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Surface Modification Technologies for Space and Planetary Applications

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Absrtact. This paper presents an overview of processes developed in our company for applications in various space and planetary environments. A number of materials including polymers, paints and other organic-based materials undergo dramatic changes and irreversible degradation of physical and functional characteristics when exposed to space or planetary environments, like in LEO, GEO or on Moon, or Mars. Protective schemes including protective coatings, mechanical metal foil wrapping or cladding, specially synthesized bulk materials, etc. are used to reduce the effects of space environment on materials and their properties. However, the protection of polymers, paints and other organic-based materials in space still remains a major challenge, especially for future long duration exploration missions to other planets or permanent space stations or for an ever-growing array of nano-, micro- and macro-satellites in VLEO, LEO and GEO orbits. Surface modification processes and advanced coatings are used increasingly to protect existing or provide new properties to polymers, paints and other organic-based materials.

A number of surface modification solutions that include treatment of the surfaces by chemical or physical processes and that differ from the traditional protective coating approaches were developed by ITL in the last 30 years that change the surface properties of treated materials, protecting them from the hazards of low Earth orbit (LEO) and Geostationary orbit (GEO) environments or providing dust mitigation properties when used in Lunar environment. Examples of their testing, characterization and applications are provided. In addition, a surface treatment process for mitigation of lunar dust effects in lunar environment was developed and will be discussed.

Keywords: Surface modification, space environment, low Earth orbit, PhotosilTM, ImplantoxTM, CarbosurfTM, SurfTexTM, Dust mitigation technology.

1. Introduction

Polymer materials, paints, graphite and polymerbased composites exposed to the space environmental factors such as atomic oxygen (AO), ultraviolet radiation and extreme thermal cycling conditions in low Earth orbits (LEO) and charged particles in geosynchronous orbits (GEO) have been shown to undergo significant accelerated deterioration of their major structural and functional properties that include surface erosion, mass loss, thermal optical properties changes, etc. (Fig. 1).

Higher energy erosion processes, such as physical sputtering, are well understood for polymers. Chemical

J.I. Kleiman jkleiman@itlinc.com reactions of polymer oxidation at thermal energies, including those by thermal atomic oxygen, are also well understood, yet only a few attempts have been made to study the basic aspects of the accelerated mechanism of polymer erosion by fast atomic oxygen (FAO) [1], [2]. This situation is due mostly to the absence of theoretical approaches for this very special energy range. The way the kinetic energy of fast reactive particles is transferred to chemical reactions is still not clear on a microscopic level. Correlations were found between FAO erosion yield of hydrocarbon polymers and their chemical content and structure [3]. A very important feature in the found relationship was the observation that carbon films and graphite were more resistant to FAO than hydrocarbon polymers that was later confirmed by long duration flight data [4]. This finding implied that one could not expect substantially increased erosion stability in hydrocarbon polymers and composite materials. Most polymers have FAO erosion yields of about (1-4)·10⁻²⁴ cm³/atom of atomic oxygen. Perfluorinated poly-

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Fig. 1. Scanning electron microscopy (SEM) analysis of different polymer materials exposed to accelerated atomic oxygen testing in low Earth orbit space environment simulator. *a*) Planar secondary electrons SEM image of a PMMA polymer exposed to a fast atomic oxygen (FAO) beam for 6 hrs, imitating $\sim 2-3$ months in space; *b*) Cross-sectional backscattered electrons compositional SEM image of a Kapton polymer exposed to a FAO beam for

6 hrs. The area marked as "masked" was protected from the AO beam; c) Planar secondary electrons SEM image of a protective film coated space polymer exposed for \sim 24 hours to the FAO beam showing strong erosion of an area that contained, most probably, a defect or a pit through which the erosion started

mers are an exception. Because of fluorine atoms in their bonding structure, their erosion yields are much lower [1], [4]. Although it was once thought that perfluorinated polymers might be the answer to the problems of polymers in LEO, there are other factors like combined effects between atomic oxygen and vacuum ultraviolet (VUV) and/or ionizing radiation or the influence of soft-X-rays that increase the erosion yields to unacceptable levels. Materials having erosion yields of the order of 10^{-24} cm³/atom are unsuitable for long-term use in the LEO environment and for space in general.

In addition to the erosion processes, the non-metallic, in particular, dielectric external materials used in many space systems are affected strongly by electrons and protons in a broad energy range, electromagnetic solar radiation (both the near and the far ultraviolet radiation), and X-ray radiation. The response of those materials to radiation depends on the type of radiation, its energy and dose that defines the total ionization losses density during the radiation penetration, and on radiation resistance of particular materials. The GEO environment, with its main radiation factors, is well documented, in comparison with LEO environment, in a number of documents and standards [5], [6], with the most damaging effects are shown to be surface charging and arcing, especially dangerous in long-term missions.

In general, the cost of developing new polymer materials and paints for use in space is very high, because of constraints on bulk optical, thermal and mechanical properties. Presently a number of different technological solutions are offered to solve the problems discussed above [7]–[9] (see also the references therein). Protection is provided by metals or by stable inorganic compounds (mostly by oxides or oxide-based surface structures). Oxide coatings are often deposited by one of a few advanced deposition techniques [10]. Also, specially selected or synthesized materials are used that are able to form oxide(s)based compounds in a top surface layer under aggressive oxidative environments due to surface conversion processes [7], [8], [10]–[15]. In special cases, mechanical protection by metal foil wrapping or cladding may be used. In addition to structural stability, preservation of important functional properties, such as optical, thermal-optical, electrical, etc. is often required [16], [17]. Deposition of advanced protective coatings, surface modification of materials, development of modern thermal control paint systems, synthesis of special silicones or other polymers with improved resistance to LEO/GEO environment are the major trends for protection.

