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Evaluation of Protective Silicone/Siloxane Coatings in Simulated Low-Earth-Orbit Environment

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A protective silicone/siloxane hybrid coating was prepared using a polysiloxane binder and nanophase silicon–oxo clusters. Siloxane clusters were formed in situ from sol–gel precursors during the UV-curing process, which is accomplished through a cationic curing mechanism at ambient temperatures. The binder of the coating was a methyl-substituted silicone oligomer, and the siloxane/silicon–oxo phase was prepared from tetraethoxysilane (TEOS). Alkoxy silane groups were also grafted onto the silicone oligomer to couple with a chain, to couple with the silicon–oxo clusters. Scanning electron and atomic force microscopy, x-ray photoelectron spectroscopy, and UV absorbance/transmittance studies were used to observe the silicone/siloxane hybrids performance in low-Earth-orbit simulators. The results show that a protective oxide layer was formed, and at moderate fluence levels (2.22×10^{21} atoms/cm^2) the silicone/siloxane hybrid coating did not exhibit microcracking and had appreciable specular transmittance.

Introduction

THROUGH the use of lightweight, high-strength composite materials, the weight of satellites and spacecraft can be drastically reduced, which is important in both the economical and efficiency aspects. However, these composites, which can replace the metallic exterior and infrastructure of satellites and space vehicles, cannot survive the aggressive environment of space unless properly protected. Resistance to degradation from the hostile conditions present in both low Earth orbit (LEO) and geosynchronous orbit is essential for the extended use of these lightweight composites in space. Ground-state atomic oxygen, deep UV radiation, and the extreme velocity of the vehicle have been recognized as the major causes of decomposition among carbon-based materials in LEO.[1,2] The UV radiation that is present in LEO is of sufficient energy to cleave organic bonds, which can lead to chain scission and cross-linking reactions in organic polymeric materials. This can lead to thermal conductivity, changes in optical and mechanical properties, embrittlement, and a decrease in strength.[3] Other factors that affect organic materials in space are thermal cycling, particulate radiation, vacuum, and micrometeoroids and debris. The need to counter the adverse effects of atomic oxygen erosion, as well as to protect from high-energy radiation and particles on organic materials, solar arrays, and other delicate instruments is of major importance.

A coating that can withstand atomic oxygen degradation, UV radiation, and atomic particles would be ideal. In addition, a coating that possesses thermal stability, flexibility, stability, and high optical transparency would be the desired protection for space vehicles constructed out of lightweight high-strength composites or other organic-based materials. High optical transparency would allow the coatings to provide protection for optical equipment, reflectors, and solar arrays. Several categories of polymers are colorless and transparent, such as polyesters or aliphatic polyimides, but have inadequate long-term thermal and atomic oxygen stability.[4,5] Some polymers do possess high thermal stability, such as aromatic polyimides, but have poor optical transparency.

Polyhedral oligomeric silsesquioxanes (POSS), which are dominated by an oxygen-to-silicon ratio of 1.5:1, have shown good resistance. Polysiloxanes and POSS contain covalently bonded reactive functionalities appropriate for polymerization or grafting. The POSS derivatives can be blended or copolymerized with many aerospace polymers and are being considered for atomic oxygen durability.[6,7] The resistance to atomic oxygen attack of silicone blended or copolymerized polymers depends not only on the oxygen-to-silicone ratio, but the fractional fill of the silicone. The challenge to make a functional use of such blends has been to find an adequately silicone-filled polymer that contains the appropriate protective silicone such that it has acceptable atomic oxygen durability, optical, thermal, and mechanical properties, as well as ease of application.

To harness the desired properties needed for protection while in the environment of space, siloxane polymers can be considered. Siloxane polymers are a class of noncarbon-based materials that have rates of erosion one to two orders of magnitude slower than organic polymers in LEO.[8,9] In addition to slower erosion rates, when exposed to atomic oxygen, siloxane polymers form a protective silicon dioxide barrier consisting of SiO_x (where x is from 1.8 to 2.0) (Refs. 10 and 11). The silica layer on the surface prevents further degradation of the polymer underneath with continued exposure to atomic oxygen.[12–14] This provides enhanced atomic oxygen resistance and will offer a self-healing mechanism if the coating is scratched or etched from debris by allowing additional atomic

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oxygen to oxidize the newly exposed silicon. However, this surface conversion from silicone to silica tends to produce tensile stresses within the surface of the oxidized silicone.[15]

A variety of approaches have been explored to identify silicone, silicone copolymers, or silicone–hydrocarbon blends that provide flexibility as well as atomic oxygen protection.[16–19] Results indicate that hybrid polymers composed of inorganic and organic polymers hold potential to survive LEO atomic oxygen attack. Although polysiloxanes possess atomic oxygen protection, thermal stability, flexibility, and stability, this is just part of the solution to achieve ideal protection from the elements of space. The UV radiation and high-energy particles can still damage siloxanes and degrade the underlying composite material as well. Therefore, to incorporate protection from those components, silicone/siloxane hybrid coatings, which are inorganic/organic hybrid materials, can be used. Silicone/siloxane hybrids are part ceramic (inorganic) and part polymer (organic or silicone) and can offer protection from atomic oxygen as well as UV radiation and high-energy particles via the in situ fabrication of nanophase silicon/metal–oxo clusters.[20,21] A synergistic effect between the inorganic and organic phases on a nanoscale is obtained through the use of phase coupling agents, which for this system are alkoxy silanes pendant from the polysiloxane chain. The synergy between the phases in this approach also is a function of the uniform distribution of the silicon–oxo clusters within the continuous siloxane phase.[22] The uniform distribution is attributed to nucleation effects of the coupling agents.[23–25]

The silicon–oxo clusters are formed through a series of hydrolysis and condensation reactions between sol–gel precursors. The reactions are given in Fig. 1. The size and domain of the silicon–oxo clusters can be controlled through the reaction conditions.[26] The reinforcing effect of the nanoscale inorganic phase can be maximized through the functionalization of the polysiloxane to accommodate bonding. The sol–gel precursor, oligomerized tetraethoxysilane (TEOS), has been found to be amenable to photoinduced cationic polymerization of cycloaliphatic epoxides. Also, the silanol groups formed can react with the cycloaliphatic epoxide to further reinforce the network. Once the coating is exposed to atomic oxygen, a protective layer of silicon oxide is formed and, with the incorporation of silicon–oxo clusters the coating should protect the composite material against atomic oxygen erosion, high-energy particles, and UV radiation.[24]

