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Facile route to nature inspired hydrophobic surface modification of phosphate glass using polyhedral oligomeric silsesquioxane with improved properties



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ABSTRACT

Hydrophobic polyhedral oligomeric silsesquioxane (POSS) molecules were utilized for the surface coating to improve the hydrophobicity of the surface of phosphate glass (Pglass). To maximize the Pglass surface hydrophobicity, protrusions on the Pglass surface were successfully prepared by Pglass particles on the surface of the bulk Pglass to mimick the lotus leaf, which has a superhydrophobic surface. The results showed that the combination of hydrophobic coating by POSS and improved roughness prepared by Pglass particles with air trapped on the Pglass surface yielded significantly increased hydrophobicity close to superhydrophobicity of lotus leaf. Chemical stability tests using ethanol and acetone confirmed stability of POSS on the Pglass surface. This result was supported by the XPS data showing an increase of bridging oxygen on the Pglass surface due to the condensation reaction between the hydroxyly functional groups of the Pglass and POSS. The relatively longer hydrophobic functional group of isooctyl compared to that of the isobutyl on the POSS cages gave larger contact angles than that of conventional silane, indicating that the POSS chemicals used are able to effectively produce the so-called "umbrella effect" mechanism that covers the intrincic hydrophilic surface of the phosphate glass using bulky molecules and grafted hydrophobic POSS chemical functional groups.

1. Introduction

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Water repellency of a solid surface is a very important property in fundamental research and practical applications related to surface structures and properties [1-4]. Water-repellent surfaces are usually prepared by low surface energy materials including alkyl chains [5-7] and fluorinated functional groups [4,8,9], showing higher contact angles. In addition, the actual contact area between water and solid surface is a critical factor that is strongly influenced by the surface roughness of solid materials. The contact angle (θ) between a flat solid surface and a liquid droplet is usually calculated using the Young's equation [10] as follows:

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \tag{1}$$

where, γ_{SV} , γ_{SL} , and γ_{LV} indicate the interfacial free energies per unit area of the solid-gas, solid-liquid, and liquid-gas interfaces, respectively. However, this equation is applicable only to a flat surface without roughness. For rough surfaces, Wenzel [11] and Cassie [12]

proposed models showing the relationship between roughness and water repellency. The Cassie model considered the air captured on the surface, which is a critical factor to achieve a hydrophobic surface. The models just mentioned show that hydrophobicity is governed by a combination of the low surface energy and surface roughness on the solid materials [13]. A number of researchers [14-18] reported application of the fundamental principle of the "lotus effect" to achieve improved contact angle and surface properties such as self-cleaning that is facilitated by water droplets moving easily on the hydrophobic surface to remove the dust from the surface of a lotus leaf. The authors just mentioned focused their research on low surface energy for increased contact angle and on understanding the relation between surface roughness and contact angle for hydrophobicity.

Other researchers have reported research efforts to achieve hydrophobic surface properties by mimicking hydrophobic surface structures in nature and their theoretical relationship between roughness of the surface and contact angle. For example, the effect of fractal structure [19,20], multiscale roughness [21,22], molecular level heterogeneity [23], and gravity [24] on hydrophobicity of surface have been studied

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Fig. 1. Schematic description of the surface modification of bulk Pglass with Pglass particles and POSS to improve hydrophobicity of the surface of Pglass.

to understand the structure of hydrophobic surfaces. Based on these theoretical studies, researchers fabricated artificial hydrophobic rough surfaces by various methods [25,26]. Shibuichi et al. [27] utilized alkylketene dimer (a kind of wax) to form a fractal surface to fabricate effective roughness. Lau et al. [28] used carbon nanotube forest to structure a rough matrix by mimicking the lotus effect using plasma enhanced chemical vapor deposition (PECVD). In addition, other reported methods were used to fabricate rough surfaces using polymer reconformation [29], lithography [30], and a multilayer method [31]. Note that when a rough surface is not composed of low-surface-energy materials, the surface is modified with low-surface-energy materials having long alkyl chain or fluorinated functional groups to achieve a larger contact angle [32,33]. According to the Wenzel model [11,34] as already mentioned, a surface with a contact angle less than 90° will show decreased contact angle as the roughness increased, indicating that an increase of roughness is effective for achieving hydrophobicity when there are low surface energy materials on the solid surface.

It is worthy to note that there are two key factors for developing superhydrophobic surfaces. The first factor is the low-surface-energy materials with long alkyl chains [6,7] or fluorine functional groups [4,8] and the second factor is roughness which has a small ratio of contact area of the solid surface-water droplet compared to the airwater droplet as already discussed. A combination of these two key factors yields superhydrophobic surfaces by coating the low surface energy materials on the prepared rough surface. The rough surface can be directly prepared either by using low surface energy materials to achieve a superhydrophobic surface or by using certain materials coated with low surface energy materials. The approach just described was used in the current research.

