JOURNAL OF SPACECRAFT AND ROCKETS
Vol. 43, No. 3, May–June 2006

Changes in Properties and Structure of Polyethylene Terephthalate Film Under Vacuum Ultraviolet

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The effect of vacuum ultraviolet (VUV) radiation on polyethylene terephthalate (PET) film was investigated on a gas-jet VUV source with a wavelength of 5–200 nm. The experimental results show that under VUV irradiation both tensile fracture strength and elongation decrease slightly. The spectral absorbance of the PET film increases noticeably with increasing dose. An absorption band mainly forms in the ultraviolet-to-visible region. X-ray photoelectron spectroscopy, Fourier transform infrared, and electron spin resonance analyses indicate that in the skin layer of PET film under VUV radiation, the C–O bonds are broken and decarbonylation occurs, leading to the formation of free radicals as well as a trend to carbonification. The scission of the macromolecule chains, the increase in radical concentration, and the carbonification are considered to be major contributors to the change of optical properties for PET film under VUV exposure.

Nomenclature

T_λ = spectral transmittance
ΔA_λ = change of spectral absorption
δ = elongation
ε = strain
σ = stress
σ_f = fracture strength

I. Introduction

POLYMERIC materials have been widely employed in spacecraft for parabolic antennas, solar wings, and thermal control systems.[1–3] Their performance in space will directly influence the reliability and lifetime of spacecraft. Vacuum ultraviolet (VUV) radiation is one of the major environmental factors causing the degradation of polymers. Although the VUV energy percentage in the total spectrum of the sun is very limited, its photoenergy is high enough to break most chemical bonds in the polymers.[4] Therefore, it is important to study the effect of VUV radiation on the chemical structure and properties of polymeric materials, such as polyethylene terephthalate (PET) film. Most published work about the effects of VUV on polymeric films was performed using various VUV lamps with which it could be difficult to obtain a VUV spectrum similar to the sun's. A gas-jet VUV source was used in this study, which could give a spectrum similar to the sun in the wavelength range from 5 to 200 nm.[4] The aim of this work was to examine the changes in chemical structure and properties of the PET film under VUV exposure.

II. Experimental

The PET film was 60 μm thick. Its molecular structure is shown in Fig. 1. The film was annealed at 70°C for 3.5 h for eliminating the influence of thermal and strain history, rinsed with analytically pure acetone and ethanol in turn, and dried in a desiccator for more than 48 h at ambient temperature before VUV exposure.

The VUV source used in this study operated on supersonic argon gas, which was excited by a high-energy electron beam to give VUV with wavelength in the range from 5 to 200 nm. Figure 2 shows the spectrum of the VUV source compared to the sun's. A VUV intensity of 0.24 W/m^2 was acquired at a distance of 70 cm from the source, corresponding to 10 times the VUV solar constant (VUV sun). In this study, the gas-jet pressure was 5 atm, the electron-beam energy was 1000 eV, and the electric current was 15 mA. The vacuum before and after the injection of argon gas into the chamber was 10^{-5} and 10^{-3} Pa, respectively. The samples were located 70 (corresponding to 10 VUV suns), 34 (40 VUV suns), and 22 cm (100 VUV suns) away from the VUV source, respectively.

Tensile tests were carried out at room temperature after the VUV exposure. The engaged surface area of the film samples was 20 × 5 mm, and the crosshead speed was 2.4 mm/min. The transmittance of the VUV irradiated samples in the wavelength range from 200 to 3200 nm was measured with a UV-3101PC scanning spectrophotometer. X-ray photoelectron spectroscopy (XPS) was performed with a VG-ESCALAB Mark-2 type spectrometer with Mg$K\alpha$ source. The vacuum of the work chamber was 10^{-6} Pa, and the pass energy 20 eV. Infrared spectra were acquired using a Perkin–Elmer System 2000 Fourier transform infrared (FTIR) spectrophotometer. The resolution of the spectrophotometer was 1 cm^{-1}. The test wave numbers were in the range from 400 to 4000 cm^{-1}. Also, the change in electron spin resonance (ESR) spectra was examined using a JES-FE3AX spectrometer, and the measurements were made at frequencies in the range of 9.434 GHz with a center field of 3364 G at room temperature. The microwave power was 1 mW, the sweep range of the magnetic field was 500 G, and the field modulation was 5 G. The signal of diphenylpicrylhydrazyl was used as a standard for the g value. The intensity of ESR spectra was normalized by the mass of the PET film and the gain of the signal.