Surface modification technologies were developed for protection and for imparting new functional properties to materials. This review will discuss the latest trends in surface modification technologies that were developed either to protect the basic properties of the materials or to change them in a desirable way, without altering the bulk properties.

The surface modification processes can roughly be divided into two broad categories; processes that were developed for protection of materials, films and structures and processes that were developed with the major goal to change or impart new functional properties to the treated surfaces. Examples of both approaches will be provided below with their practical applications to a variety of space components and systems.

2. Surface Modification Processes for Protection in LEO

Among the major characteristics of the materials to be preserved and protected in space environment, the thermal optical properties, i. e. the solar absorptance, α and the total emittance, ε play a very important role. Often, the lowest α/ε surfaces are desired, since they minimize the influence of the Sun on temperature control. For surfaces that never "see" the Sun, the choice may be made mainly for the required ε . The thermal control materials are supposed not only to establish but also to maintain the α , ε or α/ε values, i.e., the required thermal-optical properties in a particular space environment, such as in LEO.

It has been clear for a long time that such important space-related materials as back-surface metalized thin polymer films and organic black and white paints are susceptible to AO and/or ultraviolet (UV) in LEO and to radiation in GEO and should be protected [7]–[9], [16]–[31]. Carbon fiber reinforced plastic (CFRP) composites, often used as materials of spacecraft structural elements, are also susceptible to LEO environmental degradation [18], [19], [32].

Protective coatings of oxides, such as silicon and aluminum oxides, deposited on the surface of polymers or composites provide improved erosion resistance. However, it has been found that thin oxide coatings when exposed to thermal cycling in the LEO space environment may develop cracks and/or spall mostly because of interfacial stresses and differences in thermal expansion coefficients between the coatings and polymers they are supposed to protect. These destructive processes, in addition to coating defect sites, leave the underlying polymeric material exposed to FAO, possibly causing extensive surface erosion. High-quality protection of polymer-based materials in LEO, therefore, remains a major challenge, especially for future long-duration missions or deployed space stations.

Surface modification of materials for protection from the harsh space environment was initiated in the mid-90's at University of Toronto Institute for Aerospace Studies / Integrity Testing Laboratory Inc. (UTIAS)/(ITL) and other groups as a complimentary approach to coatings. Initially, two processes were developed at UTIAS/ITL [28], [33], one taking a "chemical route" [28] while the other followed the "physical route" [33]. Both processes proved to successfully protect space materials from the atomic oxygen erosion providing 10–100 times lower erosion rates than those of the unprotected materials [28]–[31], [33]–[37].

2.1. Chemical Modification Processes

In the chemical approach, the surface modification of space-approved, commonly used polymer-based materials, paints and carbon fiber-reinforced polymer (CFRP) composites enriches the top surface layers with specially selected elements that are able to form stable protective oxides or oxide-based protective surface structures in oxidative environments [28] that allows prevention of erosion and etching in LEO and in other severe oxidative environments.

The PhotosilTM process is based on a silylation reaction and allows Si to be incorporated into the sub-surface region of the originally treated material. The surface becomes a new material and attains new properties. In essence, the process involves three major steps: (a) UV/air pre- treatment (activation) of the material, (b) actual silylation, and (c) UV/air post-treatment (stabilization) of the modified material. Silvlation has been performed in past on many materials [38] that contain active functional groups, such as hydroxyl (OH), in their original structure. Most polymers, especially those used in space applications, however, do not contain active functional groups and a silvlating agent will not react with them. Activation of the surface, i. e. production of groups with active hydrogen atoms, can be accomplished using processes like UV induced oxidation, oxidizing plasmas, flame treatment, ion bombardment, or wet chemical treatment that oxidize the polymer surface [39]. For the modification processes to be effective in space applications, the active OH groups have to be created in the treated polymer material to a depth of 1 µm or more. It was established [28] that activation of most polymers using UV radiation was preferable. The activation process is believed to be a result of simultaneous excitement of polymer molecules and attack by molecular oxygen or ozone, atomic oxygen and singlet oxygen generated from molecular oxygen by the UV radiation. The physical and chemical changes occurring under photochemical oxidation involve an increase in concentration of a variety of oxygen groups, cross-linking and chain scission.

The competition of these reactions as well as the depth of UV penetration and oxidation all depend on the chemical structure of the polymer, the power and wavelength of the excitation source, time of exposure and the sample temperature during irradiation. After silvlation, the newly created structure contains hydrocarbon fragments. These fragments may interact with the atomic oxygen in LEO environment thus increasing further the erosion resistance of the surface by forming silicon-oxygen enriched compounds. The products of such oxidation processes in real space environment can, however, create additional contamination problems [3] It was found [28] that by introducing a third, stabilization stage, consisting of exposure of the silvlated polymer to UV radiation in the presence of oxygen, it was possible to create new silicon-oxygen-carbon structures that became exceptionally stable under FAO attack [28]. Although the mechanism of this transformation is not clear yet, it is believed to be of fundamental importance. Similar effects were observed for atomic oxygen resistant (AOR) polysiloxane-polyimide (AOR Kapton) film that became less susceptible to AO attack if the samples were first exposed to VUV radiation [40].

As a result of the PhotosilTM process, a newly developed organic structure containing silicon, carbon, and oxygen atoms bonded in a complex configuration is formed that slows the destruction of the polymers and thermal control paints in different oxidizing environments [28]. The chemical content of the structures formed in the sub-surface region of the treated materials includes atoms coming partially from the silylating agent and partially from the pristine polymer structure. SIMS and XPS analyses were used to estimate the depth of silylation and stabilization stages and the chemical composition of the treated regions. Considerable amounts of silicon were found, penetrating to a depth of at least $0.5 \mu m$ [41].