Specifically, in the current research, hydrophobic polyhedral oligomeric silsesquioxane (POSS) was utilized to coat the rough surface of tin fluorophosphate glass (Pglass) that was previously prepared by grafting microsize (< 75 um) Pglass particles. Note that Pglass has ultra-low glass transition temperature (T_g) and processing temperature compared to that of silicate based glasses [35,36]. The low T_g is a desired property for a wide range of applications of Pglass such as optoelectronics, bioengineering and protective coatings. In addition, the viscosity of Pglass is known to drop remarkably at relatively low

temperature, an attribute of the Pglass that is highly desirable during the Pglass processing. For example, the viscosity of Pglass (10 Pa·s) at 290 °C is same as that of honey at room temperature. Further, at 270 °C the viscosity of Pglass is less than that of Ketchup (50 Pa·s) at room temperature [35], which is a special intrinsic property of Pglass that is remarkably different from that of other inorganics like borosilicate glass material. To create a hydrophobic surface of the inorganic Pglass of this study, special organic-inorganic hybrid materials (e.g. POSS) were selected to bridge the gap between Pglass surface and hydrophobic organic functional group. Note that POSS has been widely used for bridging materials between organic and inorganic materials [37-39] due to its special chemical structure of (RSiO_{1.5})_n where R is generally organic functional groups grafted on the 3-dimensional inorganic silicate cage which is either open or closed [40]. Pglass coated by hydrophobic POSS is expected to be useful in a number of applications including optoelectronics and protective coating application. After coating hydrophobic POSS on the surface of Pglass, the coated Pglass can effectively protect the substrate from water, air that can cause surface corrosion, and electrical short on the surface of metals and electronic devices. This facile method used in the current study to increase roughness of the Pglass surface using Pglass particles described here will provide a fundamental basis for a better improvement of surface roughness. In addition, the feasibility of creating a hydrophobic coating with a number of POSS chemicals on the inorganic Pglass was evaluated in detail in this study.

2. Experimental methods

2.1. Materials and sample preparation

Tin fluorophosphate glass (Pglass) was synthesized with molar composition $50SnF_2 + 20SnO + 30P_2O_5$ using analytical grade reagents (i.e. tin(II) oxide (SnO), tin(II) fluoride (SnF₂) and ammonium dihydrogen phosphate ((NH₄)H₂PO₄)), which were purchased from Sigma-Aldrich and used as received. The mixture of reagents were melted in a carbon crucible under the conditions reported in the literature [35,41]. The molten materials in the furnace were poured onto a metal mold to yield disk-shaped pure bulk Pglass samples. In addition,

some of the pure Pglass samples were annealed at 200 $^{\circ}$ C and 250 $^{\circ}$ C up to 30 min for characterizations of the surface of bulk Pglass after the prescribed thermal treatments just mentioned.

Subsequently, a portion of the bulk Pglass samples was ground into particles and then sifted with a sieve of 75 um mesh size. To introduce a rough surface on the bulk Pglass, a disk shape of the bulk Pglass was placed on the Pglass powder in a glass bottle as depicted in Fig. 1 and rubbed about 5 times followed by tapping gently to remove the excess Pglass particles locally attached to the bulk Pglass (i.e., those particles that are not bonded via hydrogen bonds to the bulk Pglass surface). A torch flame was subsequently utilized to graft the H-bonded Pglass particles onto the bulk Pglass at elevated temperature to increase the roughness of the bulk Pglass. The Pglass particles and the surface of bulk Pglass were fused by the torch flame instantaneously.

Three types of POSS chemicals (i.e. trisilanol phenyl POSS (TSP-POSS), trisilanol isobutyl POSS (TSB-POSS), trisilanol isooctyl POSS (TSO-POSS)) used in this research were supplied by Hybrid Plastics Inc. These POSS samples with prescribed alkyl functional groups were used in this research to increase the hydrophobicity of the surface of Pglass. The bulk Pglass with the increased surface roughness using the grafted Pglass particles were coated with each POSS by dip coating. Both the bulk Pglass with fused (or grafted) Pglass particles and the pure bulk Pglass with smooth surface were dipped in a POSS/acetone solution in the concentration range of 0.1%-5.0% w/v (POSS/acetone), followed by the condensation reaction at 170-250 °C for 15 min in the furnace. A vacuum was applied for 2h at 110 °C to dry and increase the condensation reaction between P-OH of Pglass and Si-OH of POSS. In addition, three different concentrations (0.5%, 1.0% and 5.0% w/v) of TSP-POSS/acetone solution were utilized for TSP-POSS coating on the smooth surface of bulk Pglass to investigate the change of hydrophobicity of the surface of pure bulk Pglass as a function of the amount of POSS on the Pglass samples with smooth surface.

