Anti-Fog Coatings For Spacesuit Helmets

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A permanent and robust anti-fog coating was developed that is applied to the interior of polycarbonate spacesuit helmets. The coating is a mechanically resilient and permanent superhydrophilic (SHPL) layer produced by a two-step process consisting of a plasma processing pre-etch followed by the deposition of an optically transparent Diamond Like Carbon (DLC) coating to achieve an anti-fog, SHPL-DLC layer with Water Contact Angle (WCA) < 10°. The all-dry vacuum process consists of an oxygen plasma etching to engineer the surface of the polycarbonate, creating a well-controlled nanotextured morphology, which is key to the superhydrophilic properties, followed by vacuum deposited Plasma Enhanced Chemical Vapor Deposition (PECVD) DLC coating with high surface energy. The process is carried out at low temperatures compatible with polycarbonate materials and the two steps are performed back-to-back without breaking vacuum between steps. The process is readily scalable and compatible with large scale production volumes. The SHPL-DLC coating was tested for > 200 hours exposure using a breath simulator with no detrimental effect on the coating performance. The coating was also tested for exposure to cleaning fluids, IPA chemical exposure, adhesion testing per ASTM D3359, and abrasion resistance per MIL-E-12397 with no detrimental effects.

Nomenclature

BEE = Bottom Electrode Energized
CVD = Chemical Vapor Deposition
DLC = Diamond Like Carbon
EMU = Extravehicular Mobility Unit
EVA = Extravehicular Activity
HITL = Human-in-the-Loop
PC = Polycarbonate
PECVD = Plasma Enhanced Chemical Vapor Deposition
PVD = Physical Vapor Deposition
Rq = Root-Mean-Square Surface Roughness
SHPL = Superhydrophilic
SHPL-DLC = Superhydrophilic Diamond Like Carbon
SHPO = Superhydrophobic
TEE = Top Electrode Energized
WCA = Water Contact Angle
xEMU = Exploration Extravehicular Mobility Unit

I. Introduction

Anti-fog coatings are commonly used in spacesuit helmets to eliminate fogging on the interior of the face shield due to the astronaut's breathing. Currently for the Extravehicular Mobility Unit (EMU) spacesuit an astronaut applies an anti-fog liquid to the interior of the helmet bubble before each Extravehicular Activity (EVA). However, the anti-fog solution has been reported to cause eye discomfort during at least seven EVAs when the material came in to contact with a crewmember's eyes. For example, during STS-100, astronaut Chris Hadfield reported that eye irritation temporarily blinded him during his spacewalk. In addition to the foregoing, wipe-on anti-fog solutions are

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not a desirable approach for a number of reasons, including, they are not permanent, must be applied before each use, are easily compromised by cleaning and incidental contact, and are a consumable that must be tracked and supplied for each mission.

To address these shortcomings, the goal for the Exploration EMU (xEMU) pressure bubble is to use a permanent anti-fog coating or other technology that prevents fogging. The xEMU program investigated a permanent anti-fog solution, called HTAF-308, but it failed during qualification due to delamination and flaking after manned testing and was never implemented. During the Constellation spacesuit development program, NASA conducted a trade study on four different permanent anti-fog solutions that were selected based on their optical transmission, haze, adhesion, abrasion resistance, craze resistance, and cold box, steam, and human breath response tests. From that study HTAF-601 was selected as the primary option.

The HTAF-601 permanent anti-fog solution was tested throughout the xEMU design, verification, and test Human-in-the-Loop (HITL) events. However, major issues arose with the coating during HITL testing. For example, cleaning the helmet was a challenge to avoid damaging the permanent anti-fog coating. NASA tested a number of cleaning methods for the HTAF-601 coating with the goal of determining a preferred method. However, no effective method was found. For example, IPA cannot be used because it strips and delaminates the coating. Even when using a very gentle cleaning method consisting of flushing with distilled or DI water and dabbing at facial oils, the permanent anti-fog layer starts to delaminate consistently after 50 hr of use. Finally, the HTAF-601 coating is being discontinued by the vendor.

In order to address NASA's xEMU goals we developed a permanent anti-fog coating that is applied to the interior of polycarbonate spacesuit helmets. The key word here is permanent. The coating is applied once during the manufacturing process and does not need to be applied again over the life of the xEMU helmet. The specific project goals are: 1) To demonstrate anti-fogging performance of the coating using a simulated breathing steam-cycle test at 104 °F temperature, cycled for 216,000 cycles at 18 cycles per minute (200 hour exposure) with no fogging occurring on the samples and no evidence of delamination after the test. 2) Pass a cleaning test that consists of emersion in DI water and wipe testing. 3) Demonstrate that the coating is resistant to full strength isopropyl alcohol (IPA) wiping tests. 4) Demonstrate the abrasion resistance of the coating per MIL-E-12397 with no detrimental effects. 5) Demonstrate that the coating still has excellent optical transmission, adhesion and anti-fogging properties after it has been subjected to all of the aforementioned testing in combination. 6) Pass a cross-hatch tape-pull adhesion test per ASTM 3359. 7) Show that the coating does not reduce the optical transmission of the helmet assembly to less than 70% in the visible wavelengths. 8) Demonstrate that the coating can be applied to the interior of curved, hemispherical surfaces with dimensions similar to NASA xEMU spacesuit helmets.