III. Results

A. Tensile and Optical Properties

Figure 3 shows the tensile stress–strain curves of PET film before and after VUV irradiation. Figure 4 shows the changes of tensile strength and elongation for PET film irradiated with various doses of VUV. It can be seen that the strength and elongation decrease slightly, but the tensile behavior changes little. In addition, under the same doses, the tensile strength changes nonobviously with the

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Presented as Paper 2004-PO-B-4 at the 7th International Conference Protection of Materials and Structures from the Low Orbit Space Environment, Toronto, ON, Canada, 10–13 March 2004; received 29 December 2004; revision received 18 April 2005; accepted for publication 24 September 2005.

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increase of VUV intensity, and elongation decreases less for the sample irradiated with 10 and 40 VUV suns, especially for that of 40 VUV suns, but more tension tests are needed to demonstrate this phenomenon.

Figure 5 shows the spectral transmittance for PET film irradiated with 100 VUV suns. It could be seen that the absorption limit is at 322 nm and changes little with the VUV dose, but the transmittance decreases obviously with the irradiation dose, especially in the visible region. Figure 6 illustrates the effect of VUV intensity on the ΔA_λ. The ΔA_λ in the near ultraviolet region changes remarkably with the VUV intensity. Moreover, under the same VUV dose, the ΔA_λ in the ultraviolet region increased less for the PET film irradiated with 100 VUV suns than under 40 VUV suns (see curves 3 and 4), but more than under 10 VUV suns (see curves 1 and 2). Figure 7 shows the change in ΔA_λ at 322 and 600 nm with VUV dose. With increasing dose, ΔA_{322} increases rapidly at first, and then tends to level off, whereas ΔA_{600} changes almost linearly.

B. X-Ray Photoelectron Spectroscopy Analysis

Figure 8 shows the C_{1s} spectra of PET film irradiated with 100 VUV suns for different doses. Before the irradiation, the C_{1s} spectrum could be considered as composed of three peaks with binding energy at 284.6, 286.3, and 288.4 eV, in turn, as shown in Fig. 8c. The three peaks might be related to the carbon in the benzene rings, the carbon singly bound to oxygen in ethylene and that in carbonyl groups.[5,6] After VUV irradiation, C_{1s} spectra could still be characterized with three peaks, as shown in Figs. 8a and 8b. Table 1 shows the change in the corresponding areas ratio for the three peaks with VUV dose. With increasing irradiation dose, area ratio for the peak at 284.6 eV increases, but those at 286.3 and 288.4 eV decrease obviously, which indicates that decarbonylation might take place at

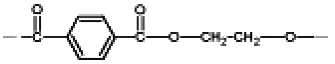

Fig. 1 Chemical structure of PET film.

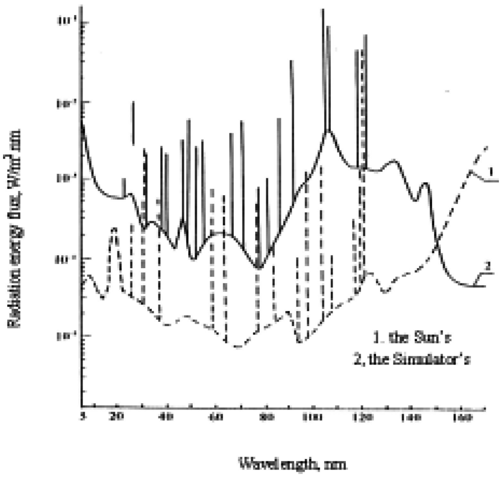

Fig. 2 Spectrum of gas-jet VUV source compared to that of the sun.

