Hydrophobic thiol-ene surfaces fabricated via plasma activation and photo polymerization

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Abstract. Alumina, such as glazed alumina for electrical insulator, operated in an open field subjects to a very harsh condition; resulting in lifetime shortening. Coating hydrophobic layer on alumina surface can help prolonging its lifetime. In this study, 25×25 mm alumina sheets were used as substrates. The hydrophobic composite polymers were prepared from (3-mercaptopropyl)trimethoxysilane(MPTMS), 2,4,6,8-tetramethyl-2,4,6,8tetraavinylcyclotetrasiloxane(TMTVSi), pentaerythritoltetra(3-mercaptopropionate)(PETMP), 2,2-dimethoxy-2-phenylaceto phenone(photoinitiator) and heptadecafluorodecylmethacrylate(HEFDMA) via the thiol-ene reaction. The alumina sheets were first activated by dielectric-barrier discharge plasma to improve its adhesion. All the polymers were found to optimize at the ratio of (MPTMS:TMTVSi:PETMP:HEDFMA) to 4:2:1:2 for coating on the alumina substrate. To enhance polymerization, 2,2-dimethoxy-2-phenylaceto phenone was also used as a photoinitiator A proper mixing sequence in the thiol-ene reaction results in film with excellent surface retention after prolong soaking in solvent such as acetone. FTIR shows that S-H and C=C functional groups have significantly changed after photopolymerization and thermally cured. The static contact angle increase from mere 53.0°±1.5° of the uncoated substrate to 120.0°±1.2° after coating. SEM shows the film with clear appearance of a few-micron thick. Under AFM, the coated surface roughness was about 9.3 nm with evenly distributed spikes of a few nanometer in height. The cross-cut test also confirmed the film was very smooth and none of the square of the films detached.

1. Introduction  
Alumina has a wide range of applications; following its outstanding properties for example very excellent insulator, excellent dielectric properties in ranges of DC to GHz frequencies, high strength and stiffness. The alumina was chosen as main material for manufacturing the high voltage insulator for electric circuit, power grid and high voltage transport power line. The glazing is normally applied in the final processing stage of alumina as a protection layer. This glaze has approximately four to six years in lifetime [1]. However, in some areas with hostile environment e.g., salty vapors in coastal area, defecation problem in roosts of birds, smoke in an industrial area and smog that emit from automobile at highways or in highly populated city; those pollutions can reduce the lifetime further [2].
There are quite a few alternatives for this problem. One way is by coating the insulator with a layer of specific property, e.g., hydrophobic layer. It can reduce time and area of interaction by the pollutions and contaminations. There are two major approaches for enhancing hydrophobic property. One approach is to apply hydrophobic molecules like fluorocarbon group on the surface by means of coating, for example, polyhedraloligomeric silsesquioxane \[3\] and polyhedraloligomeric silsesquioxanes with corner fluoralkyl modification \[4\]. The other approach is to modify surface geometric texturing by creating the micro- or nano-roughness. This approach may be achieved by chemical and physical deposition, for example, spraydeposition hydrophobic silica nanoparticles \[5\], and plasma polymerization combined with nanoparticles \[6\], and fluorinated polyhedral oligomeric silsesquioxanes \[3\].

The experiment in this work generally focuses on promoting the strong bonding and the durability by using plasma surface treatment \[7\] and the modification of composite polymer from thiol-ene. The unique characteristic of hydrophobic and the durability also can be achieved via thiol-ene modified polymer, which thiol-ene reactions are consider as a click chemistry reaction that give a high yield product, stereo-selectivity and high reaction rate \[8\].

2. Material and methods

2.1. Material
Alumina sheets (Al\(_2\)O\(_3\)) of purity 96%) were purchased from Kyocera Corporation, Japan. They were shaped to have dimension of 25 × 25 × 0.68 (W × L × Th) mm. (3-mercaptopropyl) trimethoxysilane(MPTS), 2,4,6,8 -tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (TMTVSi), Penta erythritoltetraakis(3-mercaptopropionate)(PETMP) and 2,2-dimethoxy-2-phenylacetophenonmeth acrylate(DMPA) as photoinitiator were obtained from Sigma-Aldrich. Heptadecafluoro decyl methacrylate(HDFDMA) was gained from Wako Chemicals, Japan. Prior to the experiment, alumina substrates were cleaned in an ultrasonicate bath with cleaning reagents in the series as follow; dish washing soap, acetone, ethanol, methanol, and A3 deionized water, for 15 minutes each.

