

Development of Hydrophobic Coatings for Water-Repellent Surfaces Using Hybrid Methodology

**by Amanda S. Weerasooriya, Jacqueline Yim, Andres A. Bujanda,
and Daphne Pappas**

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Weapons and Materials Research Directorate, ARL

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14. ABSTRACT Hydrophobic surfaces are of considerable interest due to their self-cleaning, wicking, water-repellent, and antimicrobial properties. Several approaches have been investigated for the development of hydrophobic and superhydrophobic materials. One in particular involves introducing surface roughness and chemical functionalities with hydrophobic end groups. In this work, hydrophobic surfaces were incorporated on ultra-high-molecular-weight polyethylene films using a three-step process. A treatment by plasma was employed before any other significant treatments to help with better adherence of particles acquired through silane wet chemistry, which was implemented to introduce surface roughness to yield a hierarchical assembly of silicon oxide (SiO ₂) nanoparticles. This was followed by plasma-enhanced chemical vapor deposition (PECVD) at atmospheric pressure to deposit a coating composed of fluorinated groups on the material. The chemical composition, wettability, and morphology of the surface were studied using water contact angle, Fourier transform infrared spectroscopy, x-ray photoelectron spectroscopy, atomic force microscopy, and scanning electron microscopy. Variations in the deposition processes of wet chemistry and PECVD were investigated. Fluorinated liquid precursors with different fluorocarbon structures and deposition time varied as well as the SiO ₂ nanoparticle loading. These parameters varied to obtain a surface with optimal distribution of particles coated with thin fluorocarbon films that exhibit hydrophobic behavior.					
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1. Introduction

Coatings that impart hydrophobic properties are of considerable interest. For applications such as aircraft windows, optical components, protective eyewear, and clothing, this type of surface is desired for the material to be soil repellent and water resistant. A prime model of a surface with these characteristics can be found in nature, specifically the lotus flower shown in figure 1. The leaves of the lotus flower have super-hydrophobic properties as a means of self-cleaning.¹

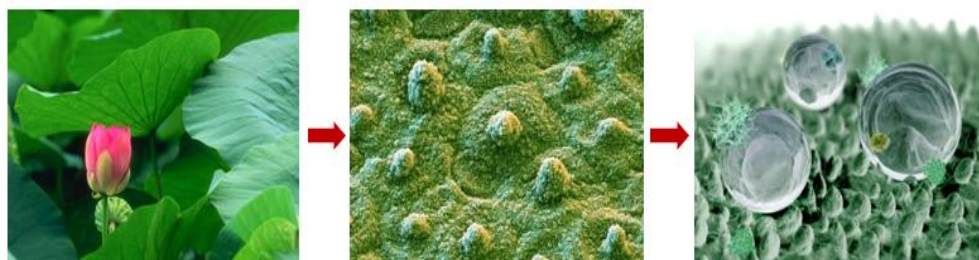


Figure 1. Lotus effect.

This is a result of the hierarchical rough structure of the leaf and the waxy layer on the surface of the leaf. To achieve a super-hydrophobic surface, the surface energy and surface roughness of a material play a key role and must be investigated. The lower the surface energy, the higher the hydrophobicity of that surface, and to further increase the hydrophobicity an appropriate surface roughness is required.² Intrigued by this effect, the goal for this study was to develop a low-cost, thin hydrophobic coating comprised of silica nanoparticles with pendant fluorocarbon chains extending toward the surface. To achieve this hydrophobic surface, wet chemistry and atmospheric pressure plasma treatment techniques were used on ultra-high-molecular-weight polyethylene (UHMWPE) (figure 2). Through wet chemistry techniques, the surface roughness of the UHMWPE was increased physically by depositing silicon dioxide (SiO_2) nanoparticles on the surface of the sample as depicted in figure 3. Plasma-enhanced chemical vapor deposition under atmospheric pressure was used to deposit a fluorocarbon coating. This technique is desirable because it does not require the use of vacuum equipment, is capable of large area deposition, produces minimal waste, and is capable of controlling the coating chemistry.

¹Marmur, A. The Lotus Effect: Superhydrophobicity and Metastability. *Langmuir* **2004**, *20*, 3517–3519.

²Liu, Y.; Chen, X.; Xin, J. H. Super-Hydrophobic Surfaces From a Simple Coating Method: A Bionic Nanoengineering Approach. *Nanotechnology* **2006**, *17*, 3259–3260.

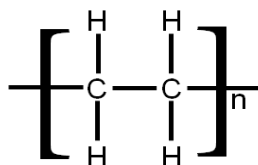


Figure 2. Chemical structure of UHMWPE.

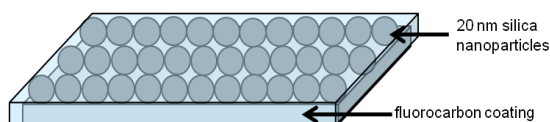


Figure 3. Proposed textured structure.

