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Atomic Oxygen Texturing of Polymers and Carbons

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ABSTRACT

Atomic oxygen, which is present in the low Earth orbit environment of space, can be used to texture the surface of polymers and some forms of carbon. It can be produced in vacuum chambers in the form of a plasma or directed beam using high voltage, radio frequency or microwave dissociation of oxygen gas. The textures that are produced are typically five microns in height or less. These textures can allow alteration of the surface properties without affecting the bulk material. Surfaces textured in this manner can experience increased or decreased static coefficient of friction, reduced water contact angle, increased diffuse transmittance and increased radiant heat transfer capability. These properties are of value for a variety of applications such as broad illumination fiber optics and as a replacement for chemical treatments to make polymers less sticky to the touch. This paper discusses the effects of various levels of atomic oxygen treatment on the transmittance, static coefficient of friction, and water contact angle for acrylic and compares the latter two with some previously measured data for other polymers and carbon. Changes in radiant heat transfer for carbon-carbon composites are also discussed.

1.0 INTRODUCTION

Alteration of surface morphology and/or surface chemistry of materials has been used as a way of enhancing some surface dependent properties without altering the properties of the bulk material. Often, this involves the use of a chemical treatment. For example, this type of treatment has been used to reduce the stickiness of natural rubber without affecting the modulus of elasticity of the bulk material. The chemicals used in these types of processes, however, have come under more strict environmental regulations in the United States of America with regard to their use and disposal. Therefore, it has become increasingly desirable to similarly alter the surface of a material using nonwet chemistry techniques. For polymers and some forms of carbon, this can be accomplished using atomic oxygen.

Atomic oxygen is the most predominant species in low Earth orbit from altitudes of ~180 to 650 km (ref. 1). It is produced by the photodissociation of molecular oxygen by photons of 243 nm in wavelength from the sun (ref. 2). Atomic oxygen is highly chemically reactive, and at modest energies can break chemical bonds and produce volatile reaction products. Carbon containing materials and those with volatile oxidation products exposed on spacecraft passing through this environment have been found to undergo natural changes in surface morphology (ref. 3). The reaction with atomic oxygen produces very fine cone structures on the surface which can be spaced as tightly as a micron or less with typical heights up to 5 μm.

In order to be able to perform more in-depth studies of the effects of atomic oxygen on spacecraft materials, systems were developed for producing atomic oxygen on the ground. Typically these systems produce atomic oxygen under a partial vacuum by using high voltage sources, microwaves or radio frequency to dissociate molecular oxygen into atomic oxygen (ref. 4). Studies primarily have focused on the rate of surface erosion and testing of techniques to prevent the reaction from occurring. As a result of the testing, however, it was found that the texture can have a beneficial effect for some material applications on Earth. Some methods of producing atomic oxygen such as radio frequency plasmas are relatively inexpensive and effective at producing surface textures which are adequate for many commercial applications.

This paper focuses on some of the surface property changes that can result from atomic oxygen texturing of acrylic and carbon. It will focus primarily on changes in static coefficient of friction, transmission of light, and water contact angle for acrylic as compared to other similarly textured polymers. Also the ability to better remove waste heat will be discussed for carbon-carbon composites. Applications for these types of surface textures are widespread and are in such diverse fields as manufacturing, medicine, home products and aerospace.

