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| 14. ABSTRACT<br>The wide applicability of non-wetting materials has generated a surge in commercial, military, and academic materials research. Previous studies have elucidated three parameters useful in the development of non-wetting surfaces: chemical functionality (high fluorine content), multiple scales of surface roughness (nano and micro), and surface geometry (re-entrant curvature). These parameters have been used in the development of materials that are superhydrophobic and superoleophobic. Although many of these surfaces exhibit the desired omniphobic character, a simple method to produce mechanically robust non-wetting coatings on various substrates has not been reported. Various nanoparticles, such as nanosilica, have been shown to provide the required surface roughness for non-wetting character in polymer systems. In the present work, a fluoroalkyl-modified nanosilica is developed and investigated to help achieve both the surface roughness and low surface energy demands of an omniphobic polymer coating. The fluoroalkyl-modification has the added benefit of increasing dispersion and compatibility in a crosslinkable fluoropolymer matrix, which is thought to be needed to produce a mechanically-robust coating. Substitution of the silanol groups on the surface of silica has been well documented using various types of coupling agents, including chlorosilanes. The present work reports the modification of a previously reported two-step, amine promoted method for modifying the surface of silica. |                             |                                   |                                          |                                                                           |                                                        |
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# Toward Mechanically-Robust Omniphobic Composite Coatings using Fluoroalkyl-Modified Silica

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## Introduction

The wide applicability of non-wetting materials has generated a surge in commercial, military, and academic materials research.<sup>1-8</sup> Previous studies have elucidated three parameters useful in the development of non-wetting surfaces: chemical functionality (high fluorine content), multiple scales of surface roughness (nano and micro), and surface geometry (re-entrant curvature).<sup>5</sup> These parameters have been used in the development of materials that are superhydrophobic and superoleophobic.<sup>1-8</sup> Although many of these surfaces exhibit the desired omniphobic character, a simple method to produce mechanically robust non-wetting coatings on various substrates has not been reported.<sup>1,2,4,5,8</sup> Various nanoparticles, such as nanosilica, have been shown to provide the required surface roughness for non-wetting character in polymer systems.<sup>1,7,8</sup> In the present work, a fluoroalkyl-modified nanosilica is developed and investigated to help achieve both the surface roughness and low surface energy demands of an omniphobic polymer coating. The fluoroalkyl-modification has the added benefit of increasing dispersion and compatibility in a crosslinkable fluoropolymer matrix, which is thought to be needed to produce a mechanically-robust coating. Substitution of the silanol groups on the surface of silica has been well documented using various types of coupling agents, including chlorosilanes.<sup>9-15</sup> The present work reports the modification of a previously reported two-step, amine promoted method for modifying the surface of silica.<sup>9,10,15</sup> The reaction scheme used for this modification is presented in Figure 1.

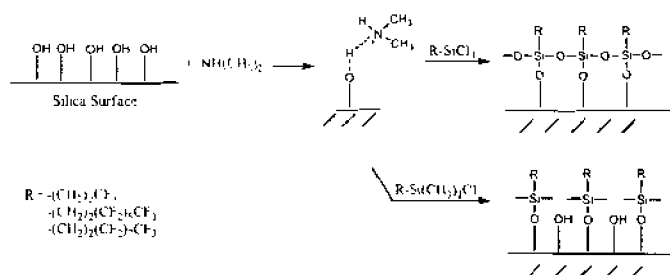


Figure 1. Reaction scheme for the modification of silica surface.

In addition to fluoroalkyl-functionalized silica, the effect of a fluorinated polyhedral oligomeric silsesquioxane (POSS) nanoparticle, (1H,1H,2H,2H-heptafluorodecyl)3Si3O12 or fluorodecyl POSS, with an extremely low surface energy ( $\gamma_s < 10$  mN/m) is investigated.<sup>1</sup> The present work focuses on the development of an omniphobic composite coating that can be easily applied to various surfaces by spray atomization or other types of spray technology.