In a previous study, hydride terminated poly(dimethylsiloxane-co-methylhydrosiloxane) was prepared and then functionalized with cycloaliphatic epoxides and alkoxy silanes via hydrosilation chemistry.[27] The pendant alkoxy silane aids in miscibility during silicone/siloxane hybrid formation and provides a site for interaction with the metal/silicon–oxo cluster, whereas the cycloaliphatic epoxide provides a reactive crosslinking site for cationic UV curing. In this study, the functionalized silicones were UV cured with TEOS oligomers to form films for LEO evaluation. Scanning electron and atomic force microscopy were used to study the physical effects atomic oxygen had on the coatings and to observe any silicon–oxo clusters formed during the crosslinking reactions. The oxidation of the silicone/siloxane hybrid surface on exposure to atomic oxygen was assessed using x-ray photoelectron spectroscopy. Thermal gravimetric analysis was also used to evaluate the thermal degradation of the coatings, and UV-visible spectroscopy was used to evaluate the optical properties of these coatings under various atomic oxygen fluence levels. Mechanical properties of the silicone/siloxane hybrid coating were also investigated before atomic oxygen exposure to provide insight on the durability of the coating during vehicle production/transport. The results of the investigation of the atomic oxygen durability under various fluence levels of the UV curable silicone/siloxane hybrid coating will be compared to the results of the presently used silicone coating DC 93-500. Analysis of these silicon coatings will provide insight into the dynamics of the materials interaction with atomic oxygen.

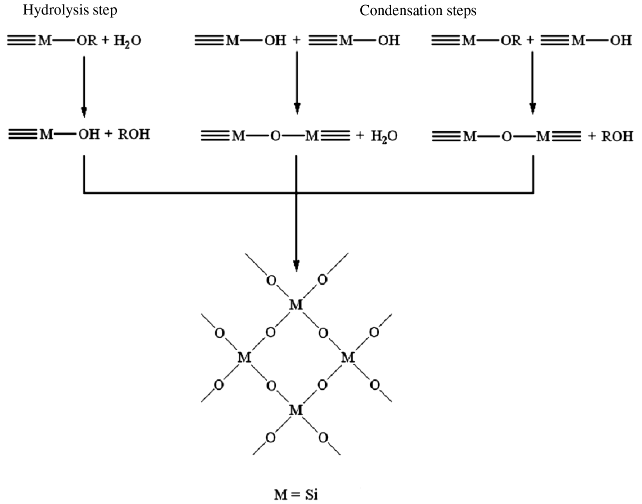


Fig. 1 In situ silicon–oxo cluster formation for nanoscale reinforcement in silicone/siloxane hybrid coatings.

Experimental

Materials

The functionalized polysiloxane and TEOS oligomers were synthesized as described earlier.[24] Toluene, supplied by Aldrich Chemical Co., was distilled and stored over molecular sieves (4A, beads, 8–12 mesh). Irgacure 250 was supplied by Ciba Specialty Chemicals and used as received. Air-sensitive materials were transferred and weighed in an inert atmosphere dry box under argon.

Instruments

Pencil harness tests were conducted according to the American Society for Testing and Materials (ASTM) method D3363-00. Taber scratch tests were performed using a Taber Shear/Scratch Tester model 502 and conforming to ASTM method G171-03. Taber abrasion tests were conducted on a Taber Industries 5130 Abraser using a CS-10 test wheel. Taber abrasion studies corresponded to ASTM method D552-93a. Thermogravimetric analysis was performed on a TGA Q 500 (Thermal Analysis). The x-ray photoelectron spectroscopy was completed on a Kratos Model ES3000 with a nonmonochromatic 120-W Al K-Alpha radiation source under a 10^{-8} torr vacuum. Scanning by electron microscopy was performed on a Hitachi S-2150 operating at 15 kV. Atomic force microscopy was performed on a multimode scanning probe microscope (Digital Instruments) using the tapping mode. Optical property changes before and after atomic oxygen exposure were made using a Perkin Elmer Lambda-19 spectrophotometer.

Coating Application

The functionalized polysiloxane was diluted with toluene, 25 wt%/wt, to reduce the viscosity. Sol–gel precursor (5 wt%/wt) and photoinitiator (3 wt%/wt) were also added to the diluted polysiloxane and thoroughly mixed. A piece of Kapton H (~10-cm diameter) was mounted onto a spinning stage and spun at a very high speed. The polysiloxane solution was dropped onto the center of the spinning Kapton sample. The sample was removed from the stage and passed through a UV-curing chamber with a belt speed of 25 ft/min and an average intensity of 150 mW/cm^2. The DC 93-500 was coated in the same manner, but placed in an oven at 80°C for 6 h to allow it to cure. Fused silica panels were also coated by both polymers in the same manner. The coating thickness was measured with a coating thickness gauge and atomic force microscopy (AFM). Both methods confirmed an average of a 2-μm thickness.

Atomic Oxygen Exposure

Samples of the silicone/siloxane hybrid coated Kapton H polyimide (coated on both sides) were compared with samples of DC 93-500 silicone-coated Kapton H (coated on both sides) for atomic oxygen durability. Optical property changes and mass loss were documented at atomic oxygen effective fluence levels of

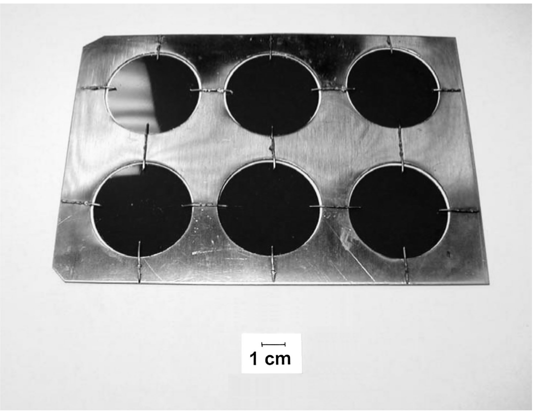


Fig. 2 Sample holder used to prevent curling of 2.54-cm-diam samples when they were exposed to atomic oxygen.