2.0 EXPERIMENTAL METHODS AND APPARATUS

2.1. Atomic Oxygen Exposure Sources

For texturing of acrylic, atomic oxygen was produced by radio frequency dissociation (100 W, 13.56 MHz) of air at pressures of ~20 to 27 Pa in a Plasma Prep II asher manufactured by Structure Probe Industries. Small coupons of acrylic approximately 2.54 × 2.54 × 0.32 cm were placed in the cylindrical vacuum chamber and exposed to various dose levels of atomic oxygen. The effective atomic oxygen dose was determined by exposing a vacuum dehydrated 2.54 cm diameter, 0.0127 cm thick piece of Kapton type H polyimide film manufactured by DuPont to the atomic oxygen during the acrylic texturing. The volume loss of Kapton per square centimeter of surface area was determined using the mass loss of the Kapton and the density (1.42 g-cm^{-3}). Using the known atomic oxygen erosion yield of 3.0×10^{-24} cm^3-atom^{-1} for Kapton in low Earth orbit, the effective atomic oxygen dose or fluence could be determined. This represents the equivalent number of oxygen atoms striking a square centimeter of the surface during the test that would cause the same measured erosion if it were exposed in low Earth orbit. The Kapton film was dehydrated in vacuum prior to weighing to eliminate errors in mass measurement due to moisture uptake. The atomic oxygen arrival in this type of system is isotropic because the sample sits inside the atomic oxygen formation region or plasma. As a result, the texture is more spread out and the resulting cones are not as tall.

For carbon texturing, more closely spaced and taller cone structures were desired so a directed beam of atomic oxygen was used. In this type of system the plasma region is located upstream from the samples and the vacuum pumping system. The lower pressure near the samples draws atomic oxygen from the higher pressure formation region so that it flows over the samples from a single direction. For these tests the directed atomic oxygen was produced by an End Hall gridless source from Commonwealth Scientific using oxygen as the feed gas. Samples were located 25 cm downstream of the source on a water cooled sample holder where they were exposed to a 90 eV beam of a mixture of atomic oxygen ions and molecular oxygen ions. Pressure in the vacuum chamber was 0.013 Pa during source operation and 1.33×10^{-4} Pa background with the source off. Polyimide Kapton was again used as an atomic oxygen dose monitor. A more complete description of the source is given in reference 5.

2.2 Property Characterization

Photographs of the acrylic and carbon-carbon composite surfaces were taken with a Cambridge 200 scanning electron microscope. Diffuse transmittance for acrylic was measured with a Perkin Elmer Lambda-9 UV-VIS-NIR spectrophotometer over the wavelength range from 250 to 2500 nm with a specular light trap in the instrument. Diffuse transmittance was of interest due to the potential use of acrylic for broad area illumination purposes.

Water contact angles for the textured and untextured acrylic surfaces were measured with a Contact Angle Measuring System Model G1, manufactured by Kernco Instruments. Demineralized water was used to produce the droplets for measurement. The contact angle was measured as the angle between the surface and a tangent line drawn parallel to the water droplet near the point at which the droplet touches the surface. Large angles indicate good water shedding ability (>90°) while angles near zero indicate that the surface is wetting.

The static coefficient of friction between two identically prepared acrylic samples was measured using an inclined plane. One of the acrylic samples was bonded to the plane and the other was gently placed on top of it so that the prepared surfaces were together. The plane was then slowly elevated until sliding was initiated between the two acrylic samples. The static coefficient of friction was computed as the tangent of the angle of inclination when sliding initiated.

Thermal emittance is used as a measure of the ability of a surface to radiate heat away from itself. An object which is a perfect radiator would have an emittance of one, while an object which cannot reject any heat would have an emittance of zero. For a diffusely reflecting surface, the hemispherical spectral emittance is in general equal to the absorptance at the same wavelength (ref. 6). Therefore, making the surface a better absorber at selected wavelengths would improve the emittance. For the carbon-carbon composite samples tested, the hemispherical spectral emittance was determined from two instruments. A Perkin Elmer Lambda-9 UV-VIS-NIR spectrophotometer was used to measure the spectral hemispherical reflectance over wavelength ranges of 250 to 2500 nm and a Perkin Elmer Hohlraum Reflectometer was used to measure over the 1500 to 15000 nm wavelength range. By overlapping the results from the two, the reflectance as a function of wavelength between 250 and 15000 nm was obtained for each sample. Since the samples were not transmissive, the spectral hemispherical emittance could be obtained by subtracting the reflectance values at each wavelength from unity. The total hemispherical emittance at each temperature of interest was obtained by integrating the emittance versus wavelength curve with respect to the blackbody curve for that temperature using the equation below (ref. 6).