To achieve these goals, Acree developed an optically transparent Superhydrophilic Diamond Like Carbon (SHPL-DLC) coating that can be applied to polycarbonate substrates. A plasma processing technique is used to produce the anti-fogging SHPL-DLC coatings. The technique is a proven semiconductor industry process carried out in a vacuum chamber and is compatible with large-scale, volume processing. The Superhydrophilic (SHPL) surface is achieved through an all-dry process consisting of an oxygen plasma etch to engineer the surface topography of the polycarbonate, creating a controlled nanotextured surface, follow by Plasma Enhanced Chemical Vapor Deposition (PECVD) of a thin DLC layer with high surface energy. The entire process takes place at low temperatures compatible with polymer processing (< 50° C). The oxygen plasma etch is a proven and effective process for polymer surface modification, cleaning and adhesion improvement.[1] Studies have shown that a high density oxygen plasma can be used to modify plastic surfaces resulting in nanotextured surface with an approximately 100-250 nm RMS roughness.[2] After coating with a high surface energy DLC the nanotextured plastic surface becomes superhydrophilic with a water contact angle WCA < 10°, so the water drops on the surface spread out and are not capable of scattering light and producing fogging. It is important to note that neither the oxygen plasma surface treatment or DLC layer by themselves produce a superhydrophilic surface. On the contrary, both are required together to produce the SHPL result.

In addition to providing a high energy surface, there are many advantages to the DLC coating. It provides a hard, abrasion resistant layer that is inorganic, highly inert and not effected by most chemicals. DLCs are commonly used in industrial applications to enhance the hardness, wear and abrasion resistance of a surface, in addition to providing protection from corrosion and chemical attack. This is in contrast to other anti-fog coatings that are almost universally based on organic or polymer chemistries and as a result tend to be soft and susceptible to chemical attack from solvents and cleaners and offer little abrasion protection.

The DLC coating provides a hard, protective surface (~100-300 nm) with high surface energy. DLCs come in many varieties and the key to producing the high surface energy is through the controlled addition of additives or dopants. DLCs with high hardness and Young's modulus and with excellent hydrophilic properties are produced by incorporating silicon (Si) into the DLC.[3] The increase in surface energy is often attributed to the gain of sp2 carbon hybridization and dangling bonds leading to a increase in the polar part of the surface energy.[3] The Si doping of the DLC is generally accomplished by using hexamethyldisiloxane (HMDSO) during the PECVD deposition process.

As a side note, superhydrophobic (SHPO) coatings were also tested in this project for their anti-fogging properties. Interestingly, by adjusting the plasma pre-treatment, through varying the power and gas flow ratios, and adjusting the DLC properties by varying the power, gasses and flow rates, a SHPO-DLC coating can be produced on polycarbonate with a WCA > 150° using the PECVD process. However, steam fog testing quickly demonstrated that SHPO coatings do not possess effective anti-fogging properties, and as a result, the investigation of SHPO coatings was discontinued.

II. Background on Superhydrophilic Surfaces

Studies conducted at Acree and by others have demonstrated that a superhydrophilic (or superhydrophobic) surface cannot be created with a high surface energy (or low surface energy in the case of superhydrophobic) coating alone.[4-6] Studies have established that wetting properties are governed by both surface chemistry and topography. In other words, two requirements must be met in order to achieve a superhydrophilic surface: (1) A surface with nanostructures or nanotextures, and (2) a high surface energy material coating. The combination is key to achieving anti-fogging surfaces with WCA < 10°.

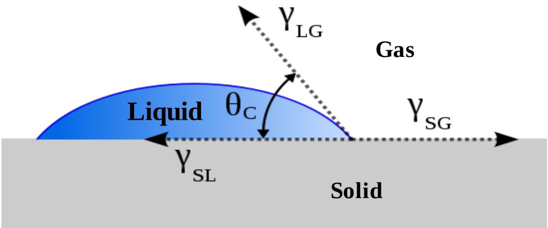


Figure 1. The contact angle, θ_C, is the angle formed by a liquid at the three phase boundaries where the liquid, gas, and solid intersect.

Wetting or non wetting properties of a surface are governed by the forces at the contact line between the solid-liquid (SL), solid-gas (SG) and liquid-gas (LG) boundaries arising from the tensions at these interfaces γ_{SL}, γ_{SG}, and γ_{LG}, as depicted in Figure 1. Projecting the liquid-gas force horizontally and establishing a horizontal force balance gives rise to Young's equation.[2]

$$\cos\theta_c = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} \quad \text{Equ. 1}$$

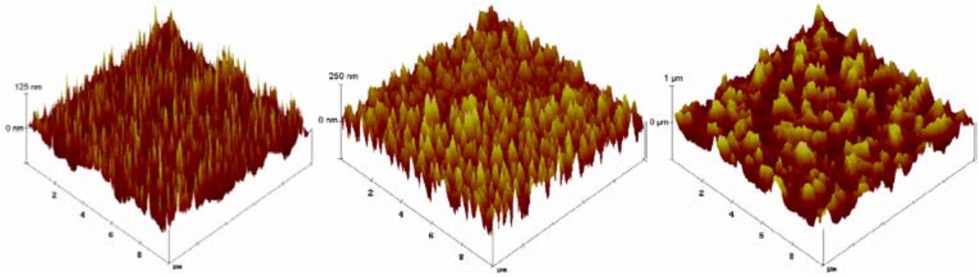
where θ_c is the contact angle. This static contact angle between a flat surface and a water droplet is generally used as a measure as to whether a coating attracts or repels water. Surfaces with $\theta_c > 90°$ are termed hydrophobic, whereas those with angles < 90° are referred to as hydrophilic. In this project, we are interested in superhydrophilic coatings that have a $\theta_c < 10°$ so the water droplets spread out and thereby do not scatter light and fog the surface.

Since most of the surfaces encountered are not ideally flat but have surface roughness, Wenzel proposed a more realistic, modified version of Young's equation.[2]

$$\cos\theta_w = r \cdot \cos\theta_c \quad \text{Equ. 2}$$

where θ_w is the Wenzel's contact angle, θ_c is the contact angle from Equation 1, r is the roughness factor with a value greater than 1 and defined as the ratio of the actual surface area of the rough surface to the geometric projected area. Since $r > 1$, Wenzel's equation predicts that texturing of the surface will not determine if a surface is hydrophilic or hydrophobic but will enhance its intensity once established through surface energy considerations. Note that the WCA measured in this project is most closely associated with θ_w .