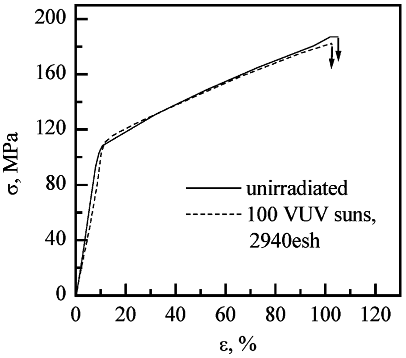

Fig. 3 Tensile stress–strain curves of PET film before and after VUV irradiation.

Table 1 Change in area ratios of fitting peaks for C_{1s} spectra of PET film after VUV irradiation

Intensity, VUV suns	Dose, esh	Binding energy, eV (area ratio, %)		
0	0	284.6 (69.6)	286.3 (17.1)	288.4 (13.3)
100	680	284.6 (84.7)	286.7 (11.3)	288.8 (4.0)
100	1600	284.6 (86.3)	286.5 (10.3)	288.6 (3.3)
100	2940	284.6 (89.4)	286.6 (8.4)	288.7 (2.2)
40	1600	284.6 (90.6)	286.4 (9.4)	——

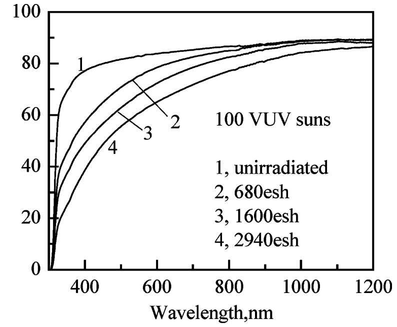

Fig. 5 Change in T_λ of PET film after irradiation with 100 VUV suns.

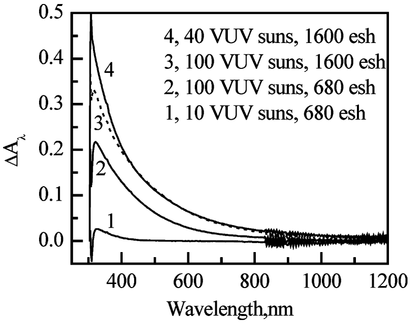

Fig. 6 Change in absorbance ΔA_λ for PET film vs intensity.

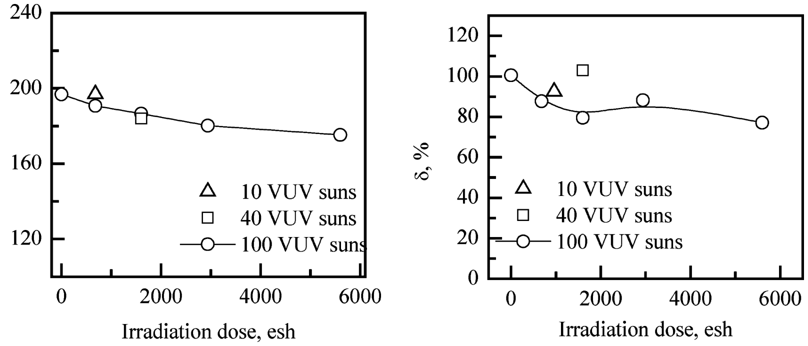

Fig. 4 Tensile fracture strength σ_f and elongation δ of PET film vs VUV irradiation dose.

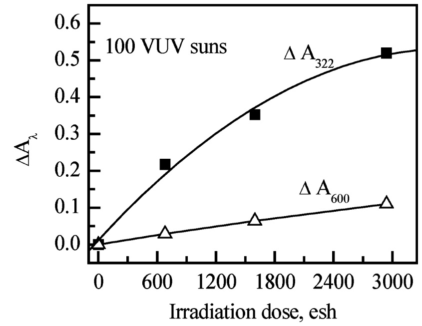

Fig. 7 **Changes in absorbance at 322 nm (ΔA_{322}) and 600 nm (ΔA_{600}) vs VUV dose for PET film irradiated with 100 VUV suns.**

