EFFECT OF SILICA TYPE ON SUPERHYDROPHOBIC PROPERTIES OF PDMS-SILICA NANOCOMPOSITE COATINGS

[1]SENNUR DENIZ, [2] BILGEN ARIKAN

[1]Assist. Prof. Dr., Department of Chemical Engineering, Yildiz Technical University, Istanbul-Turkey
[2]MSc., Department of Chemical Engineering, Yildiz Technical University, Istanbul-Turkey
E-mail: [1]sennurdeniz@gmail.com, [2]bilgenarikan12@gmail.com,

ABSTRACT

Polydimethylsiloxane (PDMS)-based coatings with superhydrophobic property prepared on various substrates by applying a suspension of suitable nanoparticles in PDMS have attracted much interest in industrial applications. Polydimethylsiloxane (PDMS)-silica nanocomposite coatings with different types of hydrophobic surface treated nanosilica were fabricated by coating a layer of fluoroalkylsilane (FAS) as a topcoat. The coating solutions of PDMS-silica were prepared by mixing PDMS with hydrophobic fumed nanosilicas having different surface groups in toluene and applied on to the cleaned aluminum alloy (Al) substrates by spray coating method. A layer of FAS-topcoat was applied on PDMS-silica nanocomposite coatings by using two different types of FAS (FAS1 and FAS2). The coated Al substrates were allowed to cure at room temperature for varying curing times. The effects of hydrophobic nanosilica and FAS types, and drying time of FAS topcoat on the surface wettability were studied. The molecular structure and crosslinking reaction of the PDMS-silica nanocomposites was characterized by Fourier transform infrared spectroscopy (FTIR). The static water contact angles (WCA) of the coatings were measured by sessile drop method using a contact angle analyzer. The PDMS-silica coatings having different types of hydrophobic silica with FAS1 topcoat were found superhydrophobic with static WCA of >150°.

Keywords: *Superhydrophobic Coating, Polydimethylsiloxane, Fumed Nanosilica, Al surface, Water Conract Angle*

1. INTRODUCTION

Superhydrophobicity has taken great interest for its self-cleaning character and superhydrophobic (SH) surfaces have extensive technological potential for various applications due to their extreme water-repellent properties [1-5]. Generally, a surface with a water contact angle (WCA) larger than $150°$ and a roll-off angle less than $10°$ is defined as superhydrophobic surface which also exhibit a self-cleaning effect and low drag for fluid flow. These surfaces are of interest in various applications, including self-cleaning windows, exterior paints for buildings, navigation ships, textiles, and applications requiring a reduction in fluid flow, e.g., in micro/nanochannels and hence promote cleaning on outdoor surfaces such as automobiles, buildings, antennas and traffic lights [6-9]. Extremely water-repellent superhydrophobic surfaces can be produced by using roughness combined with hydrophobic coatings. The wettability of a solid surface depends on both surface chemical composition and surface geometrical microstructures. Surfaces with high energy, formed by polar molecules, tend to be hydrophilic, whereas those with low energy and built of non-polar molecules tend to be hydrophobic.

Polymer nanocomposites have been fabricated to obtain the SH surfaces due to their distinctive advantages like facility of processing, cost efficiency, and feasibility of application over large area. It was demonstrated that it is possible to obtain SH surfaces by incorporating nanoparticles in low surface energy polymers like polydimethylsiloxane (PDMS) [10-12]. PDMS polymer has been intensively studied for their unique properties, such as hydrophobicity, excellent thermal stability, low glass transition temperature, good electrical properties, good weather resistance, low surface free energy, low toxicity and low chemical reactivity [13-17]. PDMS is a typical elastomeric material with low surface energy of about 20 mN/m. Recently, it has also been introduced into micro-fluidic devices as

www.eaas-journal.org

channels. Flat PDMS surface has intrinsic hydrophobicity with WCA of about 100-110° [18]. The chemical inertness of PDMS makes it useful in a variety of applications in automotive fields, microelectronic areas, aerospace and construction industries [16,19]. A large number of commercial PDMS products, such as sealants, adhesives, membrane and elastomers have been found in everywhere. In these products, silica has been broadly used as reinforcing agent to improve mechanical properties of PDMS matrix due to its inherent weak intermolecular force [20].

PDMS nanocomposite coatings with SH property have been developed by several researcher [21, 22]. PDMS-nanoparticle coatings which exhibit water repellency have been reported to impart superhydrophobicity to monument surfaces using common and cost-effective materials [21]. PDMS nanocomposite coatings filled with hydrophobic nanosilica have prepared by dispersing of silica nanoparticles in the silicone matrix [19,11]. Momen et al. have reported to apply a PDMS coating based on RTV silicone rubber on anodized aluminum surfaces to obtain a nanostructured superhydrophobic surface [12].

