

Effects of Vacuum Ultraviolet on the Structure and Optical Properties of Poly(tetrafluoroethylene) Films

Guirong Peng,¹ Dezhuang Yang,¹ Jincheng Liu,² Shiyu He¹

¹Space Materials and Environment Engineering Lab, Harbin Institute of Technology, Harbin, 150001, China

²Institute of Opto-Electronics, Harbin Institute of Technology, Harbin, 150001, China

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ABSTRACT: The effects of vacuum ultraviolet (VUV) at wavelengths of 5–200 nm on the microscopic structure and optical properties of poly(tetrafluoroethylene) (PTFE) films were investigated. X-ray photoelectron spectroscopy analysis showed that the C_{1s} spectra changed from a single peak at 292.8 eV to multiplex peaks with binding energies of 284.6, 286.6, 288.6, 290.5, and 293.0 eV after VUV irradiation at 680 esh. With an increasing irradiation dose, the C_{1s} peaks at 290.5 and 293.0 eV disappeared. After the PTFE film specimens irradiated at 1600 esh were sputtered with argon ions for 3 min, the C_{1s} peaks at 290.5 and 293.0 eV appeared again, and the height of the peaks at 286.6 and 288.6 eV increased. The content of fluorine decreased after VUV irradiation. The content of fluorine in the film surface layer decreased significantly with the increase in the VUV inten-

sity, but it did not change with the irradiation dose. Fourier transform infrared (FTIR) analysis results indicated that some conjugated bonds, such as —FC=CF—, were formed during VUV irradiation, but no CH absorption bands were observed in the FTIR spectra; this indicated that the increase in the height of the C_{1s} peak at 284.6 eV arose mainly from the carbon–carbon bonds, that is, from carbonification. The spectral transmittance of the PTFE film decreased gradually with an increasing VUV irradiation dose, and at a given dose, the lower the intensity was of the VUV irradiation, the greater the change was in the spectral transmittance. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 115–121, 2003

Key words: polytetrafluoroethylene (PTFE); irradiation; microstructure

INTRODUCTION

Polymeric materials have widely been used in spacecraft for parabolic antennas, solar battery base plates, and thermal control systems.^{1–7} Their service behavior in space will directly influence the reliability and lifetime of spacecraft. Vacuum ultraviolet (VUV) irradiation is one of the major factors causing the degradation of polymers.^{8–10} Although the VUV energy percentage of the total spectrum of the sun is very limited, its photon energy is high enough to be comparable to most chemical bonds, or even significantly higher; this can result in serious changes in the chemical and physical properties of polymers. Therefore, for the selection of materials used in such an environment, knowledge about their resistance against VUV irradiation is very important. However, most published investigations about the effects of VUV on polymers were carried out with various UV lamps,^{11–15} with which it could be difficult to obtain a VUV spectrum similar to that of the sun.¹⁶ The difference in the wavelengths of VUV can greatly influence the behavior of polymers.^{12,13,15} A gas-jet-type VUV source was

used in this work; it could give a spectrum similar to the sun's spectrum in the wavelength range of 5–200 nm.¹⁷ The aim of this study was to reveal the effects of VUV irradiation on the microstructure and optical properties of poly(tetrafluoroethylene) (PTFE) films.

EXPERIMENTAL

The PTFE film was 50 μm thick. The film was annealed at 70°C for 3.5 h, rinsed with analytically pure acetone and ethanol in turn, and dried in a desiccator for more than 48 h at the ambient temperature before irradiation.

The VUV source used in this study operated on supersonic argon gas, which was excited by a high-energy electron beam. A VUV intensity of 0.24 W/m² could be acquired at a distance of 70 cm from the source, corresponding to 10 times the VUV solar constant (VUV suns). 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 specimens were located 34 (corresponding to 40 VUV suns) and 22 cm (100 VUV suns) away from the VUV source.

The X-ray photoelectron spectroscopy (XPS) spectra were acquired with a VG-Escalab Mark-2 spectrome-

Correspondence to: G. Peng (gr8599@yahoo.com.cn).