2. Experimental Systems and Procedures

2.1 Cylindrical Atmospheric Plasma System (Pretreatment)

Prior to any other treatment, a cylindrical atmospheric pressure plasma system was used to pretreat the UHMWPE. This system consists of two high-voltage electrodes and one grounded electrode (see figure 4). Plasma in this system is created between the lower rotating electrode and the set of upper high-voltage electrodes.³ Connected to the top electrodes is the gas-handling system, which leads the gas from the tanks to the electrodes and bubbler system that is connected to the top electrodes. The bubbler vaporizes the precursor, which is carried to the plasma via helium gas. When the power supply is turned on, a voltage is applied causing electrons to flow between the two electrodes and excite gas molecules. Under the relaxation stage, the gas atoms and molecules emit photons that make the gas glow. A power density of $1.5 \text{ W} \cdot \text{cm}^{-2}$ was used in this study.

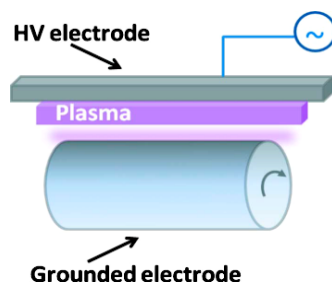


Figure 4. Cylindrical system used in study.

³Pappas, D. Status and Potential of Atmospheric Plasma Processing of Materials. *Journal of Vacuum Science & Technology A* **2011**, 29, 020801.

2.2 Water Vapor Plasma Pretreatment

To ensure that silica particles adhered to the UHMWPE film, a pretreatment using the cylindrical atmospheric plasma system was used. The pretreatment serves to create reactive chemical groups on the surface of the inert UHMWPE for subsequent processing. The UHMWPE films were first cleaned in ethanol to rid the material of disparities and residues prior to treatment, and then the samples were left to air dry. Once the films were dried completely, the samples were mounted onto the cylinder in the plasma system using Kapton tape. Ultra-high-purity helium gas (99.999%) was administered with a flow rate of 12,000 standard cubic centimeters per minute (sccm) to ignite the plasma. A volume of 40.0 mL of water was put into the bubbler system and heated to 25 °C. The samples in this study were treated for 1.32, 5.28, or 10.56 s.

2.3 Wet Chemistry Process

After the pretreatment of UHMWPE films using the cylindrical atmospheric plasma system, silane coupling chemistry was used to incorporate nanoparticles for a textured surface to increase the surface roughness of the material. The wet chemistry method involved a two-step process. The first step entailed using 3-glycidyloxypropyl trimethoxysilane (GPS) (figure 5) to create a cross-linked siloxane network with pendant epoxy groups to allow silica nanoparticles to adhere to the surface. A 50-mL 1.0% (w/w) GPS in methanol solution was created. To do this, 0.5 g of GPS and 49.5 g of methanol were weighed out and mixed together using a magnetic bar and stir plate for 10 min. Next, the pretreated UHMWPE films were placed in the solution individually. Each sample was immersed in the solution for 60 s then left to air dry. Once dried, they were put in an oven set at 70 °C for 1 h. After heating, the samples were taken out and a solution of LudoxTMA (34-wt% SiO₂ suspension in H₂O) in an ethanol/H₂O solution was created. Various weight-percent loadings of LudoxTMA in ethanol/H₂O were studied from 0.5% to 2%. This was accomplished by making another solution with a total volume of 50 mL of ethanol/deionized (DI) water (90:10 v/v) with amounts of LudoxTMA shown in table 1 for the appropriate weight-percent of LudoxTMA. Once the appropriate amount was weighed out, the LudoxTMA was mixed with the 90:10 ethanol/H₂O mixture with the magnetic bar and stir plate for 10 min. The same dip-coating process that was used for the GPS solution was used for the Ludox solution. The samples were placed in the oven for 1 h at 70 °C. After drying in the oven, the films were taken out and placed in an ethanol bath to free the surface of particles that were not chemically bonded to the surface of the UHMWPE.

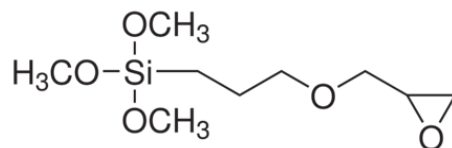


Figure 5. GPS chemical structure.

Table 1. Ludox weight-percent values.

Ludox (wt%)	Amount of Ludox Mixed With 50 mL Ethanol/DI Water (90:10 v/v) (g)
0.5	0.73
0.75	1.09
1.0	1.46
1.5	1.48
2.0	1.49

2.4 Micropulsed Plasma Jet

A micropulsed atmospheric pressure plasma jet (APPJ) system was used to deposit a fluorocarbon coating on the nanotextured UHMWPE. The APPJ system consists of a quartz tube (2-mm outer diameter) with copper tape at the bottom (high-voltage electrode) and an aluminum (Al) stage covered in quartz (ground electrode) (figure 6). Helium gas was flowed into the plasma jet at a flow rate of 3000 sccm. The precursors used were pentafluorophenyl triethoxysilane (FAS-5) and heptafluoro-1,1,2,2-tetrahydrodecyl triethoxysilane (FAS-17) (figure 7). The duty cycle was varied from 25% to 50% and the deposition time was varied from 60 to 180 s.