In most of the previous studies, hydrophilic nanosilica particles or in situ prepared hydrophobic nanosilica was incorporated in PDMS matrix to create roughness and subsequently treated with FAS to reduce surface energy of the films [9-11]. In our present work, superhydrophobic PDMS-silica nanocomposite coatings with a topcoat of low surface energy fluoroalkylsilane (FAS) were fabricated by using different types of hydrophobically modified fumed silica nanoparticles containing different surface functional groups dispersed in RTV silicon matrix on Al substrate by spray coating. The effect of microstructure and roughness on the wettability of the nanocomposite coatings was studied. The wetting property of the coating surface was determined by static water contact angle measurements. The chemical compositions of the as-prepared films on aluminum substrates were analyzed using a Fourier transform infrared spectroscopy (FTIR). The optimal process conditions of nanocomposite coatings, such as drying time, and the surface group types of nanosilica were investigated for the superhydrophobic properties of coated Al surfaces.

2. EXPERIMENTAL STUDY:

2.1 Materials

PDMS (RTV 615 type) was obtained from GE Bayer Silicones (Germany) as a two-component system, consisting of a vinyl-terminated pre-polymer (RTV A) and a crosslinker containing several hydrosilane groups (RTV B). Dynasylan® F8263 (FAS1, fluoroalkylsilane formulation, ready-to-use in isopropanol) and Dynasylan® F8261 (FAS2, tridecafluorooctyl triethoxysilane, $CF_3(CF_2)_5CH_2CH_2Si(OR)_3$) were purchased from Evonik, Germany, and toluene from Merck Chemicals. Dibutyl tin dilaurate (DBTDL) was purchased from Fluka. Hydrophobic fumed silica nanoparticles having different surface groups (CAB-O-SIL® types; TS-530; TS-610, and TS-720) were supplied from Cabot Sanmar Ltd, USA. The typical properties and hydrophobic surface groups of the treated grades of CAB-O-SIL® fumed silica recommended for coatings are shown in Table 1 and Fig. 1.

Table 1. Typical Properties of Surface Treated Hydrophobic Fumed Nanosilicas [22].

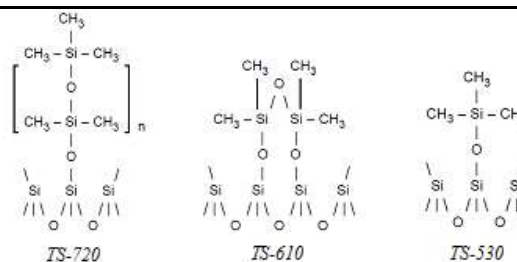| CAB-O-SIL® fumed silica code	Surface Treating Agent	BET Surface Area (m^2/g)	pH (4% slurry)	Carbon Content (wt .%)
TS-530	Hexamethyldisilazane	320	5.5	4.25
TS-610	Dimethyldichlorosilane	130	>4.0	0.85
TS-720	Dimethylsilicone Fluid	200	NA	5.4

Figure 1. Surface Chemistry of CAB-O-SIL® Hydrophobically Treated Fumed Silicas.

2.2 Preparation of PDMS-Silica Nanocomposite Coatings with Different Types of Treated Fumed Silica

PDMS solution (10 wt. %) was prepared by mixing PDMS RTV 615 A (10.0 g) with toluene (90 ml) till a homogenous clear solution was obtained and making up to 100 ml. Dynasylan® 8263 was used as FAS1 directly. FAS2 solution (2 wt. %) was prepared by dissolving 0.20 g of Dynasylan® 8261 in 10 ml ethanol. PDMS-silica solution was prepared by mixing the PDMS solution (5 ml) with ultrasonically dispersed solution of fumed silica

(0.20 g) in toluene. DBTDL (4 wt. %) was added to this solution and further stirred magnetically for 1 h. The final solution of PDMS-silica dispersion was applied on to the cleaned aluminum (Al) substrates by spraying technic using a spray gun with 1.0 mm diameter nozzle. The atomizing air pressure was maintained at about 2 atm. The coated Al substrates were cured for 24 h at room temperature. After that, two types of FAS topcoat were applied on PDMS-silica nanocomposite coatings by spraying of FAS1 and FAS2 solutions in double passes to incorporate sufficient amount of FAS in the topcoat. All coatings with FAS double layer topcoat were dried at room temperature for 1 h and 24 h and heated at 100°C for 1 h. A group of coatings were immediately heated at 100°C for 1 h after FAS coating without drying at room temperature.

2.3 Characterization of PDMS-Silica Nanocomposite Coatings

Fourier Transform infrared spectroscopy (FTIR) spectra of the samples were measured using KBr pellet technique with an infrared analyzer. The chemical structures of PDMS nanocomposites were analyzed by using a Nicolet NEXUS 670 Spectrometer by attenuated total reflection infrared spectroscopy (ATR-IR).

