An Analysis of the Changes in the Structure and Tensile Properties of Polytetrafluoroethylene Films Under Vacuum Ultraviolet Irradiation

Guirong Peng, Hongbin Geng, Zushun Lü, Dezhuang Yang, Shiyu He

Harbin Institute of Technology, Harbin 150001, People's Republic of China

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ABSTRACT: The effect of 5–200 nm of vacuum ultraviolet (VUV) irradiation on the structure and tensile properties of polytetrafluoroethylene (PTFE) films was investigated. The change in structure before and after VUV irradiation was evaluated with differential scanning calorimetry (DSC) and electron spin resonance (ESR) analysis. DSC analysis results showed that the melting point, melting enthalpy, and crystallization enthalpy increased and the maximum crystallization temperature decreased a little with increasing VUV dose. It was deduced from the DSC data that the molecular weight of the PTFE films decreased and the destruction of the crystal structure took place under VUV irradiation. The ESR results showed that the radicals formed under VUV irradiation were chain-end radicals and peroxy radicals, which may have been formed due to the scission of carbon-to-carbon bonds. The tensile fracture strength and elongation decreased with increasing VUV irradiation dose. Under the same irradiation dose, the tensile properties were more sensitive to the lower VUV intensity. The decrease in the molecular weight and the destruction of crystal structure might have been the major reasons for the deterioration of the tensile properties. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1494–1497, 2004

Key words: polytetrafluoroethylene (PTFE); irradiation; structure; tension; ESREPR

INTRODUCTION

Polytetrafluoroethylene (PTFE), such as Teflon film, has been widely used as a thermal control material in spacecraft. The property evolution of Teflon film in the space environment has been investigated,[1–5] but few studies have involved microstructural changes. Moreover, when the effect of vacuum ultroviolet (VUV), irradiation was studied, most of the experiments were carried out with various ultraviolet lamps.[6–9] It is difficult for these to give high accelerating factors and a VUV spectrum similar to Sun's. The studies in refs. 7 and 9 showed that the VUV irradiation with various wavelengths had different influences on the Teflon properties. Also, van Eesbeek et al.[8] pointed out that the monochromatic and polychromatic VUV irradiation had various effects. The gas-jet-type VUV source with wavelengths from 5–200 nm used in this study could give a spectrum very similar to Sun's and high accelerating factors. The aim of this study was to reveal changes in the structure and tensile properties of PTFE film under VUV irradiation.

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

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EXPERIMENTAL

A gas-jet-type simulator was used as the VUV source, in which a supersonic jet of gas mixture of Ar and Kr flowed into a vacuum chamber and was excited by an electron beam and which emitted VUV rays with wavelengths of 5–200 nm through an open aperture into another high-vacuum chamber (10^{-7} torr) to irradiate the film samples. The VUV irradiation intensity was approximately 252 erg/cm^2 at a 70-cm distance away from the source.

The PTFE film used in this study was 50 μm thick. The specimens were annealed for 3.5 h at 70°C, rinsed with analytically pure acetone and ethanol in turn, and then stored in a desiccator for more than 48 h at ambient temperature. Tensile tests were carried out at room temperature. The engaged surface area of the film specimens was 20 × 5 mm. The crosshead speed was 2.4 mm/min.

Thermal analysis was carried out with a Setaram DSC-141 type analyzer (France). The specimens were heated from −150 to 380°C at a heating rate of 10°C/min, kept at 380°C for 2 min, cooled at a rate of −10°C/min to 240°C, and then rapidly cooled to −150°C. Also, a heating from −150 to 380°C at a rate of 10°C/min was performed again for the second additional analysis. The cooling medium used was liquid nitrogen. Nitrogen gas, at a flow rate 20 mL/min, was used as the protective inert ambience. Also, the change in the electron spin resonance (ESR) spectrum was examined with a JES-FE3AX type spectrometer (Shimidzu, Kyoto, Japan), and the measurements were made at frequencies of 9.434