## Experimental

**Materials.** Hi-Sil 233 (synthetic hydrated amorphous silica, 22 nm avg. diameter) was obtained from PPG Industries. Fluoro-compounds, (3,3,3-trifluoropropyl)trichlorosilane, (3,3,3-trifluoropropyl)dimethylchlorosilane, (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane, (tridecafluoro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane, (heptafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane, and (heptafluoro-1,1,2,2-tetrahydrodecyl)dimethylchlorosilane were purchased from Gelest, Inc. and were used as received without further purification. Anhydrous dimethylamine was obtained from Aldrich. 1H,1H,2H,2H-heptafluorodecyl polyhedral oligomeric silsesquioxane (fluorodecyl POSS) was synthesized according to the literature method.<sup>4</sup> Chloroform was received from Aldrich and passed through an activated alumina column to remove water. Viton Extreme ETP-600S was obtained from DuPont. Asahiklin AK-225G (1,3-Dichloro-1,1,2,2,3-pentafluoropropane) was used as received from AGC Chemicals Americas, Inc. Steel and aluminum Q-panel substrates were obtained from the Paul N.

Gardner Company, Inc. Glass microscope slides were obtained from Aldrich, cleaned with acetone and air dried before use.

**Instrumentation.** Surface modified silica was analyzed by TGA-MassSpec analysis (TA Instruments Q5000 IR, Pfeiffer-Vacuum Thermostat GSD301 MS system), DRIFTS (Nicolet 6700 FT-IR with DRIFT Smart Collector) and Elemental Analysis (Perkin Elmer 2400 Series II CHNS/O Elemental Analyzer). Contact angle studies of composite films were performed on a DataPhysics OCA 20 goniometer. Imaging of composite films was obtained via scanning electron microscopy (FEI Quanta 600), atomic force microscopy (Digital Instruments Dimension 3100), and optical profilometry (Veeco Wyko NT9300).

**Modification of Silica Surface.** The two-step amine-promoted method illustrated in Figure 1 was used for the modification of the Hi-Sil 233 silica surface. Hi-Sil 233 (2 g) was initially dried overnight under dynamic vacuum (10 mTorr) at 200-215 °C. Dimethylamine gas was then introduced to the dried silica under static vacuum to atmospheric pressure. The dried silica was then left in the dimethylamine environment for approximately 24 h with mechanical agitation via magnetic stir-bar. Under nitrogen 60 mL of chloroform was added to the Hi-Sil 233, followed by 1 mL of chlorosilane, and finally, an additional 20 mL of chloroform. The slurry was allowed to stir overnight in a nitrogen environment. The surface modified Hi-Sil 233 product was then recovered by filtration and subsequently washed with chloroform (10 mL x3). The modified silica was further purified by Soxhlet extraction using chloroform and AK225G. Both Soxhlet extractions were allowed to proceed for approximately 24 hours. The modified silica samples were then dried under ambient conditions and then in a vacuum oven at 110 °C. The vacuum oven treatment was implemented to cure the trichlorosilane modified silica products (horizontal polymerization), as well as to dry the products.

**Composite Coating Deposition.** A 5 wt% stock solution of Viton Extreme ETP-600S in AK-225G was used to prepare suspensions of modified-silica. The concentration of modified-silica in the fluoropolymer solutions varied from 0-20wt%. Fluorodecyl POSS was blended into suspensions at a concentration of 5mg/mL. Spray atomization of the composite coatings was achieved using an airbrush system (Paasche Airbrush Company, VLSTPRO double-action siphon feed). Glass, aluminum, and steel substrates were sprayed at a distance of approximately 20 cm. The thickness of the coatings was varied from one pass (~2 sec spray) to several passes (~10 sec spray). The coated substrates were air dried for one hour followed by oven drying for approximately 12 hours at 60 °C.