In another experiment, Isobutyl trimethoxy silane (IBTM-silane) (supplied by Gelest Inc.) was utilized as a control for coating the Pglass surface to compare the hydrophobicity among the surfaces coated by IBTM-silane, TSB-POSS, and TSO-POSS. The Pglass bulk samples were dip-coated in the water/ethanol (1:1) solution including hydrolyzed IBTM-silane. Note that for the silane coupling agent, the silanol formation via hydrolysis is necessary because silanes need to be hydrolyzed to have hydroxyl group for physical and chemical interaction with hydroxyl groups of Pglass. In addition, the 140 °C condensation temperature was applied because of the low evaporation temperature (154 °C) of IBTM-silane. A molar concentration of 6.32×10^{-3} mol/L (equivalent to a concentration of 0.5% w/v) was used for all the three samples (i.e. samples dip-coated with IBTM-silane, TSB-POSS, and TSO-POSS).

2.2. Characterizations

2.2.1. Scanning electron microscopy (SEM) – energy dispersive X-ray spectroscopy (EDX)

The surface modified bulk Pglass with Pglass particles and POSS were characterized using SEM and EDX to investigate the morphology and the distribution of elemental composition of the surface. The surface of the samples was coated with silver using Quorum Emitech K550X sputter coater to decrease the electric charge on the surface of the samples. FEI Quanta 200 scanning electron microscope (SEM) operating with 20 kV and energy dispersive X-ray spectroscopy (EDX) was carried out on the samples with Thermo Scientific NSS Spectral Imaging System with NSS 2.2 X-Ray Microanalysis Software.

2.2.2. Contact angle

Water contact angle measurement was carried out via the sessile drop technique using FTA200 optical contact angle measurement system (FTA Inc.) connected to Prosilica GC750 camera (Allied Vision Technologies). The obtained data from the contact angle measurements were analyzed with FTA32 software. A sessile drop of $10 \,\mu$ l of distilled water was deposited with a syringe on the surface of the pure bulk Pglass and the surface-modified bulk Pglass with Pglass particles for roughness and POSS molecules for hydrophobicity in air at room temperature. To reduce the influence of the size difference of the water drop, the contact angle measurement was started within 5 s after depositing the water drop on the surface of samples. Contact angles were measured 5 times at one point within 5 s, and repeated for a minimum of at least 3 different points for each sample. The average and standard deviation of these data were calculated and reported in this manuscript.

2.2.3. Chemical stability of POSS-modified surface.

Chemical stability tests of the POSS-modified surface of the bulk Pglass with Pglass particles were performed by observing the relationship between the change in the time evolution and the water contact angles. The contact angles of the surface-modified samples with the three types of POSS (i.e. TSB-POSS, TSO-POSS, and TSP-POSS) were measured and the samples were subsequently immersed into acetone and ethanol solvents for 10 min and 60 min, respectively, to dissolve the POSS molecules. The immersed samples were shaken about 10 times in the solvents before being taken out and then dried in the atmosphere for 5 min and followed by vacuum drying for 1 h at 110 °C to evaporate the solvent completely.

2.2.4. X-ray photoelectron spectroscopy (XPS)

XPS spectra were obtained on the rectangular samples (1 cm \times 1 cm \times 2 mm) using a Kratos AXIS 165 spectrometer equipped with monochromatic Al-K α X-rays at 12 kV and 12 mA as the excitation radiation in UHV, 5 \times 10⁻⁹ Torr. A charge neutralizer was utilized to reduce surface charging on the surface modified Pglass samples with POSS because a non-conductive material usually accumulates the positive charge in the area irradiated by the x-ray beam which can cause a decrease of the kinetic energy of the emitted photoelectrons resulting in a shift of peaks to higher binding energy in the spectrum [42–44]. The obtained spectra were fit and deconvoluted using a Gaussian curve-fitting method in Origin software (OriginLab Corp.).