2.22×10^{21} and 1.38×10^{22} atoms/cm^2. Kapton H witness samples were used to determine the effective atomic oxygen fluence as described in Ref. 28. All substrates used for the evaluation and fluence witnesses were made of 2.54-cm-diam × 0.127-mm-thick Kapton H polyimide. An additional set of silicone/siloxane hybrid and DC 93-500 coated samples were made and were scratched before atomic oxygen exposure using finger wiping of laboratory dust. This was done to see whether minor abrasion of the coatings surface would cause preferential cracking of the silicone coatings with atomic oxygen exposure. Samples of the silicone-coated Kapton H were punched out and vacuum dehydrated for 48 h before weighing to minimize mass uncertainty due to weight loss as recommended by ASTM E 2089-00.

Atomic oxygen testing was performed in an SPI Plasma Prep II (13.56-MHz) radio frequency plasma asher. The ashers are typically operated on air at a pressure of 20–26.7 Pa (150–200 mtorr). The samples were held down by fine wires attached to a metal frame (Fig. 2) lying on a glass plate to minimize curling of the samples with atomic oxygen exposure from only one side. Curling typically occurs for silicone-coated samples that are coated on one side and could allow atomic oxygen to attack the uncoated back of the samples which would compromise the sample weight loss data. The plasma asher was operated at a Kapton effective flux of 9.21×10^{15} atoms $\cdot$ cm^{-2}/s.

Cross-contamination witness samples were placed in the plasma ashers next to the silicone-coated samples to assess the degree of silicone transport and resulting contamination. Tests were performed before sample exposures to validate that any contamination deposited would be a result of the samples contained within the plasma asher. Thicknesses of deposited contaminants were measured using a Dektak 6M stylus profilometer that scanned the contamination-coated fused silica slide from the deposited area to an area that was protected from contamination deposition by means of a tightly fitted aluminum foil mask.

Results and Discussion

The presence of atomic oxygen, high-energy particles, UV radiation, and thermal cycling in LEO make organic-based material degradation of great concern for spacecraft. The exposure of most silicones to atomic oxygen in LEO results in the steady conversion to silicon oxides, which can offer protection but can also lead to surface cracking and flaking. A need exists for a silicon-based self-healing coating that is free from such surface cracking and can be effectively used for material protection in LEO. A protective silicon/siloxane hybrid coating was prepared using a polysiloxane binder and nanophase silicon–oxo clusters to protect against the aggressive LEO environment. It was proposed that the polysiloxane will react with the atomic oxygen to form a silica layer on the surface. This silica layer protects from additional atomic oxygen exposure, whereas the nano-sized silicon–oxo clusters can offer UV-radiation (290–400 nm) and high-energy particle protection. Protection from all but the very nearest UV radiation can be accomplished through the incorporation of titanium sol–gel precursors.[29] Ground-based LEO simulators were used for evaluating the atomic oxygen durability over a range of fluence levels, of thin silicone/siloxane hybrid coatings on a Kapton H substrate.

The abrasion and scratch resistance of the cured coating were studied to determine how susceptible it is to physical damage. The Taber abrasion and scratch tests yielded a value of 183 wear cycles per mil and a scratch value of 50 g. Both of these values are low and show that the coating has poor abrasion resistance. These values were checked using the pencil hardness test, which gave a value of 2B/B. This value is also low, and this trend could be the result of the very low glass transition temperature of the coating, which is approximately −130°C. Such a low glass transition temperature makes the coating soft and vulnerable to damage. Varying the pendant groups on the silicone to raise the glass transition of the coating could be a potential answer in improving the abrasion resistance. Not surprisingly, this is the subject of further research.[24]

Thermal gravimetric analysis was performed to observe the thermal stability of the silicone/siloxane hybrid coating and the DC 93-500. Irreversible changes to the crosslinked structure of silicone polymers unavoidably occur at high temperatures due to chain scission or oxidative cross linking.[30] In an inert atmosphere depolymerization occurs with the loss of volatile products, mostly low molecular weight cyclic oligomers, but is often catalyzed by traces of acids, bases, water, or residual catalyst used in the polymers original production.[31] Typically, depolymerization occurs near 400°C for reasonably pure polydimethylsiloxane.[32] Figure 3 shows the comparison of the thermal stability of the silicone/siloxane hybrid and DC 93-500 coatings.

Thermal gravimetric analysis of the cured silicone/siloxane hybrid coating illustrates the loss of small molecular weight oligomers in the early stages of the analysis as depicted by the gradual decrease in weight percent until 400°C. The DC 93-500 does not exhibit this weight loss in the early stages of the analysis as a result of being vacuum stripped during its production, which eliminates any low molecular weight species. As expected, the depolymerization occurs near 400°C for both of the samples tested with the DC 93-500, showing a slightly higher degradation temperature as a result of its high purity. The range of molecular weights gives way to the multiple slopes the silicone/siloxane hybrid curve exhibits. Also note that the silicone/siloxane hybrid sample generated a small amount of residue (∼11%), which can be attributed to the silicon–oxo clusters formed during the polymerization process and high molecular weight chains that may not have completely volatized/degraded.

The thermal degradation of the DC 93-500 is drastically different than the silicone/siloxane hybrid coating's profile. The major degradation slope starting at approximately 400°C shows a more thermally stable compound with a broader degradation range from 400 to 730°C as opposed to the silicone/siloxane hybrids range of

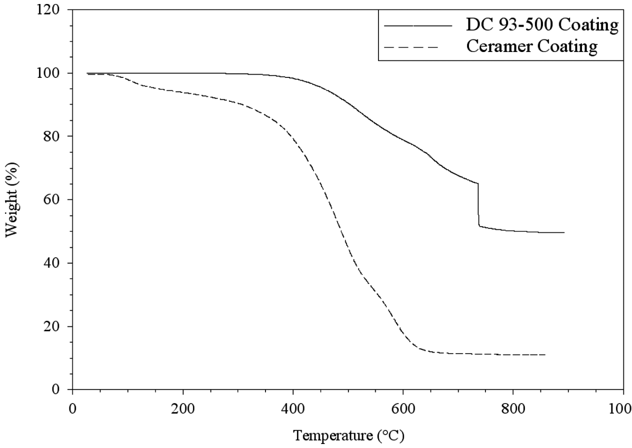


Fig. 3 Thermal gravimetric analysis of silicone/siloxane hybrid coating with 5% sol–gel precursor and DC 93-500.