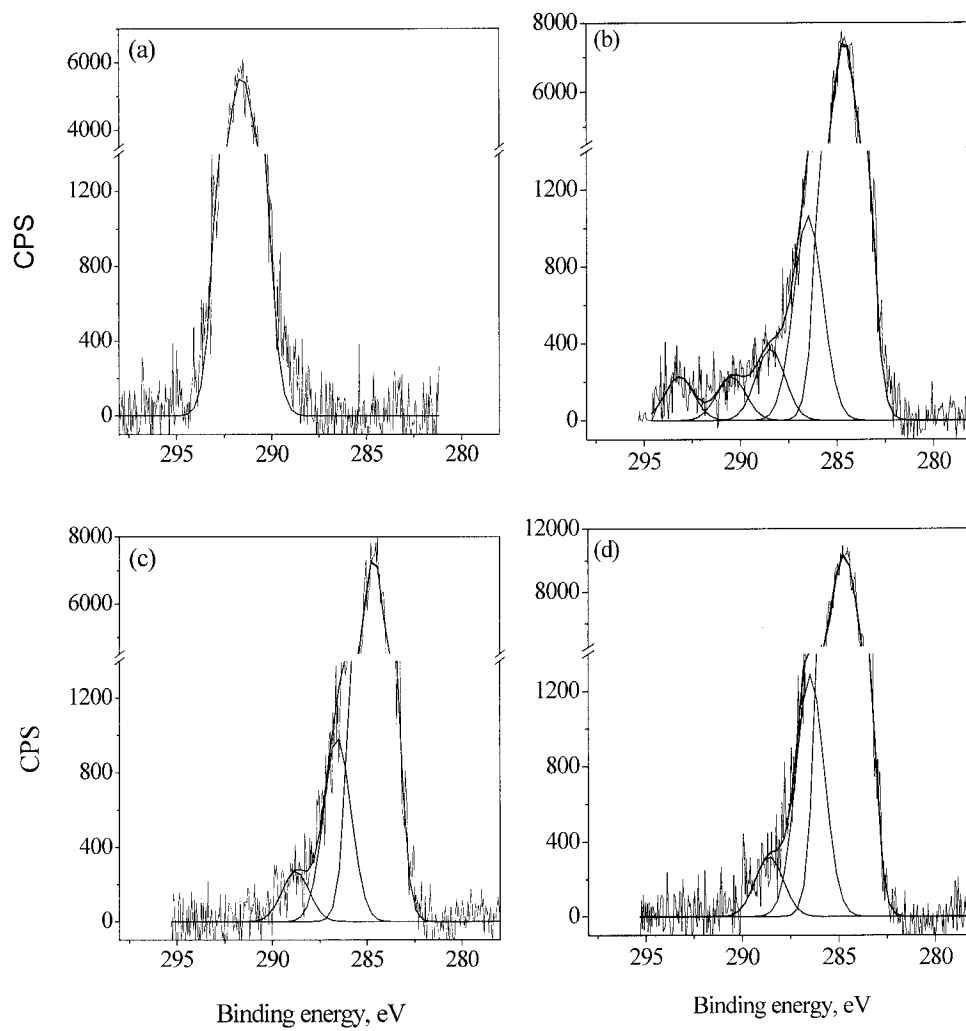


Figure 1 C_{1s} spectra of PTFE films after irradiation with 100 VUV suns at various doses and their Gauss fitting peaks: (a) not irradiated, (b) 680 esh, (c) 1600 esh, and (d) 2940 esh.