3. Results and discussion

3.1. Characterization of pure Pglass surface

A glass surface such as calcium phosphate glass generally has hydrophilic properties with contact angles of about 20-60° due to the hydrophilic [45-47]. The tin fluorophosphate glass (Pglass) showed about 80° of contact angle due to the fluorine in the Pglass composition as shown in Fig. 2. The Pglass containing fluorine has a unique fundamental advantage of less hydrophilic surface compared to that of other typical hydrophilic glasses [47]. The migration to surface of fluorinated compound with hydrophobic property is well known [4,48,49]. For example, Tan et al. [50] reported results of phase separation of fluorinated urethane phase to the surface of the bulk samples due to the low surface energy of fluorinated segments, which is consistent with the result reported by Chapman et al. [51]. The authors just mentioned reported the alignment of fluorocarbon segments of polymer chains on the surface of polymer materials due to the low surface energy of fluorinated side chains. In addition, Clifford [52] reported that phosphate and fluorine cause phase separation in the glass phase. Further, Vogel [53] reported that replacement of oxygen ion by fluorine ion increased the phase separation in silicate glass.

We found an evidence supporting less hydrophilicity of the surface of bulk Pglass according to the distribution of Pglass compositions. Fig. 3(a, b) showed the composition analysis results by EDX on the surface of bulk Pglass and the Pglass particles from the inside of the pure bulk Pglass, respectively. This figure indicates that there is a significant difference of fluorine composition between the surface of bulk Pglass (16.3 wt%) and the Pglass particle (9.7 wt%) from the inside of



Fig. 2. (a) Contact angle o n the surface of pure bulk Pglass and (b) schematic of the functional groups of the Pglass surface.

bulk Pglass. This difference of composition of fluorine element is conjectured to be the result of the movement of the hydrophobic fluorinated Pglass molecules to the surface of bulk Pglass. Fluorine in the glass generally disrupts the glass network and replaces bridging oxygen by non-bridging fluorine, which might produce relatively small fluorinated Pglass molecules, and facilitate the phase separation tendency in Pglass materials [52,54].

As shown in Fig. 4 the XPS spectra of Sn describes the ratio of Sn-F₂O and Sn-O₂F on the surface of Pglass and the fracture surface of Pglass. According to this figure, the ratio of the amount of Sn-F₂O to Sn-O₂F is 1.6%:98.4% on the fracture surface of the bulk Pglass, indicating

that the Sn atoms connected with one fluorine is a major portion of the inside of the bulk Pglass, which is consistent with the result reported by York-Winegar [55]. However, the XPS data obtained from the surface of the bulk Pglass showed 45.5%:54.5% for Sn-F₂O to Sn-O₂F, indicating that there is more Sn connected with two fluorine atoms on the surface of bulk Pglass. These results suggest that the Pglass molecules with tin connected with two fluorine atoms were phase-separated and moved to the surface of Pglass during the synthesis and cooling process because the molecules with more non-bridging fluorine are small and hydrophobic as already discussed. Overall, the Pglass showed less hydrophilicity due to the fluorine elements on the surface different from other



Fig. 3. EDX results of the surface of (a) the pure bulk Pglass and (b) the Pglass particle as described in the text.



Fig. 4. XPS spectra of (a) the fractured surface of bulk Pglass and (b) the surface of bulk Pglass.

Table 1

Contact angle data on samples after POSS coating on the smooth surface of bulk Pglass.

Sample (TSP-POSS/acetone)	Contact angle (°)	Std
Pure TFP 0.1% w/v 0.5% w/v 1.0% w/v 5.0% w/v	81.6 84.8 91.6 89.4 91.3	2.64 2.31 1.21 1.93 0.34
3.070 W/V	91.5	0.54

Table 2

Calculated contact angle for rough surface (θ) as a function of the roughness factor (R_f) for various arbitrary contact angles for smooth surface (θ_0) from the Wenzel model.

	$R_{f}(1)$	R _f (1.2)	R _f (1.5)	R _f (1.7)	$R_{f}(2.0)$		
Initial angle (θ_0)	Angle of rough surface (θ)						
50	50	39.5	15.4	< 0	< 0		
70	70	65.8	59.1	54.4	46.8		
90	90	90.0	90.0	90	90		
110	110	114.2	120.9	125.6	133.2		
130	130	140.5	164.6	> 180	> 180		



Fig. 5. Contact angle of the smooth surface of bulk Pglass with TSB-POSS, TSO-POSS, and TSP-POSS coating.

glasses which have very strong hydrophilic surface. It is plausible to propose that the fluorinated Pglass molecules prepared by replacing bridging oxygen with non-bridging fluorine are phase separated in the samples, causing less hydrophilicity on the surface of the bulk Pglass.



Fig. 6. Contact angle (θ') for hydrophobic rough surface with trapped air as a function of the wetted solid surface area fraction (f1) for various contact angles with respect to the Cassie model. (Superposition of actual contact angle data obtained from samples prepared by the surface coating with \blacktriangle : TSP-POSS, \bigcirc : TSB-POSS, \blacksquare : TSO-POSS).