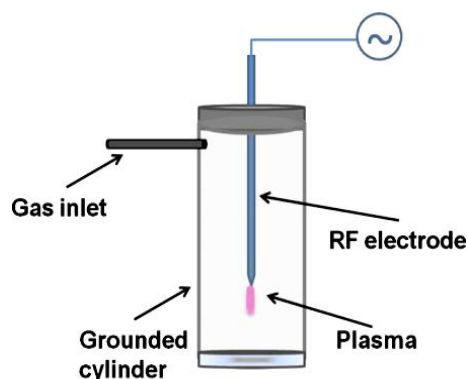


Figure 6. Plasma jet used in this study.

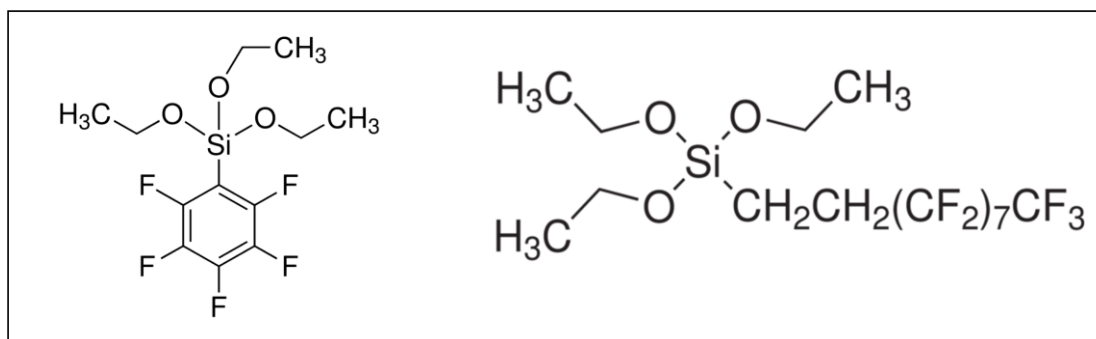


Figure 7. Chemical structure of FAS-5 (left) and FAS-17 (right).

2.5 Sample Characterization

2.5.1 Static Water Contact Angle (WCA)

WCA is measured using a goniometer of a given material when it is desired to find out how hydrophobic or hydrophilic a material is. If the contact angle measurement taken is closer to or higher than 70° , the material being tested is considered “hydrophobic” or nonwetable. The higher the angle, the more hydrophobic it is. If the contact angle measurement taken is closer to 0° , the material is considered more hydrophilic. The more hydrophilic a material is, the smaller the angle will be.

With the goniometer, a drop of water with a volume around $0.2\ \mu\text{L}$ is placed on the surface of a substrate. A camera captures an image of the water droplet when it comes into contact with the surface. A LabVIEW* program is used to calculate the contact angles that are formed on the substrates from the image. A minimum of four drops were placed on each sample to ensure validity when measuring contact angles in this study.

2.5.2 Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy (ATR-FTIR)

ATR-FTIR was used to study the chemical composition of UHMWPE, before and after silane chemistry and the deposition of the fluorocarbon-like coating. A horizontal ATR (HATR) bench top, the ATR crystal holder, and a clamp were used with the Thermo-Nicolet 670 FTIR spectrometer. A zinc selenide ATR crystal was used in this study to scan the mid-IR region of $4000\text{--}650\ \text{cm}^{-1}$. OMNIC software was used to operate the FTIR and collect spectrum. Prior to collecting scans, the ATR crystal is cleaned with ethanol and a background spectrum is collected to subtract out the presence of CO_2 and water vapor from the spectrum of the sample. After recording the background spectrum, the sample is placed on the ATR crystal and a force is applied to the sample using a clamp to establish good contact between the sample and the crystal. Then the spectrum of the sample is collected. All spectra were acquired using a resolution of $4\ \text{cm}^{-1}$ and a total of 64 scans each.

2.5.3 X-Ray Photoelectron Spectroscopy (XPS)

XPS was used to obtain elemental composition of the surface. This is accomplished by irradiating the material with x-ray beams that penetrate up to 10 nm in depth with a Kratos Axis Ultra X-ray XPS system equipped with a hemispherical analyzer. A 100-W monochromatic Al $K\alpha$ ($1486.7\ \text{eV}$) beam irradiated a $1\text{-} \times 0.5\text{-mm}$ sampling area with a take-off angle of 90° . The base pressure in the XPS chamber was held between 10^{-9} and 10^{-10} Torr. Elemental high-resolution scans for C1s, F1s, and O1s were taken in the constant analyzer energy mode with 20-eV pass energy. Energy correction for high-resolution C1s spectra was done using 285.0 eV as the reference peak corresponding to the aliphatic carbon-carbon, C-C group in the modified and pristine UHMWPE films. Peaks at 101, 285, 530, and 685 eV correspond to silicon, carbon, oxygen, and fluorine, respectively.

*LabVIEW is copyrighted by National Instruments Corporation, Austin, TX.