Recent studies agreed well with the above models and further establish that superhydrophilic properties can only be achieved by having a surface with a modified topography combined with a high surface energy coating. Studies at Acree and by others have shown that a high density oxygen plasma can be used to roughen surfaces of polycarbonate and other plastics resulting in nanotextures with approximately 100-250 nm RMS roughness.[2] Figure 2 shows the surface topography using atomic force microscope analysis of oxygen plasma treated plastic samples after 1, 2 and 5 minutes of etching time. It can be seen that the surface morphology and amplitude of the surface roughness is a strong function of the process duration. In plasma etching of polymers, atomic oxygen free radicals produced by high density plasmas are the etching agent. During the etching process, atomic oxygen attacks the carbon-carbon molecular bonds in the polymer backbone and removes the molecule efficiently from the polymer.



1 min etching **2 min etching** **5 min etching**

Fig. 2. AFM images of oxygen plasma treated polymer samples.

III. Background on DLC Coatings

DLC is an amorphous carbon coating with high mechanical hardness, chemical inertness, and optical transparency. Carbon forms a great variety of crystalline and disordered structures because it can exist in three hybridizations: sp3, sp2 and sp1. The strong sp3 covalent bonding confers the above mentioned desirable properties of DLC coatings and its percentage varies dependent upon deposition methods and conditions. Therefore, DLC is often referred to as a family of coatings with differing properties and tradeoffs.[7] In general, DLC provides extremely high hardness, high elastic modulus, and low coefficient of friction. These attractive characteristics have led to strong technological interest in DLC for many applications including tribology, MEMS, electronics, data storage, optics, automotive, aerospace, and medical industries.

Table 1. General DLC Properties.

Material	Young's Modulus, GPa	Poisson's Ratio	Hardness, GPa	Stress, GPa	Optical Transparency
Bulk Diamond	1141	0.07	>100	---	Excellent
Diamond (CVD)	891	0.07	31 to 100	---	Excellent
DLC, ta-C (Arc deposited)	662	0.202	30 to 50	-9	Visible absorption
DLC, a-C (Sputter)	369	0.3	10 to 40	-1.5	Visible absorption
DLC, a-C:H (PECVD)	85	0.3	3 to 15	-0.5	Excellent

Table 1 shows the physical properties of common DLC coatings. While some DLC coatings are deposited using chemical vapor deposition (CVD), the process is performed at several hundred degrees centigrade and therefore not appropriate for polymer materials, hence the use of PECVD in this project, which allows deposition at a much lower temperature. Most DLCs, including the coatings in this study, contain hydrogen as a dopant. The introduction of hydrogen serves several purposes: (1) dangling bonds are passivated and the graphitic phase removed increasing transmission, and (2) the intrinsic stress in the coating is reduced allowing thicker coatings to be deposited. The hydrogen also tends to reduce the hardness and Young's Modulus of the DLC coating, making it more compatible with soft plastic materials. Even with the lower hardness, the hardness of hydrogenated DLC is still many orders of magnitude higher than that of polycarbonate, and hence, provides much better abrasion and scratch resistance compared to uncoated PC.

In order to form the anti-fogging coatings, a DLC with high surface energy is desired so that in conjunction with the nano-structured topography a superhydrophilic surface is produced. The DLC coating not only provides a high surface energy layer for the SHPL, but also provides a hard protective layer that is inert to most chemicals and abrasion resistant. Previous studies have indicated that DLCs with high surface energy are produced by the introduction of Si as a dopant.[3] The increase in surface energy is often attributed to the gain of sp2 carbon hybridization and dangling bonds leading to an increase in the polar part of the surface energy.[3]

IV. Experimental Setup and Analytical Measurements

A. PECVD Coating Process

PECVD is a vacuum coating process that is a variation on Chemical Vapor Deposition (CVD) where plasma is used to energize a chemical gas and create reactive radicals that chemically combine on the surface of the part to form the coating. The advantage of PECVD over standard thermal CVD is that the deposition reactions take place at much lower temperatures and higher reaction rates, allowing a wide range of complex materials to be coated at low temperatures (typically 20° C to 40° C).

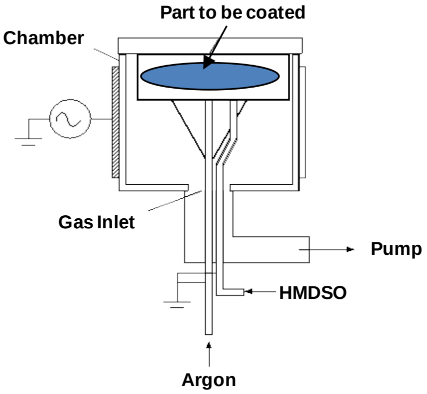


Figure 3. Schematic of PECVD system.

A general schematic of a PECVD system is shown in Figure 3. The process is carried out under vacuum in a pressure range of about 10 mTorr to 30 mTorr. The basic components of a PECVD coating system consist of the vacuum chamber, high vacuum pumps, various vacuum gauges, gas distribution manifold with gas feeds, and an rf power supply that is connected to upper and lower electrodes inside the chamber to energize the gas mixture. Figure 4 shows a picture of a PECVD coating system at Acree. In this picture the system is setup in a parallel plate configuration that is used to coat flat specimens such as the test coupons that were produced during the course of this project. In order to coat curved or more complex geometries, generally electrodes with curved shapes will be used, as described in more detail in Section VI below.