3.2. Effect of POSS coating on hydrophobicity of the smooth Pglass surface

As already mentioned, Pglass has a hydrophilic surface because the contact angle is about 80° less than 90°, which means that the surface cannot repel water completely. To improve hydrophobicity of the surface of bulk Pglass, various concentrations of TSP-POSS in acetone were applied for hydrophobic coating on the bulk Pglass using a dip coating method because TSP-POSS is known to exhibit hydrophobic properties as reported in the literature [56,57]. The obtained contact angle data are listed in Table 1 for the surface of the uncoated Pglass and coated Pglass with various TSP-POSS concentrations. The contact angles gradually increased from 81.6° to 91.3° with increasing TSP-POSS concentration from 0% w/v to 5.0% w/v (POSS/acetone). A contact angle of more than 90° was achieved using TSP-POSS coating on the bulk Pglass. To protect metal substrates or electric circuits in electronic devices completely from the water vapor, improved hydrophobic surfaces are desirable. Note that superhydrophobicity can be generally achieved by the combination of low surface energy property of surface material and surface roughness. According to the Wenzel model [11,34] (modified from Young's equation), for a water droplet in contact with a homogeneous rough surface without air pockets, the contact angle is calculated by this Eq. (2) below.

$$\cos\theta = R_f \cos\theta_0 \tag{2}$$

where, θ_0 is the contact angle for a smooth surface, θ is a rough surface, and R_f (> 1) is a roughness factor defined as the ratio of the solid-liquid area (A_{SL}) to its projection on a flat plane (A_{FP}), $R_f = A_{SL}/A_{FP}$. Based on



Fig. 7. SEM images of the surface of (a) the pure bulk Pglass, (b) the bulk Pglass with particles, (c) the bulk Pglass with distribution of protrusions prepared by Pglass particles, and (d) bulk Pglass fused with Pglass particles as described in the text.



Fig. 8. Effect of POSS type and concentration on contact angle.

the Wenzel model, hydrophobicity of a smooth surface with a contact angle greater than 90° will be improved as the R_f is increased. In contrast, the contact angle for the rough surface will be decreased with increasing R_f when θ_0 is less than 90°. The calculated contact angles from Eq. (2) are listed in Table 2.

To achieve superhydrophobic surface on the Pglass using

hydrophobic POSS, the roughness should be applied on the bulk surface and more hydrophobic POSS will be more effective according to the Wenzel model. The TSB-POSS and TSO-POSS used here are good candidates due to their hydrophobic functional groups (i.e., isobutyl and isooctyl, respectively). Three different POSS (TSP-POSS, TSB-POSS, and TSO-POSS) were coated on the smooth surface of bulk Pglass using the dip coating process already described in the experimental section. As expected, the contact angle of the surface of bulk Pglass coated with TSB-POSS and TSO-POSS are found to be larger than that of the TSP-POSS coated sample. The TSB-POSS and TSO-POSS-coated surfaces showed contact angle of $95.2^{\circ} \pm 0.79^{\circ}$ and $95.3^{\circ} \pm 1.29^{\circ}$, respectively, which is larger than $91.6^{\circ} \pm 1.21^{\circ}$ obtained from the TSP-POSS as shown in Fig. 5. These contact angles (greater than 90°) have potential ability to yield superhydrophobic surface with roughness as predicted by the Wenzel model (Eq. (2)), (see Table 2).

3.3. Effect of applying roughness on the surface of bulk Pglass using Pglass particles

Surface roughness is a critical factor to achieve superhydrophobicity on the surface of materials as reported by many researchers [10,19,27,32,58,59]. Cassie et al. [12,60,61] reported that air pockets in the surface can effectively enhance the hydrophobicity of a rough surface according to the following Eq. (3):

$$\cos\theta = f_1 \cos\theta_1 + f_2 \cos\theta_2 \tag{3}$$

where, the contact angle θ' of a rough hydrophobic surface with trapped air is the combination of a surface area fraction f_1 with a contact angle θ_1 for water-solid surface and the other surface area fraction f_2 with a contact angle θ_2 for water-air surface, indicating that f_2 represents the area fraction of trapped air. Eq. (3) can be modified by assuming the water contact angle for air is 180° [10,60] as follows:



Fig. 9. (a) SEM image and (b) EDX result on the surface of bulk Pglass coated with 0.5% w/v TSP-POSS/acetone and (c) SEM image and (d) EDX result on the surface of bulk Pglass coated with 5.0% w/v TSP-POSS/acetone.