The XPS results obtained from a number of treated polymers and thermal control paints as well as a lacing tape product used on the International Space Station (ISS) confirmed that considerable changes occur in the treated regions [41]. The high-resolution spectrum of the C 1s region contained a new peak at 283.2 eV that may be indicative of a Si-C bonding in a carbide structure. The ratios between Si, C, and O are characteristic for each material and depend on the chemical structure of the original polymer. The XPS data for the thermal control paints indicate sharp increases in silicon and oxygen contents in the outer portion of the surface region with a decrease in carbon content and a nearly total disappearance of nitrogen, as a result of PhotosilTM treatment [41]. These results verify the incorporation of silicon-containing groups and confirm the modification of the sub-surface region of the original material.

No mass loss or morphology changes were evident for the PhotosilTM treated polymer samples after fast atomic oxygen (FAO) testing to a fluence of $\sim 4 \cdot 10^{20}$ atoms/cm².

Moreover, the XPS surface content of samples before and after the FAO testing was practically the same for all analysed samples [41]. The FAO test results for the other PhotosilTM treated samples showed that the erosion yields were about two orders of magnitude lower than the erosion yield of untreated polymer samples (Table 1, Fig. 2) [41].

In general, the unprotected polyurethane-based paints exhibited considerable surface erosion following FAO exposure, and more predominant erosion after oxygen plasma asher testing, while the treated ones did not show significant sign of erosion [41].

A number of PhotosilTM – treated paints (A276: Z306 and Z306) along with respective control (untreated) samples were tested at UTIAS/ITL and at the Marshall Space Flight Center (MSFC) Atomic Oxygen Beam Facilities [41]. These samples were exposed to a minimum fluence $5 \cdot 10^{20}$ atoms/cm² of a 5 eV atomic oxygen beam that is equivalent to 3–4 months of exposure in LEO, with the changes in mass and optical properties being measured.

Material	Treatment	Erosion yields [cm ³ /atom]
Kapton 500 HN	Control (untreated)	4.3×10^{-24}
	Photosil	$\leq 5.5 imes 10^{-26}$
DEEK	Control (untreated)	2.8×10^{-24}
FEEK	Photosil	$\leq 7.9 imes 10^{-26}$
Grow Doint (1276:7206)	Control (untreated)	$1.0 imes10^{-24}$
Gray Paint (A276:Z306)	Photosil	$\leq 7.0 imes 10^{-26}$
Black Paint (Z306)	Control (untreated)	6.2×10^{-25}
	Photosil	$\leq 6.5 imes 10^{-26}$
White Paint (A276)	Control (untreated)	5.1×10^{-25}
	Photosil	$\leq 2.6 \times 10^{-27}$

Table 1. Erosion yields of untreated and PhotosilTM-treated materials after exposure to the highly oxidative environment (FAO)



Fig. 2. SEM micrograph of lacing tape surface (the insert shows the actual appearance of the tape) exposed to oxygen plasma (Effective Fluence $\sim 2.0 \cdot 10^{20}$ atoms/cm²) before and after PhotosilTM treatment. Magnification 2000x. (*a*) Untreated surface, masked section (*b*) Untreated surface, exposed section. (*c*) Treated surface, masked section; (*d*) Treated surface, exposed section. The black line separates the masked and unmasked regions on the surface



Fig. 3. Scanning electron microscopy analysis of A276:Z306 paint after FAO+VUV exposure at AOBF of MSFC (FAO Fluence ~ $5 \cdot 10^{20}$ atoms/cm²): (*a*) Control (untreated) and (*b*) PhotosilTM-treated. Magnification 500x. The inserts show regions of the surfaces enlarged further to 2000x times



Fig. 4. Mass change of pristine and Photosil-treated Aeroglaze paints during FAO testing at ITL (FAO fluence is ~ 2.10²⁰ at/cm²)

During the test at MSFC, the samples were also exposed to approximately 780 equivalent sun-hours of vacuum UV radiation.

SEM examination of the surfaces of the treated and exposed paint samples, as shown in F ig. 3, clearly demonstrated that the PhotosilTM treatment and the surface conversion process during FAO exposure provide a stabilized surface after FAO or FAO/VUV exposure. All samples that exhibited no mass loss exhibited no surface morphology changes on a microscopic level (an example is provided in Fig. 2 *b*). On the other hand, SEM micrographs of the untreated paints show highly eroded surface, exposing the pigments (an example is provided in Fig. 2 *a*).

The measured mass loss and mass loss yields for untreated and Photosil[™]-treated A276 (white paint), Z306 (black paint) and A276: Z306 (grey paint) following ground-based accelerated testing in three different atomic oxygen beam facilities (AOBF) facilities [41] are presented in Fig. 4 and Fig. 5. The data is only used for comparing the AO stability between pristine and surface- treated paints. Mass loss yields are higher in oxygen plasma test, as expected. This is attributed to the fact that in the plasma system the materials are also subjected to UV/VUV radiation, excited state neutrals, and energetic ions, all of which can affect the material erosion rate. All three AO facilities confirm the protective capability of the PhotosilTM treatment.



Fig. 5. Mass loss yields of polyurethane-based coatings

The results from measurements of the thermal optical characteristics of pristine, PhotosilTM- treated and PhotosilTM/FAO-tested polyurethane-based paints indicated that the paints after surface treatment have maintained their original thermal optical properties, even after FAO exposure [41]. Both solar absorptance and thermal emittance values remained essentially unchanged within the experimental uncertainty ($\alpha = \pm 0.02$ and $\varepsilon = \pm 0.01$). The slight increase of the thermal emittance of the untreated samples after AO exposure might be due to roughening of the surface by non-uniform erosion of the paint [41].