2.2. Preparation of thiol-ene solution
The main composition polymers in this work were MPTMS, HDFDMA, TMTVSi, and PETMP. They were synthesized via thiol-ene reaction. MPTMS and TMTVSi were mixed first in acetone solution as ratio 1:1:15 respectively; with 2\%wt of photo initiator (DMPA). During this process, the solution was maintained to mix well by using the magnetic stirrer overnight. The full-composition of thiol-ene solution was synthesized as follow; first by adding HDFDMA and PETMP into the mixture of MPTMS + TMTVSi solution and maintain the ratio at 4:2:2:1:15 \%wt (MPTMS:TMTVSi:HDFDMA:PETMP:Acetone). The mixture was ultra sonicated for 30 minutes and stirred overnight by the magnetic bar before usage for coating.

2.3. Plasma surface treatment
The surface of alumina sheets were activated by the dielectric barrier discharge plasma. The dielectric barrier discharge is generated using alternating current in RF frequency in the gap between the electrodes. The sample was placed at the center of the gap. Argon was fed at 1 liter/minute into the chamber during the process. The plasma surface treatment process was conducted at RF power of 34 W for 5 minutes.

2.4. Film coating
The films on the surface of alumina consist of MPTMS+TMTVSi, HDFDMA and PETMP. Alumina sheets were coated by the spin-coating technique. The thickness of the thiol-ene films was varied
through rotation speed. Spin-coating time in the coating process was fixed at 30 seconds to ensure complete evaporation of solvent.

2.5. UV photopolymerization and curing
After coated by the pre thiol-ene films, alumina substrates were exposed to UV-A light at 368 nm to activate the thiol-ene reaction. They were placed at the distance of 5 cm below the UV-A lamp. The UV intensity was approximately 51 mW/cm². After finishing the photopolymerization, the alumina substrate was transferred to oven for curing; at 45°C for 2 hours.

2.6. Characterization

2.6.1. Contact angle. The angle was obtained by measure the angle of the liquids droplet on the surface of sample. ImageJ with plug-in drop snake was used such a measurement. The surface free energy of the sample was calculated via the Fowkes equation $\gamma = \cos \theta + 1 = 2(\gamma_1^a)^2(\gamma_1^d)^2 + (\gamma_2^a)^2(\gamma_2^d)^2$. The equation requires at least two contact angles from different liquids. In this work, water ($\gamma = 72.3$ mN/m) and diiodomethane ($\gamma = 50.88$ mN/m) were chosen for high and low surface tension liquids, respectively.

2.6.2. Adhesiveness test. Alumina substrates were divided to two groups; one group was plasma-treated on their surface before coating with polymeric films. For comparison, alumina substrates with their surface untreated were used as the second group. The samples were tested for their mechanical durability or adhesiveness according to the paint and varnishes “cross-cut” test following the ISO 2409:2013 [9] standard.

2.6.3. Vibrational spectroscopy and surface morphology. Fourier transform infrared (FT-IR) spectra were obtained by using a Nicolet 6700 FT-IR spectrometer. The vibrational spectra were collected in the range between 4000-650 cm⁻¹ in wavenumber. The surface morphology of the sample was obtained by scanning electron microscope (SEM, JEOL JSM 6400). The 3D surface profiles and surface roughness were obtained by atomic force microscope (AFM, SII SPA 400).

3. Result and Discussion

3.1. Synthesis characterization, and chemical composition of full-composition

The component of molecules in the full-composition films was synthesized via the thiol-ene reaction as described in the previous section. The coating solution before photopolymerization has consisted of the MPTMS+TMTVSi, HDFDMA and PETMP. In the last step of thiol-ene reaction, the thiol PETMP has four available sides for bonding the with -ene group (MPTMS+TMTVSi and HDFDMA). There are five possible structures that can occur in the final process, namely $A_0B_4, A_1B_3, A_2B_2, A_1B_1$ and $A_2B_0$ ($A = $ MPTMS+TMTVSi and $B = $ HDFDMA) with the possibility of 6.25%, 25%, 37.5%, 25%, 6.25%, respectively. Various functional groups characterized by their vibrational frequency in FT-IR.

**Figure 1** shows FTIR spectra of three different films coated on alumina. When adding TMTVSi to MPTMS, the characteristic vibration peaks at 1260, 1050 and 1000 cm⁻¹ of Si-O-Si band, which give the evidence of the thiol-ene polymer network formation [5], have evidently stood out in comparison
to the case MPTMS+HDFDMA. The presence of =C-H peaks at 790 and 700 cm\(^{-1}\) from TMTVSi well noted. Also evident in the spectrum of MPTMS+TMTVSi is the peak at 1400 cm\(^{-1}\) of Si-O. In the case of full-composition film (solid line in Figure 1), where MPTMS, TMTVSi, HDFDMA and PETMP were mixed, there appeared the characteristic vibration peak of 1730 cm\(^{-1}\) of C=O from PETMP. The greater proportion of C=C with their characteristic peaks at 1050 and 1000 cm\(^{-1}\) and the presence of C-F in range of 1300-1000 cm\(^{-1}\) in the full-composition film have lessen the otherwise prominence peaks of Si-O-Si in this region.

