Effects of Atomic Oxygen and Ultraviolet in Low Earth Orbit on Low Surface Energy Polymer Film

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ABSTRACT: Effects of atomic oxygen (AO) and ultraviolet (UV) on a polymer film with surface energy of 8.0 mJ m^{-2} derived from poly(1H,1H-perfluorooctyl methylacrylate) were investigated by contact angle measurements, X-ray photoelectron spectroscopy, and atomic force microscope. The film was exposed to AO with a flux of 6.73×10^{15} atoms cm^{-2} s^{-1} and UV with intensity of 15.8 mW cm^{-2} at wavelength of 200–450 nm, respectively. It is found that AO and UV irradiation resulted in the reduction of film thickness, change of wettability, and increase of surface energy, and AO exhibited more serious effects than UV on the fluorinated polymer film. Reduced rate of thickness of the film was almost proportional to the AO exposure time. After exposed to AO and UV irradiation, the surface energy of the film increased to 17.3 mJ m^{-2} and 11.0 mJ m^{-2}, respectively. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 329–334, 2011

Key words: atomic oxygen; ultraviolet; low earth orbit; low surface energy; fluoropolymer

INTRODUCTION

Polymers are extensively used in spacecraft due to their high strength-to-weight ratio and a variety of mechanical, thermal, electrical, thermo-optical, and surface properties; however over the last two decades, it has been well established that polymers undergo severe degradation because of many environmental factors in low earth orbit (LEO) such as thermal cycling, plasma, ultraviolet (UV), radiation, etc., resulting in reduced material lifetimes. Thus, the influence of individual constituent of the space environment on polymer materials and their synergistic effects should be understood for proper selection of polymers for specific functions. To do this, in-flight materials exposure experiments conducted on spacecraft should be the most suitable method; however, due to the high cost and the limited availability of in-flight experiments, and the demands for accelerated tests simulating long duration missions, it is necessary for ground simulation systems to study the space environment effects on materials.

Atomic oxygen (AO) and UV are the main constituents of space environment in LEO, which are especially harsh toward almost all of the polymers used in spacecraft. Many efforts had been made to investigate the influence of AO and/or UV on polymers, such as polysiloxanes (silicones), polyurethanes, polyesters, acetals, acrylics, fluorocarbons, polyamides, polyimides, etc., which proved that AO, due to its high chemical reactivity and high impinging energy ($\sim$ 5 eV) to material surfaces, is one of the most important factors eroding polymeric materials used in space, and UV radiation can enhance the damage of AO to materials.[1–12] To our knowledge, few reports have been made on the influence of AO and UV on polymers with ultra-low surface energy, which are composed of fluorocarbon or fluorosilicone polymer with pendant perfluoroalkyl groups[13–18] and can be used as creep barrier materials for space lubricants because their surface energies are lower than the surface tensions of most space lubricants.[19]

In this study, we studied the effects of a simulated LEO environment of AO and UV on an ultra-low surface energy polymer coating, and X-ray photoelectron spectroscopy (XPS), ellipsometer, and contact angle (CA) machine were employed to make the assessment.

EXPERIMENTAL

Materials

1H,1H-perfluorooctyl methacrylate was purchased from Alfa Aesar (China), which was purified by

distilling under reduced pressure. Azobisisbutyroni-trile (AIBN, Shanghai Chemical Reagent, China) was recrystalized in methanol before use. 1,1,2-Trichloride-1,2,2-trifluoro-ethane (CFC113) was obtained from Tianjin Chemical Reagents Corporation (China) and used without further purification.