Fig. 10. SEM image of (a) nature inspired hydrophobic Pglass surface modified by Pglass particles for roughness and POSS coating for low surface energy, and (b) the surface structure of lotus leaf having super-hydrophobicity. (Fig. 10(b) is reproduced with permission from Ref. [15]. Copyright (1997), Springer Nature).



Fig. 11. Schematic description of microstructure of the surface of bulk Pglass with protrusion, TSO-POSS coating, and trapped air for enhanced hydrophobicity.

$$\cos\theta = f_1 \cos\theta_1 + (1 - f_1) \cos 180^o \tag{4}$$

 $\cos\theta' = f_1 \cos\theta_1 - (1 - f_1) \tag{5}$

where, $f_1 + f_2 = 1$ and the equation can be rewritten as following:

$$\cos\theta = f_1 \cos\theta_1 - f_2 \tag{6}$$

where, θ' is the contact angle of a hydrophobic rough surface composed of two different materials (i.e. solid and air), f_1 and f_2 are the fractions of solid surface and air in contact with water droplet, respectively, and θ_1 is the contact angle for the water-solid surface. The dependence of the contact angle on the fraction of solid surface in contact with water droplet is presented in Fig. 6 as calculated from Eq. (6) (Cassie model). This model implies that even if the contact angle of the smooth surface is less than 90°, it can achieve the superhydrophobicity with a small number of f_1 with air trapped in the surface. The actual contact angle data obtained from the samples modified with the three different POSS samples used in the current study are shown together in Fig. 6, which indicates that the roughness (f_1) of the samples is 0.3–0.4. This result suggests that contact angles can be increased if the roughness of the samples has a f_1 value smaller than 0.3. Overall, the contact angle would significantly increase with decreasing f_1 , indicating that the decrease of contact area between solid and water droplet on the hydrophobic rough surface with air trapped would increase the contact angle.

Note that hydrophobicity is the combination of hydrophobic materials and rough surface with air pockets in the surface as reported in the literature. TSB-POSS and TSO-POSS were applied in this study to achieve relatively smaller surface energy due to the alkyl chains on the POSS cage with the roughness of the surface of bulk Pglass. As already described in Fig. 1 in the experimental section, the micro-sized (< 75 um) Pglass powder was applied on the bulk Pglass and fused (or grafted) on the bulk surface using a torch flame. The instantaneously melted Pglass particles and the bulk Pglass surface were fused together and connected chemically as shown in Fig. 7. The micro-sized protrusions formed by Pglass particles enhanced the roughness of the surface of bulk Pglass for hydrophobicity. Fig. 8 shows effects of POSS type and concentration on the contact angles of the samples with the rough surfaces. The obtained maximum contact angles of the POSS-coated samples were obtained at a concentration of 0.5% w/v (POSS/acetone), showing 125.7°, 130.7°, and 138.2° of contact angles prepared by using

Table 3

Chemical stability of coated-POSS on the surface of bulk Pglass.

the TSP-POSS, TSB-POSS, and TSO-POSS, respectively. This result shows a significant improvement in the contact angle of the samples with rough surfaces compared to that of the samples with the smooth surface shown in Fig. 5. There is a significant change of the contact angle due to the roughness increase with trapped air in the surface of Pglass as expected. These results confirm that the hydrophobic property of the surface is the result of a combination of the surface energy of materials and the roughness with trapped air on the surface.

Another result illustrating the critical effect of roughness for hydrophobicity is shown in Fig. 9, indicating that higher concentration of POSS on the surface of bulk Pglass decreased the hydrophobicity significantly reported earlier in Fig. 8. For example, the concentration of 0.5% w/v TSP-POSS achieved 125.7° while 5.0% w/v TSP-POSS vielded a contact angle of only 96.4° contact angle. The roughness of the bulk Pglass surface with 0.5% w/v TSP-POSS shown in Fig. 9(a) was greater than that of the bulk Pglass surface with 5.0% w/v TSP-POSS as shown in Fig. 9(c), which indicates that the relatively thick POSS layer covered a small size of protrusion and reduced the roughness of the surface, resulting in a decrease of the contact angle. The EDX data (Fig. 9(b)) with 0.5% w/v TSP-POSS showed that the compositions of elements at positions #1 and #2 are quite similar to each other, indicating a homogeneous coating. However, in Fig. 9(d) with 5.0% w/v TSP-POSS the compositions of carbon and silicon elements from POSS molecules at position #1 (i.e. C = 23.2%, Si = 1.3%) are larger than that of position #2 (i.e. C = 18.4%, Si = 0.7%), indicating that more POSS was coated on the surface of the bulk Pglass than on the surface of the protrusion. This result is another evidence of the thick POSS coating on the bulk Pglass surface, causing the decrease of the roughness of the surface of samples and the associated reduced contact angles.