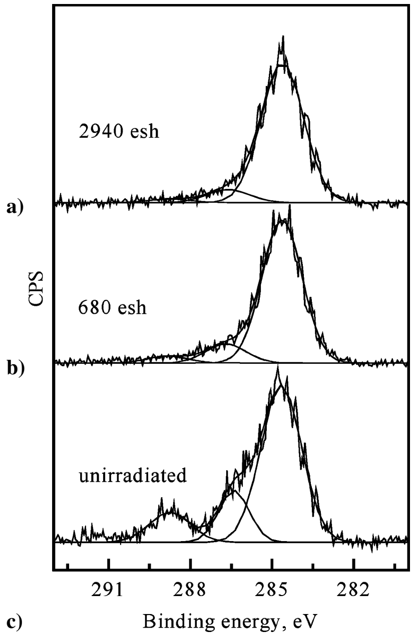

Fig. 8 ***C_{1s}*** **spectra of PET film irradiated with 100 VUV suns for a) 2940, b) 680, and c) 0 esh.**

the surface and that carbon with binding energy 284.6 eV, like that in benzene rings, might condense on the surface, which seems more significant for the PET film irradiated with 40 VUV suns.

Figure 9 shows the change in O_{1s} spectra after VUV irradiation. Before irradiation, the O_{1s} spectrum could be fitted to two Gauss peaks with binding energy 531.8 and 533.3 eV, respectively. The former could be attributed to the oxygen in carbonyl, and latter to oxygen singly bound to carbon.[5,6] After irradiation, the intensities of both peaks decrease. From the preceding XPS analysis, it is believed that the single bonds of carbon to oxygen in PET molecules could be broken under VUV radiation, further resulting in decarbonylation.

C. Fourier Transform Infrared Analysis

The FTIR spectra for PET film before and after VUV irradiation are shown in Fig. 10. The absorption peaks at 3627 and 3545 cm^{-1} are due to vibration of the hydroxyl group.[7,8] After VUV irradiation, the two peaks are enhanced, indicating that the content of end hydroxyl groups might be increased to some extent. In addition, several new peaks are observed in the region from 1680 to 1530 cm^{-1}. These peaks could be attributed to the change in substitute groups on benzene rings.[7,8] The peak at 1785 cm^{-1} is from the absorption of anhydride groups.[7,8]

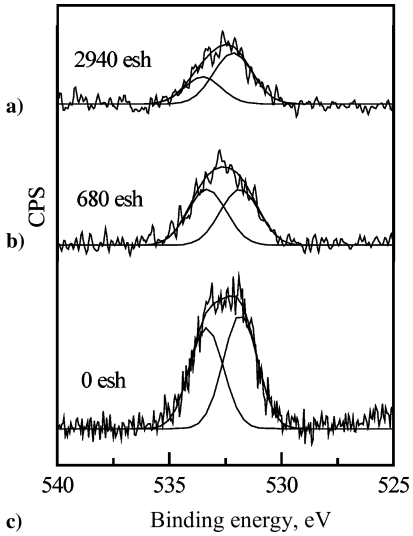

Fig. 9 ***O_{1s}*** **spectra of PET film irradiated with 100 VUV suns for a) 2940, b) 680, and c) 0 esh.**

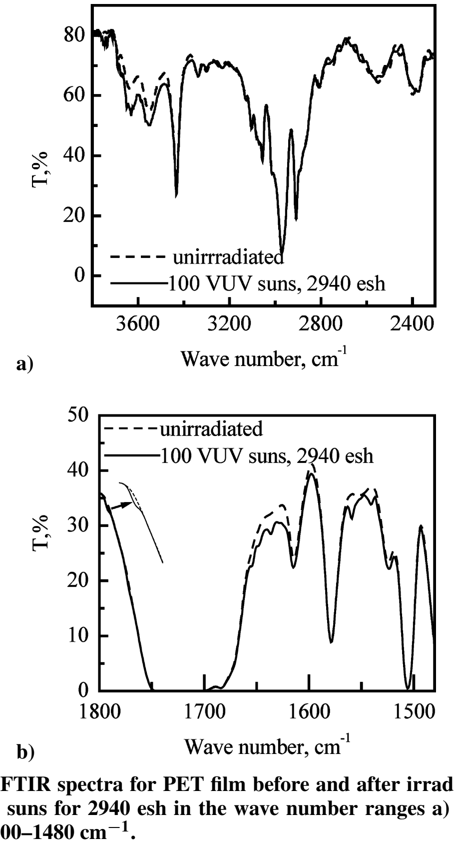

Fig. 10 **FTIR spectra for PET film before and after irradiation with 100 VUV suns for 2940 esh in the wave number ranges a) 3700–2300 and b) 1800–1480 cm^{-1}.**