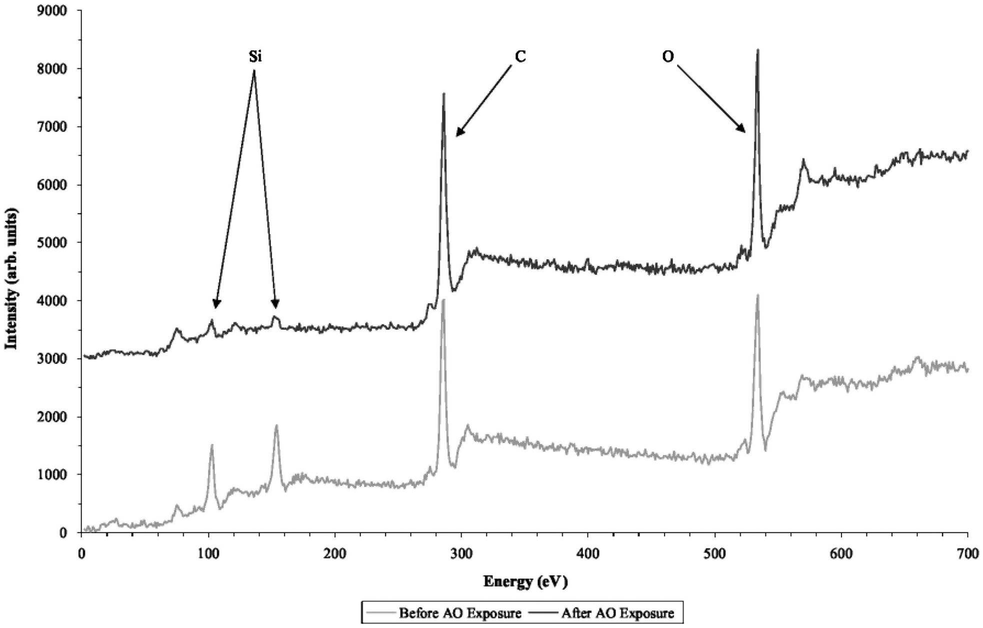


Fig. 4 XPS spectrum of cross-linked methyl-substituted polysiloxane before and after atomic oxygen exposure.

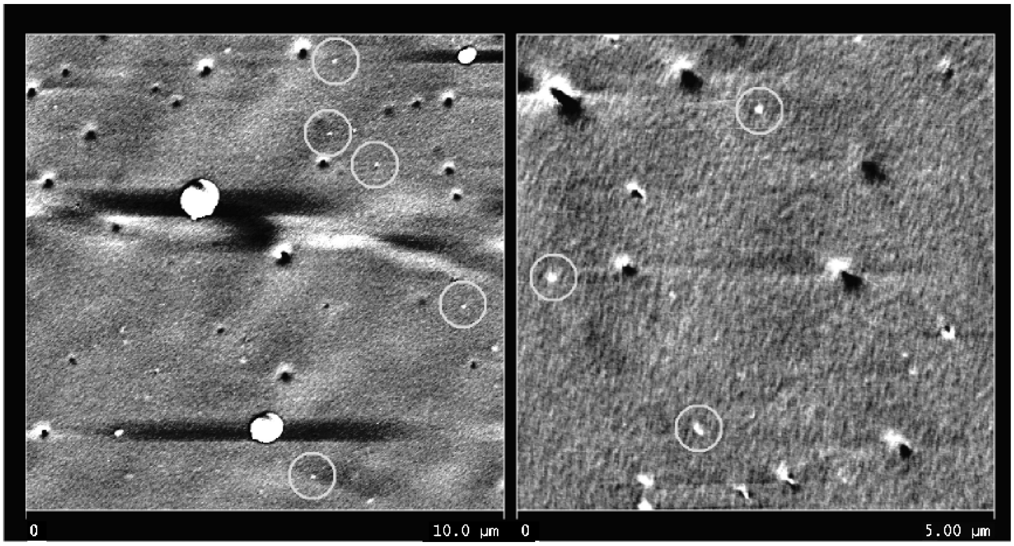


Fig. 5 AFM images of cross-linked methyl polysiloxane substituted with 5% sol–gel precursor.

400–650°C. The extreme degradation of approximately 11.5 wt% at 730°C for the DC 93-500 is very unusual and has been observed in subsequent analyses. This could be attributed to the sample achieving its absolute highest temperature before total decomposition of the sample. The sharp slope is then followed by a residue segment, which accounts for 50% of the remaining weight. Because the cured DC 93-500 is composed of approximately 40–60% of various types of silica (dimethylvinylated, trimethylated, and methylated), these components could account for the residue left after analysis.

The x-ray photoelectron spectroscopy was performed to confirm the presence of a protective oxide layer (Fig. 4). Note that sputtering was not performed during the analysis to ensure that only the surface of the samples was analyzed. The initial x-ray photoelectron spectroscopy (XPS) spectrum shows high amounts of both silicon and oxygen, which is expected because these elements are present in the polymer backbone. After atomic oxygen exposure the oxygen peak increased, whereas the silicon peaks decreased. This is anticipated due to the protective oxide layer possessing a high amount of oxygen compared to silicon. The oxide layer should be composed of silicon atoms the valences of which are filled by oxygen atoms, yielding a SiO_x network. The presence of carbon after exposure to atomic oxygen is due to impurities on the surface of the film such as dust, dirt, etc., and is, therefore, always present.[26]

Another important aspect of the coating is the presence of the silicon–oxo clusters. When the AFM is used in the tapping mode, it can be possible to detect hard (silicon–oxo clusters) and soft (polymer) regions within the cross-linked polymer network. These clusters provide additional protection against high-energy particles and deep UV light (200–260 nm). Figure 5 is an AFM image of a sample with 5 wt%/wt sol–gel precursor added before casting. The silicon–oxo clusters are visible in the subjected sample (highlighted with a circle). The average size for the methyl-substituted polysiloxane nanophase is 125 nm. Figure 5 shows a dispersed and uniformly sized nanophase, which could be attributed to the small size of the pendant methyl group allowing more freedom to the growing nanoclusters.