The advantage of PECVD deposition is that it can deposit uniform layers on large, 3-dimensional, complex shaped objects because the entire volume of the system is filled with the reactive deposition plasma, so all surfaces are coated. The volume plasma is created capacitively by energizing the electrodes shown in Figure 4 using an RF power supply operating at 13.56 MHz. To produce the DLC coatings a mixture of Ar and acetylene (C_2H_2) are introduced into the vacuum chamber through the gas manifold. For this project in order to produce DLCs with high surface energy for the SHPL coatings, Si is introduced into the DLC as a dopant. To this end, HMDSO (hexafluoroethane, $C_6H_{18}OSi_2$) is introduced into the chamber as a gas by bubbling Ar through the liquid HMDSO outside the chamber in a special flow tank (not shown in the figure) and flowing the mixture into the vacuum chamber.

The properties of the DLC can be controlled over a wide range by varying the process settings, such as, process pressure, rf power, flow rates of the various gasses, electrode spacing and geometry, and electrode polarity. A large number of experiments were conducted in the course of this project to optimize the DLC superhydrophilic coating properties. The coating properties were first optimized using water contact angle and optical transmission measurements on 1” x 3” flat polycarbonate samples, with the goal of producing coatings with WCA < 10° and optical transmission in the visible T > 85%. Once these goals were reached, samples were prepared and measured for anti-fogging performance, steam exposure, chemical resistance, abrasion resistance, etc., as detailed below.

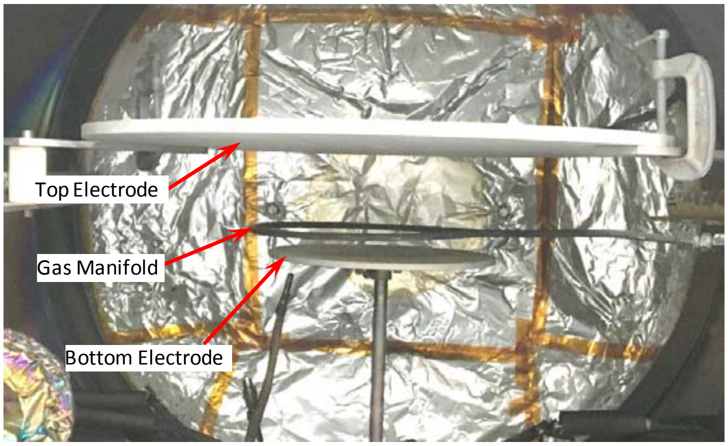


Figure 4. View of PECVD setup.

Another advantage of the PECVD process is that the same setup is used to produce the nanotextured surfaces. By introducing O_2 and Ar gasses and creating a plasma by applying power to the rf electrodes, the polycarbonate surface is modified on a nano-scale. This allows the SHPL-DLC coatings to be efficiently produced without breaking vacuum between processing steps. The general procedure for applying the SHPL-DLC coating is: 1) the parts are loaded into the coating system, 2) the chamber is pumped down to low pressure, 3) the plasma etch step is performed, 4) the DLC is deposited, and 5) the chamber is vented back to atmospheric pressure and the parts removed. The entire process takes about two hours.

B. Description of Analytical Measurements and Tests

A number of analytical measurement and tests were performed on the samples during the course of the project. The measurements and test methods used are:

1) Fogging and Breath Simulation Testing: A custom built fogging test system was constructed at Acree. A picture of the system is shown in Figure 5. The system consists of an off-the-shelf steam humidifier that was modified by adding a “chimney” made from Kapton plastic in order to better direct the steam flow and to control the steam temperature, which was established at 104° F. The samples are mounted to a rotating platen driven by a variable speed motor set to 18 rpm and the temperature of the steam is constantly monitored using a thermocouple connected to a Fluke meter. When running, the samples alternatively pass through the steam, and then out into room air, and back into the steam 18 times per minute, simulating human breathing. The samples are mounted to the platen with the coated surface facing down so they receive full and direct steam exposure. The system was used to both verify anti-fogging properties by simple observation of the degree of fogging while in operation and to perform the long-term breath exposure testing, which consists of passing the samples through the steam for 216,000 cycles (200 hours or 8.3 days). All of the other tests listed in this section were performed before and after the 200 hour steam exposure test to ensure that there was no degradation of the SHDL-DLC coating properties, including anti-fogging properties.

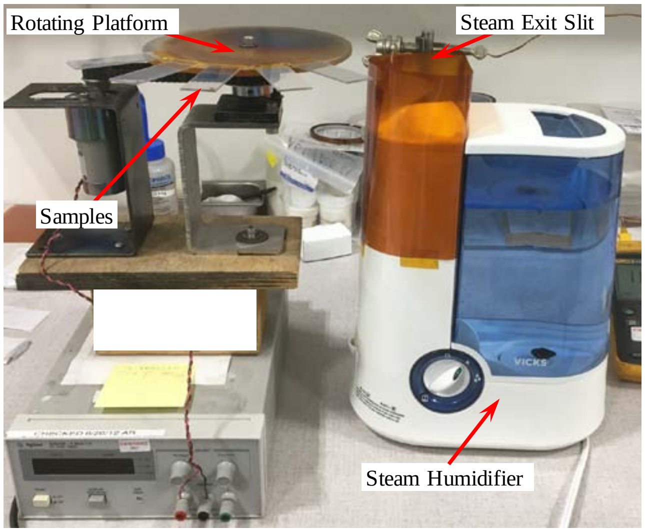


Figure 5. Breath simulation setup.

2) Water Contact Angle (WCA): The water contact angle is measured using a goniometer with a telescopic camera system connected to a computer. The system works by applying a precise and measured drop of purified water to the surface of the sample, imaging the drop using the camera, and feeding the image to the computer. The computer then uses software to calculate the angle between the drop and the substrate surface. The contact angle, θ_C, is the angle formed by the liquid at the three phase boundaries where the liquid, gas, and solid intersect.[8] The WCA measurement gives a quick indication of the surface energy and the hydrophilic (high surface energy) or hydrophobic (low surface energy) properties of the surface. In general, for superhydrophilic coatings WCA $< 10°$ whereas superhydrophobic surfaces have WCA $> 150°$. The idea is to measure and optimize the superhydrophilic properties of the SHPL-DLC coating, which can be used to quickly optimize and down-select the most promising coatings and be correlated with the antifogging performance.