Fig. 10(a) shows the morphology of the POSS-modified surface of bulk Pglass with increase of the roughness using Pglass particles, which is remarkably similar to the morphology of the surface of the lotus leaf [6,15]. This obtained nature-inspired surface effectively enhanced hydrophobicity of the surface of bulk Pglass. Furthermore, if the f₁ value of solid-water contact ratio can be reduced with regular and sharp protrusion of Pglass particles on the bulk Pglass surface, superhydrophobicity with more than 150° of contact angle could be achieved in this system using hydrophobic POSS. The illustrative schematic description in Fig. 11 shows the microstructure of the surface of bulk Pglass with protrusion prepared using Pglass particles as already described. This rough surface shown was coated by TSO-POSS and has trapped air. The water droplet could not contact directly with the surface of bulk Pglass due to the hydrophobic isooctyl chains on POSS cages on the protrusion of Pglass particles and the trapped air on the surface.

3.4. Chemical stabilization of POSS on the bulk Pglass surface.

Chemical stability tests were conducted using acetone and ethanol to investigate the stability of the coated POSS on the surface of bulk Pglass due to the solvent's outstanding ability to dissolve POSS. In addition, the surface of bulk Pglass was completely wetted by acetone because acetone has both polar and nonpolar properties. The contact angle of the hydrophobic bulk Pglass samples with roughness and hydrophobic POSS was measured after chemical stability tests using the acetone and ethanol for 10 min and 60 min. Before taking samples from

Time	TSP-POSS, 0.5% w/v		TSB-POSS, 0.5% w/v		TSO-POSS, 0.5% w/v	
	Acetone	Ethanol	Acetone	Ethanol	Acetone	Ethanol
0 min 10 min 60 min	$\begin{array}{rrrr} 125.3^{\circ} \ \pm \ 2.76^{\circ} \\ 122.4^{\circ} \ \pm \ 4.86^{\circ} \\ 125.1^{\circ} \ \pm \ 5.07^{\circ} \end{array}$	$\begin{array}{rrrr} 124.8^{\circ} \ \pm \ 3.84^{\circ} \\ 124.1^{\circ} \ \pm \ 1.77^{\circ} \\ 124.3^{\circ} \ \pm \ 3.56^{\circ} \end{array}$	$\begin{array}{rrrr} 129.1^{\circ} \ \pm \ 1.03^{\circ} \\ 128.7^{\circ} \ \pm \ 1.20^{\circ} \\ 128.4^{\circ} \ \pm \ 1.03^{\circ} \end{array}$	$\begin{array}{rrrr} 128.0^{\rm o} \ \pm \ 2.70^{\rm o} \\ 127.4^{\rm o} \ \pm \ 1.89^{\rm o} \\ 128.5^{\rm o} \ \pm \ 1.95^{\rm o} \end{array}$	$135.4^{\circ} \pm 1.51^{\circ}$ $135.1^{\circ} \pm 1.69^{\circ}$ $133.4^{\circ} \pm 1.99^{\circ}$	$\begin{array}{rrrrr} 134.4^{\circ} \ \pm \ 2.00^{\circ} \\ 134.8^{\circ} \ \pm \ 2.39^{\circ} \\ 134.5^{\circ} \ \pm \ 5.05^{\circ} \end{array}$



Fig. 12. The XPS O 1s spectra of (a) the surface of pure bulk Pglass and (b) the TSP-POSS coated surface of bulk Pglass.



Fig. 13. The structural effect on the contact angle of bulk Pglass as a function of the coating materials of (a) IBTM-silane, (b) TSB-POSS, and (c) TSO-POSS.

each solvent after the test time, the samples were shaken vigorously. The contact angles measured in the chemical stability test using acetone and ethanol solvents from 0 min to 60 min are listed in Table 3. Note that the contact angles of samples in the stability test in the acetone and ethanol did not change significantly, indicating that POSS molecules coated on the Pglass are stable due to the chemical bonds between the hydroxyl group of Pglass and POSS as expected, and as previously reported by other researchers [35,62,63]. Chemical reaction between Si-OH of 3-((methacryloyloxy) propyl) trimethoxysilane (MEMO) and P-OH of 2-(methacyloxyloxy)ethyl phosphate (EGMP) resulting in formation of P-O-Si bonds by thermal curing at 120 °C was reported by Kannan [62]. In addition, Styskalik et al. reported that P-O-Si bonds are formed by the condensation of Si-OH and P-OH at 150 °C, which is a lower temperature than 170–250 °C applied for the condensation reaction between POSS and Pglass in our experiments.