$$\varepsilon(T_A) = \frac{\int_0^\infty \varepsilon_\lambda(\lambda, T_A) e_{\lambda b}(\lambda, T_A) d\lambda}{\sigma T_A^4}$$

where

ε_λ emittance at wavelength λ

$e_{\lambda b}$ blackbody hemispherical spectral emissive power at wavelength

σ Stefan Boltzmann Constant

T_A Temperature of Interest

The Hohlraum reflectometer and the integration technique are discussed in more detail in reference 7.

3.0 RESULTS AND DISCUSSIONS

3.1 Polymer Texturing

Acrylic undergoes changes in surface morphology upon reaction with atomic oxygen which can be seen in the scanning electron photomicrographs in figures 1(a) to (e). The surface of untreated acrylic is rather featureless, but with a small amount of atomic oxygen exposure very small finely spaced cones are developed. As atomic oxygen reacts further with the surface, the finely spaced cones are eroded down to a fine texture before wider and deeper craters begin to form. Because many properties are a function of surface texture, and atomic oxygen dose greatly affects the size of texture on the surface, the dose level of atomic oxygen can be used to tailor surface properties.

Transmittance of light is one property that is affected by this change in texture. Figure 2 shows a plot of the diffuse transmittance of acrylic as a function of the effective atomic oxygen fluence. For low fluences the surface texture is very fine so short wavelengths are easily scattered while longer wavelengths are not. As the surface loses its fine texture and becomes more flat, the acrylic becomes more specularly transmitting and scatters light less. As ever finer textures give way to broader features, the diffuse transmittance shifts to higher levels for longer wavelengths. Changing the atomic oxygen dose level can allow for tailoring of the optical properties of an acrylic surface. This can have a wide range of applications from illumination display panels, to broad area illumination fiber optics. The ability of a surface to shed water is also affected by the extent of atomic oxygen texturing. Figure 3 contains a plot of the water contact angle for acrylic as a function of atomic oxygen fluence. A combination of small surface features and oxygen functionalities may allow water to soak in thereby reducing the contact angle. A greatly reduced contact angle can be observed for the first two atomic oxygen fluence levels. As the surface begins to smooth out and develop larger features, the contact angle recovers to near that of the original acrylic. Many polymers and carbon also become wetting at low atomic oxygen fluence levels. Table I contains a comparison of the water contact angle for a few polymers and pyrolytic graphite with acrylic. A more complete listing of polymer contact angle information is contained in reference 8. The ability to tailor the surface wetability can have application in many areas such as the improvement of a polymer’s ability to hold ink for printing purposes.

Static coefficient of friction is also dependent on the texture resulting from atomic oxygen exposure. Figure 4 contains a plot of the static coefficient of friction between identically prepared surfaces for acrylic as a function of atomic oxygen fluence. The plot indicates that the friction coefficient increases very rapidly and appears to level off with increased atomic oxygen exposure. For very low fluence levels, the fine surface texture is not very robust and is easily deformed and scraped from the surface. As the texture grows, however, it becomes a more stable and integral part of the surface and is much harder to deform. The stiffness of the texture appears to help increase the ability of the textured acrylic surface to cling to itself. Table II contains a summary of some data for other polymers and pyrolytic graphite in comparison to the acrylic. In general, it appears that polymers that have a low modulus experience a decrease in static coefficient of friction with atomic oxygen exposure, while those that have a high modulus exhibit an increase in the friction coefficient This ability to tailor the static coefficient of friction can have applications in areas of bondability and handleability of surfaces. Further data regarding static coefficient of friction and the effect of atomic oxygen texturing on it can be found in reference 8.