Synthesis of PPFOMA

The polymer used for AO and UV exposure test in this experiment was prepared via bulk polymerization of 1H,1H-perfluorooctyl methacrylate using AIBN as an initiator in the similar procedure of the literature for the perfluroacrylates, as shown in Supporting Information Figure S1.[16] A reaction vessel was charged with 4.68 g (10 mmol) of 1H,1H-perfluorooctyl methacrylate and 16.4 mg (0.1 mmol) of AIBN and degassed for 30 min with nitrogen under stirring. The mixture was then heated to 70°C and kept for 6 h. The obtained colorless solid was cooled to room temperature and then purified by being dissolved in CFC113 and precipitated in methanol. The three times purification of dissolved precipitate offered the poly(1H,1H-perfluorooctyl methacrylate) (PPFOMA). Infrared (IR; KBr, cm^{-1}): 2975, 2925 (C—H stretching), 1762 (C=O stretching), 1460, 1410 (CO—O$^-$ stretching), 1245, 1215 (CF$_2$ stretching), 1150 (C—O stretching). The glass transition temperature (T_g) and melting temperature (T_m) were 64.5 and 186.5°C, respectively, and the starting decomposition temperature (T_d) was 313.0°C. Figure S2 and S3 in Supporting Information display its IR spectrum and DSC and thermogravimetric analysis curves, respectively.

Film formation

The polymer films were prepared on Si-wafer by spin-coating of PPFOMA solution in CFC113 with concentration of 1 wt % followed by heating for 1 h at 60°C. The thickness of the films was 150 nm measured by ellipsometer. The CAs for water and diiodomethane (DIM) were 123° and 102°, respectively, and the surface energy was 8.0 mJ m^{-2}.

AO exposure

A ground-based simulation facility at Lanzhou Institute of Chemical Physics was used in this study, which uses a microwave power source to excite O$_2$ and produces oxygen plasma. An electromagnetic field was applied to manipulate the oxygen plasma, which was accelerated by an electric field produced by negatively biased metallic plate. The accelerated oxygen plasma beam collided with the metallic plate allowing the neutralization of the oxygen plasma by the negative charges on the plate and rebounding of the neutralized oxygen plasma to form neutral AO

beam with impingement kinetic energy. The neutral AO beam with impingement kinetic energy was then manipulated to collide with the samples. Details about this facility have been reported in our previous works.[20,21] The flux of the AO was 6.73 × 10^{15} atoms cm^{-2} s^{-1}, which was calculated using Kapton-H films (thickness: 50 μm) as reference. The film samples were exposed to AO for 10–180 s in the pressure of 4.0 × 10^{-3} Pa.

UV exposure

The films were exposed to UV excimer light with wavelength of 200–450 nm in the pressure of 4.0 × 10^{-3} Pa using a mercury Xenon lamp as source. The intensity of the UV excimer light at the sample position was determined to be 15.8 mW cm^{-2} using a UV monitor. The films were exposed to the UV excimer light for 10–300 min.

Measurements

The film surface before and after AO and UV exposure was characterized by XPS, which was carried out on a PHI-5702 multifunctional spectrometer (Physical Electronics Inc., Eden Prairie, MN) using Al Kα radiation and the binding energies were referenced to the C$_{1s}$ line at 284.8 eV from adventitious carbon. Infrared spectroscopic measurements were conducted on a TENSOR 27 instrument (BRUCKER, Ettlingen, Germany, KBr disks). Thermal stability was determined with a thermogravimetric analyzer (STA 449 C, Netzsch, Serb, Germany) over a temperature range of 25–900°C at a heating rate of 10°C min^{-1} under N$_2$ atmosphere. The surface morphology of the film was imaged using an atomic force microscope (AFM, Nanoscope III, Veeco Instrument, Santa Barbara, CA) in contact tapping mode. The thickness of the film was measured on an ellipsometer (L116E, Gaertner, Skokie, IL). The wettability of the films was performed on a DSA 100 CA instrument (Kruss, Hambury, Germany), and deionized water and DIM (99%, Aldrich) were chosen as testing liquids because significant amounts of data are available for them. The static CA measurement of the films was determined at 25°C by CA goniometry using a Krüss GH-100 goniometer interfaced to image capture software via injecting a 5-μL drop of the test liquid onto the surface. A two-liquid geometric method was employed to determine the surface energy (γ).[22,23]