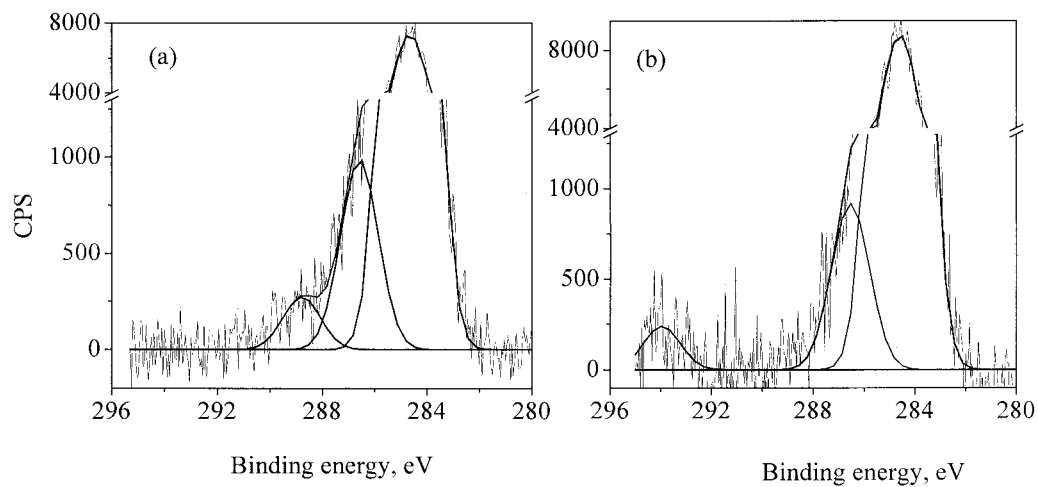


Figure 2 C_{1s} spectra and their Gauss fitting peaks of PTFE films irradiated at 1600 esh at different VUV intensities: (a) 100 and (b) 40 VUV suns.

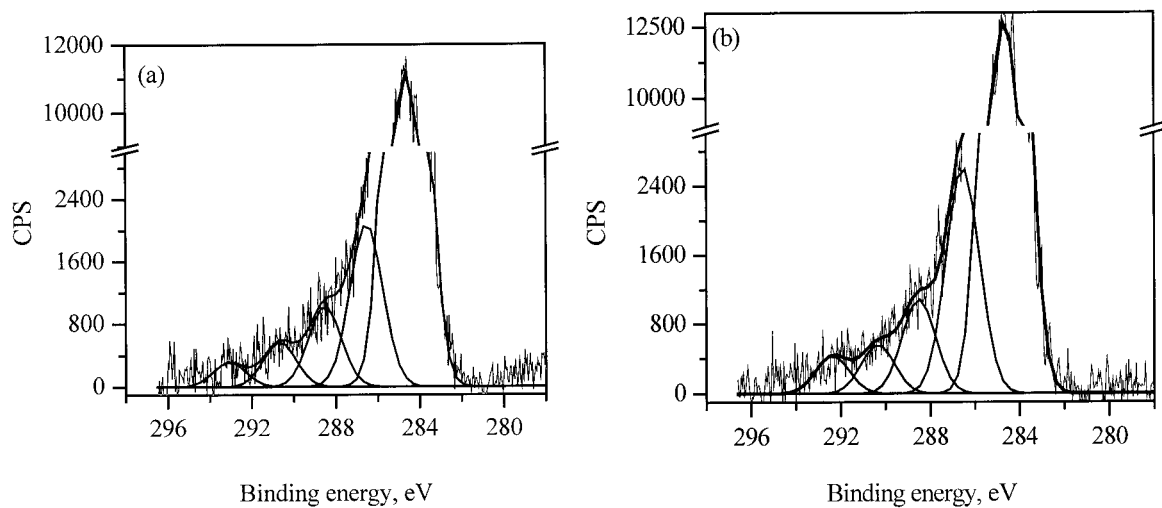


Figure 3 C_{1s} spectra after sputtering with argon ions for 3 min of PTFE films irradiated at 1600 esh at different VUV intensities: (a) 100 and (b) 40 VUV suns.