WCA of the coatings were measured by sessile drop method using a contact angle analyzer, (KSV Theta Attention). Measurements were made using tangent line-fitting mode. The drop volume for WCA measurements was 10 µl. Deionized milli Q water (surface tension: 71 mN/m) was used for measurements. An average of five measurements was taken for reporting WCA and the error in measurements were within ±2°. The static contact angles are measured to study the wetting property of the hydrophobic coatings. There are different models prescribed on the wetting phenomenon by Young, Wenzel and Cassie-Baxter (Fig. 2). The wettability of an ideal flat surface in terms of water contact angle is described by the Young's equation (Eq. 1);

$$\cos(\theta_Y) = (\gamma_{sg} - \gamma_{sl})/\gamma_{lg} \qquad (Eq.1)$$

where γsg, γsl and γlg represent the interfacial tensions of solid-gas, solid-liquid and liquid-gas respectively. Typically, the observed surfaces are not ideally flat but they are rough. Wenzel modified Young's formula (Eq. 2) by assuming that the liquid filled up the protrusions on the rough surface as shown Fig. 2a;

$$\cos(\theta_W) = r \cos(\theta_Y) \qquad (Eq. 2)$$

where θ_W, θ_Y are the Wenzel's and Young's contact angle and r is termed as the roughness factor. Roughness factor is defined as the ratio of the actual area of a rough surface to the projected area on the horizontal plane. Thus surface roughness plays an important role in determining the wetting behavior along with the chemical composition. It enhances the hydrophobicity of the surface with $\theta_Y > 90°$ and hydrophilicity of the surface with $\theta_Y < 90°$. For the heterogeneous wetting where the surface is in contact with liquid forms a composite of the air and solid, Cassie–Baxter modified Wenzel's equation (Eq. 3) as;

$$\cos\theta_C = -1 + r\, f(\cos\theta_W + 1) \qquad (Eq. 3)$$

where θ_C is the Cassie's contact angle and f is the contact area between water droplet and the solid surface. This equation gives the contact angle for rough surface with air trapped between the grooves on the surfaces and the droplet rests on a composite of the solid and air as shown in Fig. 2b. The range of applicability of Wenzel's or Cassie–Baxter's equation is decided by using Pierre-Gilles de Gennes equation for threshold roughness r_t for air trapping (Eq. 4).

$$r_t = 1 + [(\tan^2\theta)/4] \qquad (Eq. 4)$$

For low surface roughness ($r < r_t$), the contact angle is given by Wenzel's equation and beyond the threshold roughness ($r > r_t$), air pockets are trapped and Cassie–Baxter's equation must be used to evaluate the contact angle. These two are the widely studied wetting states but a very little attention is paid to the surfaces where even though the contact angle is large, water drop sticks to the surface. It was also demonstrated that at least one more wetting state exists on the textured surfaces namely Cassie impregnated wetting state. Where a liquid film impregnates a texture ahead of the droplet protrusions are filled with liquid and the solid surface ahead of the droplet is dry, as depicted in Fig. 2c.
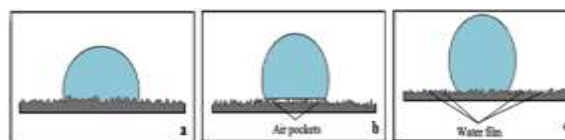

Figure 2. Different Models of Wetting States; (a) Wenzel, (b) Cassie-Baxter, (c) Cassie Impregnated Wetting State.

3. RESULTS AND DISCUSSION

3.1. Static Water Contact Angle Measurement

Table 2 lists the water contact angle of the hydrophobic and superhydrophobic coatings studied in the present work. The WCA of bare

ISSN2305-8269

www.eaas-journal.org

aluminum alloy surface also was hydrophilic with WCA of 67° ± 2 indicating the hydrophilic nature of this surface. The WCA of PDMS (room temperature vulcanized silicon rubber, RTV615) was 105° ± 1.5 which clearly showed that this surface was hydrophobic. On the other hand, the PDMS-silica nanocomposite coatings prepared with FAS1 topcoat and different types of nanosilica containing different hydrophobic surface groups were superhydrophobic with WCA of >150. The WCAs of PDMS-silica coatings with FAS1 and FAS2 topcoats prepared by different types of hydrophobic surface treated silica were measured between 163° and 126°.

Table 2. WCAs of PDMS-Silica Nanocomposite Coatings Prepared by Different Types of Hydrophobic Nanosilica with Varying Drying Time.