3.2 Carbon Texturing

From the previous section, it was shown that some forms of carbon such as pyrolytic graphite can be textured using atomic oxygen to alter the water contact angle and static coefficient of friction of the surface. An increase in the surface texture can also allow a material such as a carbon carbon composite to better radiate heat away from itself. Figure 5 contains some scanning electron photomicrographs of a two dimensional weave carbon-carbon composite produced by Rohr Industries. Figure 5(a) shows the surface as received, and figure 5(b) contains the image taken after atomic oxygen texturing. By using the directed beam to texture the surface, very finely spaced, tall cones could be produced. Unlike on the acrylic sample textured in the isotropic plasma, these cones start small and continue to grow in height until they reach a limiting height rather than eroding into a broader texture. The improvement in radiative heat loss produced by the structure is shown in the total emittance as a function of atomic oxygen fluence data for various temperatures which is contained in figure 6. Values of total thermal emittance of 0.8 or higher are desired for many radiator applications. Texturing allows this level to be achieved easily over a broad range of temperatures. A more complete description of this testing is given in reference 9.

4.0 CONCLUSIONS

Atomic oxygen texturing of polymers and some forms of carbon can produce significant changes in surface properties that can have broad applications in many fields of interest. Texturing can allow tailoring of optical properties, alter the ability to shed or retain water, improve the bondability or handleability, and improve heat rejection. Careful selection of the material and the atomic oxygen exposure level can lead to improved surface properties that can enhance the performance of many products for both terrestrial and aerospace use.

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TABLE I.—WATER CONTACT ANGLE FOR PRISTINE AND ATOMIC OXYGEN EXPOSED POLYMERS

Material	Untreated	Exposed to an atomic oxygen fluence level of 1×10^{20} atoms-cm^{-2}
Acrylic	56 ± 5°	7 ± 2°
Cellulose acetate[a]	52 ± 1°	10 ± 1°
Polycarbonate[a]	74 ± 1°	10 ± 1°
Natural rubber[a]	91 ± 2°	24 ± 1°
Pyrolytic graphite[a]	110 ± 1°	4 ± 1°

[a]Data for these materials contained in reference 8.

TABLE II.—STATIC COEFFICIENT OF FRICTION FOR LIKE ON LIKE PRISTINE AND ATOMIC OXYGEN EXPOSED POLYMERS

Material	Untreated	Exposed to an atomic oxygen fluence level of 1×10^{-2} atoms-cm^{-2}
Acrylic	0.69 ± 0.01	0.80 ± 0.01
Cellulose acetate[a]	0.44 ± 0.03	1.29 ± 0.06
Polycarbonate[a]	0.41 ± 0.02	0.83 ± 0.02
Natural rubber[a]	0.86 ± 0.10	0.51 ± 0.03
Pyrolytic graphite[a]	0.48 ± 0.01	0.55 ± 0.02

[a]Data for these materials contained in reference 8.