RESULTS AND DISCUSSION

Effects of AO and UV on the thickness of the low surface energy films

Both AO and UV exposure exhibited evident erosion to the low surface energy films. Figure 1 shows the
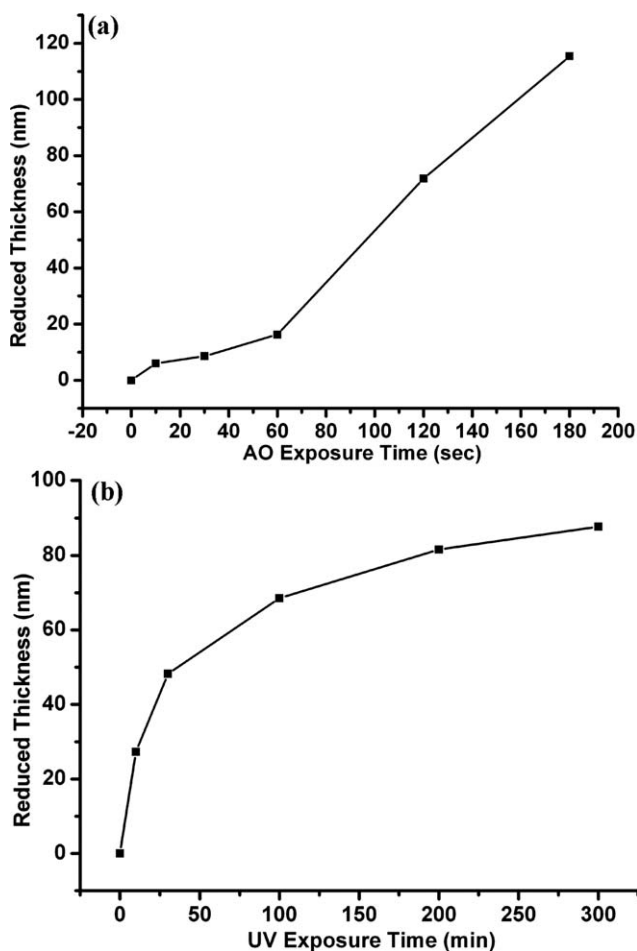
Figure 1 Reduced thickness of the fluorinated polymer film after AO (a) and UV (b) exposure.

reduced thickness of the films after the AO and UV exposure. As shown in Figure 1(a), when exposed to AO with flux of 6.73×10^{15} atoms cm^{-2} s^{-1}, the thickness of the polymer film decreased rapidly along with the exposure time. The erosion rate of AO to the film was almost proportional to the exposure time, which is 1.03×10^{16} atom cm^{-2} nm^{-1} when exposure time was 180 s. Figure 1(b) showed the erosion rate of UV exposure to the films. It shows that the erosion rate of UV to the film decreased along with the exposure time, which was 2.73 nm min^{-1} within the initial 10 min exposure and decreased to 0.061 nm min^{-1} when the exposure time increased from 100 to 200 min. Comparison of Figure 1(a,b) obviously interpreted that the erosion rate of UV exposure was much smaller than that of AO exposure, indicating that AO plays more important role in the erosion of the low surface energy film than UV. The main reason that AO and UV exhibited different erosion rate to the perfluoroalkyl polymer film should be their different erosion mechanism. The dominant erosion mechanism of AO to the perfluoroalkyl polymer film should be scission,

whereas the erosion mechanism of UV should be the synergistic effects of scission and cross linking.[2,24] The 5 eV AO could break the C—C bond followed by the release of volatile C_nF_m and/or C_nH_m fragments,[2,24] which resulted in the fast reduction in film thickness. On one hand, although the UV irradiation could break the C—C bond and release the volatile C_nF_m fragments leading to the reduction in film thickness, on the other hand, it could cause cross linking for C—H constituent thereby no mass loss occurred;[24] thus, UV irradiation exhibited lower erosion rate to the perfluoroalkyl polymer film than AO irradiation.