Coating code	Drying Time of FAS Topcoat (h)	WCA (θº)
PDMS-530- FAS1	0	**163**
PDMS-530- FAS1	1	152
PDMS-530- FAS1	24	147
PDMS-610- FAS1	0	**157**
PDMS-610- FAS1	1	147
PDMS-610- FAS1	24	151
PDMS-720- FAS1	0	**144**
PDMS-720- FAS1	1	145
PDMS-720- FAS1	24	135
PDMS-530- FAS2	0	**145**
PDMS-530- FAS2	1	137
PDMS-530- FAS2	24	132
PDMS-610- FAS2	0	**143**
PDMS-610- FAS2	1	138
PDMS-610- FAS2	24	128
PDMS-720- FAS2	0	**138**
PDMS-720- FAS2	1	128
PDMS-720- FAS2	24	126

PDMS-silica coatings with FAS1 topcoat showed an increase in WCA for all types of treated fumed silica in the same drying time with respect to the coatings with FAS2 topcoat prepared for all drying times. Fig. 3 depicts the WCA variation of PDMS-silica nanocomposite coatings having FAS topcoat with drying time. It can be seen that the WCA of PDMS-silica nanocomposite coatings having FAS topcoat almost linearly decreased with an increase in drying time for FAS1 and FAS2. The FAS topcoating on PDMS-silica nanocomposite coatings prepared by the different types of treated silica had formed a relatively higher nanoroughness on the surface of PDMS-silica coating with FAS1 for each silica type. The smaller the drying time of PDMS-silica coatings with FAS topcoat led to the higher the WCA of PDMS-silica coating. It can be attributed that the formation of FAS topcoating for both FAS1 and FAS2 without drying was completed quite easily than that of FAS coating for drying time of 1 and 24 h at room temperature.

Images of water drop on PDMS-silica nanocomposite coatings with FAS1 topcoat prepared by three different types of surface treated silica are shown in Fig. 4. For all silica types, the WCA values of PDMS-silica nanocomposite coatings prepared by FAS1 topcoat were found to be higher according to that of the coating prepared by FAS2 for all drying times. The PDMS-silica coatings with FAS1 topcoats prepared with silica TS-530, -610 and -720 without drying time were superhydrophobic with static WCA of 163°, 157°, and 145°, respectively. The WCAs of the PDMS-silica coatings with FAS1 topcoats prepared with silica TS-530 and -610 was found to improve with increasing the surface area of silica type. WCA value of PDMS-silica coating with FAS1 topcoat prepared with silica TS-720 showed a decrease in WCAs for all drying times. It can be attributed that the big surface groups and the smaller surface area of silica TS-720 inhibited the impregnation of silica particles into the PDMS

22

matrix and the particles were not to be surrounded by PDMS polymer chains.
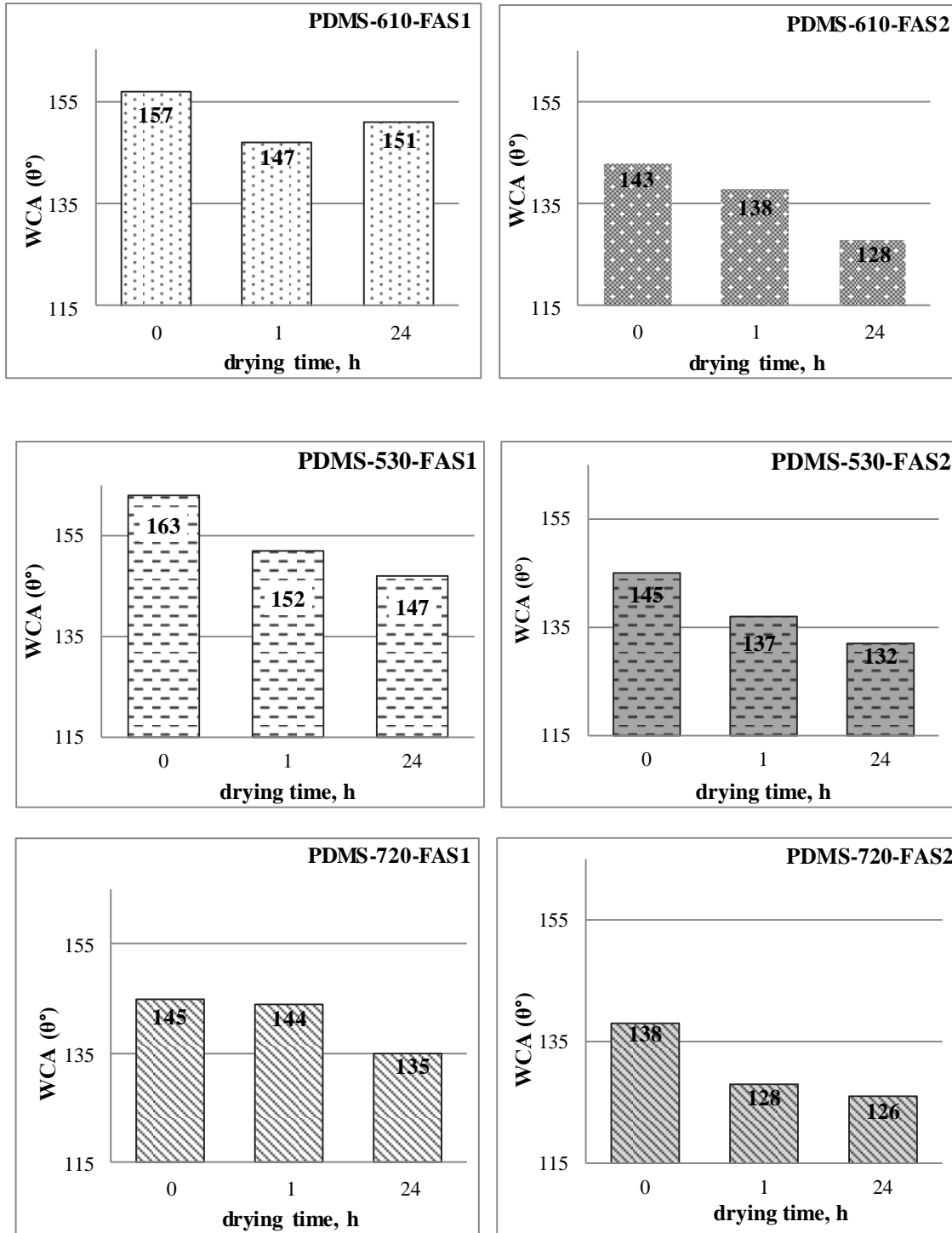