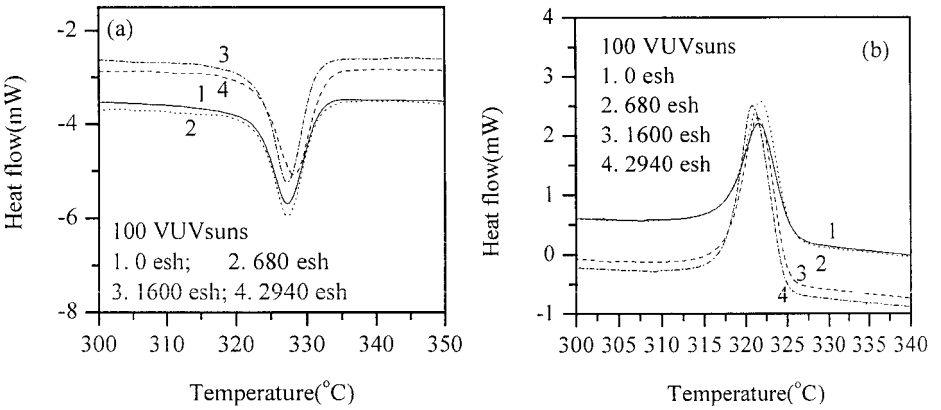

Figure 1 DSC plots of PTFE irradiated at different doses with 100 VUV/Suns for the first (a) heating and (b) cooling.

GHz with a center field of 3364 G at room temperature. The microwave power was 1 mW, the sweep range of magnetic field was ±250 G, and the field modulation was 5 G. The signal of diphenyl picryl hydrazyl was used as a standard for the g value.

RESULTS AND DISCUSSION

Differential scanning calorimetry (DSC) analysis

Figure 1 shows the plots for the first heating and cooling DSC analysis and Figure 2 shows the plots for the second heating DSC analysis for the melting/crystallization transition in PTFE film irradiated at various VUV doses. The thermal characteristics for melting and crystallization are given, from Figures 1 and 2, in Table I, in which ΔH_{m1} is the melting enthalpy in the first heating DSC curves, T_{m1} is the corresponding endothermic peak temperature (or maximum crystallization temperature), ΔH_c is the cooling crystallization exothermal enthalpy, T_c is the corresponding exothermic peak temperature, ΔH_{m2} is the enthalpy in the second heating DSC analysis, and T_{m2} is the corresponding peak temperature. As shown in Table I, both ΔH_{m1} and ΔH_{m2} increased after VUV irradiation, whereas T_{m1} and T_{m2} increased a little with increasing dose. ΔH_c also increased, but T_c decreased slightly with increasing VUV dose. The change in ΔH_c was related to the variation in molecular weight.[10] Therefore, the relation of molecular weight with irradiation dose was deduced, as shown in Figure 3. The number-average molecular weight (M_n) decreased with VUV dose.

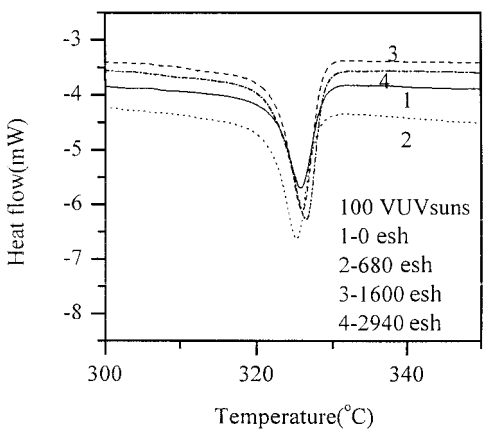

Figure 2 DSC plots of PTFE irradiated at different doses with 100 VUV Suns for the second heating.

The first heating DSC characteristic data revealed the complex effects of the change in molecular weight and crystal structure. However, high temperatures eliminated the effects of thermohistory and processing, and change in the data of the second heating resulted from the change in the molecular weight. That is, the decrease of the molecular weight led to the decrease in the activatation energy of crystallization and resulted in a more regular crystal structure and an increase in crystallinity. Therefore, the change in the data of the second heating further confirmed the change in molecular weight.