3) Optical Transmission Measurement: The spectral transmission of the coated samples was measured using a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer at Acree. The samples are measured over the visible range, 400 and 800 nm. The goal is to show that the coating does not reduce the optical transmission of the coated samples to less than 70% through the visible range.

4) Cross-Hatch Tape-Pull Adhesion Test: The adhesion of the coatings was measured using a tape-pull test per ASTM D3359 Method B, Class 4B using the specified 3M #250 tape. This is the most severe of the various tape-pull methods and involves scratching a cross-hatch pattern into the coating prior to performing the test. The test specifies inspection of the sharp corners for delamination. This test was performed on each sample before and after the steam exposure and other mechanical and chemical tests to ensure no degradation of coating adhesion.

5) Abrasion Resistance Test: Abrasion testing was performed using a modified version of the moderate abrasion test per MIL-C-48497. The test consists of using a Taber type linearly oscillating stage, to which the sample is affixed, and running the sample back-and-forth under an abrasive tip with a fixed normal load. The test conditions used were: Number of strokes = 50, Stroke Length = 2.3 cm, Normal Load = 3.5 psi, Abrading Tip = CleanWipe wiper. The test was modified by using the CleanWipe instead of the usual cheesecloth. This was done because the MIL-C-48497 test was originally designed for glass optical components, not plastics, and the cheesecloth is too aggressive for polycarbonate, even when uncoated, producing abrasion and scratch marks.

6) Water Cleaning Test: The water cleaning test is designed to test the coating for exposure to typical cleaning procedures that may be required over the life of the spacesuit helmet. The samples were submerged in DI water for approximately 5 minutes, wiped with a Kimwipe cleaning cloth, and then blown dry with air. This procedure was repeated at least three times on each sample. The anti-fogging, adhesion, optical transmission and abrasion resistance were measured before and after the water test to ensure no degradation of coating properties.

7) Chemical Exposure and Cleaning Test: In the chemical exposure test the samples were saturated with isopropyl alcohol (IPA) and then wiped using a Kimwipe cleaning cloth and allowed to dry. The test was repeated at least three times on each sample. The anti-fogging, adhesion, optical transmission and abrasion resistance were measured before and after the chemical exposure test to ensure no degradation of coating properties.

V. Experimental Results and SHPL-DLC Coating Development

A large number of experiments were conducted in the course of this project. In the early stages it was not clear whether a superhydrophobic or superhydrophilic coating would work better in terms of anti-fogging performance. As a result, experiments were conducted to develop both types of coatings on polycarbonate. Anti-fogging testing as described in Section IV-B quickly demonstrated that superhydrophilic coatings far outperformed superhydrophobic coatings for antifogging performance, and as a result, superhydrophobic coatings were no longer pursued and instead effort was put into developing and optimizing the superhydrophilic coatings.

Table 2. Deposition parameter ranges investigated.

Parameter	Range Investigated	Unit
Working Pressure	1 to 30	mTorr
Ar/O_2 Ratio	0.5 to 68.0	N/A
RF Power	100 to 600	Watts
Plasma Etch Time	10 to 60	min
$HMDSO/O_2$ Ratio	0.16 to 4.5	N/A
DLC Deposition Time	3 to 45	min
Electrode Polarity	+ or -	N/A
DLC Thickness	10 to 1,000	nm

Table 2 shows the range of parameters over which experiments were conducted. As can be seen from the table the parameter range is quite large. To develop the SHPL coatings the first step was to create the nanotextured surface topography. Figure 6 shows the measured Rq on various polycarbonate samples versus RF power during the O_2 etch process, where Rq is the root-mean-square surface roughness and is the square root of the sum of the squares of the individual peaks and valleys on the surface from the mean line. Rq is measured at Acree and calculated automatically using a Dektak 3030*ST* Surface Texture Analysis System. For the Figure 6 data the chamber pressure was maintained at 28 mTorr, the treatment duration was 30.0 minutes, and the O_2/Ar partial pressure ratio was 1:1. The top electrode was energized for this data (TEE), meaning that the RF power was connected to the top electrode (See Figure 4) and the bottom electrode was grounded. It is interesting to note that as the power is increased at first the sample becomes rougher, higher Rq, but with increased power the surface actually becomes smoother.

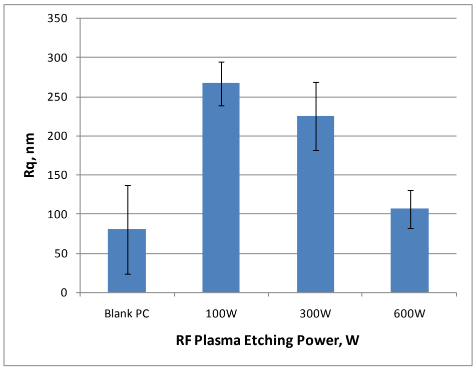


Figure 6. Rq surface roughness vs. Etch power with TEE.

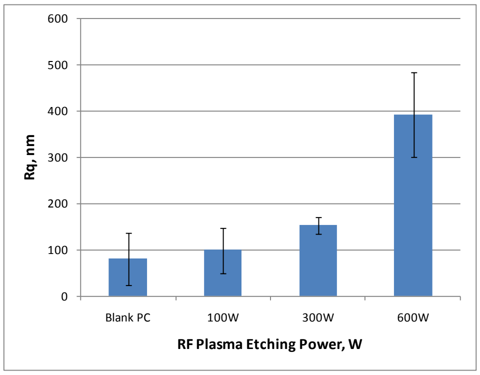


Figure 7. Rq surface roughness vs. Etch power with BEE.