Figure 3. *The WCAs Variation of PDMS-Silica Nanocomposite Coatings with the Drying Time.*

www.eaas-journal.org

PDMS-530-FAS1
θ = 163°
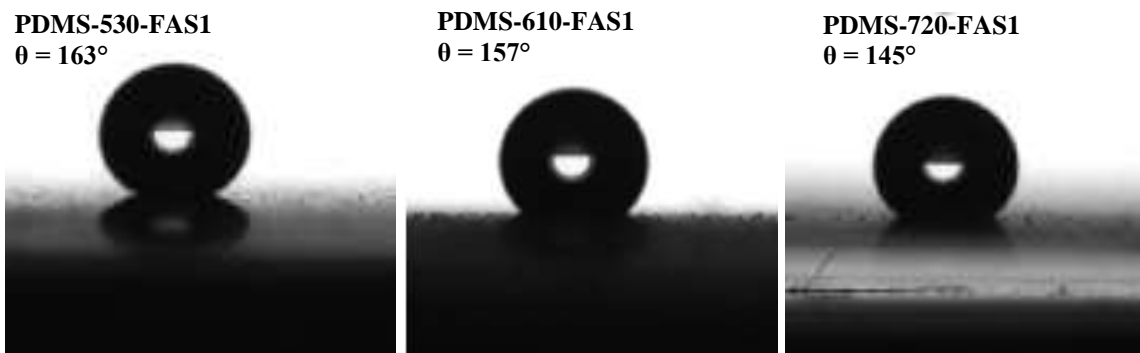
PDMS-610-FAS1
θ = 157°

PDMS-720-FAS1
θ = 145°

Figure 4. Images of Water Drop on PDMS-Silica Nanocomposite Coatings Prepared by FAS1 Topcoat and Different Types of Hydrophobic Silica without Drying Time.

3.2. FTIR Characterization of PDMS-silica Nanocomposites

The FTIR spectroscopy is a powerful tool that combines enhanced visualization of chemical information which was used to investigate the functional groups present in the coatings. The FTIR spectra of coatings were obtained by detaching coatings from the substrate and spectra were recorded in transmission mode using the detached powder.

Typical PDMS formulations are polymerized by mixing a "base", consisting mainly of long PDMS monomers capped by vinyl groups, with a "curing agent", consisting of shorter PDMS monomers with silicon hydride groups [24-26]. It is a two-component system: (a) RTV A that contains a dimethylvinyl terminated pre-polymer and the Pt-catalyst, and (b) RTV B that contains the cross-linker with several hydride groups. When mixed with a platinum catalyst, the liquid polymerizes resulting from the addition of silicon hydrides across vinylic double bonds. The curing of the PDMS (RTV 615) was occurred via Pt-catalysed hydrosilylation reaction to form a densely cross-linked polymer network. The hydrosilylation (addition reaction) relies on the ability of the hydrosilane bond of the crosslinker ($\equiv$SiH) to add across a carbon-carbon double bond that belongs to the pre-polymer in the presence of Pt catalyst (Fig. 5)[28]. In the ideal case, the SiH may react only with the $-CH=CH_2$ groups along the prepolymer chains, allowing a good control over the crosslinks distribution.
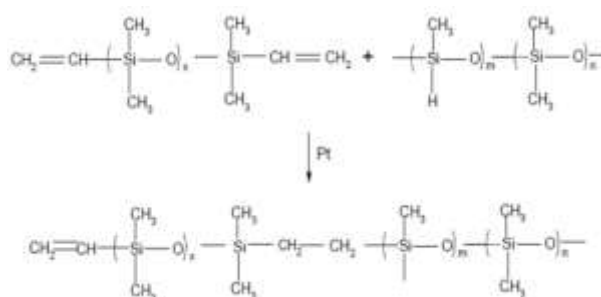
Figure 5. Scheme of the Crosslinking Reaction for the Silicon Network Formation of Polydimethylsiloxane (RTV 615 A and B) [27].