Currently, the PhotosilTM technology is used to protect polymer-based parts and painted external components of NASA's Canadarm2 systems [31]. PhotosilTM has been used, as well, to treat painted external components of the Special Purpose Dexterous Manipulator (SPDM), a sophisticated evolution of the Canadarm installed onboard the International Space Station [31]. Fig. 4 shows some space hardware that was treated by the PhotosilTM process (Fig. 6).

2.2. Physical Modification Processes

High energy ion beam sources were used to modify space-bound materials in order to provide new protective properties to their surfaces.

A method of surface modification of advanced polymers, graphite and carbon-based composites named ImplantoxTM based on high-dose ion implantation with Si, Al, Si + Al, Si + B, Si + Al + B, Y, Sm, Gd and special oxidative post-treatment was developed [30], [33]–[37] that dramatically increased the erosion and oxidation resistance of polymer-based materials together with substantial improvements in mechanical, electrical, and optical properties.

In the ImplantoxTM process, a high-dose single or binary ion implantation of metals or semi- metals is performed into polymers that when combined with a special oxidation post-treatment following ion implantation produces a graded oxide(s)-based surface layer, with a variable degree of carbonization, chemically bonded to the original polymer, and highly resistant to erosion and oxidation.



Fig. 6. Examples of space hardware treated by the PhotosilTM process: *a*) Canadarm2 (left) approaching a grapple fixture mounted on the Special Purpose Dexterous Manipulator (SPDM) Source: <u>https://spaceflight.nasa.gov/gal-lery/images/station/crew-26/html/iss026e011832.html</u>); *b*) The grapple fixture. It is attached to a payload for the end effector of the Remote Manipulator System (RMS) robot arm to grasp it and maneuver it. The grapple fixture is painted with polyurethane-based gray (Aeroglaze® A276:Z306) and black (Aeroglaze® Z306) paints; *c*) Optical target plate/rod. The assembly is used as a visual alignment aid to assist in positioning the RMS robot arm end effector over the grapple spike for capture. The visual cues of the target and rod are painted with black (Aeroglaze® Z306) paint with white (Aeroglaze® A276) markings; *d*)–*g*) External space components on the ISS treated by PhotosilTM

Based on computer simulation and experimental studies, the implantation energy range required to produce a 50– -100 nm thick, modified, protective oxide-based layer in most of the treated materials was determined to be 20–50 keV and the required ion dose range was found to be 10¹⁶–10¹⁷ ions/cm² [33], [35]. The types of oxides, the degree of surface carbonization, i. e. the surface content of oxide(s)based structures and the amount of carbonized (graphitized) phases in the modified surface layers can be varied and controlled in a wide range of parameters. Various surface-sensitive properties of the modified layers, such as mechanical, optical, electrical, etc. can be tailored and controlled by the conditions of ion implantation and the following oxidative post- treatment. It was confirmed in a number of studies that surface treatment by ImplantoxTM:

 protects polymers and composites from space environment in low Earth orbits,

 increases the oxidation resistance in highly oxidative environments, such as atomic oxygen, ozone, oxygen plasmas,

- improves the durability of polymeric materials and coatings,

- allows tailoring of the degree of hydrophobicity and hydrophilicity

 allows tailoring of optical and thermal-optical surface properties, including refraction, reflection, color, and degree of transparency.

It is important to note that ImplantoxTM as well as the PhotosilTM processes are not coating processes. During the ImplantoxTM process, the surface layers of the treated material are modified., eliminating the problems of adhesion, thermal mismatch and change in dimensions. Virtually all hydrocarbon polymers, carbon and carbon fiber-reinforced polymer (CFRP) composites can be modified by ImplantoxTM. The process is a low temperature process, allowing for low melting temperature materials to be treated. Since this surface treatment technology is based on ion- implantation in vacuum, it is absolutely clean and environmentally friendly. No hazardous materials are used or released in this process.

While most polymer samples, immediately after the implantation process, exhibit a carbonized surface layer and are opaque prior to exposure to FAO, a partial or full recovery of the original color and optical transmission was observed after FAO treatment of the implanted samples, with the degree of recovery depending on the implantation conditions and on the FAO dose. The observed changes in optical transmission is a further indication of the conversion of at least the top surface of the implanted layer to a colorless oxide-based surface layer in the presence of atomic oxygen. It was shown that, depending on the time and the conditions, the whole implanted subsurface region or only the top portion of it can be converted to a graded oxidebased structure. In the last case, a carbonized layer is still left underneath the implanted region that allows developing a new, three-layer graded structure. These options were named subsequently, as full or partial surface conversion.

The control samples of pristine graphite, when exposed to FAO, eroded strongly and underwent a color change, turning matt-black (small circle in Fig. 7 *c*). On the contrary, implanted graphite (high-dose Si or Si + B) samples withstood the FAO exposure without any visible erosion signs turning sky-blue (Fig. 7 *d*, the sky-blue circle marked with an arrow).



Fig. 7. Color, optical transmission and surface morphology effects after FAO exposure: full stability is achieved in ion-implanted DuPont Mylar (*a*) and DuPont Kapton (*b*) (inside the small circles. Erosion of untreated graphite is shown in-side the black circle (*c*) and full protection of implanted graphite is shown in the sky-blue circle (*d*)

These stabilization and protection effects can be explained by examining the surface content of the implanted materials after FAO testing. A certain amount of carbon was removed from the surface of every material in the interaction with FAO. The stoichiometry of the surfaces (Table 2) suggests that protective, oxide-based layers were developed during the conversion processes. This suggestion is fully confirmed by high-resolution XPS that shows the formation of implanted metals⁻ oxides at the surface as illustrated in Table 2 [36].