Effects of AO and UV on the surface properties of the low surface energy film

Effects of AO on the wettability and surface energy of the film are listed in Table I. It showed that very short time of AO exposure resulted in the drastic decrease of static CAs for water and DIM, which decreased from 123° to 96° and from 102° to 85°, respectively, and, thereby, surface energy of the film increase from 8.0 to 17.3 mJ m^{-2}. However, along with the increase of the AO exposure time, static CAs for water and DIM and surface energy of the film became almost constant. It can be explained that the outmost surface of the film without AO exposure exhibited mildly higher atomic proportion of fluorine than the calculated one because of the preferential orientation of the pendent perfluoroalkyl toward the surface at higher temperature,[16–18] which resulted in the bigger static CAs and lower surface energy of 8.0 mJ m^{-2}, whereas short time AO exposure (10 s) could erode the outmost surface of the film and lead to the decrease of atomic proportion of fluorine imparting the film higher surface energy of 17.3 mJ m^{-2}. Then, although longer AO exposure (30, 60, or 180 s) resulted in the sharp decrease of the thickness of the film, atomic proportion of fluorine on the film surface kept constant; thus, static CAs for water and DIM and surface energy of the film became almost constant. The explanation was also confirmed by the XPS measurement. Supporting Information Figure S4 shows the XPS survey spectra of the film with different AO exposure time, and the surface atomic composition of the film is listed in Table I. It can be seen that the atomic proportion of fluorine on the polymer film surface is 56.7% and the ratio of F/C is 1.56, both of which are larger than the calculated ones; whereas, after 10–180 s AO exposure, the atomic proportion of fluorine became 43.2–44.2%, and the ratio of F/C became 0.97–1.00, which is lower than the calculated ones. It can also be found that the atomic proportion of both C and O on the polymer film surface increased from 36.3 to 44.7% and from 7.0 to 12.1% after 10 s AO

TABLE I
Wettability, Surface Energy, and Surface Analysis Results of the Film
Before and After AO Exposure

AO exposure time (s)	Contact angle (°)		γ (mJ m^{-2})	Atomic concentration found (%) (calculated)		
	Water	DIM		C	F	O
0	123	102	8.0	36.3 (41.4)	56.7 (51.7)	7.0 (6.9)
10	96	85	17.3	44.7	43.2	12.1
30	98	85	16.7	42.9	44.2	12.9
60	97	86	16.7	43.6	43.9	12.5
180	97	86	16.7	44.6	44.1	11.3

exposure, respectively, and then both of them almost kept constant. The facts of decrease of F together with increase of C and O of the film after AO exposure indicated that the surface was composed of more polymer backbone groups and ether groups after the outmost surface of the film with higher $-CF_2$ and $-CF_3$ groups and was erased by AO, which are more hydrophilic than $-CF_2$ and $-CF_3$ groups, resulting in the decrease of CAs for water of the film. Half-an-hour AO exposure was also carried out, which showed that the sample became hydrophilic. The reason should be that the fluorinated polymer film had been completely eroded by AO and the bare surface of silicon-wafer was hydrophilic after AO exposure. The results suggested that the surface energy of the fluorinated polymer film kept <20 mJ m^{-2} until it was seriously eroded under the condition of AO irradiation.