Fig. 6 presents infrared spectra of crosslinked PDMS. The IR spectrum of PDMS contains the typical peaks of the C-H methyl stretch at 2965 cm^{-1}, the C=C stretch at 1480 cm^{-1}, the silicon-methyl bond (Si-CH$_3$ deformation) at the range of 1260-1280 cm^{-1}, and 805 cm^{-1}, and two broad Si-O-Si stretches at 1100 cm^{-1}[28,29]. The unreacted vinyl and hydrosilane (SiH) groups (after crosslinking) can be determined by the presence of absorption band at 1410 cm^{-1} (for vinyl) and 2140 cm^{-1} (for SiH) [30].
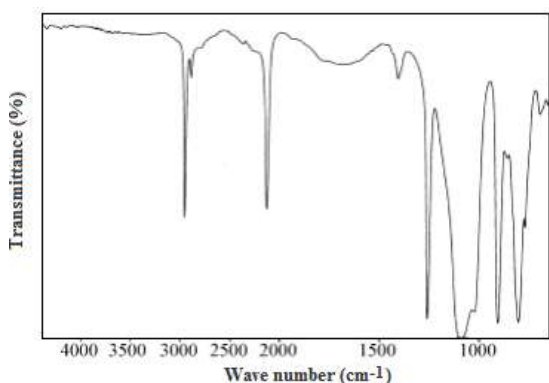
Figure 6. Infrared Spectra of Crosslinked PDMS [28].

The FTIR spectra shown in Fig. 7a and b consist of bands related to the vibrations and deformation of both fumed nanosilicas and PDMS-silica nanocomposites structural units. Fig. 7b displays intense absorption peak for spectra of a values at

1090 cm^{-1}, which is due to Si-O-Si asymmetric stretching vibration indicating the presence of silica network in the coatings. The Si-O-Si peak splits into bands separated at 1020 cm^{-1} and 1090 cm^{-1}. Appearance of the peak between 3100 cm^{-1} and 3500 cm^{-1} is due to the stretching vibration of hydroxyl group, indicates an incomplete condensation of the Si-OH in the hybrid matrix and the peak at around 1700 cm^{-1} is due to physically adsorbed water. The weak bands observed from 2960 cm^{-1} to 3000 cm^{-1} for all spectra are assigned to, symmetric and asymmetric stretching of C-H bond respectively and a band at 1300 cm^{-1} is due to the bending of C-H. The characteristic absorption bands of the CH_3 groups for PDMS at near 2980, 1390, 1255 and 780cm^{-1} were observed in the FTIR spectra of the PDMS-silica coatings.
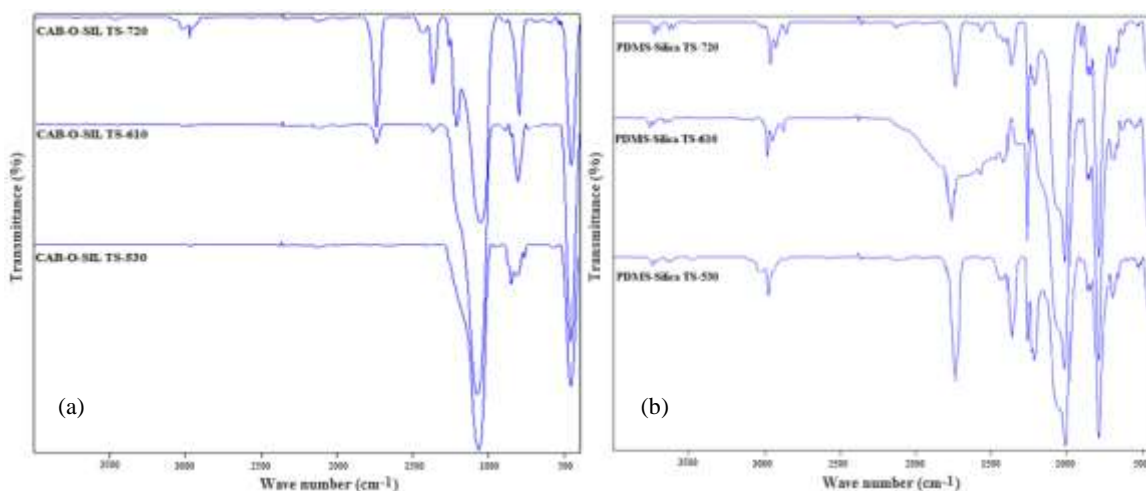

Figure 7. FTIR Spectrums of; a) Fumed Silicas, and b) PDMS-Silica Coatings with FAS1 Topcoat Prepared by Different Types of Fumed Silica without Drying.