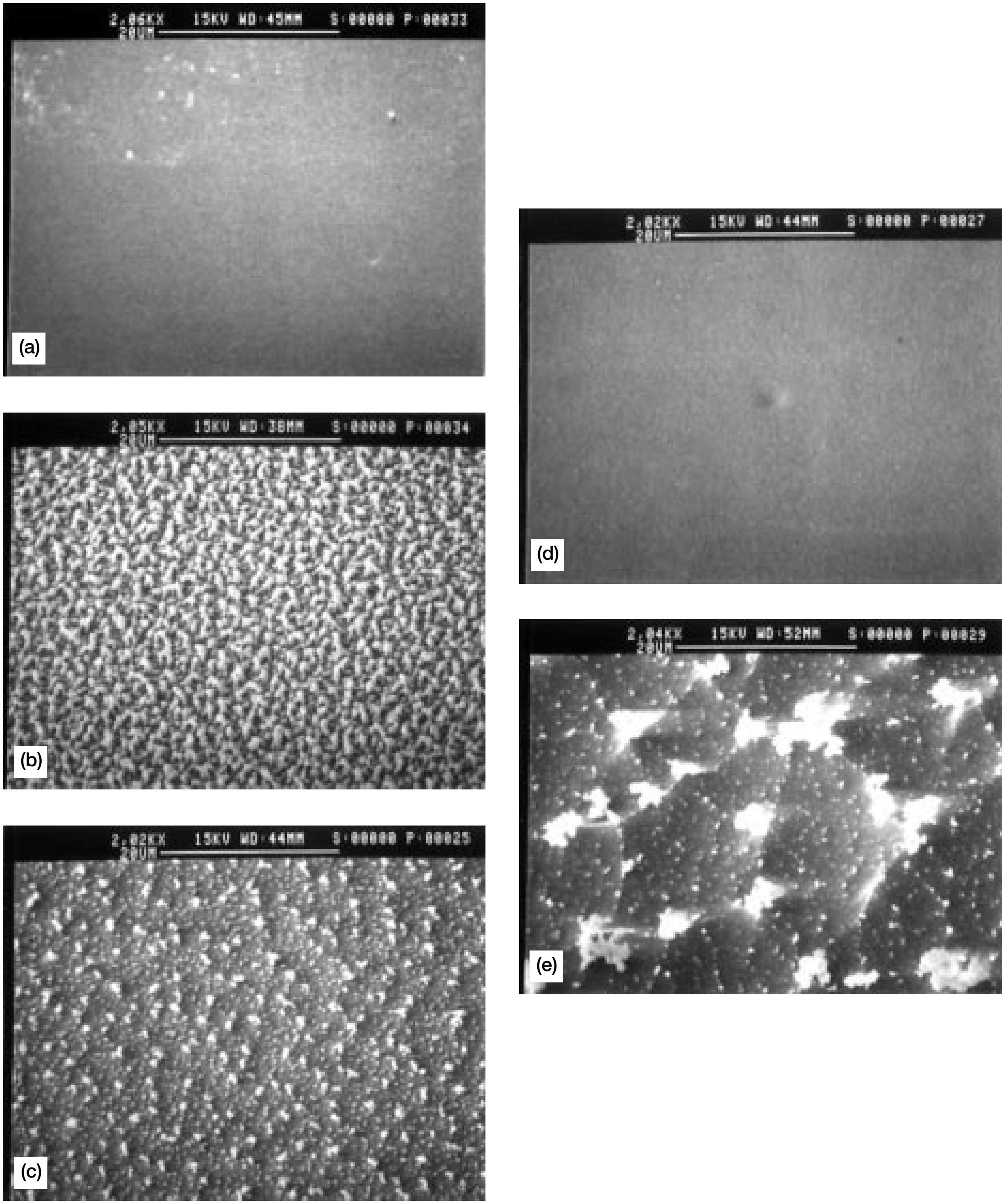

Figure 1.—Scanning electron photomicrographs of acrylic surfaces. (a) Untreated. (b) Exposed to an atomic oxygen effective fluence of 9.6×10^{19} atoms–cm^{-2}. (c) Exposed to an atomic oxygen effective fluence of 4.9×10^{19} atoms–cm^{-2}. (d) Exposed to an atomic oxygen effective fluence of 1.3×10^{21} atoms–cm^{-2}. (e) Exposed to an atomic oxygen effective fluence of 2.0×10^{21} atoms–cm^{-2}.