ter with an Mg $K\alpha$ source (Thermo VG Scientific, West Sussex, UK). The vacuum of the work chamber was 10^{-8} Torr, and the pass energy was 20 eV. IR spectra were acquired with a PerkinElmer System 2000 Fourier transform infrared (FTIR) spectrophotometer (Per-

kin Elmer, Shelton, CT). The resolution of the spectrophotometer was 1 cm^{-1} . The test wave numbers were in the range of $400\text{--}4000\text{ cm}^{-1}$. The transmittance of the VUV-irradiated specimens in the wavelength range of $200\text{--}3200\text{ nm}$ was measured with a UV-

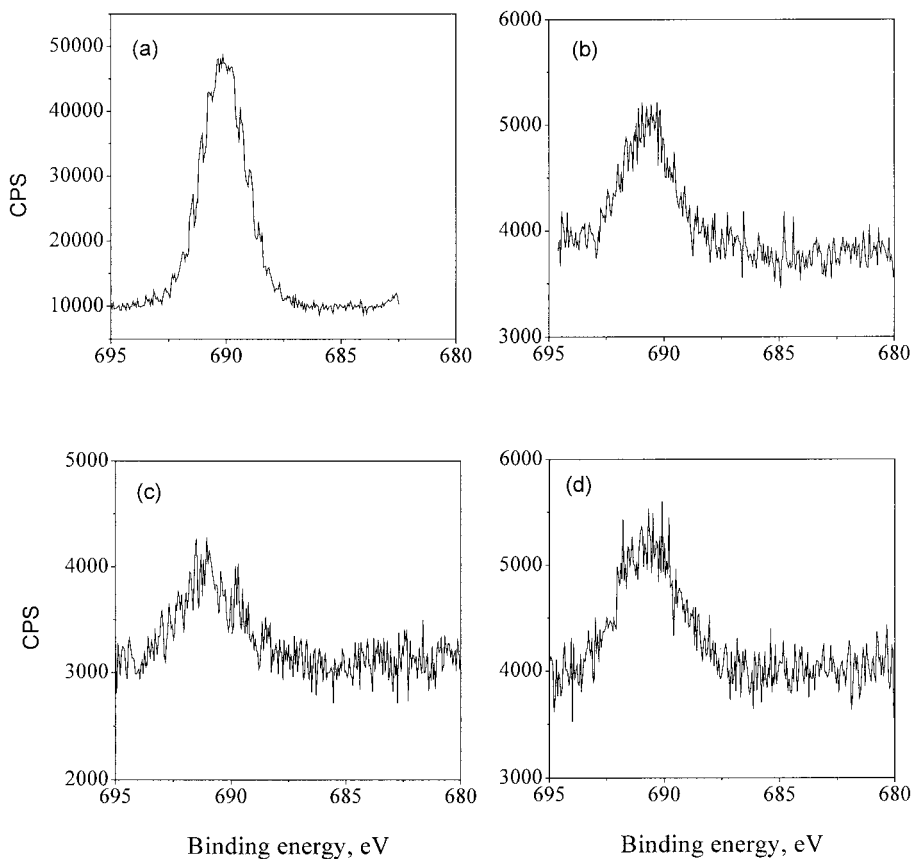


Figure 4 F_{1s} spectra of PTFE films after irradiation with 100 VUV suns at various doses: (a) 0, (b) 680, (c) 1600, and (d) 2940 esh.

3101PC scanning spectrophotometer (Shimadzu, Kyoto, Japan).

RESULTS AND DISCUSSION

XPS analysis

Figure 1 shows the C_{1s} spectra and their peak fitting results for PTFE films irradiated with VUV at different doses. From Figure 1(a), it can be seen that the C_{1s} spectrum before irradiation revealed only one symmetrical peak at 292.8 eV, which could be assigned to CF_2 . The spectrum also indicated that there was no significant contamination of the PTFE film. For the specimens irradiated at 680 esh, the C_{1s} spectra showed a major peak at 284.6 eV with a small shoulder on the side of higher binding energy, as shown in Figure 1(b). From fitting with Gauss peaks, the C_{1s} spectrum can be considered to arise from the Gauss peaks at 284.6, 286.6, 288.6, 290.5, and 293.0 eV, which could be attributed to the species of carbon bound to carbon, hydrogen, and fluorine in various proportions, such as CF_2 , CF_2CH_2 (the C_{1s} binding energies were 290.9 and 286.4 eV, respectively), $CHFCHF$ (the