The major appeal of the ion implantation approach over conventional inorganic coatings is that the difficulties associated with brittleness, mismatch of coefficients of thermal expansion, and change in surface morphology are mitigated by creation of a graded surface modified region.

The surface modification process Implantox[™] was used to evaluate the feasibility of the methodology to affect the surface composition and to achieve full erosion protection in a number of polymer samples that were implanted with selected ion species using single, binary or triple combinations of ions and then exposed to a reactive oxidizing atmosphere or tested in the atomic beam facility. In addition, two materials with designed bulk properties to with

Implanted Ions	Concentration of elements detected by XPS (at %)				
	С	0	Si	Al	Other
		Kapton			
Si	17.0	54.0	29.0	-	-
Si-B	24.0	46.0	30.0	_	_
Si-Al	30.5	45.6	5.4	17.5	0.9
Si-Al-B	30.7	44.6	6.4	17.1	1.4
PEEK					
Si	41.2	39.7	19.1	-	-
Si-Al	37.4	41.0	5.6	13.1	2.8
Graphite					
Si	40.0	41.90	16.6	_	1.5
Si-B	38	44.1	15.6	-	2.0

Table 2. XPS data for surface composition of implanted polymers after FAO testing, (at. %) [Ref. 34]

stand atomic oxygen erosion were also treated, namely, TOR-LMTM and TOR-NCTM (both names are trademarks of Triton Systems Inc. [12], [13]). A series of experiments were conducted in which ion implantation of phosphorus (P), silicon (Si), and combined phosphorus + silicon (P+Si) was performed into both TOR materials. It was shown that, in all cases, the surface conversion under AO exposure represents the main mechanism of full protection by the ImplantoxTM treatment. A strong decrease of surface resistivity has been shown to be an additional positive outcome of ImplantoxTM treatment of thin film space polymers [42].

In another technique, using plasma immersion ion implantation and deposition (PIII&D), successful results were obtained in surface modification of an aluminum alloy Al2024 and silicon [43] and some space polymer materials [44]. Surface modification of aluminum alloys can lower the coefficient of friction and improve the resistance to fatigue of this alloy, while application of this treatment to silicon wafers can result in protection against radiation damage for silicon solar cells Using a source named VAST (Vaporization of Solid Targets), solid elements were vaporized in a high-pressure glow discharge, being further ionized and implanted/deposited in a low-pressure cycle, with the aid of an extra electrode [43].

Three plasma processing systems based on the same PIII technique have been used in the improvement of surface properties of different materials important for aerospace and space applications [43], [44]. Metal plasma PIII of Al and Mg was used for surface protection of such polymers as Kapton, Mylar and polyethylene [44]. A rigid polymer UHMWPE was also treated with nitrogen PIII to produce a protective DLC-like layer [44]. When Kapton and Mylar were treated with different elements like Mg and Al, very good protection was achieved in control plasma experiments against erosion by atomic oxygen [44].

3. Surface Modification Processes for Imparting New Functional Properties

Surface modification can also be used for imparting new properties to materials. In this area of research, the use of ion beams has proven to be very successful.

Ion beam texturing is a well-known phenomenon [45]. Most ion-sputtered polymer surfaces develop cone or spire-like features. The applications of ion beam textured polymers for adhesion improvement, biomedical applications, electrical properties changes, wettability properties changes, etc. was studied and described by numerous workers [32], [45]–[49]. It was shown, for instance, that the etch rates of PTFE, depending on the ion beam power density and target temperature, range from 3 to 1700 μ m/h [48]. A few examples when the use of ion-beam treatment was successful in developing new processes for space applications are discussed below.

3.1. Surface Texturing Process – SurftexTM

A surface modification texturing process was developed for texturing back-metallized Teflon thermal control materials [50], [51] that were applied to camera and light equipment on the International Space Station using an adhesive. The developed surface texturing process is based on ion-beam bombardment of the surface with noble gases. As a result of such treatment, the specularity of back- metallized Teflon thermal control films can be reduced, with the surface morphology changing from metallic-like and shiny to complete milky, white appearance.

An optimization of the process parameters allowed achieving a strong texturing effect. Fig. 8 shows the total and diffuse reflectance of a 127 μ m thick back-metallized Teflon sample after its surface was treated with argon ions. As can be seen from Fig. 8, most of the light was reflected diffusely, with the diffuse reflectance almost equalling the total reflectance.

The surface of the treated film attains rough morphology with well-developed cone or spike-like features (Fig. 9 d through Fig. 9 f).

Due to high specular reflectance properties of the back-metalized Teflon (Fig. 9 *a*) that negatively affected the performance of the video cameras on the MSS, a requirement arose to make these surfaces highly diffusive, without changing their thermal optical properties. The developed texturing process reduced substantially the specularity of back-metallized Teflon thermal control films (Fig. 9 *b*) by changing the morphological appearance of their surfaces in a controlled manner from a mirror-like and shiny to complete milky, white appearance without significantly affecting the thermal optical properties [50]. As a result, the problem of excessive glare of the silver- Teflon films was solved [50]. Mechanical abrasion treatments did not change the high diffuse reflectance properties of the surfaces allowing for their handling and processing [50].



Fig. 8. Total (RT) and diffuse (RD) reflectance measurements for a back-metallized Teflon sample after an exposure to an Argon gas ion-beam



Fig. 9. Optical images of Silver/Teflon samples before (*a*) and after (*b*) treatment with the texturing process. Coins are placed in front of the samples to demonstrate the total loss of reflectance in the treated sample. Images in c-*e* show a gradually enlarged surface, demonstrating the achieved roughness. *f*) Cross-sectional image of the sample, demonstrating the surface profile of the ion-beam treated sample

The space hardware covered with the textured backmetallized Teflon is used on the ISS in open space routinely and an example of a camera that was exposed to the open space environment between June 2002 and June 2006 and delivered back to MDA around November 2006 is shown in Fig. 10 [52].