4. CONCLUSION

A type of the PDMS-silica nanocomposite coatings with FAS topcoat formed by the two different types of FAS solution on Al surface was prepared by using the different types of treated fumed silica with varying drying times. WCAs of PDMS-silica coatings with FAS topcoat prepared by different types of hydrophobic treated silica were found between 163° and 126°. The PDMS-silica nanocomposite coatings with FAS topcoat possessed the good superhydrophobicity for the coatings prepared by FAS1 solution at 100ºC without drying time. The PDMS-silica coatings with FAS1 topcoats prepared with silica TS-530, -610 and -720 were superhydrophobic with static WCA of 163°, 157°, and 145°, respectively. The WCAs of the PDMS-silica coatings with FAS1 topcoats prepared with

silica TS-530 and -610 was found to improve with increasing the surface area of fumed nanosilica and the types of silica surface groups. The analysis through FTIR indicated that silica particles were dispersed in PDMS matrix. These coatings can be applied by spraying on larger area of Al substrates.

Therefore, it is a simple and cost-effective method to obtain superhydrophobic surfaces.

Acknowledgements

REFERENCES:

[1] X. Li, D. Reinhoudt, M. Crego-Calama, "What do we need for a superhydrophobic surface? A review on the recent progress in the preparation of superhydrophobic surfaces" *Chemical Society Reviews*, Vol. 36, No. 8, 2007, pp. 1350-1368.

[2] D. Oner, T. J. McCarthy, "Ultrahydrophobic Surfaces. Effects of Topography Length Scales on Wettability", *Langmuir,* Vol. 16, No. 20,2000, pp. 7777-7782.

[3] Z. Yoshimitsu, A. Nakajima, T. Watanabe, K. .Hashimoto, "Effects of Surface Structure on the Hydrophobicity and Sliding Behavior of Water Droplets", *Langmuir,* Vol. 18, No. 15, 2002, pp. 5818-5822.

[4] (a) N. A. Patankar, "On the Modeling of Hydrophobic Contact Angles on Rough Surfaces", *Langmuir ,* Vol. 19, No. 4, 2003, pp. 1249-1253; (b) B. He, N.A. Patankar, J. Lee," Multiple Equilibrium Droplet Shapes and Design Criterion for Rough Hydrophobic Surfaces", *Langmuir*, Vol. 19, No. 12, 2003, pp. 4999-5003.

[5] A. Marmur, "The Lotus Effect: Superhydrophobicity and Metastability" *Langmuir,* Vol. 20, No. 9, 2004, pp. 3517-3519.

[6] H.J. Song, Z.Z. Zhang, X.H. Men, "Superhydrophobic/superhydrophilic surfaces from a carbon nanotube based composite coating", *Applied Physics A,* Vol. 91, 2008, pp. 275-280.

[7] C.T. Hsieh, F.L. Wu, W.Y. Chen, "Super water- and oil-repellencies from silica-based nanocoatings", *Surface and Coatings Technology,* Vol. 203, No.22, 2009, pp. 3377-3384.

[8] C.-T. Hsieh, Y.-S. Cheng, S.-M. Hsu, J.-Y. Lin, "Water and oil repellency of flexible silica-coated polymeric substrates", *Applied Surface Science,* Vol. 256, No. 16, 2010, pp. 4867-4872.

[9] X. Huang, X.L. Fang, Z. Lu, S. Chen, "Reinforcement of polysiloxane with superhydrophobic nanosilica", *Journal of Material Science,* Vol. 44, No. 17, 2009, pp. 4522-4530.

[10] B.J. Basu, V.D. Kumar, C. Anandan, "Surface studies on superhydrophobic and oleophobic polydimethylsiloxane-silica nanocomposite coating system", *Applied Surface Science*, Vol. 261, 2012, pp. 807- 814.

[11] T. Bharathidasana, S.V. Kumarb, M.S. Bobjib, R.P.S. Chakradhara, B.J. Basu, "Effect of wettability and surface roughness on ice-adhesion strengthof hydrophilic, hydrophobic and superhydrophobic surfaces", *Applied Surface Science,* Vol. 314, 2014, pp. 241-250.

[12] G. Momen, M. Farzaneh, R. Jafari, "Wettability behaviour of RTV silicone rubber coated on nanostructured aluminium surface", *Applied Surface Science,* Vol. 257, No. 15, 2011, pp. 6489-6493.

[13] D. Chen, Y. Liu, H. Zhang, Y. Zhou, C. Huang, C. Xiong, "Influence of Polyhedral Oligomeric Silsesquioxanes (POSS) on Thermal and Mechanical Properties of Polydimethylsiloxane (PDMS) Composites Filled with Fumed Silica", *Journal of Inorganic Organometallic Polymers and Materials*, Vol. 23, No. 6, 2013, pp. 1375-1382.