**Figure 1** FTIR spectra of coated alumina

**Figure 2.** Contact angle of Alumina sheet (AS), and alumina coated with MPTMS (M), MPTMS + TMTVSi (MT), MPTMS+HDFDMA (MH), full-composition (FC)

### 3.2. Contact angles

Contact angles of water and diiodomethane on the bare and coated alumina are shown in Figure 2. Water contact angle were found to increase when alumina was coated. The contact angle on the polymer film become larger with more composition added, (as labeled as M, MT, MD and FC in Figure 2). Similar trend was also observed with diiodomethane contact angle. Among all these films, film with MPTMS+HDFDMA shows the high of water contact angle of 130°± 1.5°. It can be understood that the fluoroalkyl function group in HDFDMA play an essential role. The full composition film, which contains HDFDMA also exhibit large water contact angle of 120°±1.2°. This water contact angle is smaller than that of the MPTMS+HDFDMA film because of the lesser HDFDMA ratio in the molecular structure.

### 3.3. Adhesiveness test

In this experiment, plasma was utilized to treat alumina surface in comparison with untreated surface. The result is shown in Table 1. The films with TMTVSi in the structure provide the greatest adhesiveness in the cross-cut test. Another interesting result is the plasma surface treatment also improved adhesiveness. This effect is more significant in the case of films with no TMTVSi.
Table 1 Classification of films from “cross-cut” test

| Type of film                  | Classification |
|-------------------------------|----------------|
| M on untreated substrate     | 2              |
| M on plasma-treated substrate| 1              |
| MH on untreated substrate    | 4              |
| MH on plasma-treated substrate| 3              |
| FC on untreated substrate    | 0              |
| FC on plasma-treated substrate| 0              |

3.4. Surface morphology

The bare and coated alumina surface were characterised for their surface morphology by SEM as shown in Figure 3. The bare surface is rough and very porous (Figure 3(A)). After coating, the surface becomes less rough and less porous (Figure 3(B)-(E)). MPTMS films (as shown in Figure 3(A)) was very thin, the underlying alumina surface was clearly seen. With further additional composition of HDFDMA (Figure 3(C)) or TMTVSi (Figure 3(D)) and eventually HDFDMA, TMTVSi, PETMP (Figure 3(E)) to MPTMS, the films became more viscous and resulting in thicker films. Films with TMTVSi in their content reveal very smooth surface (Figure 3 (D-E)). It can be concluded that the chemical composition of the coating film play highly significant role to the surface hydrophobicity.

![SEM image at ×3500 magnification of alumina (A) bare sheet and (B) coated with MPTMS (C)MPTMS+HDFDMA (D) MPTMS +TMTVSi and (E) full-composition](image1)

Figure 3 SEM image at ×3500 magnification of alumina (A) bare sheet and (B) coated with MPTMS (C)MPTMS+HDFDMA (D) MPTMS +TMTVSi and (E) full-composition

![AFM 3D image of coated alumina surface (a) MPTMS (b) MPTMS+HDFDMA (c) MPTMS+TMTVSi (d) full-composition. Please note the huge difference in the height](image2)

Figure 4 showed AFM images of MPTMS, MPTMS+HDFDMA, MPTMS+TMTVSi and full-composition (MPTMS+HDFDMA+TMTVSi +PETMP), respectively. The first two cases, showed very high value for roughness (≈ 66.7 and 79.4 nm), while the last two cases had much less roughness (≈ 5.9 and 9.3 nm). Also, in the case of MPTMS+TMTVSi and full-composition films, there appeared nanospike-like patterns. There nanometer high structures were found to evenly distributed all over the surface. This structure may be explained by the Cassie-Baxter model rather than the Wenzel model [10]. However, the applicability of such explanation is doubtful in this nanometer range.
4. Conclusion
We have successfully synthesized the hydrophobic films from MPTMS, TMTVSi HDFDMA and PETMP by the thiol-ene reaction. The alumina sheets were activated by DBD plasma before coating the hydrophobic films. Plasma activation has significantly promoted the adhesiveness between films and substrate. The hydrophobic films have significantly enhanced the water contact angle of the alumina surface from $53.0^\circ \pm 1.5^\circ$ to $120.0^\circ \pm 1.2^\circ$. The films have also greatly improved the smoothness of the alumina sheet. The nanometer-high spikes have been observed on this hydrophobic film. Further improvements for higher yield of the mixtures from the thiol-ene reaction and for higher water contact angle (toward superhydrophobic) are necessary. In summary, the hydrophobic film from MPTMS, TMTVSi, HDFDMA, and PETMP synthesized by the thiol-ene reaction together with plasma activation on the substrate prior to the coating has a great potential as super-hydrophobic coating on alumina with the property to withstand corrosive environment.

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