Fig. 10. Visual appearance of the camera CLPA S/N 206 (TVC S/N 209) (stored in a clean room at MDA) after delivery in November of 2006

3.2. Ion-beam Processes With and/or Without Simultaneous Surface Reconstruction

A number of ion-beam based surface modification processes with and/or without simultaneous surface reconstruction were developed at ITL for various space applications. Brief description of the processes and a few examples of their application to various space products are presented below.

3.2.1. Charge Dissipative Ion-beam Treatment Process – CarbosurfTM

A surface modification technology, CarbosurfTM that was developed to achieve charge dissipative properties on the surface of polymers is based on the controlled carbonization of the surface layer of thin polymer films [53], [54]. Temperature stable surface resistivity (SR) in the charge dissipative range, from ~2 MΩ/sq up to 150 MΩ/sq, has been achieved on hydrocarbon and partially fluorinated polyimides, due to surface carbonization, using specially selected ion beam treatment conditions [54]. The created surface resistivity can be tailored to the desired values for particular applications on a variety of space polymer films. The CarbosurfTM treatment is performed using ion beams of rare gases, without affecting the mechanical and any other properties of the polymeric material underneath, and may be scaled-up using industrial high-intensity ion beams.

The main advantage of surface carbonization over technologies currently available is a low temperature dependence of the achieved surface resistivity and excellent RF performance. As an example, results of SR behavior at room temperature and with temperature varying in the range from -150 °C to +150 °C for two treated polymers, namely, CP1 treated by Ar⁺ ion beam and Kapton HN exposed to Kr⁺ ion beam, are presented in Table 3 and Fig. 11, respectively [53]. It is clear from Fig. 11 that the temperature dependence is quite slow and at low temperatures the ion beam treated samples still keep the surface resistivity in the appropriate range of values. Table 3 presents the results of surface resistivity measurements on polymer films after ion beam treatments performed with Ar⁺, and Xe⁺. The Ar⁺ treatments have been performed at higher - Ar⁺(I) and lower - Ar⁺(II) energies, to illustrate both ion mass and ion beam energy influence.

The other important feature of the CarbosurfTMtreated materials, i. e. their full RF permeability, is demonstrated in Table 4. The significant distinction of the developed surface carbonization technology from deposition of semi conductive coatings is that the CarbosurfTM treatment is "graded" into the material thus eliminating any sharp interfaces that could be a weak point of the alternate coatings' technologies [53].



Fig. 11. Resistivity over temperature for ion beam treated Kapton HN and CP1 thin (1 mil) polymer films

As can be seen from Table 3, repeatable desired values of surface resistivity for the candidate materials for sunshield antennas were achieved using different ion mass gasses (Kr, Ar) and different ion beam energies ($Ar^+(I)$ or $Ar^+(II)$). The numbers in parentheses in the first column indicate ion beam surface treatments with different parameters. CP1 is a high-performance fluorinated polyimide polymer material used in space. Kapton HN is a high-performance polyimide polymer used extensively in space.

Materials / Surface treatment	Surface resistivity at room temperature, ρ (Ohm/sq.)			
	Xe^+	$\operatorname{Ar}^{+}(I)$	$\operatorname{Ar}^{+}(\operatorname{II})$	
CP 1 White (1)	0.75×10 ⁷	2.5×10^{8}	1.3×10 ⁷	
CP 1 White (2)	0.8×10^{7}	3×10 ⁸	3×10 ⁷	
CP 1 (1)	0.6×10^{7}	5×10 ⁸	1.3×10^{7}	
CP 1 (2)	0.75×10^{7}	5.2×10 ⁸	6×10 ⁷	
Kapton HN (1)	1.5×10^{7}	5×10 ¹⁰	3×10 ⁹	
Kapton HN (2)	1.3×10^{7}	3.5×10 ¹⁰	1.9×10 ⁹	

 Table 3. Surface resistivity of thin (1 mil) polymer films after moderate energy ion beam treatment at room temperature [Ref. 50]

Table 4. Waveguide measurements after different modes of moderate-energy ion beam treatment of thin space polymer films[Ref. 50]

	Description	Worst case, 26.5 to 41 GHz			
Sample #		Insertion Loss	Return Loss	Insertion Phase	
		dB	dB	degrees	
	Clear CP 1 (untreated)	-0.012	-34.1	1.49	
31	Ar ⁺ CP 1	-0.012	-34.1	1.51	
32	Kr ⁺ CP 1	-0.018	-34.4	1.33	
34	Xe ⁺ CP 1	-0.008	-33.7	1.33	
	Kapton HN (untreated)	-0.015 to -0.025	-30 to -31	1.7 to 2.1	
4-K1	Xe ⁺ Kapton	-0.014	-31.1	1.7	
33	Kr ⁺ Kapton	-0.024	-31.5	1.68	

3.2.2. Charge Dissipative Ion-beam Treatment Process – Carbosurf+TM

A novel ion-beam surface treatment process with simultaneous surface renewal (IB/SSR) providing chargedissipative properties to the treated surfaces was developed at ITL [55], [56] and successfully used for treatment of a large number of variously shaped and sized flat conductor cables (FCC) on both sides that are being used in various applications in aerospace, space and commercial programs (Fig. 12).



Fig. 12. Optical image of the short and long FCC's (a) and a portion of the FCC demonstrating the grooved nature of its surface (b)

The results of surface resistivity (SR) measurements of the front side of FCC's, used as interconnects in solar panel arrays on satellites in Geostationary (GEO) orbit, averaged around 10 M Ω /sq for short FCC units and around 8 M Ω /sq for long units. The SR values for back sides averaged around 18 M Ω /sq for both short and long FCCs. These values remained unchanged during ~ 1 month storage of the treated FCCs at lab conditions, and after a following 2.0–2.5 year's storage.