[14] D. Yang, W. Zhang, R. Yao, B. Jiang, "Thermal stability enhancement mechanism of poly(dimethylsiloxane) composite by incorporating octavinyl polyhedral oligomeric silsesquioxanes", *Polymer Degradation and Stability*, Vol. 98, No. 1, 2013, pp. 109-114.

[15] Y. Zhang, Y. Mao, D. Chen, W. Wu, S. Yi, S. Mo, C. Huang, "Synthesis and characterization of addition-type silicone rubbers (ASR) using a novel cross linking agent PH prepared by vinyl-POSS and PMHS", *Polymer Degradation and Stability,* Vol. 98, No. 4, 2013, pp. 916-925.

[16] E. Yilgor, T. Eynur, C. Kosak, S. Bilgin, I. Yilgor, O. Malay, Y. Menceloglu, G.L. Wilkes, "Fumed silica filled poly(dimethylsiloxane-urea) segmented copolymers: Preparation and properties", *Polymer*, Vol. 52, No. 19, 2011, pp. 4189-4198 .

[17] M. Jin, X. Feng, J. Xi, J. Zhai, K. Cho, L. Feng, L. Jiang, "You have full text access to this contentSuper-Hydrophobic PDMS Surface with Ultra-Low Adhesive Force", *Macromolecular Rapid Communications,* Vol. 26, No. 22, 2005, pp. 1805-1809.

[18] M. T. Khorasani, H. Mirzadeh, "You have full text access to this contentIn vitro blood compatibility of modified PDMS surfaces as superhydrophobic and superhydrophilic materials", *Journal of Applied Polymer Science,* Vol. 91, No. 3, 2004, pp. 2042-2047.

[19] M.W. Simon, K.T. Stafford, D.L. Ou, "Nanoclay Reinforcement of Liquid Silicone Rubber", *Journal of Inorganic*

Organometallic Polymers and Materials, Vol. 18, No. 6, 2008, pp. 364-373.

[20] M.I. Aranguren, E. Mora, C.W. Macosko, "Compounding Fumed Silicas into Polydimethylsiloxane: Bound Rubber and Final Aggregate Size", *Journal Of Colloid and Interface Science*, Vol. 195, No. 2, 1997, pp. 329-337.

[21] P.N. Manoudis, I. Karapanagiotis, A. Tsakalof, I. Zuburtikudis, B. Kolinkeová, C. Panayiotou, "Superhydrophobic films for the protection of outdoor cultural heritage assets", *Applied Physics A*, Vol. 97, 2009, pp. 351-360.

[22] X. Ding, S. Zhou, G. Gu, L. Wu, "Facile fabrication of superhydrophobic polysiloxane/magnetite nanocomposite coatings with electromagnetic shielding property", *Journal of Coatings Technology and Research,* Vol. 8, no. 6, 2011, pp. 757-764.

[23] Brochure-CAB-O-SIL-Treated-Fumed-Silicas -for-Polyols-Used-in-Polyurethanes, http://www.cabotcorp.com/solutions/products-plus/fumed-metal-oxides/hydrophobic.%20(1).pdf. Cabot Co.,

[24] Product Technology for Silicone Heat Cured Elastomers, General Electric Silicones, http://www.gesilicones.com/silicones/americas/business/portfolio/hce/workshops/paperproducttech.shtml.

[25] S.J. Clarson, J.A. Semlyen, *Siloxane Polymers*, Prentice Hall, Englewood Cliffs, NJ 1993.

[26] D.J. Campbell, K.J. Beckman, C.E. Calderon, P.W. Doolan, R.M. Ottosen, A.B. Ellis, G.C. Lisensky, "Replication and Compression of Surface Structures with Polydimethylsiloxane Elastomer", *Journal of Chemical Education,* Vol. 76, No. 4, 1999, pp. 537-541.

[27] Nela Stafie, *Poly(Dimethyl Siloxane)-Based Composite Nanofiltration Membranes For Non-Aqueous Applications,* Ph.D. thesis, University of Twente, Enschede, The Netherlands, 2004.

[28] A.R. Wheeler, G. Trapp, O. Trapp, R.N. Zare, "Electroosmotic flow in a poly(dimethylsiloxane) channel does not depend on percent curing agent", *Electrophoresis*, Vol. 25, No. 7-8, 2004, pp.1120-1124.

[29] Socrates, G., Infrared and Raman Characteristic Group Frequencies, John Wiley & Sons, West Sussex, England, 2001.

[30] J. Pickering, D. van der Meer, G. Vancso, "Effects of contact time, humidity, and surface roughness on the adhesion hysteresis of polydimethylsiloxane", *Journal of Adhesion Science and Technology,* Vol. 15, No. 12, 2001, pp. 1429-1441.