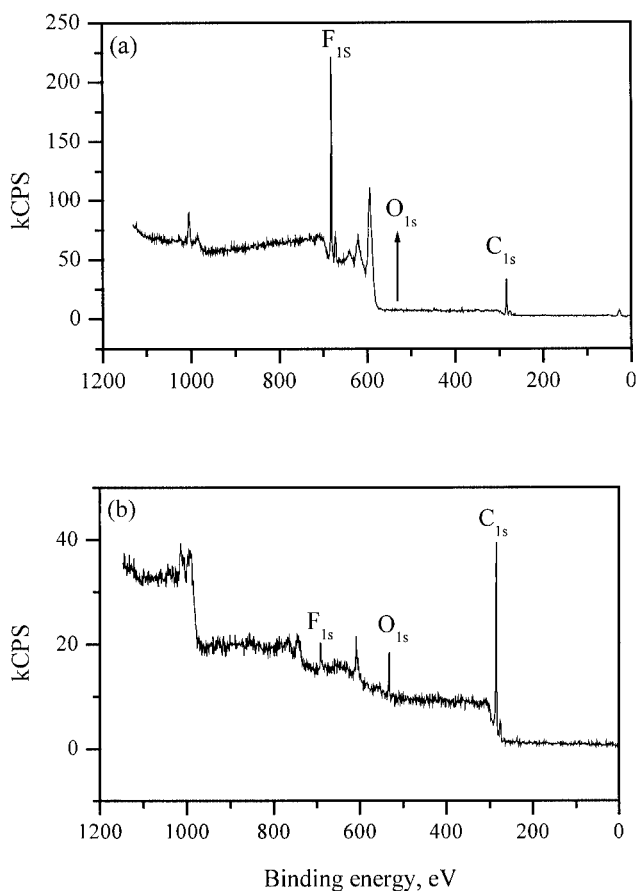


Figure 5 XPS survey spectra of (a) a pristine PTFE film and (b) a PTFE film irradiated with 100 VUV suns at 680 esh.

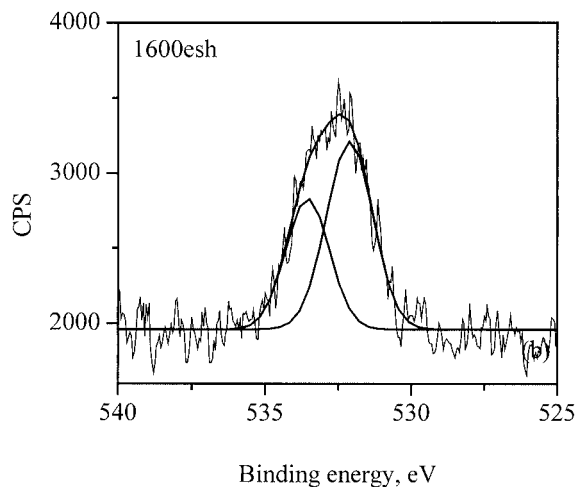


Figure 6 Peak fitting results for the O_{1s} spectrum of a PTFE film after irradiation with 100 VUV suns at 1600 esh.

C_{1s} binding energy was 288.2 eV), and CH_2CH_2 (the C_{1s} binding energy was 284.6 eV).¹⁸⁻²³ With a further increase in the VUV dose, the C_{1s} peaks at 290.5 and 293.0 eV disappeared, but no obvious changes for the C_{1s} peaks at 286.6 and 288.6 eV were observed, as shown in Figure 1(c,d). Figure 2 indicated the influence of the VUV intensity on the C_{1s} spectrum at a given irradiation dose. Under the higher VUV intensity, the C_{1s} spectrum could be fitted to three characteristic peaks [Fig. 2(a)]. As for the lower VUV intensity [Fig. 2(b)], only the C_{1s} peaks with binding energies of 284.6 and 286.6 eV were observed, as shown in Figure 2(b). Also, a peak at 294 eV appeared, which might be a shake-up peak due to the π bonds; this indicated that some conjugated groups, such as $-FC=CF-$, were formed.¹⁸