Figure 7 shows Rq data versus power with the bottom electrode energized (BEE). The process settings are the same as Figure 6, namely chamber pressure 28 mTorr and O_2/Ar partial pressure ratio 1:1, except the treatment duration was shortened to 20.0 minutes, since the BEE configuration gives a more aggressive result. Note that with the BEE setup a much higher surface roughness is achieved for a given power and the surface roughness increasing monotonically with power. Additional testing demonstrated that after the DLC coating was deposited the BEE samples produced better SHPL surfaces with lower WCAs and better anti-fogging properties. As a result, the BEE configuration was used to produce all of the tested SHPL samples.

Figure 8 shows typical WCA results during the development of the SHPL coatings for a) uncoated polycarbonate (shown for comparison), b) DLC coated polycarbonate with no plasma etching, and c) DLC with plasma etching. The figure clearly illustrates the beneficial effect of the plasma etch step. With no plasma etch the WCA = 21.6°, which is about the lowest value achievable with just the DLC alone and the surface is not superhydrophilic. However, with the plasma etch step added to create the nanostructure surface topography, the WCA becomes almost 0° and is clearly superhydrophilic (WCA < 10°). Note that the DLC was already optimized for the highest surface energy possible (lowest WCA) by adjusting the Si dopant, power levels, etc., prior to combining both the etch and DLC, and yet WCA = 21.6° is the lowest value the DLC was able to achieve alone. For these samples the bottom electrode was energized and the DLC deposition power was 300 W.

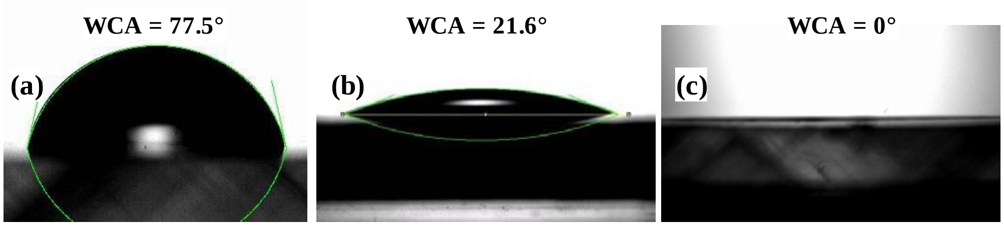


Figure 8. WCA measurements. a) Uncoated polycarbonate. b) DLC with no plasma pretreatment. c) DLC with plasma pretreatment.

Figure 9 demonstrates the anti-fogging properties of the SHPL-DLC coatings. The tests were conducted using the fogging test setup as described in Section IV-B. The samples were held over the stream exit port for 3 seconds and then the images were taken. Figure 9 (a) is for uncoated polycarbonate and is included for comparison. Notice the significant fogging on the surface. Figure 9 (b) is a SHPL-DLC coated sample that is fresh from the coating system prior to exposure to the 200 hour steam test, water cleaning test, IPA chemical exposure test, etc.. Notice there is no fogging of the surface whatsoever. Figure 9 (c) is a SHPL-DLC coated sample that was subjected to 200 hour steam exposure, the water cleaning test, the IPA chemical exposure test, and the MIL-C-48497 abrasion test. Note that even after all of these tests and exposure the coating anti-fogging properties are excellent and have not diminished.

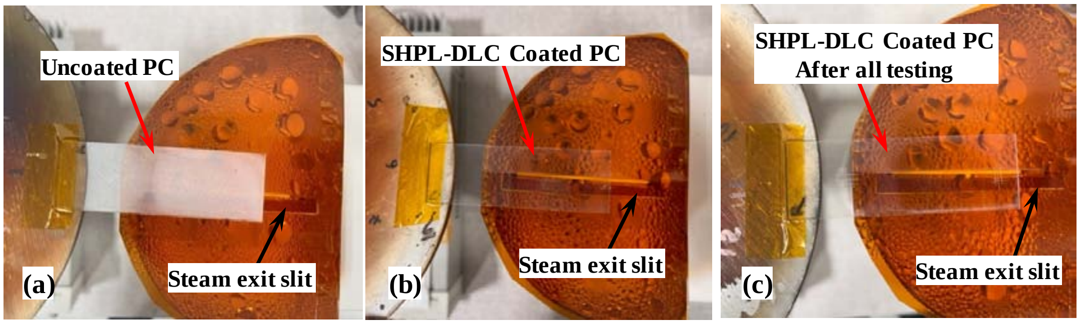


Figure 9. Anti-fogging properties of: a) Uncoated polycarbonate. b) SHPL-DLC freshly deposited. c) SHPL-DLC after 200 hour breath exposure, water cleaning test, IPA immersion testing, and MIL-C-48497 abrasion testing.

Figure 10 shows photomicrographs of SHPL-DLC coatings after ASTM D3359 cross-hatch adhesion testing. Figure 10 a) is for a freshly deposited SHPL-DLC coating. Figure 10 b) is for a SHPL-DLC coating that has undergone the 200 hour steam exposure test, water cleaning test, IPA immersion testing, and MIL-C-48497 abrasion testing. Note that for both samples no coating is removed by the tape, indicating excellent adhesion. In particular, coating failure will occur at the edges and sharp corners of the scribes, but no coating is removed.

Figure 11 shows the samples after the MIL-C-48497 abrasion testing. Figure 11 a) is uncoated polycarbonate and is shown for comparison. Figure 11 b) is the SHPL-DLC coating that was freshly deposited. Figure 11 c) is the SHPL-DLC coating after 200 hour steam exposure, water cleaning test, and IPA immersion testing. Note that no scratches or streaks are produced on any of the samples. All of the samples pass the test and the conclusion is that the SHPL-DLC coating does not degrade the scratch and abrasion resistant of the polycarbonate. If anything it is expected that the SHPL-DLC coating will enhance the abrasion resistance of the polycarbonate.