To study the potential microcracking and/or delamination on exposure to atomic oxygen, photographs of the samples were taken after the samples were subjected to two different fluence levels: 2.22×10^{21} and 1.38×10^{22} atoms/cm^2. Figures 6a and 6b show photographs of the silicone/siloxane hybrid and DC 93-500 coatings on both the Kapton H and fused silica substrates. Figure 6a does not

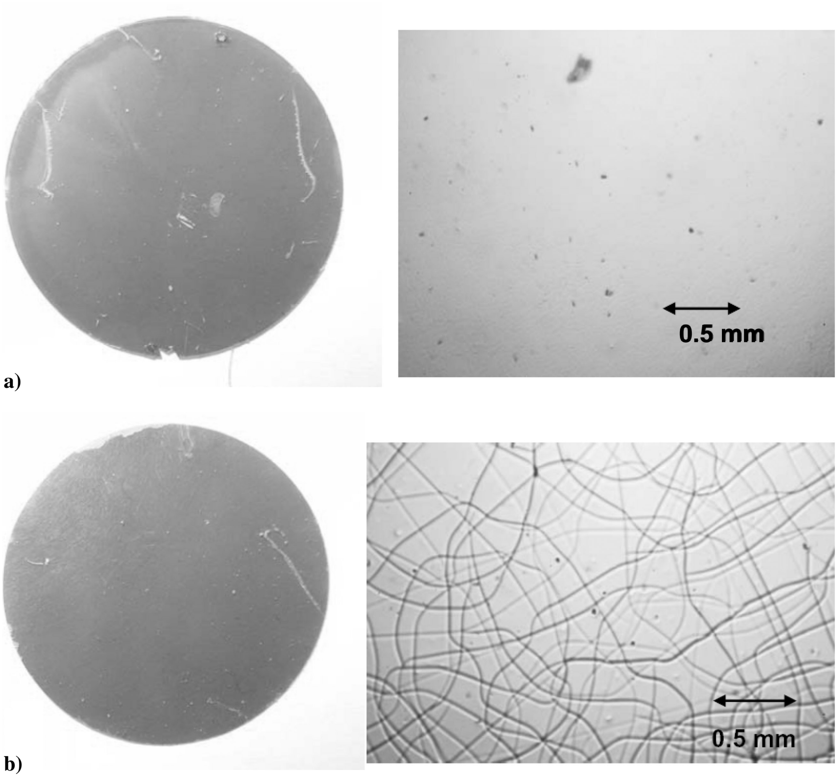


Fig. 6 Photographs of a) silicone/siloxane hybrid and b) DC 93-500 coated Kapton H and fused silica after atomic oxygen exposure to moderate fluence levels (2.22×10^{21} atoms/cm^2).

show any evidence of microcracking of the coatings or other physical damage at 2.22×10^{21} atoms/cm^2, a moderate fluence level. This stability could be attributed to the coating's homogenous dispersed nanophase, which allows for a more uniform distribution of the stresses caused by the growing silica layer. The DC 93-500 coated samples show evidence of microcracking in Fig. 6b, which could be contributed to a nonuniform system. Such nonuniformity can create areas of limited and appropriate protection when dealing with the growing surface stresses. Once a coating fails cracks propagate throughout the surface, as shown in Fig. 6b.

Figure 7 provides more insight to the homogenous composition of the two coatings and shows that both samples exhibit extreme microcracking and delaminate from the substrates. However, Fig. 7a shows a more complete failure in comparison to the localized areas that the DC 93-500 exhibits. This is further reinforcement that the silicone/siloxane hybrid possesses a more homogeneous composition due to the entire coating experiencing failure.

The stresses developed within the surface of the silicone/siloxane hybrid coating during the high atomic oxygen fluence level were enough to overcome the internal stresses of the coating causing complete failure and delamination. That the silicone/siloxane hybrid coating detaches from the substrate allows for greater coating mass loss due to atomic oxygen attack on both the front and back surfaces of the coating. This causes greater shrinkage and opening of the cracks, thus allowing atomic oxygen to attack the underlying Kapton H. However, both samples show failure at such high fluences.

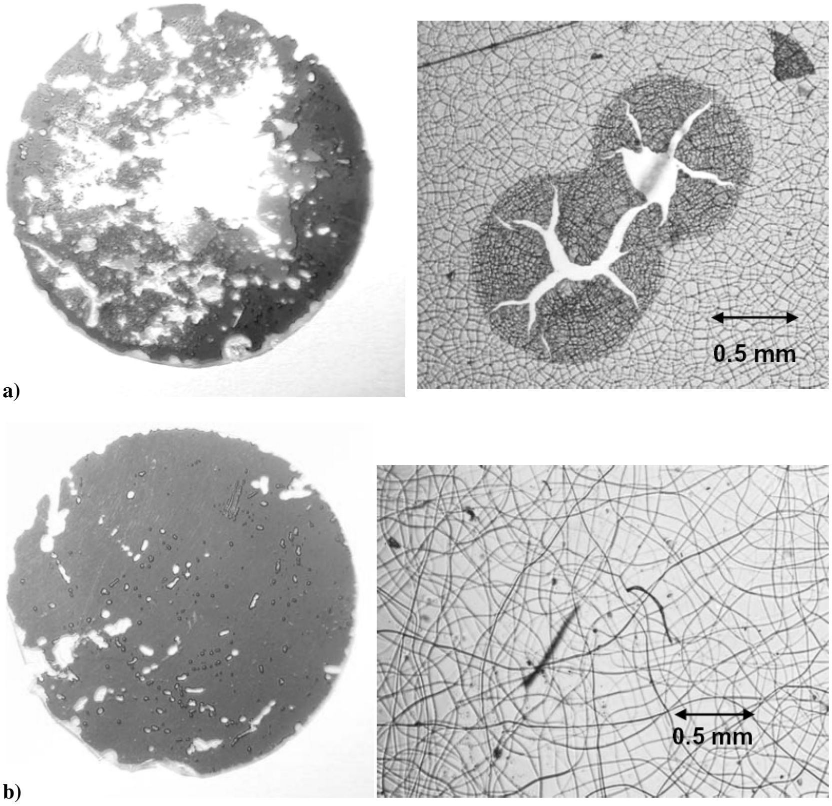
The mass loss of coated Kapton H as a function of atomic oxygen fluence for both the silicone/siloxane hybrid and DC 93-500 coatings is shown in Fig. 8.

Figure 8 shows that the silicone/siloxane hybrid and the DC 93-500 coatings provide significant atomic oxygen protection for most fluences. However, at fluences above 1.0×10^{22} atoms/cm^2, the silicone/siloxane hybrid coating develops apertures due to microcracking, and the rate of oxidation of the underlying Kapton H greatly increases. The magnitude of the cracks is greater than those developed in the DC 93-500 coating, which accounts for the extreme mass loss. There did not seem to be significant differences in atomic oxygen protection in the laboratory dust abraded coatings. This is thought to be due to the fact that the very shallow scratches created did not penetrate the coatings.