Figure 3 shows the C_{1s} spectra for specimens sputtered by argon ions for 3 min after irradiation at different VUV intensities at 1600 esh. The C_{1s} peaks with the binding energies of 290.4 and 292.6 eV appeared again, and the height of the C_{1s} peaks with binding energies of 286.6 and 288.6 eV increased to some extent. No obvious differences were observed in

TABLE 1
Change in Composition in the Surface Layer of PTFE Film After VUV Irradiation in Terms of XPS Quantitative Analysis

Intensity (VUV suns)	Dose (esh)	C_1 (%)	F_1 (%)	C/F
0	0	37.0	63.0	0.6
100	680	96.1	3.9	24.6
100	1600	94.2	5.8	14.5
100	2940	96.2	3.8	25.3
40	1600	89.6	10.4	8.6

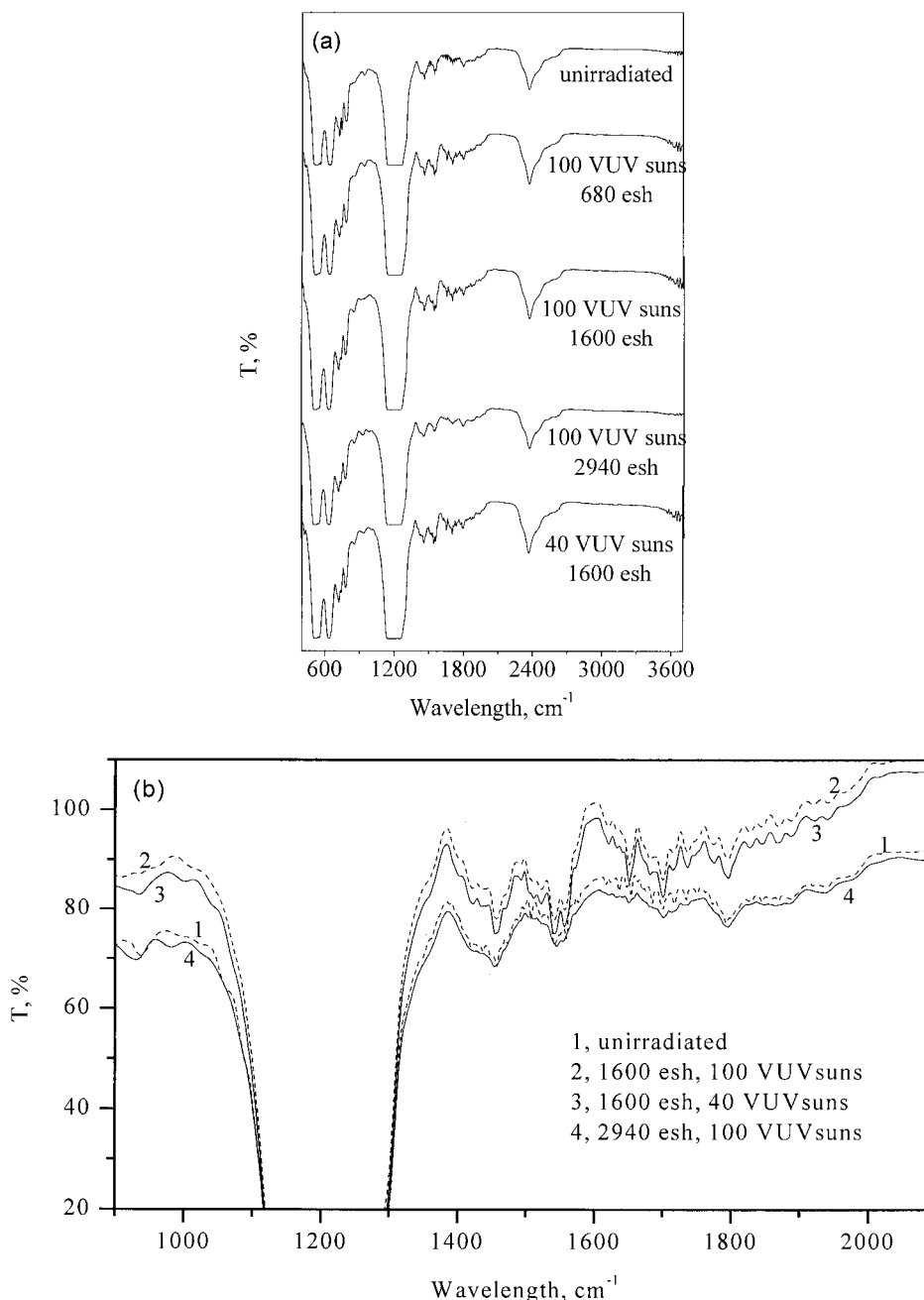


Figure 7 FTIR spectra of PTFE films before and after VUV irradiation at (a) 400–3600 and (b) 900–2100 cm^{-1} .

the C_{1s} spectra for PTFE films irradiated at different VUV intensities.

As for the F_{1s} spectra, with an increasing VUV irradiation dose, no significant changes in the F_{1s} binding energy were observed, but the intensity of the full width at half-maximum was broadened, as shown in Figure 4. Because the creation of CHFC and CF_2CH_2 would change the binding energy of F_{1s} to some extent,^{18,20,23} the broadening of F_{1s} spectra demonstrated that the changes in the microstructure caused by VUV irradiation agreed with the changes in the C_{1s} spectra.