Effects of UV on the wettability and surface energy of the film are listed in Table II. It showed that even after 300 min UV irradiation, static CAs of the film for water and DIM were still larger than 110° and 90°, respectively, indicating the film is still hydrophobic and oleophobic, and surface energy of the film was <11.0 mJ m^{-2}. It indicated that UV exposure showed slight effects on the wettability and surface energy of the film. The XPS survey of the films shown in Supporting Information Figure S5 and the surface analysis results listed in Table II consist with the results of static CAs and surface

energy. It showed that after UV exposure, even as long as 300 min, the atomic proportion of fluorine on the surface of the film was 51.9%, which was 0.2% higher than the calculated value 51.7%; thus, the film still exhibited hydrophobicity, oleophobicity, and low surface energy. The reason should be that although UV can erode the fluorinated polymer film, the UV exposure using a UV source with a power of 15.8 mW cm^{-2} can heat the film to $\sim 60°C$, which lead to the low surface energy groups such as $-CF_3$ and $-CF_2$ move to the outmost surface of the film because of their preferential orientation toward the surface.[16–18] This also explained why the erosion rate of UV irradiation decreased along with the increased exposure time. Aforementioned, UV irradiation can, on one hand, lead to mass loss and, on the other hand, cause cross linking of C—H constituent; thus, when the UV exposure time was short, the cross-linked proportion was small and the perfluoroalkyl groups could easily orientate toward the surface, which were eroded quickly by UV irradiation causing fast erosion rate to the film thickness. While the cross-linked proportion increased with the UV exposure leading to fewer rest perfluoroalkyl groups being able to orientate toward the surface, thereby resulted in a low erosion rate to the film.

Figure 2 shows the effects of AO and UV on the surface morphology of the film. It showed the surface morphology of the film after 10 or 30 s AO exposure [Fig. 2(b,c)] did not exhibit evident variation

TABLE II
Wettability, Surface Energy, and Surface Analysis Results
of the Film After UV Exposure

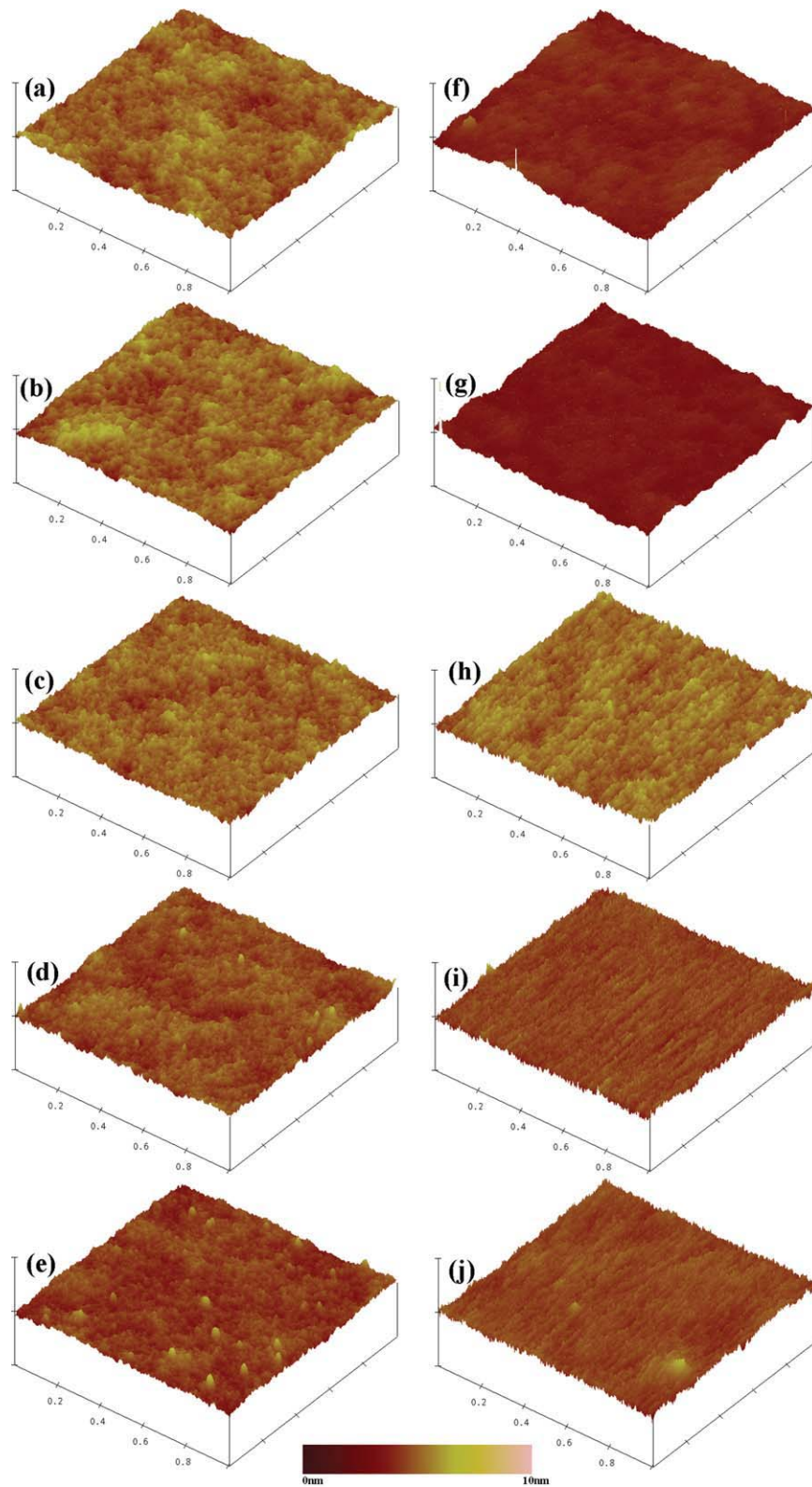| UV exposure time (min)	Contact angle (°)		γ (mJ m^{-2})	Atomic concentration (%)		
	Water	DIM		C	F	O
10	123	102	8.0	36.9	54.9	8.2
30	122	101	8.3	36.8	54.8	8.4
100	121	101	8.3	36.9	54.3	8.8
200	117	96	10.2	40.3	52.7	7.0
300	114	94	11.0	39.1	51.9	9.0