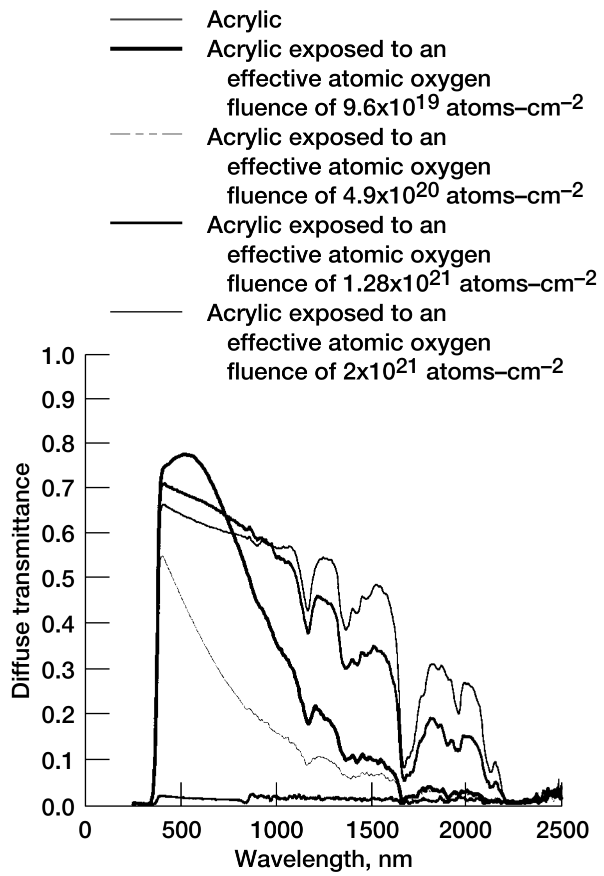

Figure 2.—Diffuse transmittance of acrylic versus wavelength as a function of atomic oxygen effective fluence.

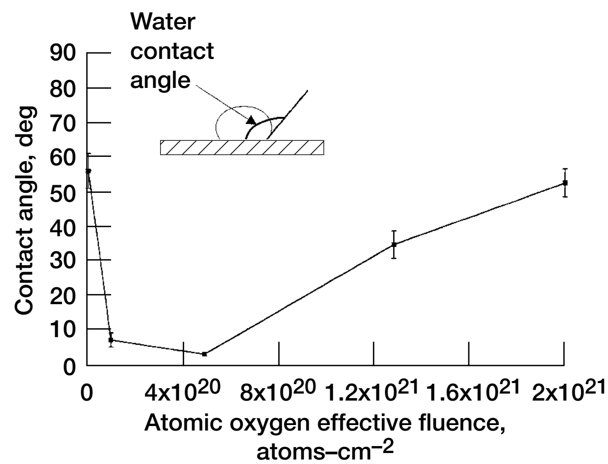

Figure 3.—Water contact angle for acrylic as a function of atomic oxygen effective fluence.

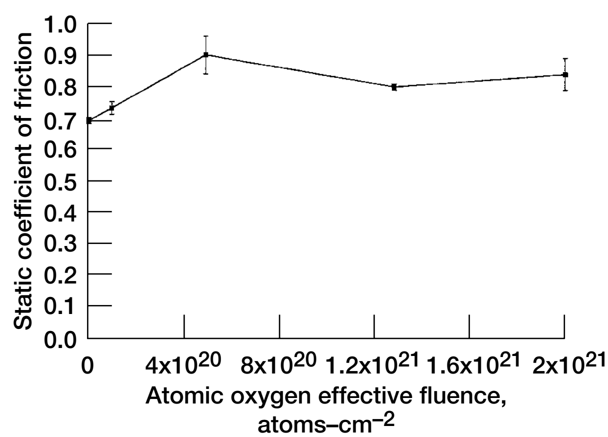

Figure 4.—Static coefficient of friction between identical acrylic surfaces as a function of atomic oxygen effective fluence.