Extended long-term ground-based GEO environment simulation testing experiments (15 years space equivalent) that involved simultaneous exposure to all three GEO environmental factors, i. e. protons, electrons, and UV have been performed on two specially selected FCC sets. These sets included pristine and IB/SSR-treated FCCs, with both front and back FCC surfaces being exposed. As can be seen from Fig. 13 that presents the SR data for three ion-beam treated FCCs vs. GEO exposure equivalent testing time, after 15 years of GEO equivalent testing all tested front and back surfaces of ion-beam treated FCCs remained fully charge-dissipative.

The SR additionally decreased in all tested, or aged ion-beam treated FCCs to the end of GEO aging, attaining SR values in a narrow range of (3–7) M Ω /sq after 15 years of GEO space equivalent exposure, confirming the presence of the phenomena of so-called radiation-induced or enhanced surface conductivity [57]–[59].



Fig. 13. SR data for three ion-beam treated FCCs vs. GEO exposure equivalent testing time

Table 5 summarizes the results of three GEO simulating ground-based tests. The data in the last column illustrate the stability of the post-GEO-aging SR values following a continuous storage of the FCCs in laboratory conditions, verified by regularly repeated SR measurements during almost 2 years.

 Table 5. The SR values for FCCs before and after simulated GEO exposure, or GEO aging

	Surface Resistivity (SR) (M Ω /sq)				
Sample ID	Ion-Beam Treated	4 yrs equiv. of GEO space exposure	15 yrs equiv. of GEO space exposure	Final*	
Short FCC (back side)	19.3	16.3	7.1	7.2	
Short FCC (front side)	11.2	5.4	2.8	3.1	
Long FCC (back side)	13.1	4.2	4.1	5.2	

*- SR data - the values stable after 1 month, and later - after 2 years of storage

As can be seen from Table 5, the surface conductivity obtained on the insulating space polymer films is almost insensitive to space radiation during the 15 years in GEO.

3.2.3 Innovative Thermal Control Materials for Space and Lunar Exploration

For long-term Lunar exploration, the external thermal control space materials should be with static charge control surface properties and, at the same time, satisfy flexibility requirements and the thermal limits of the Moon environment. The high efficiency materials, like, for example, the ITO/TeflonFEP/Ag/Inconel or ITO/Teflon FEP/Al/Inconel would be highly preferable in such applications. However, these products have quite narrow temperature limits, from -60 °C to +70 °C that do not satisfy and are not compatible with the thermal limits of the Lunar environment [60]. Beyond the mentioned above limits, the thermal expansion coefficient's mismatch between the hard and quite brittle ITO and soft TeflonFEP is causing ITO cracking and possible spallation. Even for the widely used ITO/KaptonHN/Al there have been concerns about not enough ITO coating's flexibility when used for curved materials surfaces.

Due to high efficiency and high environmental stability of many current white space inorganic, mostly silicate, paints, using them as thermal reflector materials in Lunar exploration would be the preferred choice. At the same time, we have seen in our numerous space materials testing experiments in the vacuum dusty simulators that the silicate paints, collected from various manufacturers, demonstrated one of the highest accumulation, retention, and retention efficiency of dust simulants, during and after dusting, due to the porous nature of the silicate binders in the paints (Fig. 14) [61]. It looks like the dust fills up the surface opened pores and stays there, mostly by interlocking, meaning that the use of those white pants on the Moon is, at least, questionable.

Taking into account the deficiencies discussed above, we extended our work on development of innovative space materials that could replace the ITO/TeflonFEP/Ag/Inconel or ITO/TeflonFEP/Al/Inconel for applications in Lunar environment. Our undoped and specially doped super coatings were deposited first onto front surfaces of back metallized KaptonHN, i. e. KaptonHN/Al (Sheldahl production). Top quality various DLC-like and N-, Si, or Si+O doped DLC thin coatings were deposited at different deposition regimes and substrate temperatures. As a result of this work, uniform, highly flexible, chargedissipative coatings, with high adhesion, adjustable SR values and with indications of dust mitigation properties have been deposited on KaptonHN/Al samples and then on product prototypes of $0.5 \text{ m} \times 1.5 \text{ m}$ in size that can be used, depending on the type and number of doping elements, for LEO, GEO, or Lunar applications. Information on the thermal optical properties and surface resistivity for N-DLC coatings deposited on Kapton/Al in comparison with standard (Sheldahl) ITO/Kapton/Al are presented as an example in Table 6 [61]. It can be seen, that the performance efficiency on the innovative thermal control product is even slightly better, than the ITO coated Kapton/Al. For comparison, similar data for DLC(N)/Teflon FEP/Ag/Inc, for Textured Teflon FEP/Ag/Inc and for Photosil-treated Kapton HN are also given.

As can be seen from F ig. 14, the N-DLC coatings deposited on Kapton 500HN demonstrated one of the lowest retention efficiencies in the dusting experiments.