D. Electron Spin Resonance Analysis

Figure 11 is the ESR spectra of PET film after VUV irradiation. The g value is 2.004 with linewidth 9G, somewhat larger than typical carbonaceous organic free radicals (2.002–2.003 and ≈3G, respectively).[9] The slightly larger g and linewidth might be due to the electrons that are delocalized in the aromatic rings and double bonds of carbon to oxygen.[10] The radical of $OC—\dot{C}_6H_3—CO$ could remain stable until 160°C, but the radical $O—\dot{C}H—CH_2—O$ could easily be destroyed by light and heating.[11,12] Therefore the observed radicals in this work might be the stable radicals $OC—\dot{C}_6H_3—CO$. The radicals could be destroyed with small molecules such as CO and CO_2 released,[13] which are detected by the mass spectrograph attached to the radiation source in the work, indicating that decarbonylation takes places assuredly.

On the basis of ESR analysis, the free radical concentration could be estimated using the formula in Ref. 14. As shown in Fig. 12, the free radical concentration increases rapidly and then tends to level off with the increase of VUV dose. This trend is similar to that of

ΔA_{322} vs dose in Fig. 7, demonstrating that the change of optical properties has a relation with the free radicals.

IV. Discussion

The single bond of carbon to oxygen in the constitutive unit of PET is weaker and easier to break. The breaking could result in the formation of an isolated carbonyl group. The isolated carbonyl is unstable and easy to stabilize by decarbonylation. The formed radicals in the stabilization could further condense and lead to carbonification to some extent. This process is Norrish I, as shown in Fig. 13a. On the other hand, carbonyl could capture the hydrogen at the γ position, inducing displacement of the γ hydrogen and further scission of the macromolecule chain with the formation of alkenes. This is the Norrish II process, as shown in Fig. 13b.

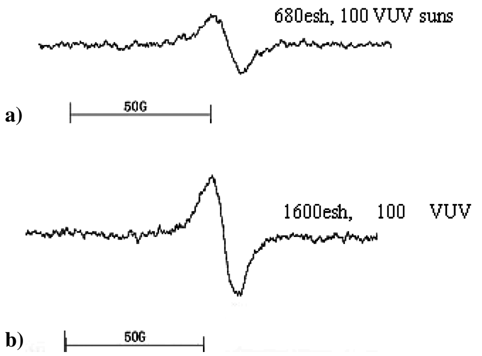

Fig. 11 ESR spectra for PET film irradiated with 100 VUV suns for a) 680 and b) 1600 esh.

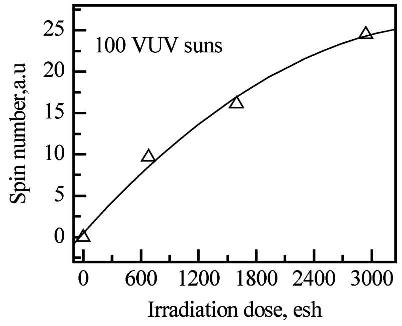

Fig. 12 Relative radical amount vs dose for the PET film irradiated with 100 VUV suns.

Former XPS analysis results indicated that the content of benzene rings increased whereas that of carbonyl decreased after VUV irradiation of PET film. Moreover, the FTIR analysis results demonstrate that the content of end hydroxide increased and the substitute group of benzene rings changed. In addition, stable radicals formed after VUV irradiation. All of these results indicated that the PET film degraded mainly according to Norrish I, as shown in Fig. 13a.

The similar trends for the concentration of radicals and the change of absorbance at 322 nm with irradiation dose demonstrate that the change of optical properties has some relationship to the radicals. The formation rate of radicals is proportional to the intensity and dose of VUV, whereas the annihilation rate and the after reaction of radicals would be influenced by the concentration, the longevity of the radicals, and the ambient temperature. Under lower-intensity VUV, for lower radical formation rate, the annihilation rate for the radicals is lower, too, and the radicals might undergo more significant after-reaction and then change to more stable ones. On the other hand, ΔA is proportional to the concentration of the matter that has been absorbed in the region. Therefore, the optical properties change with the increase of dose and were influenced by intensity.