To further examine the concept of a self-healing coating, the samples were exposed to atomic oxygen (5.0×10^{20} atoms/cm^2), mildly abraded with dust, and then reexposed to atomic oxygen (1.5×10^{21} atoms/cm^2). Once scratched, the newly exposed silicone should oxidize when reexposed to atomic oxygen, repairing the damage done to the coating. Scanning electron and atomic force microscopy were used to examine the effects atomic oxygen had on the scratched surface. Figures 9a and 9b show an AFM image of the abraded and abraded/reexposed silicone/siloxane hybrid coating. Figure 9a visibly shows the areas of damage by revealing the soft unoxidized coating underneath the hard oxidized surface. Furthermore, Fig. 9a shows that the damage done to the surface did not fully penetrate the coating because the depth of the scratches is approximately 1.5 μm.

Figure 9b shows that the scratched area has been oxidized as indicated by that region's hardness being equal to the rest of the original oxidized area. This shows that minor abrasions can be mended with the atomic oxygen and prolong the lifetime of the coating, which is advantageous because microcracking exposes an uncoated surface to the LEO environment and the rapid degradation contributes to the loss of the long-term durability of the composites used in space vehicle construction.[33]

Scanning electron microscopy (SEM) was employed to examine the surface of the coating after abrasion and reexposure to atomic oxygen for physical damage. Figure 10 shows two SEM photographs taken at different locations on the coating. The photographs do not show evidence of reoxidation due to the silica layer being very thin (~100 Å), but they do show that no microcracking or undercutting is evident. The SEM photographs also show that the scratches did not fully penetrate the coating because the underlying Kapton H is not observed. Figure 11 is an SEM photograph of a silicone/siloxane hybrid sample subjected to a high fluence (1.38×10^{22} atoms/cm^2) and shows delamination and microcracks developed in the coating. Figure 11 also shows the underlying Kapton H substrate, which has been damaged as a consequence of atomic oxygen exposure. The scratches on the silicone/siloxane hybrid coating are never fully repaired, but rather the newly exposed polysiloxane is reoxidized



a)

b)

Fig. 7 Photographs of a) silicone/siloxane hybrid and b) DC 93-500 coated Kapton H and fused silica after atomic oxygen exposure to high fluence levels (1.38 × 10^{22} atoms/cm^2).

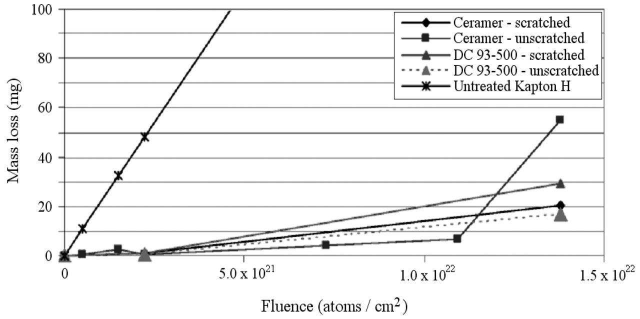
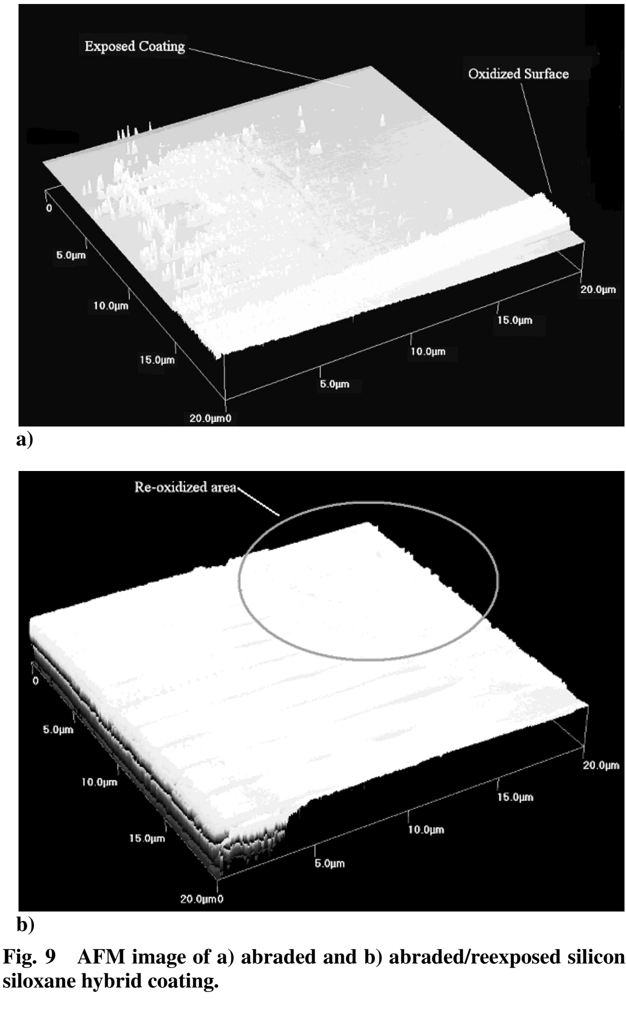


Fig. 8 Mass loss of coated Kapton H as function of atomic oxygen fluence for both silicone/siloxane hybrid and DC 93-500 coatings.

to prevent further atomic oxygen erosion. The scratches were still visible on the surface.

UV/visible spectroscopy was performed to observe the change in optical properties with increased atomic oxygen fluence. Total absorbance, transmittance, and reflectance were studied for both the silicone/siloxane hybrid and DC 93-500 coatings. Figures 12a–12c show the optical properties of the silicone/siloxane hybrid coating. Figure 12a shows that as atomic oxygen exposure increases, the absorbance for the wavelengths between 250 to 800 nm also increases. This is expected due to the characteristic nature of silica being UV absorbent in that region (290–400 nm) (Ref. 34). Figure 12a is also further confirmation of the SiO_x surface formed on the surface when comparing the overlaying spectra. The unexposed silicone/siloxane hybrid coating still shows a slight absorbance in the UV region that is due to the incorporated silicon–oxo clusters within the coating. With increasing atomic oxygen fluence the absorbance increases, attributable to the heavier oxidation of the surface into silica. Figure 12b shows the expected reduction in transmittance with increased atomic oxygen exposure.

Figure 12c shows that no change in reflectance was observed with increased atomic oxygen fluence. The optical properties of



a)

b)

Fig. 9 AFM image of a) abraded and b) abraded/reexposed silicone/siloxane hybrid coating.