Table II shows the effect of VUV intensity on the DSC characteristic data of the PTFE films. T_{m1} and T_{m2}, ΔH_{m1} and ΔH_{m2}, T_c and ΔH_c were different for various VUV intensities. Compared with that under the intensity of 100 VUV suns, ΔH_{m1} was smaller, but ΔH_{m2} and ΔH_c changed more significantly for the PTFE film irradiated with 40 VUV Suns. We deduced that the molecular weight decreased more rapidly under the lower intensity

TABLE I
DSC Data of PTFE Irradiated for Various VUV Doses with 100 VUV Suns

Dose (esh)	ΔH_{m1} (J/g)	T_{m1} (°C)	ΔH_c (J/g)	T_c (°C)	ΔH_{m2} (J/g)	T_{m2} (°C)
0	24.45	327.18	−20.35	321.8	18.91	325.22
680	29.65	327.35	−26.11	321.9	22.06	325.21
1600	31.41	327.34	−26.14	321.6	23.71	325.85
2940	31.28	328.18	−29.40	320.8	25.24	326.35

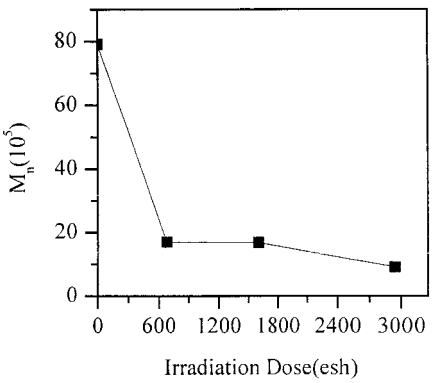

Figure 3 Change in molecular weight of PTFE films with the VUV irradiation dose.

VUV irradiation, indicating that the lower intensity VUV was more sensitive to the degradation of the PTFE film.

ESR analysis

The ESR spectrum of the PTFE film irradiated at an intensity of 100 VUV Suns for 1600 esh is shown in Figure 4. This revealed three peaks with g values of 2.004, 2.014, and 2.023. In general, the radicals in the PTFE film after irradiations have two types,[4,11–14] including the main chain radical —CF_2—$\dot{C}F$—CF_2– and the chain-end radical —CF_2—$\dot{C}F_2$. The ESR spectrum for the main-chain radicals was a ten-line one with hyperfine splitting values of 91 and 33 G, whereas that for the chain-end radicals was a three-line one with a hyperfine splitting of 16 G. The g value for both type radicals was 2.004. When the main-chain radical and the chain-end radical can contacted with enough oxygen, they could be changed into peroxy radicals. One is —F_2C—CF_2—$CF_2(O\dot{O})$—CF_2—CF_2– with $g_{\parallel} = g_{\perp} = 2.02$, and the other is —$F_2C$—$CF_2$—$CF_2$—O—$\dot{O}$ with $g_{\parallel} = 2.01$ and $g_{\perp} = 2.02$. Oshima et al.[14] and George et al.[4] showed that under proper conditions, the complex spectra induced by chain radicals and chain-end radicals were changed to symmetrical ones, which was attributed to peroxy radicals. The ESR spectrum shown in Figure 4 was asymmetrical, and the g values were 2.004, 2.014, and 2.023, indicating that the spectrum was caused by the superposition of peroxy radicals and a part of chain-end radicals. Chain-end radicals could have been formed when the carbon-to-carbon bonds in PTFE molecules were broken, and the scission of carbon-to-carbon bonds could have led to the decrease in molecular weight. A part of the radicals could have been terminated immediately after their formation. The termination rate is proportional to the concentration of formed radicals. Thus, under VUV irradiation with a lower intensity, a lower concentration of radicals would have been formed, the radicals could have lived for a longer time, and the after-reaction of the radicals was more serious. Therefore, the molecular weight of PTFE film irradiated with the lower VUV intensity decreased more rapidly.

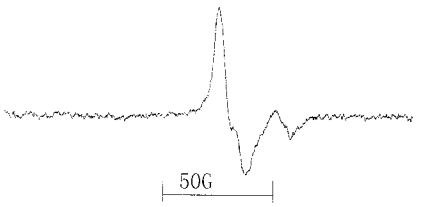

Figure 4 ESR spectrum of PTFE film irradiated at an intensity of 100 VUV Suns for 1600 esh.