2.5.4 Atomic Force Microscopy (AFM)

AFM was used to study the morphology of the surface of the sample. Surface roughness measurements and phase imaging were acquired to detect variations in composition, viscoelasticity, and other properties. A cantilever with a 35- μm -long silicon probe at the end of the beam was used to scan the substrate's surface. A frequency of 300 kHz was applied across the surface of the substrate. A scan area of $5 \times 5 \mu$ with a scan rate of 0.5 Hz was used.

2.5.5 Scanning Electron Microscopy (SEM)

An FEI Nova NanoSEM operating in both field-emission and immersion modes under nominal accelerating voltages of 1–3 eV was also used to study the morphology of the surface. All images were captured at a magnification of 20,000.

3. Results and Discussion

3.1 Nanotextured Surfaces Using Silane Wet Chemistry

3.1.1 Surface Wettability

The wetting behavior of UHMWPE films that were pretreated by the cylindrical plasma system and coated with different weight-percentages of LudoxTMA (shown in table 1) were studied through WCA. In figure 8, the effect of pretreatment time on WCA of the samples is shown. Generally, UHMWPE films exposed to He-H₂O plasma at longer pretreatment times were found to contain the highest concentration of silica nanoparticles on the surface of the sample. This is a result of the higher surface concentration of functional groups created on the surface of UHMWPE films, which in turn increases the number of available sites for GPS and Ludox to chemically react and form chemical bonds at the surface. In relation to the 0.5-wt% Ludox and 1-wt% Ludox, the 0.75-wt% Ludox was found as the weight-percent loading solution with the highest contact angle.

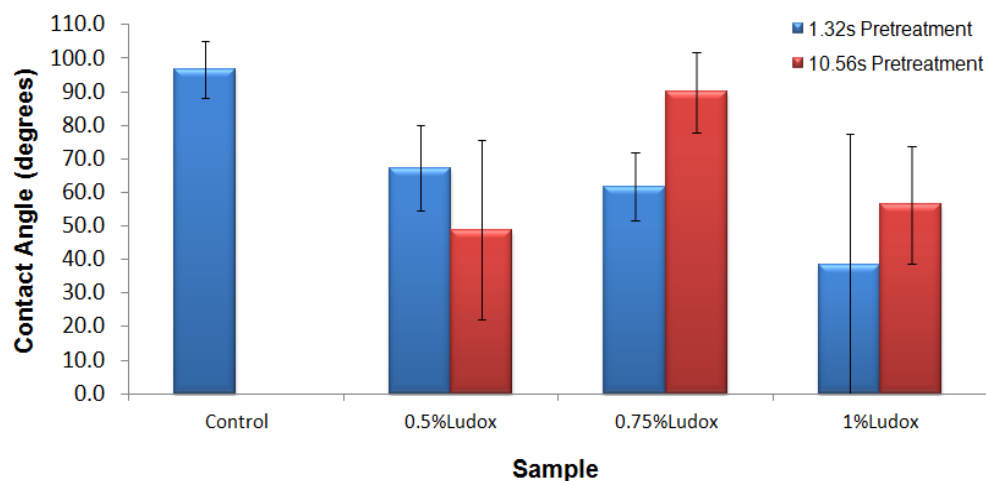


Figure 6. Effect of pretreatment time on WCA of samples 1-wt% GPS varying Ludox weight-percent.

3.1.2 ATR-FTIR

Data were collected by ATR-FTIR for the samples that were pretreated, coated with 1-wt% GPS in methanol solution, and coated with various weight-percentages of LudoxTMA in an ethanol/DI water solution. In figure 9 (left), a spectrum of the UHMWPE treated with 1-wt% GPS is shown with untreated UHMWPE spectrum. In this graph, the additional new peaks that appear in treated UHMWPE were identified as Si-O and Si-O-Si stretching bands at 3370 and 1100 cm^{-1} , respectively. In figure 9 (right), representative spectra of the UHMWPE untreated and treated with the 1-wt% GPS and 1-wt% LudoxTMA show the presence of Si-O and Si-O-Si stretching bands at 3400 and 1080 cm^{-1} , respectively, but at higher concentrations than the UHMWPE that was solely treated with the pretreatment method by plasma and the 1-wt% GPS. In this spectrum, a shift in the peaks is seen and the Si-O-Si peak is more defined, indicating that silica nanoparticles are present on the surface of UHMWPE films.

