS nano 6, no. 8 (2012): 6569-6577.
- [25] Briscoe, B. J., and K. P. Galvin. "The effect of surface fog on the transmittance of light." Solar Energy 46, no. 4 (1991): 191-197.
- [26] Yilbas, Bekir Sami, Haider Ali, Mazen M. Khaled, Nasser Al-Aqeeli, Numan Abu-Dheir, and Kripa K. Varanasi. "Influence of dust and mud on the optical, chemical, and mechanical properties of a PV protective glass." *Scientific reports* 5 (2015): 15833.
- [27] Quan, Yun-Yun, and Li-Zhi Zhang. "Experimental investigation of the anti-dust effect of transparent hydrophobic coatings applied for solar cell covering glass." *Solar Energy Materials and Solar Cells* 160 (2017): 382-389.