Innovative Thermal Control Materials for Space Application	Doping gases	Solar absorptance, (α)	Thermal emittance (ε)	Performance efficiency $\xi = (\alpha/\epsilon)$	Surface Resistivity (Ohm/sq)
Carbosurf+ technology	N/A	Slightly Changed	Almost	Slightly	
On Kapton 100HN			unchanged	Changed	$[3-4] \times 10^{6}$
On Kapton 50E					
For GEO application and space					20×10^6
antennas					
DLC(N)/KaptonHN/Al	Nitrogen	0.52	0.85	~0.61	10 ⁵ –10 ⁹ (on request)
KaptonHN/Al, Sheldahl					
(For comparison)	N/A	0.49	0.81	~0.60	Insulating
ITO/Kapton100/Al; Sheldahl					
(For comparison)	N/A	0.54	0.81	~0.67	$[2-10] \times 10^3$
DLC(N)/Teflon FEP/Ag/Inc	Nitrogen	0.23	0.81	~0.28	$\sim 60 \times 10^6$
Textured Teflon FEP/Ag/Inc	N/A	0.12	0.81	0.15	N/A
Photosil – Chemical Process	N/A	Slightly Changed	Slightly Changed	Slightly Changed	N/A

Table 6. Summary of Thermal Control Materials and Processes for Space Application



Fig. 14. Lunar dust slimulant accumulation and retention efficiency for a nymber of materials exposed in ITL's lunar environmental simulator

Only a few papers exist in the literature with some examples of DLC successful deposition trials on Teflon PTFE, mostly for medical applications, with no SR values provided there [62], [63]. We also succeeded depositing our coatings on Teflon PTFE films of different thicknesses and with different Teflon PTFE substrate surface finish. We, however, did not find any data on deposition of DLC coatings on Teflon FEP, that we have been interested in, considering to develop a high-efficiency static control thermal control material for potential lunar application. We investigated the possibilities of depositing the DLC coatings on the back-metallized Teflon FEP, which proved to be a real challenge. We developed a technological process of applying a DLC- like coating on Teflon FEP, with SR values in charge dissipative range. The developed technological process required a special innovative surface pretreatment with follow-up deposition of a thin intermediate layer, on which the specially doped super-coatings were deposited in the required SR range. Data on these materials are also presented in Table 6. The performance efficiency of this product prototype is significantly better, then for the Kapton-based ones.

Full surface analysis of all developed innovative materials was conducted, using survey and high- resolution XPS. SR measurements were made right after deposition and then on a monthly basis in lab environment for \sim 8 months (with monitoring still on-going). Abrasion resistance testing and the thermal optical measurements were also performed. Thermal cycling down to Liquid Nitrogen temperatures, with visual appearance and SR measurements have been successfully done on these materials as well. These innovative material samples (Table 6) were exposed to the LEO space environment in ram and wake directions in the MISSE-17 materials experiment that was completed in November 2023 and is ready for return on SpX-30 in December 2023 after six months in the LEO space environment [64].

4. Conclusions and future trends

Surface modification technologies present a viable alternative for protection and impartation of new functional properties to polymers, paints and other carbon-based materials and structures used in space. Surface modification processes have been developed to provide an alternative solution to the problems caused by different space environment factors to polymer-based materials, composites and paints used in LEO/GEO spacecrafts. The developed processes allow the atomic oxygen erosion to be reduced drastically by creating a self-healing protective layer that al-

References

lows, in turn, protection of the major functional properties like the thermal optical properties.

Ion-beam based surface modification treatments also imparted new functional properties to surfaces like reduced glare or increased surface conductivity that extended the use of traditional space materials in space and planetary applications.

The materials' science field is developing at a tremendous paste. Nanotechnology is the buzz word of the 21 Century. All topics discussed in this review are greatly influenced already by the new nanomaterials and new technological processes and solutions associated with them. It is not hard to envision that most of the technological approaches including deposition processes, surface modification processes, bulk material technologies, etc. will undergo dramatic changes and improvements in the near future with many such developments already well under way.

While there certainly will be a "delay" for the new solutions to get from the "drawing boards" and laboratories into the actual production and acceptance by the space industry, we should expect a very exciting time ahead of us, where these approaches will be discussed, criticized and either accepted or rejected in the upcoming professional meetings, publications, etc.

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Технології модифікації поверхні для космічних і планетарних застосувань

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Анотація. У цій статті представлено огляд процесів, розроблених в нашій компанії для застосування в різних космічних і планетарних середовищах. Ряд матеріалів, включаючи полімери, фарби та інші матеріали на органічній основі, зазнають кардинальних змін і незворотної деградації фізичних і функціональних характеристик під впливом космічного або планетарного середовища, наприклад, на НОО, ГСО, Місяці або Марсі. Для зменшення впливу космічного середовища на матеріали та їхні властивості застосовують захисні схеми, що включають захисні покриття, механічне обгортання або облицювання металевою фольгою, спеціально синтезовані сипучі матеріали тощо. Однак захист полімерів, фарб та інших матеріалів на органічній основі в космосі все ще залишається серйозною проблемою, особливо для майбутніх довготривалих дослідницьких місій до інших планет або постійних космічних станцій, а також для постійно зростаючої кількості нано-, мікро- і макросупутників на низьких, низькоорбітальних і географічних орбітах. Процеси модифікації поверхні та сучасні покриття все частіше використовуються для захисту існуючих або надання нових властивостей полімерам, фарбам та іншим матеріалам на органічній основі.

За останні 30 років ІТЛ розробив низку рішень з модифікації поверхні, які включають обробку поверхонь хімічними або фізичними процесами і відрізняються від традиційних підходів до нанесення захисних покриттів, що змінюють властивості поверхні оброблених матеріалів, захищаючи їх від небезпек низької навколоземної орбіти (НОО) і геостаціонарної орбіти (ГСО) або забезпечуючи властивості пилопоглинання при використанні в умовах Місяця. Наведено приклади їх випробувань, характеристик і застосувань. Крім того, було розроблено процес обробки поверхні для зменшення впливу місячного пилу в місячному середовищі, який буде обговорено.

Ключові слова: модифікація поверхні, космічне середовище, низька навколоземна орбіта, PhotosilTM, ImplantoxTM, CarbosurfTM, SurfTexTM, mexнологія зменшення пилу.