Tensile properties of the PTFE films

Figure 5 shows typical tensile stress–strain curves for PTFE films before and after VUV irradiation. After VUV irradiation, the tensile fracture strength and elongation decreased. Figures 6 and 7 show the change in the tensile fracture strength and elongation of the PTFE films with irradiation dose at various VUV intensities. The tensile fracture strength and elongation decreased with VUV dose. Under a given irradiation dose, the tensile fracture strength decreased with decreasing VUV intensity. The decrease in VUV intensity showed a similar effect on the elongation of the PTFE films, although the elongation did not obviously change for the specimens irradiated with intensities lower than 40 VUV Suns.

The change in tensile properties could have been related to the change in microstructure. The DSC and ESR analysis results showed that the chain scission of PTFE molecules occurred under VUV irradiation, which could have resulted in a decrease in molecular weight and could have affected the crystal structure to some extent. Because the strength of the PTFE films is believed to be sensitive to molecular weight,[15] the decrease in molecular weight would inevitably result in a decrease in tensile properties.

TABLE II
DSC Data of PTFE Film Irradiated with Various VUV Intensities for 1600 esh

Intensity (VUV Suns)	ΔH_{m1} (J/g)	T_{m1} (°C)	ΔH_c (J/g)	T_c (°C)	ΔH_{m2} (J/g)	T_{m2} (°C)
100	31.4082	327.34	−26.1417	321.59	23.7128	325.85
40	28.1415	327.5	−26.4558	321.93	24.3917	325.72

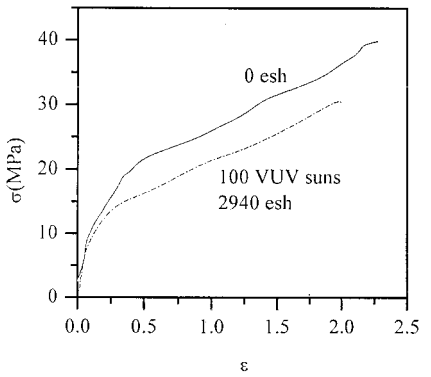

Figure 5 Typical tensile stress (σ)–strain (ε) curves of the PTFE films before and after VUV irradiation.

CONCLUSIONS

1. The DSC analysis showed that under VUV irradiation, the melting enthalpy, melting point, and ΔH_c increased with irradiation dose, whereas T_c decreased a little. We deduced that the molecular weight of the PTFE films decreased under VUV irradiation. At a given dose, VUV irradiation with a lower intensity resulted in a larger increase in ΔH_c and, thus, a greater decrease in molecular weight.
2. ESR analysis showed that for PTFE films irradiated with VUV radiation, the scission of carbon-to-carbon bonds in the molecular chains of PTFE film occurred, resulting in a decrease in molecular weight.
3. Under VUV irradiation, the tensile fracture strength and elongation decreased with increasing irradiation dose. At a given dose, with the decrease in VUV intensity, the tensile fracture strength and elongation decreased. The decrease in molecular weight and the change in the crystal structure of the PTFE films under VUV irradiation were the major reasons for the deterioration in the tensile properties.

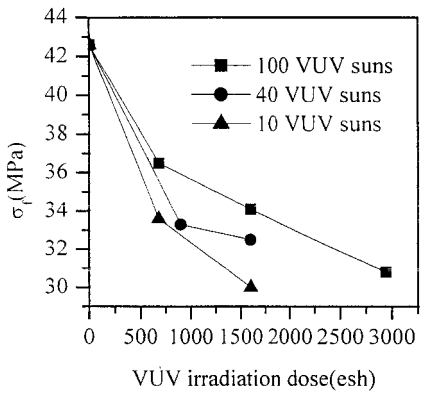

Figure 6 Change in tensile fracture strength (σ_f) of the PTFE films with irradiation dose for various VUV intensities.

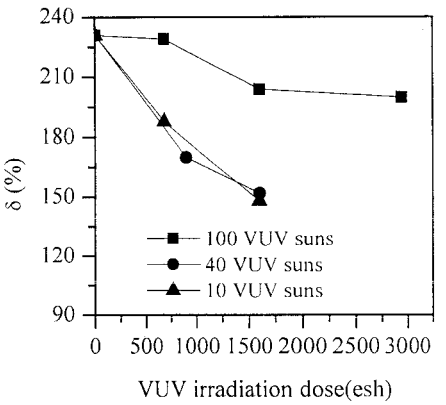

Figure 7 Change in elongation (δ) of the PTFE films with irradiation dose for various VUV intensities.

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