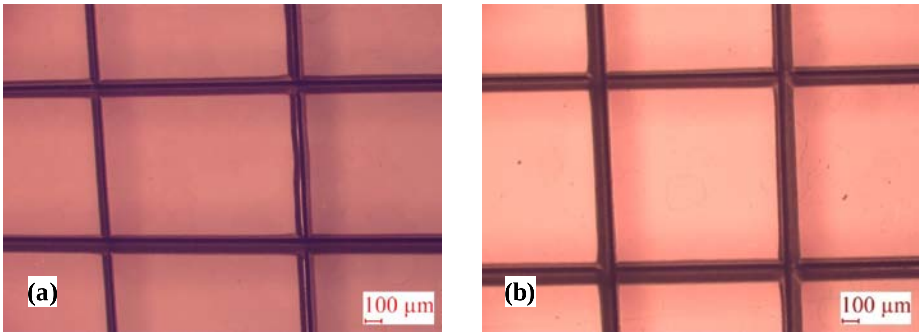


Figure 10. Photomicrographs of the SHPL-DLC coating after ASTM D3359 cross-hatch adhesion test. a) SHPL-DLC freshly deposited. b) SHPL-DLC after 200 hour steam exposure, water cleaning test, IPA immersion testing, and MIL-C-48497 abrasion testing.

Figure 12 shows optical transmission measurements in the visible region for a number of samples. The samples are as follows: (a) Uncoated polycarbonate. (b) SHPL-DLC coated polycarbonate. (c) SHPL-DLC coated polycarbonate after 200 hour steam exposure. (d) SHPL-DLC coated polycarbonate after 200 hour steam exposure, water cleaning test, and IPA chemical exposure test. (e) SHPL-DLC coated polycarbonate after 200 hour steam exposure, water cleaning test, IPA chemical exposure test, and MIL-C-48497 abrasion testing. As is evident from Figure 12, the SHPL-DLC coating has little effect on the optical transmission of the polycarbonate. The average transmission over the visible (400 nm to 800 nm) for the uncoated polycarbonate is T_{avg}(a) = 82.2 %. For the newly coated SHPL-DLC on polycarbonate T_{avg}(b) = 81.5 %, a drop of only 0.7% and is not discernable to the eye. Even after the 200 hour exposure to steam, the water cleaning test, the IPA chemical test, and the abrasion test, the average optical transmission over the visible range is T_{avg}(e) = 79.3 %, a change of 2.9% and is still not discernable to the eye.

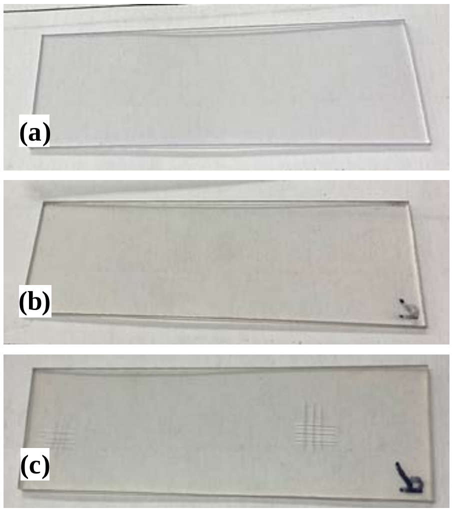


Figure 11. Photo of samples after MIL-C-48497 abrasion testing. a) Uncoated polycarbonate. b) SHPL-DLC freshly deposited. c) SHPL-DLC after 200 hour steam exposure, water cleaning test, and IPA immersion testing.

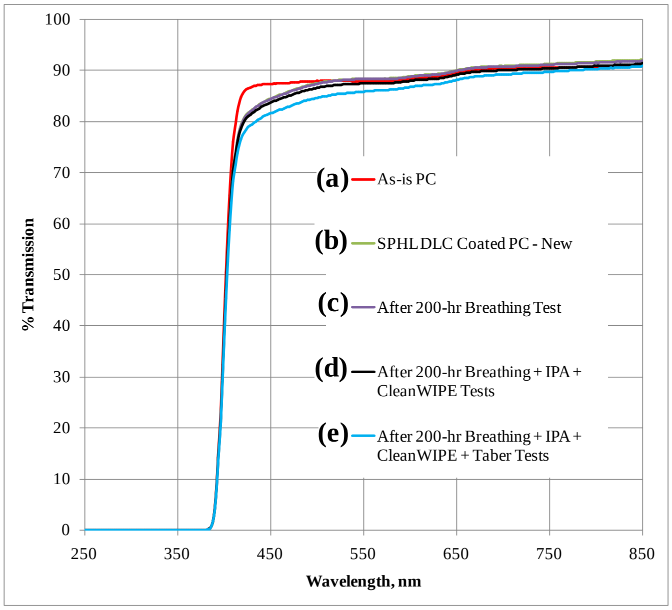


Figure 12. Optical Transmission vs. Wavelength

VI. Coating Domes and Curved Surfaces with SHPL-DLC

The PECVD process is well suited for coating curved surfaces and is capable of coating virtually any shape. To coat curved surfaces the electrodes are designed to match the general contours of the substrate. Figure 13 shows a few examples of polycarbonate domes that were coated during the project. The domes range in size from about 7” to 9” in diameter and were selected because they roughly match the dimensions of typical spacesuit helmet face shields.

Figure 13. Pictures of polycarbonate domes used for coating tests.

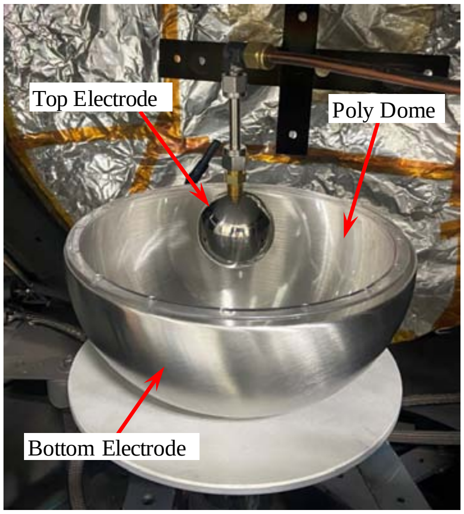


Figure 14. Picture of PECVD setup used to apply SHPL-DLC anti-fogging coating to curved shapes.