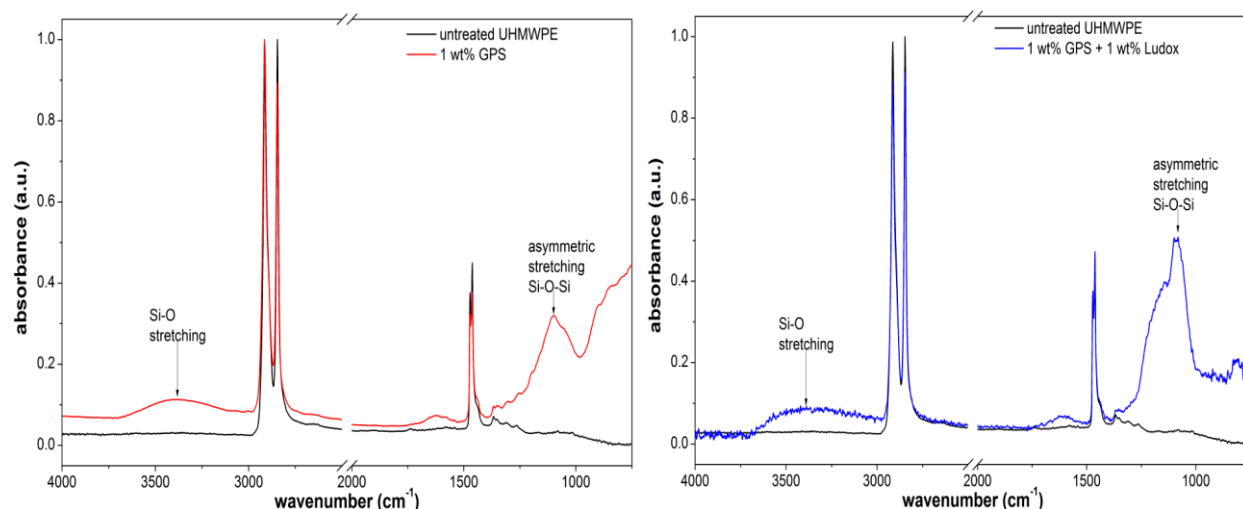


Figure 7. ATR-FTIR spectra of GPS (left) and GPS+Ludox (right).

3.1.3 XPS

Samples pretreated by plasma and subjected to the silane wet chemistry were characterized by XPS. In figure 10, it is shown that as pretreatment time increases, generally the silicon atomic concentration decreases while the carbon concentration remains relatively higher. This is observed with the surfaces with 0.5- and 0.75-wt% loading of silica nanoparticles. However, the 1-wt% loading of silica nanoparticles shows the opposite trend, as it has the highest concentration of silicon on the surface after longer exposure to the plasma pretreatment. In addition, XPS confirms the findings obtained from FTIR analyses.

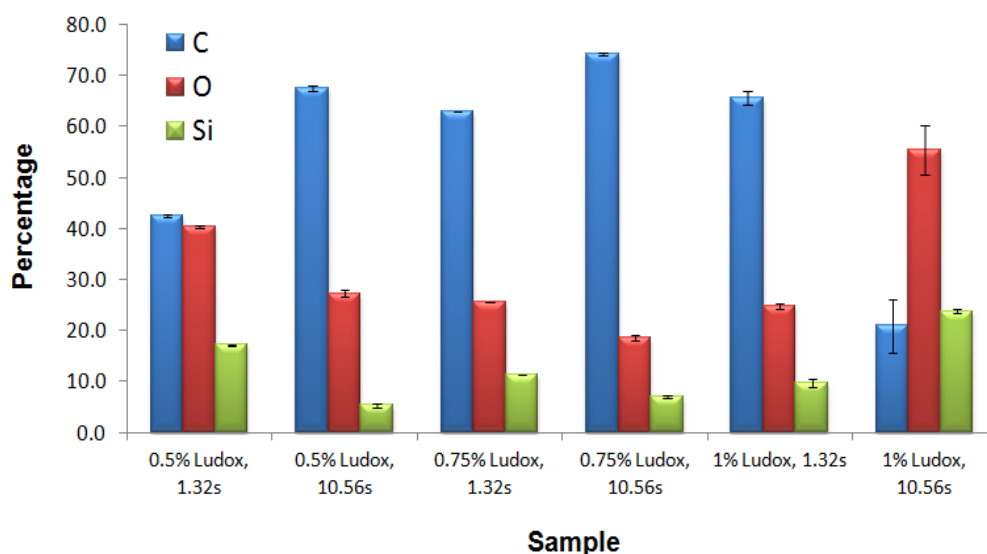


Figure 8. Effect of pretreatment time on XPS of samples 1-wt% GPS varying Ludox weight-percent.

3.1.4 AFM

AFM data was gathered for the untreated UHMWPE and 1-wt% GPS sample with various loading of silica nanoparticles. Shown in figure 11 (left) is the AFM image of a control untreated UHMWPE film. The root-mean-squared (RMS) roughness was measured to be 15.9 ± 4.6 nm. Shown in figure 11 (right) is an AFM image of a UHMWPE sample that was pretreated in plasma for 10 s with 1-wt% GPS and 1-wt% LudoxTMA. The RMS of this sample was found to be 18.1 ± 1.2 nm, proving that the overall roughness of the surface increased due to the nanotexturing effect brought about by the silica nanoparticles (figure 12). The SEM image shown in figure 13 is a magnified look at the surface of the same sample in figure 12 where phase imaging of the surface clearly shows the packing of nanoparticles on the surface.