Figure 4

Figure 2 AFM images of the film: (a) unexposed, (b–e) exposed to AO for 10, 30, 60, and 180 s, and (f–j) exposed to UV for 10, 30, 100, 200, and 300 min. The scan area is 1×1 μm and all the Z-scales are 10 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with the original one [Fig. 2(a)], whereas it presented some punctate shapes with 60 s AO exposure [Fig. 2(d)], and the punctate shapes increased with 180 s AO exposure [Fig. 2(e)]. The reason that the films with different time AO exposure exhibited little variation in surface morphology should be its high erosion effects to organic materials, that is, the high corrosive AO can break all the chemical bonds including C—C, C—F, C—H, and C—O bond on the film surface, which resulted in an equal erosion rate everywhere on the film surface.[2] Figure 2(f–j) showed the surface morphology of the film after UV irradiation. It was notable that 10 and 30 min UV exposure resulted in very smooth surfaces, and 100, 200, and 300 min UV exposure resulted in surfaces with bigger roughness than the ones with 10 and 30 min UV exposure, but smaller than the nonirradiation one. The reason should be that the UV irradiation can easily break the C—C bond of perfluoroalkyl groups on the outmost surface of the film and cause the perfluoroalkyl groups orientating to the surface at the same time, thereby a very smooth surface could be obtained for short time UV exposure; whereas, along with the increased UV exposure, more and more cross linking of C—H constituent brought by UV irradiation occurred, which modified the surface layer and caused a more rough surface than the short time exposure one.

CONCLUSION

The effects of AO and UV exposure on the fluorinated polymer film with surface energy of 8.0 mJ m^{-2} were investigated. It is found that both AO and UV can erode the low surface energy film, causing the reduction of film thickness, change of wettability and increase of surface energy, and AO has more serious effects than UV on the fluorinated polymer film. After AO and UV exposure, the surface energy of the film increased to 17.3 and 11.0 mJ m^{-2}, respectively, until it was seriously eroded under the irradiations.

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