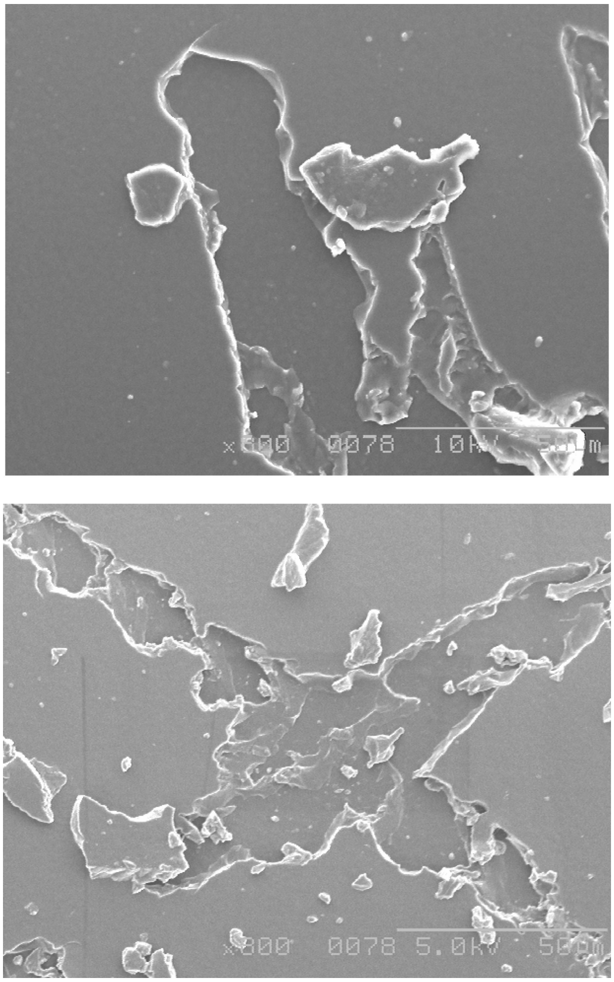


Fig. 10 SEM photographs of silicone/siloxane hybrid coating after it was scratched and reexposed.

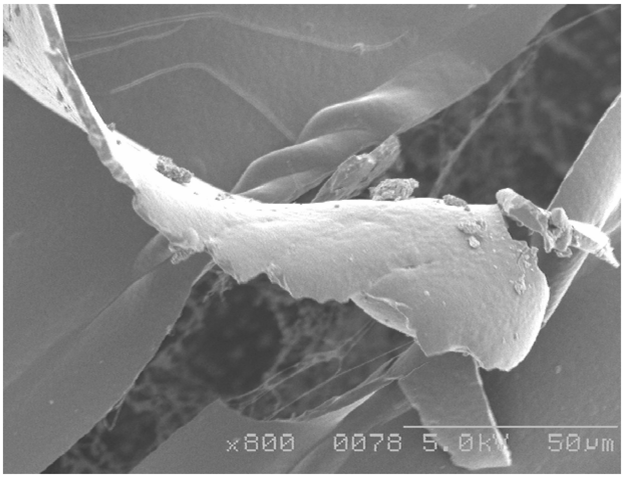


Fig. 11 Silicone/siloxane hybrid coating under high fluence showing delamination and microcracks.

DC 93-500 were also studied (Figs. 13a–13c). Figure 13a shows the absorbance of DC 93-500 before oxidation, which shows a different spectrum when compared to the spectra of the unexposed silicone/siloxane hybrid coating. The DC 93-500 does not show any absorbance in the UV region as a result of its not containing the nanophase silicon–oxo clusters. This shows that the DC 93-500 does not provide UV protection for the coated substrate, which could result in severe damage to materials that are sensitive to UV radiation. UV protection will only begin once the surface is

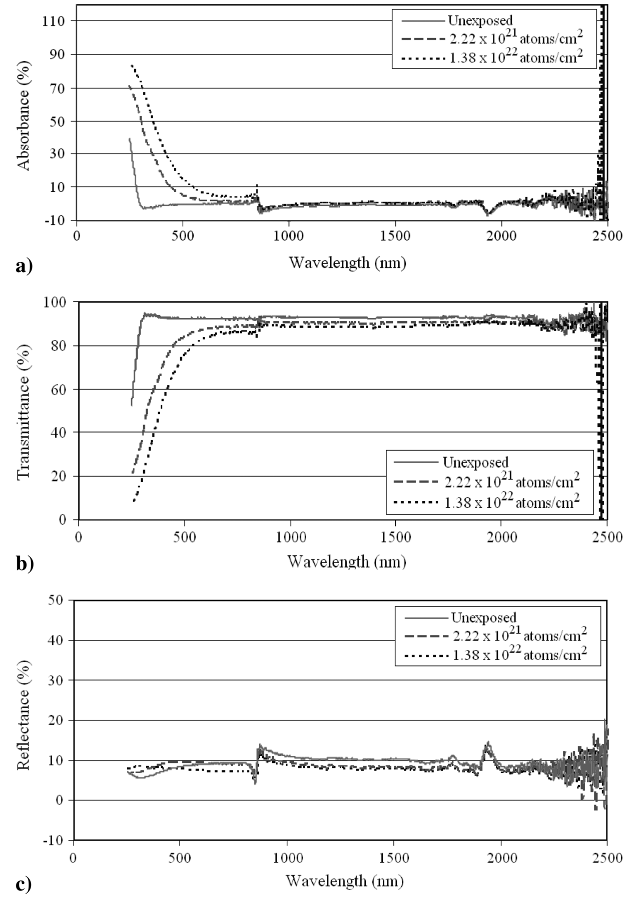


Fig. 12 Atomic oxygen effects on optical properties a) absorbance, b) transmittance, and c) reflectance for silicone/siloxane hybrid coated fused silica.