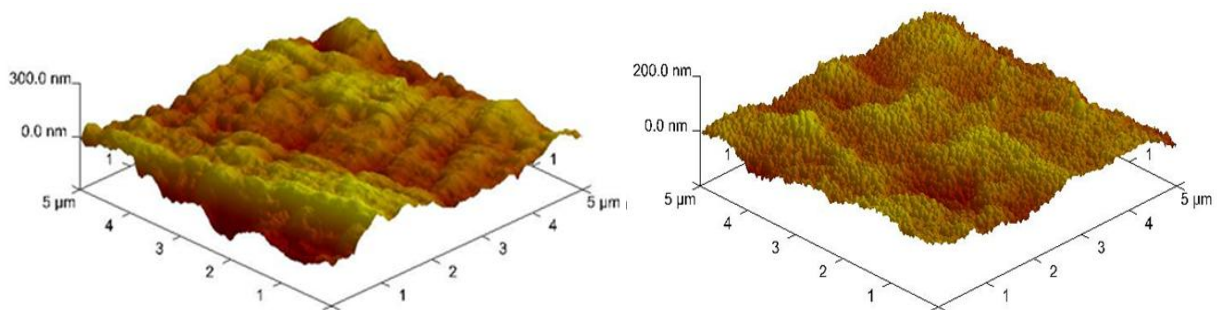


Figure 9. AFM image of untreated UHMWPE (left) and of 1-wt%-loading Ludox, 10-s plasma pretreated sample (right).

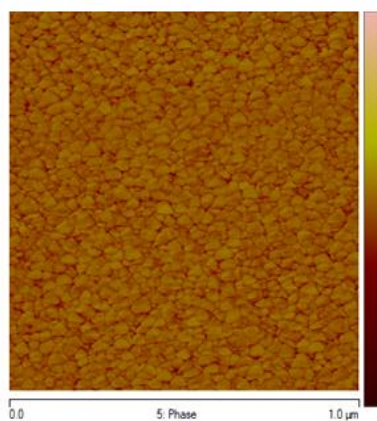


Figure 10. AFM image close-up of GPS+Ludox sample.

3.1.5 SEM

SEM was used to evaluate the dispersion of silica nanoparticles on the surface of UHMWPE films. A SEM micrograph of the UHMWPE film pretreated for 10.56 s in He-H₂O plasma with 1-wt% GPS, and 1-wt% Ludox is shown in figure 13. This micrograph shows that the silica nanoparticles are well dispersed on the surface of UHWMPE. In general, higher silica particle loading resulted in better coverage.

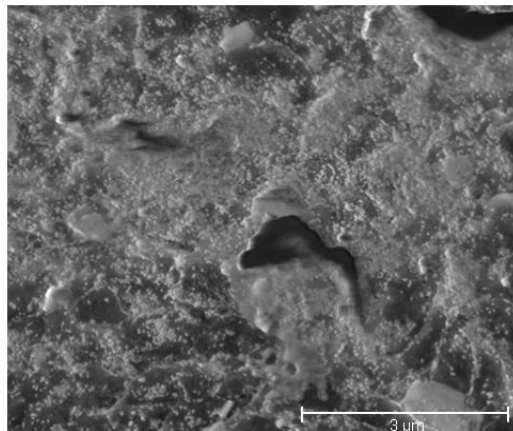


Figure 11. SEM image of GPS+Ludox sample.

3.2 Deposition of Fluorocarbon-Like Coatings on Nanotextured UHMWPE Films

3.2.1 Wetting Assessment

WCA measurements were taken on nanotextured UHMWPE films with the fluorocarbon coating deposited from each of the precursors used (FAS-5 and FAS-17). Figure 14 is a graph of the contact angles and how the GPS- and Ludox-treated samples compared differently with the samples treated with FAS-5 and FAS-17. The FAS-17 precursor through the plasma jet resulted in the highest contact angle regardless of Ludox weight-percent loading. The higher angles associated with the FAS-17 coating demonstrate that the straight chain length structure and the number of fluorocarbon groups yields surfaces that exhibit increased hydrophobicity than coatings deposited using the FAS-5 precursor. For the most part, the GPS- and Ludox-treated samples resulted in the lowest contact angles compared with the samples with the fluorocarbon coating. This can be due to the hydrophilic nature of the silica nanoparticles. With the FAS-17 precursor, the contact angle of the sample measured higher than the contact angle of the untreated UHMWPE.

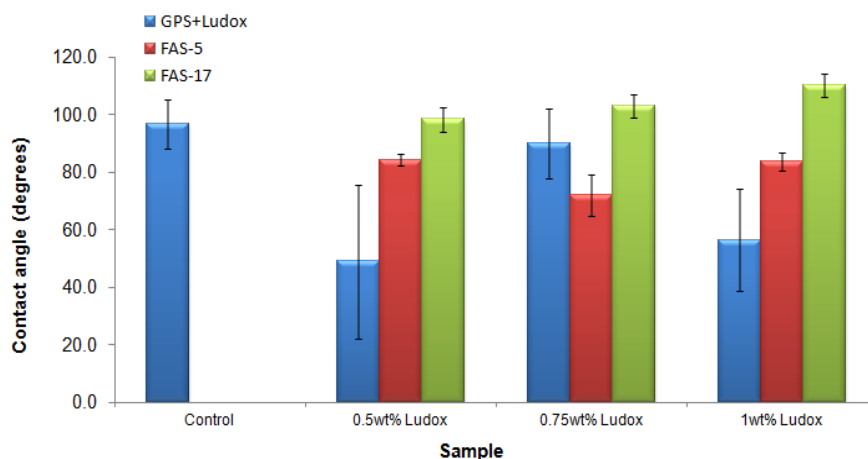


Figure 12. Effect of Ludox weight-percent on contact angle of samples treated for 180 s with FAS-5 and FAS-17.