The XPS O 1s spectra was conducted to estimate the ratio of the nonbridging oxygen (NBO) to bridging oxygen (BO) on the surface of pure Pglass and POSS-coated Pglass. Generally, the BO is related to P-O-P linkage and the NBO is associated with terminal oxygen such as $P-O^-$ including P-O-Sn in the Pglass as discussed by Brow et al. [64]. The obtained XPS O 1s spectra was deconvoluted to show the peaks that represent BO and NBO as shown in Fig. 12. The obtained data show that 64.9% of BO and 35.1% of NBO are observed on the surface of pure Pglass. After TSP-POSS coating on the bulk Pglass, the BO was increased to 70.0% and NBO was decreased to 30%. This finding is attributed to the formation of new chemical bonds of P-O-Si increasing BO and decreasing NBO, which is consistent with the result of chemical stability of POSS on the surface of Pglass. In addition, a portion of BO signal from the POSS-coated Pglass sample might be due to the BO in Si-O-Si of POSS as reported in previous research [35]. Interestingly, the ratio of BO to NBO was 64.9%: 35.1% in the O 1s spectra of the pure bulk Pglass surface in our results which is different from the results of 5%:95% reported by York-Winegar et al. [55] and 5.1%:94.9% reported by Kim et al. [35] on the fractured surface of pure bulk Pglass. As already discussed, we believe that phase separation occurred during the melting and cooling process of Pglass and the relatively hydrophobic molecules with BO were phase-separated to the surface of the pure bulk Pglass.

3.5. Umbrella effect of POSS for hydrophobicity

The water repellent property of POSS-coated Pglass was increased due to the hydrophobic functional groups (i.e. phenyl, isobutyl, and isooctyl) on the POSS cage. To further investigate the chemical structure effect of the coating materials for hydrophobicity, a fixed molar concentration of IBTM-silane and TSB-POSS was applied on the bulk Pglass, and then the contact angle was measured. Note that TSB-POSS and IBTM-silane both have isobutyl functional groups. Fig. 13 shows an increase of contact angle that is consistent with the structural effect of hydrophobic molecules on the bulk Pglass. In fact, the contact angle of a water droplet on TSB-POSS-coated sample (131.0°) showed higher than that of the IBTM-silane coated sample (126.3°), indicating that there is a structural effect of functional groups for hydrophobicity. The bulky POSS molecules can cover a relatively wide area of the hydrophilic substrate and have higher contact points with water droplet in the contact angle measurement in agreement with the so-called "umbrella effect" reported in the literature [65–69]. As expected, the longer alkyl functional groups (isooctyl, 138.2°) apparently produced a larger contact angle than that of the shorter alkyl functional group (isobutyl, 131.0°) due to the higher contact point between the relatively longer isooctyl functional groups and water droplets (see Fig. 13).

4. Conclusions

The results of this study showed that it is possible to significantly improve hydrophobicity of Pglass surface using various POSS chemicals with hydrophobic functional groups such as phenyl, isobutyl, and isooctyl on the POSS cage and Pglass particles for increase of roughness. Interestingly, the surface of pure bulk Pglass showed a less hydrophilic property compared to that of typical glasses (e.g. borosilicate glasses) due to the fluorine in the Pglass molecules. The combination of the increased surface roughness using Pglass particles and low surface energy from the hydrophobic POSS produced significantly improved hydrophobicity close to superhydrophobicity on the surface of bulk Pglass as predicted by the Cassie model, which considers trapped air in the surface of substrate.

The chemical stability test using acetone and ethanol showed that the POSS samples used here were strongly chemically bonded to the surface of Pglass. Acetone used as a solvent in POSS/acetone solution for dip coating of Pglass did not change the hydrophobicity of the Pglass surface, indicating that POSS and Pglass were chemically bonded via a condensation reaction between Si-OH of POSS and P-OH of Pglass as supported by the observed increased ratio of BO to NBO due to the obtained Si-O-P bond. It was observed that bulky POSS molecules with low surface energy functional groups and longer hydrophobic alkyl chains increased the contact angle because they can cover the hydrophilic surface effectively. This study showed that nature-inspired Pglass surface morphology, resembling lotus leaf, was successfully prepared by using Pglass particles for roughness and hydrophobic POSS for low surface energy. This result is theoretically consistent with that predicted by the Cassie model, which considers air trapped in the surface. Hydrophobically coated Pglass with ultra-low Tg and low processing temperature has the potential to be efficiently used as a sealant and a coating material to protect metal substrates and electronic devices from corrosion and electric short circuits due to water vapor and liquid water, indicating that the materials of this study might be useful for a wide range of industrial applications such as electronic device, biomedical applications, and optoelectronics.

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