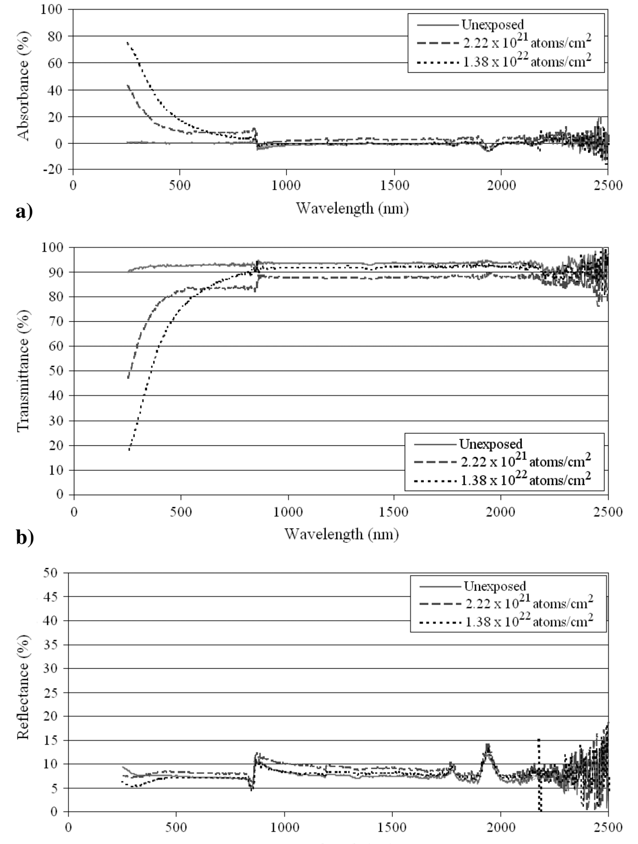


Fig. 13 Atomic oxygen effects on optical properties a) absorbance, b) transmittance, and c) reflectance for DC 93-500 coated fused silica.

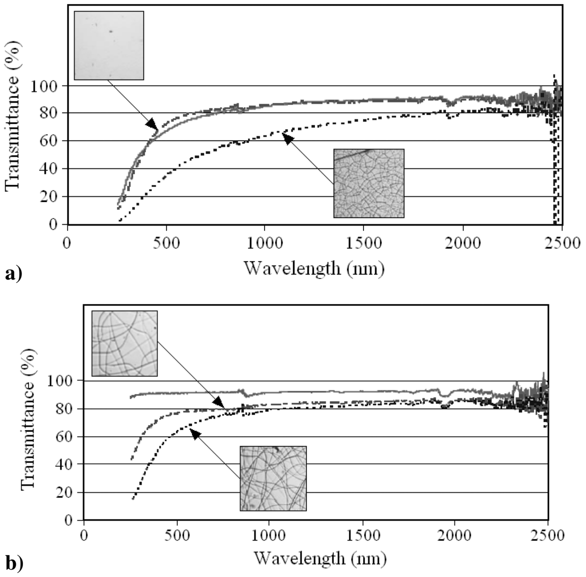


Fig. 14 Effects microcracks have on transmittance for a) silicone/siloxane hybrid and b) DC 93-500 coatings on fused silica: ——, unexposed; – – – –, 2.22×10^{21} atoms/cm^2; and - - - -, 1.38×10^{22} atoms/cm^2.

exposed to atomic oxygen and the silica layer is formed. The absorbance values for the DC 93-500 are slightly lower than those of the silicone/siloxane hybrids due to the lack of silicon–oxo clusters. As with the silicone/siloxane hybrid coating, the DC 93-500 transmittance values decreased with an increasing absorbance, and there was no change in the reflectance.

The transmittance spectra (Figs. 12b and 13b) for both coatings show an increase in transmittance as atomic oxygen fluence is increased, which could contribute to microcracking. UV-visible spectroscopy was used to further investigate this Kapton H witness sample that was microcracked as shown in Figs. 14a and 14b. Figure 14a shows the same transmittance for both the unexposed coating and the sample after moderate atomic oxygen exposure. Microcracking had a significant impact on the transmittance of the coating. Note that the results presented for the silicone/siloxane hybrid in Fig. 14 do not agree with the results presented in Fig. 12b. Figure 14a verifies that microcracking affects transmittance; therefore, Fig. 12b suggests that the silicone/siloxane hybrid coating cracked under moderate fluence because the transmittance has skewed from the original. Fluence levels could have shifted to higher levels during the experiment, causing the silicone/siloxane hybrid coating to microcrack; further studies would need to be considered to verify this. Figures 14a and 14b also show that the severity of the cracks is proportional to the loss in transmittance. The silicone/siloxane hybrid coating experienced delamination, which dropped the transmittance drastically. The DC 93-500 does not completely delaminate, which is the cause for the slightly higher transmittance. The specular transmittance degradation caused by atomic oxygen exposure is, to some extent, attributable to increased absorption for wavelengths $<$800 nm, as well as to microcracking.

Many silicone coatings used on LEO spacecraft have a history of causing contamination on spacecraft as a result of the evolution of volatile silicones and with subsequent oxidation and conversion to silica on neighboring spacecraft surfaces. Cross-contamination tests were performed separately on the silicone/siloxane hybrid and DC 93-500 coating using fused silica witness slides adjoined to the silicone coating samples. Results indicated that there was transport of short chain silicone oligomers to the fused silica that resulted in a silica deposit of 857 Å for an effective fluence of 1×10^{22} atoms/cm^2 for the silicone/siloxane hybrid, but no measurable contamination from the DC93-500. This was attributed to the lack of vacuum stripping of the silicone, whereas the DC 93-500 was vacuum stripped. A no-sample test of the facility did, in fact, result in no observable deposit of oxidized silicone.

The mechanical properties of the silicone/siloxane hybrid coating show that it is very susceptible to damage and would need to be tailored to raise the glass transition temperature by replacing the methyl groups with cycloaliphatic groups. The adhesion of the coating to the substrate could also account for the poor mechanical properties of the coating. The silicone/siloxane hybrid coating produced cross-contamination of silica on witness slides that suggests that the silicone/siloxane hybrid should be vacuum stripped to prevent the transport of short chain oligomers that can result in contamination. A variety of space environment simulations would also need to be considered.

Conclusions

Exposure of the silicone/siloxane hybrid coating to atomic oxygen resulted in a protective oxide layer formed on the surface confirmed through XPS and AFM. Atomic oxygen exposure of silicone/siloxane hybrid and DC 93-500 coated Kapton H and fused silica slides indicates the silicone/siloxane hybrid coating has an advantage over DC93-500 coatings for moderate (up to 2.22×10^{21} atoms/cm^2) Kapton effective atomic oxygen fluences. The silicone/siloxane hybrid coating, at this fluence, resulted in low mass loss of coated Kapton H samples and did not show evidence of the extended microcracking that occurred for the DC 93-500 coating. At high fluence levels (1.38×10^{22} atoms/cm^2) both the silicone/siloxane hybrid and DC93-500 fail. The lack of microcracking at moderate fluence levels results in superior specular light transmittance for the silicone/siloxane hybrid coating and may allow its use as atomic oxygen protective coatings over solar arrays or other optical equipment.

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