3.2.2 Chemical Analysis

To assess the effect of the addition of other chemical groups associated with the fluorinated precursors, ATR-FTIR and XPS analyses were conducted on these modified coatings. Spectra were collected using ATR-FTIR of the nanotextured UHMWPE films coated with FAS-5 and FAS-17 precursors. The spectrum produced from the sample treated with the FAS-5 precursor is shown in figure 15 (left). Identified absorbance bands corresponding to chemical groups found in the precursor validates that the coatings deposited on UHMWPE films have fluorine-containing groups in addition to other chemical groups, likely due to interaction with the plasma species and atmosphere. The new peaks correspond to the Si-O, benzene, carbon-fluorine (CF), a fluorine (F) atom bonded to an aromatic, an aromatic bonded to Si atom, Si-OH, CH_2F , Si-F, and CF groups. In figure 15 (right), a spectrum of the FAS-17-coated sample is shown. From this graph there is proof that fluorine-containing groups are present in the coating on the sample but dissimilar to that of the FAS-5 coating. The distinctive region in the FAS-17-coated sample lies in the $1380\text{-}950\text{-cm}^{-1}$ range. The most intense bands were found to be that of the Si-O-Si group and the CF_2 groups. The strong absorption bands for the CF_2 groups is an indication of a highly fluorinated coating.

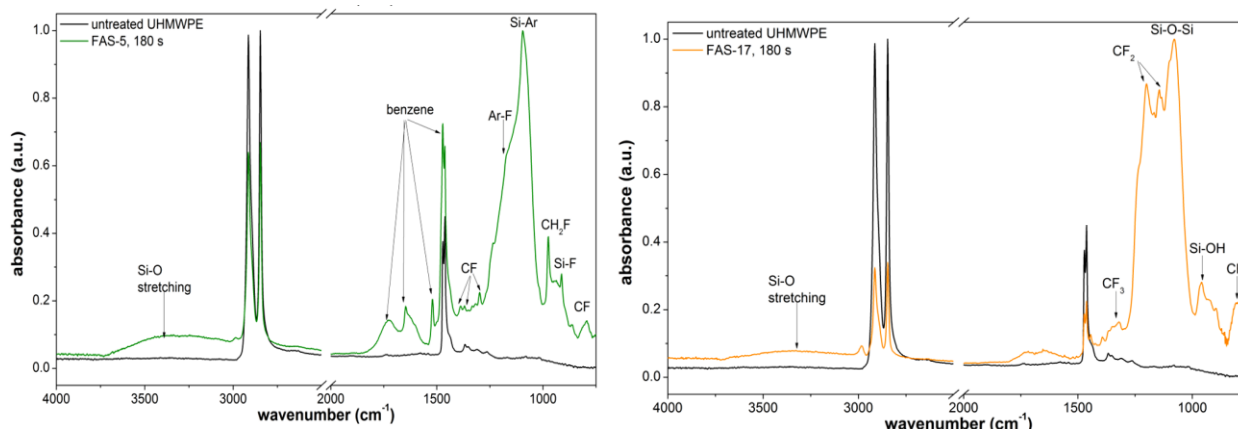


Figure 13. ATR-FTIR spectrum of samples treated with FAS-5 (left) and FAS-17 (right).

The UHMWPE samples that were subjected to pretreatment, silane wet chemistries, and then coated with FAS-5 or FAS-17 were characterized by XPS (figure 16 shows variations in atomic concentration of samples treated with FAS-5 or FAS-17). Shown in figure 17 is a graph of the atomic concentration of carbon, oxygen, fluorine, and silicon. The sample treated with 1-wt% Ludox and plasma-treated with the precursor FAS-17 showed the largest concentration of fluorine in the coating. The 1-wt% Ludox sample and plasma-treated with the precursor FAS-5 showed the second largest concentration in fluorine. Compared with the 0.75-wt%-Ludox-treated samples, the 1-wt%-Ludox-treated samples had higher fluorine percentages.

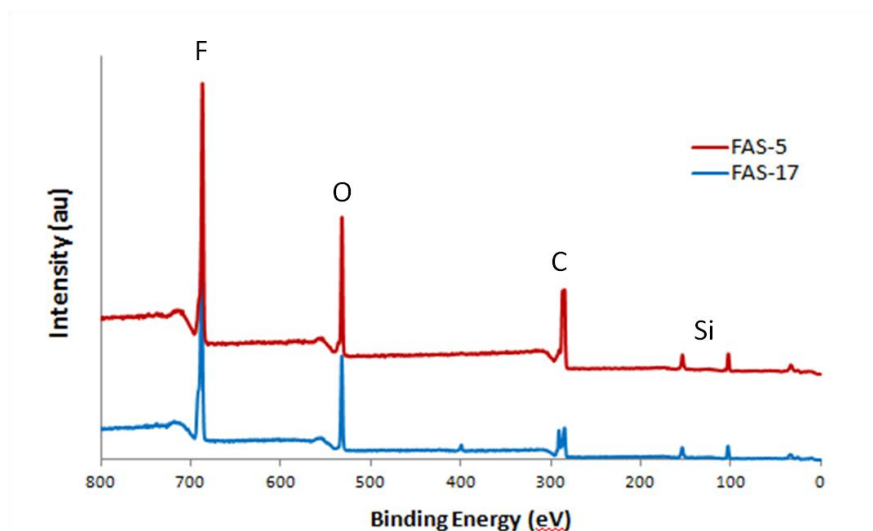


Figure 14. XPS spectra of 5-s pretreated sample varying precursor.