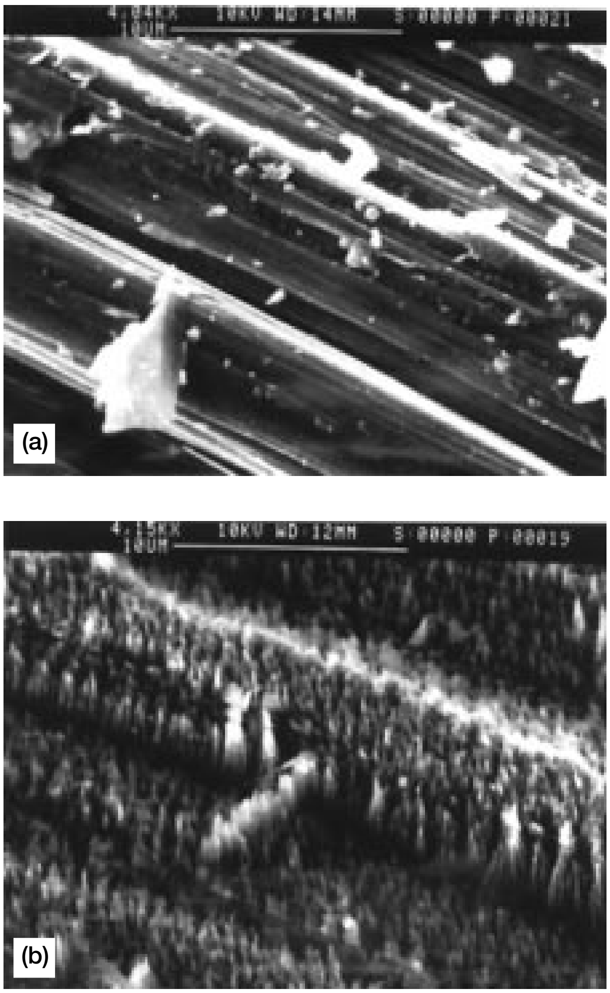

Figure 5.—Scanning electron photomicrographs of carbon-carbon composite from Rohr Industries. (a) As received. (b) After exposure to an atomic oxygen effective fluence of 4x10^{20} atoms–cm^{-2}.

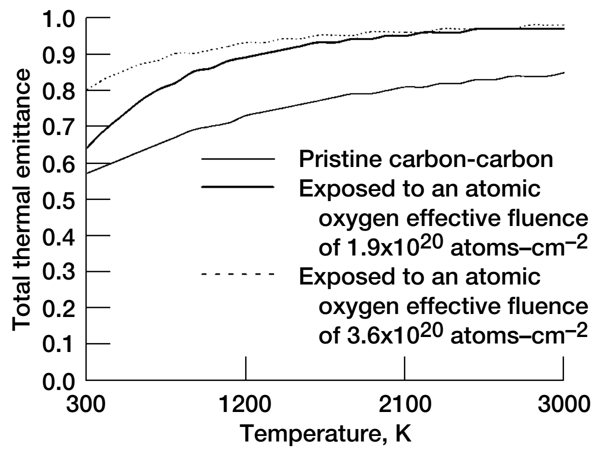

Figure 6.—Total thermal emittance versus temperature for a carbon-carbon composite material from Rohr Industries as a function of atomic oxygen effective fluence.

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Atomic oxygen, which is present in the low Earth orbit environment of space, can be used to texture the surface of polymers and some forms of carbon. It can be produced in vacuum chambers in the form of a plasma or directed beam using high voltage, radio frequency or microwave dissociation of oxygen gas. The textures that are produced are typically five microns in height or less. These textures can allow alteration of the surface properties without affecting the bulk material. Surfaces textured in this manner can experience increased or decreased static coefficient of friction, reduced water contact angle, increased diffuse transmittance and increased radiant heat transfer capability. These properties are of value for a variety of applications such as broad illumination fiber optics and as a replacement for chemical treatments to make polymers less sticky to the touch. This paper discusses the effects of various levels of atomic oxygen treatment on the transmittance, static coefficient of friction, and water contact angle for acrylic and compares the latter two with some previously measured data for other polymers and carbon. Changes in radiant heat transfer for carbon-carbon composites are also discussed.

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