Figure 5(a,b) shows the XPS survey spectra of PTFE films before and after VUV irradiation. No O_{1s} signals were observed before VUV irradiation, whereas the O_{1s} peak appeared after the irradiation. Through peak fitting to O_{1s} , as shown in Figure 6, the O_{1s} peaks could be considered to arise from $\text{C}=\text{O}$ and $\text{C}-\text{O}$, for which the O_{1s} binding energies were 532 and 533.6 eV, respectively.¹⁸ It can also be seen in Figure 5 that after VUV irradiation, the intensity of the F_{1s} peak decreased, whereas that of the C_{1s} peak increased significantly. The quantitative analysis results for the

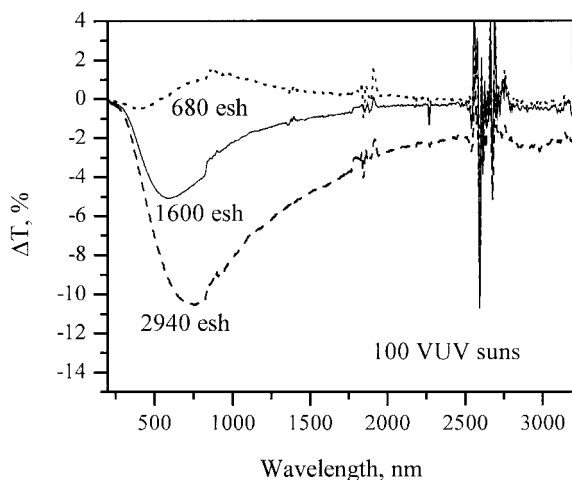


Figure 8 Changes in the spectral transmittance with the VUV dose for PTFE films irradiated with 100 VUV suns.

changes in the contents of carbon and fluorine in the surface layer are shown in Table I. After VUV irradiation, the content of fluorine obviously decreased. The content of fluorine decreased significantly with an increase in the VUV intensity, but it did not change with the irradiation dose. The changes in the contents of carbon and fluorine might indicate that carbonification occurred in the surface layer. When enough oxygen existed, ablation would take place for polymers irradiated with ultraviolet;^{24–26} when no oxygen existed, carbonification could take place during irradiation.²⁵ The surface color of PTFE films changed gradually from semitransparent white to brown during VUV irradiation, and this testifies to the appearance of carbonification. This may be one of the major sources of C_{1s} peaks at 284.6 eV.