On the other hand, the changed benzene rings could have great absorption in the ultraviolet and visible regions.[8,11,12] Otherwise, the colorless PET film was changed to brown after VUV irradiation indicated the condensation of benzene rings and further the carbonification, which could have great influence on the transparency of PET film. As discussed in a previous study,[15] the increase of intensity could lead to more significant carbonification for the more obvious local heating effects. Therefore, the changes of optical properties with VUV intensity and dose might be a cooperative effect of radicals and others, processes such as carbonification. On the other hand, for most of the energy of VUV to be absorbed within 1 μm thickness, the significant change in this layer could not be obviously revealed by tensile properties, although a small decrease in mechanical properties was observed.

V. Conclusions

VUV radiation is a major factor of space environments. Under VUV radiation, tensile properties of PET film did not change a lot, whereas the optical ones varied noticeably. With increasing irradiation dose, the tensile fracture strength and elongation decreased slightly, and the spectral absorbance increased remarkably in the ultraviolet-to-visible region. Under the same VUV dose, ΔA_λ in the ultraviolet region increased more significantly for the PET film irradiated with 40 VUV suns in the experimental intensity region.

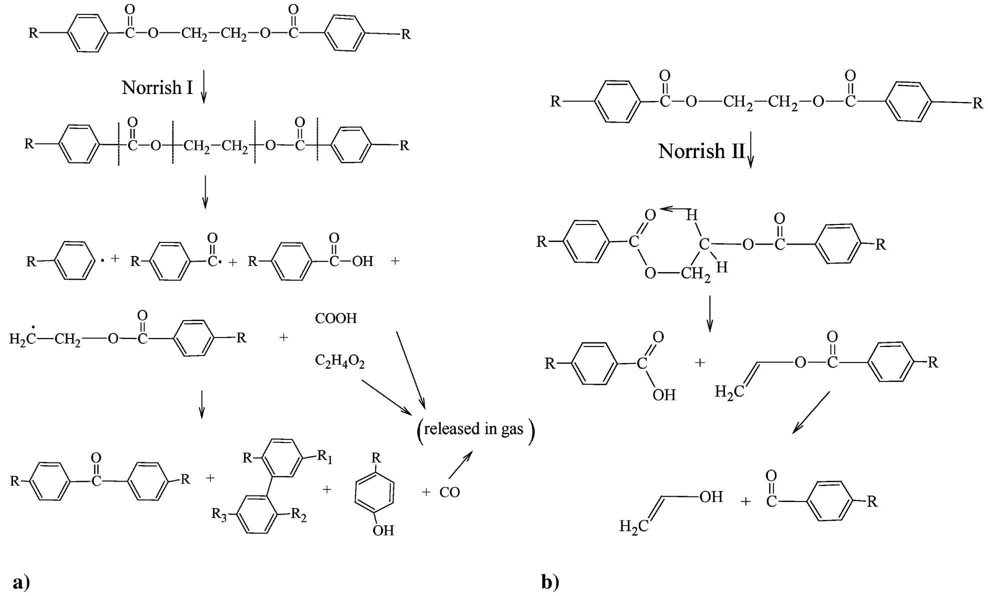

Fig. 13 Changes in chemical structure of PET molecules under VUV irradiation in terms of the a) Norrish I and b) Norrish II reactions.

XPS, FTIR, and ESR analyses indicated that in the skin layer of PET film irradiated with VUV, the C–O bonds could be broken and decarbonylation could occur, forming free radicals of benzene rings. As a result, the condensation of the benzene rings was increased, and then a trend of carbonification or the richening of carbon appeared. The increase in free radical concentration and carbonification would cause degradation in optical properties for the PET film under VUV radiation. The changes of optical properties with VUV intensity and dose might be a cooperative effect of radicals and other processes such as carbonification.

Acknowledgments

The financial support of the National Basis Research Foundation of China under Grant G19990650 is greatly appreciated. The authors are grateful to Ruiyun Zhan of the Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, for the valuable discussions of ESR analysis.

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Associate Editor