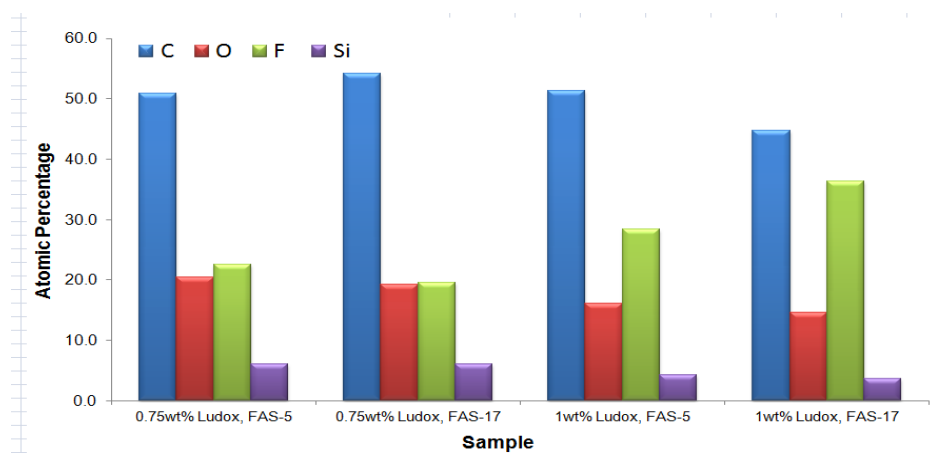


Figure 15. Effect of Ludox weight-percent on XPS of samples treated for 180 s with FAS-5 or FAS-17.

3.2.3 Surface Morphology

SEM analysis was performed on the nanotextured UHMWPE film's plasma that was treated with the precursor FAS-5 for 180 s; the SEM micrograph is shown in figure 18 (left). The particles appear to be as big as 2 μm , indicating that the particles act as nucleation sites for the coating to deposit and grow. Comparing this sample treated by FAS-5 with the sample treated by FAS-17 shown in figure 18 (right), the particles are much larger in diameter. The FAS-17 seems to deposit a thinner coating on the particles, unlike what was seen with the silica particles coated with the FAS-5 precursor.

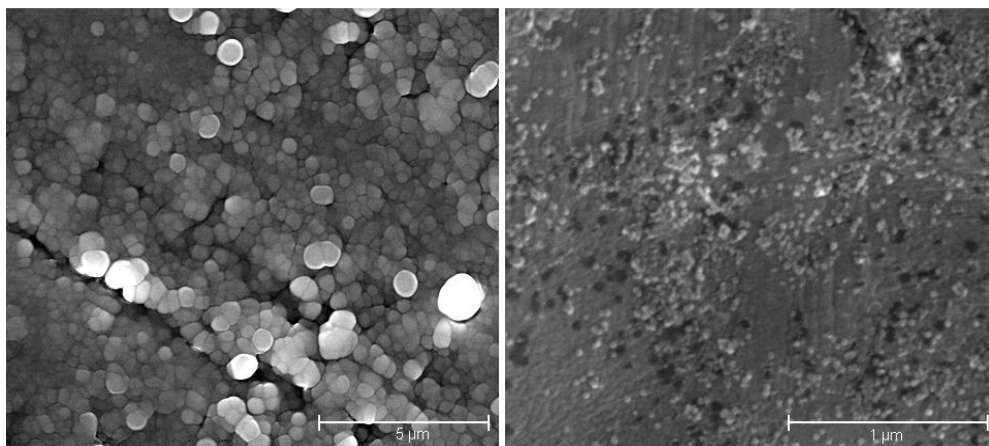


Figure 16. SEM of GPS+Ludox +FAS-5 (left) and GPS+Ludox+FAS-17 (right) samples.

4. Conclusions

Microstructural analysis shows that the processes used to create the hydrophobic coating proved to be successful. A fluorocarbon coating was successfully deposited onto the UHMWPE. There was an approximately 25% increase in WCA measurements of the bare substrate after 1 min of exposure to the plasma. It was found that longer pretreatment times resulted in more Ludox silica nanoparticles adhering to the surface of the UHMWPE, leading to lower WCAs, and that longer deposition times resulted in a higher fluorine concentration in the coating. This hybrid methodology of using combined plasma and wet chemistry was a very cost-efficient method for creating water repellency, by creating nanotextured features through SiO_2 nanoparticles and depositing fluorocarbon-like coatings to achieve hydrophobicity on surfaces.

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