IR analysis

Figure 7(a) shows FTIR spectra from 400 to 3600 cm^{-1} before and after VUV irradiation. No significant changes were observed before and after VUV irradiation. There were no absorption peaks corresponding to CH_3 , CH_2 , and CH in the range of 2800–3100 cm^{-1} ; this indicated that no CH bonds formed during VUV irradiation. This also illustrated that the carbonification occurred under the VUV irradiation.

Figure 7(b) shows FTIR spectra from 600 to 2100 cm^{-1} for PTFE films before and after irradiation with VUV. A new absorption band at approximately 981 cm^{-1} was observed that might be associated with the increase in the proportion of CCF_3 .²⁷ In addition, the absorption bands became more obvious between 1600 and 1900 cm^{-1} after VUV irradiation, and this indicated that conjugated bonds, such as $-\text{FC}=\text{CF}_2$ (1785 cm^{-1}), $-\text{FC}=\text{CF}-$ (1730 and 1717 cm^{-1}), and $-\text{FC}=\text{C}$ (1671 cm^{-1}), were formed.^{28,29}

Optical properties

Figure 8 shows the changes in the spectral transmittance after irradiation with 100 VUV suns at various doses. Under the lower dose of VUV irradiation, the spectral transmittance decreased a little and even increased slightly at wavelengths from 540 to 1300 nm. With the irradiation dose increasing further, the spectral transmittance decreased significantly in the visible-to-near-infrared region. Figure 9 shows the influence of the VUV intensity on the spectral transmittance of PTFE films. At a given dose, the spectral transmittance decreased more under irradiation of lower VUV intensity.

The changes in the spectral transmittance could be related to the changes in the microstructure, as shown in XPS and FTIR analyses. The carbonification and the conjugated bonds could significantly reduce the spectral transmittance of the PTFE films. In addition, the photon energy of VUV is high enough to break down the chemical bonds in polymers to form active radicals, and the radicals could be trapped and live for quite a long time, even for several months. They could also contribute to the decrease in the transmittance. The greater decrease in the transmittance under lower intensity VUV irradiation might be related to the lower formation rate of the radicals. However, all of these require other experiments for proof.

CONCLUSIONS

1. After VUV irradiation, the ratio of fluorine decreased, whereas the ratio of carbon increased in the surface layers of PTFE films. The content of fluorine decreased significantly with an increase in the VUV intensity, but it did not change with the irradiation dose.

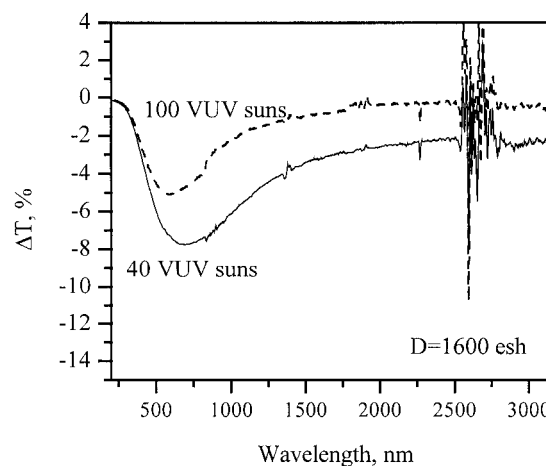


Figure 9 Changes in the spectral transmittance with the VUV irradiation intensity at a given dose for PTFE films.

2. Under VUV irradiation, the number of CF₂ groups decreased, whereas the number of CCF and CCF₂ groups and conjugated bonds increased; this indicated that carbonification took place in the surface layers of PTFE films. Lower intensity VUV irradiation at larger doses induced a more complete change in the surface structure.
3. The spectral transmittance for the PTFE films decreased gradually with an increase in the VUV irradiation dose and more significantly under lower intensity VUV irradiation.

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