## Results and Discussion

**Fluoroalkyl-Modified Silica.** The degree of fluoroalkyl substitution of the silanol groups on the surface of silica was determined using IR, TGA-MS, and elemental analysis data. TGA-MS data exhibits thermal degradation at elevated temperatures, which suggests covalent attachment of the fluoroalkylsilanes to the silica surface. Fluorinated ion fragments, corresponding with the weight loss at elevated temperatures (400-650 °C), were observed in mass spectra data for all modified silica products. TGA data was also used to quantify coverage by measuring the weight loss from 400-650 °C. Elemental analysis was used to measure the carbon content of the modified silica products, which provides yet another indication of coupling agent surface coverage. Preliminary TGA, elemental analysis, and surface coverage data are presented in Table 1. The surface coverage (wt%) was calculated from elemental analysis data (C wt%), assuming all carbon content resulted from the addition of coupling agent.

Table 1. Modified Hi-Sil233 TGA and Elemental Analysis Data

| Coupling Agent                                                                                                       | %weight loss from 400-650°C | %C content | surface coverage (wt%) |
|----------------------------------------------------------------------------------------------------------------------|-----------------------------|------------|------------------------|
| None                                                                                                                 | 1.61                        | 0.1        | 0                      |
| CF <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> SiCl <sub>3</sub>                                                    | 7.57                        | 2.6        | 10.3                   |
| CF <sub>3</sub> (CF <sub>2</sub> ) <sub>7</sub> (CH <sub>2</sub> ) <sub>2</sub> SiCl <sub>3</sub>                    | 10.02                       | 3.4        | 11.4                   |
| CF <sub>3</sub> (CF <sub>2</sub> ) <sub>7</sub> (CH <sub>2</sub> ) <sub>3</sub> Si(CH <sub>3</sub> ) <sub>2</sub> Cl | 11.56                       | 4.4        | 14.0                   |
| CF <sub>3</sub> (CF <sub>2</sub> ) <sub>7</sub> (CH <sub>2</sub> ) <sub>3</sub> SiCl <sub>2</sub>                    | 14.82                       | 4.1        | 13.5                   |
| CF <sub>3</sub> (CF <sub>2</sub> ) <sub>7</sub> (CH <sub>2</sub> ) <sub>2</sub> Si(CH <sub>3</sub> ) <sub>2</sub> Cl | 14.62                       | 5.4        | 16.6                   |

**Composite Coatings.** The hydrophobicity and oleophobicity of the composite films were investigated by measuring the static, advancing, and receding contact angles of deionized water and hexadecane. Preliminary

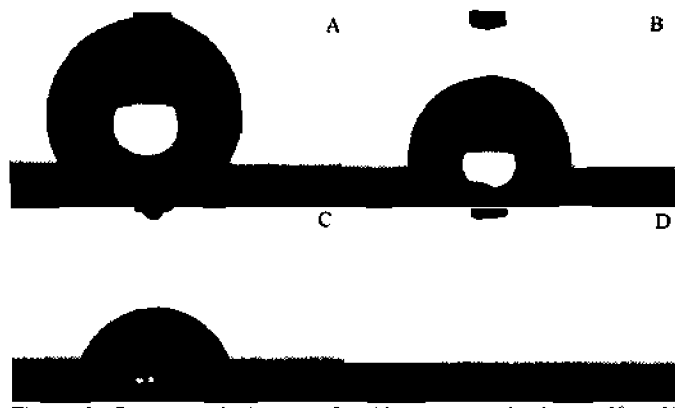
contact angle studies display superhydrophobicity with low hysteresis for all coatings containing fluoroalkyl-modified silica. Preliminary static contact angle results are presented in Table 2.