Figure 14 shows the PECVD setup used to coat the inside surface of the domes. For this particular setup a 7.2” diameter dome is being coated. The top electrode is a 2” diameter metal ball that has been drilled with a symmetrical hole pattern and is used to distribute the precursor gasses. The top electrode functions as both the electrode plate and the gas distribution manifold. The bottom electrode is a semicircular metal bowl that is 7.8” in diameter and is energized with the 13.56 MHz RF power. The process steps to produce the SHPL-DLC coating on a curved surface are the same as those on a flat surface using the parallel plate system shown in Figure 4. The etch step is first carried out using a mixture of O_2 and Ar gas, followed by the SHPL-DLC deposition using Ar and HMDSO. The gas flows and power levels are adjusted slightly to optimize the coating for the curved surface. Note that a tight fit between the bottom electrode and the polycarbonate dome is not necessary in order to produce a high quality, uniform thickness SHPL-DLC coating. For the example shown in Figure 14 the difference in diameter between the PC dome and the bottom metal electrode is 0.6” (15 mm) and yet the coating produced is uniform with no rainbow effects and excellent anti-fogging properties over the entire surface. To illustrate this Figure 15 shows a PC dome before and after coating. The SHPL-DLC coating is not perceptible on the dome.

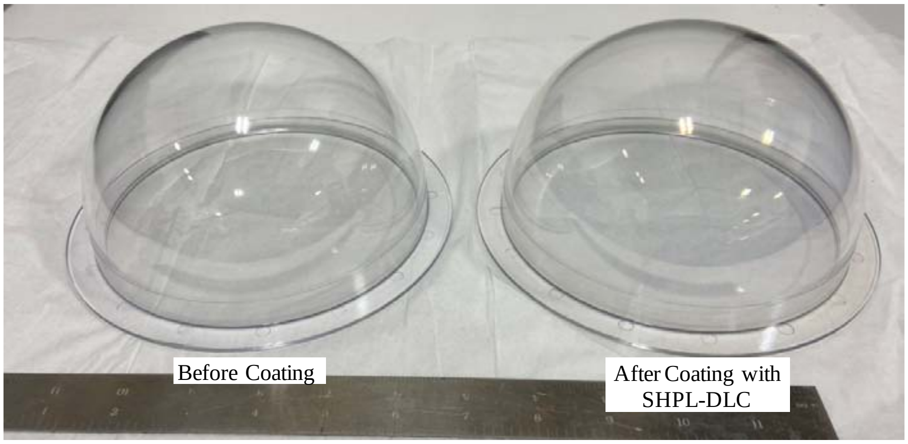


Figure 15. Polycarbonate domes before and after coating with SHPL-DLC anti-fogging coating.

Fogging tests were performed on the PC domes using the fog testing setup. The domes were held over the steam exit point exposing the inside surface for about 3 seconds and then removed and photographed. Figure 16 shows the results of the tests. The dome on the left (a) is uncoated polycarbonate and the fogging on the inside of the dome is significant. The dome on the right (b) was coated with the SHPL-DLC and the surface has no fogging whatsoever. Note that both domes were exposed to the steam source for the same amount of time and the difference between the uncoated dome and SHPL-DLC coated dome is clear and obvious.

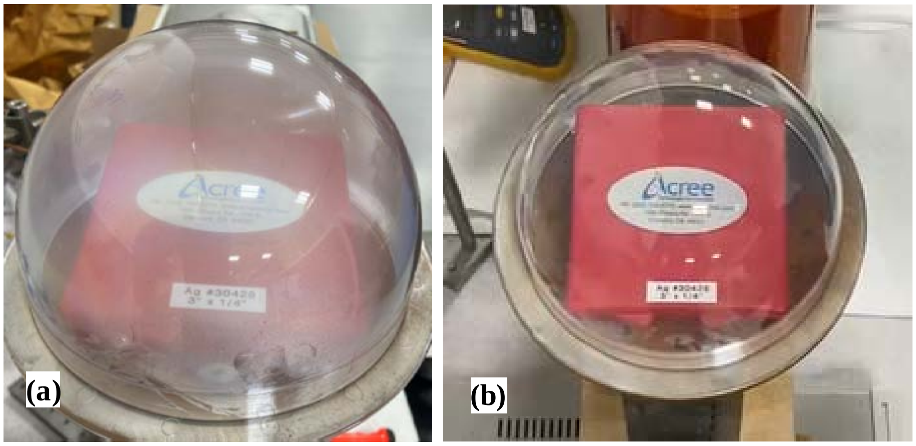


Figure 16. Pictures showing results of fogging tests on (a) uncoated polycarbonate dome and (b) SHPL-DLC anti-fogging coated dome. Note that there is no fogging on the coated dome.

VII. Conclusion

Fogging on the inside of spacesuit helmets is a longstanding and persistent problem for NASA. Currently there is no effective anti-fog treatment suitable for use that meets NASA requirements. NASA’s goal moving forward is to develop and use a permanent anti-fog coating that prevents fogging inside of spacesuit helmets. In this project a permanent superhydrophilic anti-fogging DLC coating was developed on polycarbonate material that has excellent anti-fogging properties and meets NASA environmental and exposure requirements. The coating is deposited in a vacuum system using a PECVD process that is scalable to large production volumes and can be used to coat parts of almost any size and shape, including domes. The coating is robust and was demonstrated to not degrade due to extended steam exposure (200 hours), exposure to cleaning using DI water, and is resistant to chemical exposure and has excellent abrasion properties.

Acknowledgments

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