**Table 2. Water Contact Angles on Composite Coatings**

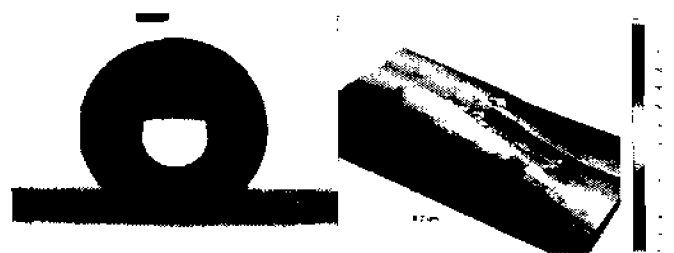
| Coating Composition <sup>1</sup>                                                                        | Average Static Contact Angle (°) |
|---------------------------------------------------------------------------------------------------------|----------------------------------|
| Blank                                                                                                   | 107                              |
| 20 wt% unmodified Hi-Sil 233                                                                            | 0                                |
| 5 wt% fluorodecyl POSS                                                                                  | 135                              |
| 20 wt% $\text{CF}_3(\text{CH}_2)_2\text{SiCl}_3$ modified Hi-Sil 233                                    | 164                              |
| 20 wt% $\text{CF}_3(\text{CH}_2)_2\text{SiCl}_3$ modified Hi-Sil 233 + 5wt% fluorodecyl POSS            | 166                              |
| 20 wt% $\text{CF}_3(\text{CF}_2)_2(\text{CH}_2)_2\text{SiCl}_3$ modified Hi-Sil 233                     | 161                              |
| 20 wt% $\text{CF}_3(\text{CF}_2)_2(\text{CH}_2)_2\text{Si}(\text{CH}_2)_2\text{Cl}$ modified Hi-Sil 233 | 165                              |
| 20 wt% $\text{CF}_3(\text{CF}_2)_2(\text{CH}_2)_2\text{SiCl}_3$ modified Hi-Sil 233                     | 165                              |
| 20 wt% $\text{CF}_3(\text{CF}_2)_2(\text{CH}_2)_2\text{Si}(\text{CH}_2)_2\text{Cl}$ modified Hi-Sil 233 | 164                              |

<sup>1</sup>Viton Extreme ETP-600S containing different fillers sprayed on glass.

The coating containing unmodified Hi-Sil 233 initially displayed hydrophobicity (Figure 2a), followed by wicking to finally produce a completely wetted surface. This observation is illustrated in Figure 2. It is worth noting that, although the volume of the droplet does decrease due to evaporation, wetting was observed on the coating containing unmodified silica – a “coffee stain appearance.” This behavior was not observed for coatings containing silica particles modified with fluoroalkyl chlorosilanes. This suggests that the untreated silica particles produced a multi-scaled rough surface necessary for wetting-resistance, but the hydrophilic silanol groups on the surface are causing the water to wet the coating. The hydrophobic modified-silica produces multi-scaled rough surfaces with low surface energies, which remain superhydrophobic after contact with water for an extended period of time. A water droplet in contact with such a coating for several minutes is shown in Figure 3



**Figure 2.** Contact angle images of a 10  $\mu\text{L}$  water droplet on 20 wt% unmodified silica coating on glass (a) initially, (b) after 2 min, (c) after 5 min, and (d) after 7 min.



**Figure 3.** Water contact angle (10  $\mu\text{L}$ ) and AFM image (6.2 x 3.4  $\mu\text{m}$ ) of composite coating containing 20 wt%  $\text{CF}_3(\text{CF}_2)_2(\text{CH}_2)_2\text{SiCl}_3$  sprayed onto a glass slide.

Slow hexadecane-wetting was observed in coatings containing modified silica. Wetting-resistance was improved with increasing modifier chain length, i.e.  $-(\text{CH}_2)_2(\text{CF}_2)_2\text{CF}_3 > -(\text{CH}_2)_2(\text{CF}_2)_2\text{CF}_3 > -(\text{CH}_2)_2\text{CF}_3$ . This is presumably due to the higher F/H ratio on the surface of the silica particles.

## Conclusions

A method has been developed for the surface modification of nanosilica using fluoroalkyl silanes. The modified silica products have been suspended into solutions of crosslinkable fluoropolymer and deposited onto various substrates by spray atomization to produce non-wetting surfaces. The introduction of fluorodecyl POSS into the fluoropolymer solutions and silica suspensions was investigated.

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