

Degradation of Polyimide Film under Vacuum Ultraviolet Irradiation

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ABSTRACT: The degradation of PI film irradiated with VUV in a wavelength of 5 to 200 nm is investigated. The results show that transparency of PI film decreases obviously after irradiation and more obviously for the film irradiated with VUV of higher intensity. In addition, the absorption line red-shifts for the PI film. The XPS and FTIR analyses results indicate that decarbonylation and the condensation of the benzene group take place under the irradiation and that carbonification takes place under 100

VUV suns. The change of optical property could be attributed to the stabilizing of the conjugation group and as well as to the carbonification to some extent. The character of VUV on polymer degradation is discussed. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1370–1374, 2004

Key words: vacuum ultraviolet (VUV); irradiation; polyimide (PI); transparency; XPS

INTRODUCTION

Polyimide (PI) film is widely used in spacecrafts as insulator, second surface mirror, and exterior surface protection materials.^{1–5} Most of the investigations of effects of vacuum ultraviolet (VUV) radiation on these polymers are carried on sources with wavelengths longer than 110 nm. The previous investigation shows that the wavelength range and spectrum of VUV have significant influence on degradation of polymers.^{6,7} We carried out a series of investigations⁸ on the effects of VUV on polymers with a modern VUV source that can give off VUV spectrum in 5 to 200 nm to simulate that of the Sun's. In this study, degradation of PI film under the irradiation of VUV in 5 to 200 nm is discussed.

EXPERIMENTAL

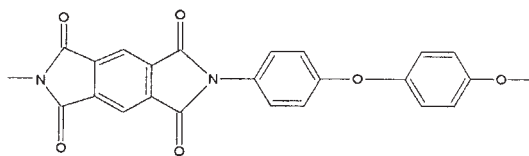
The VUV source used in this study operated on supersonic argon gas, which was excited by a high energy electron beam. A VUV intensity of 0.24 W/m² could be acquired at a distance of 70 cm from the source, corresponding to 10 times the VUV solar constant (VUV suns).⁸ In this study, the gas jet pressure was 5 atm, the electron-beam energy was 1,000 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 at 34 cm (corresponding to 40 VUV suns) and 22 cm (100 VUV suns) away from the VUV source.

The chemical structure of PI film (from Shanghai Research Institute of Synthetic Resins) of 40 μm is PMDA-ODA is shown as in Scheme 1. 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. The crosshead speed was 2.4 mm/min. The transmittance of the VUV irradiated specimens in the wavelength range of 200 to 3200 nm was measured with a UV-3101PC scanning spectrophotometer from SHIMDZU, Kyoto, Japan.

The X-ray photoelectron spectroscopy (XPS) spectra were acquired with a VG-ESCALAB Mark-2 type spectrometer with MgKα source, which was manufactured by Thermo VG Scientific in West Sussex, England. The vacuum of the work chamber was 10⁻¹⁰ Pa, and the pass energy was 20 eV. IR spectra were acquired with a Perkin-Elmer System 2000 Fourier transform infrared (FTIR) spectrophotometer, which was manufactured by Perkin-Elmer Inc., Shelton, USA. The resolution of the spectrophotometer was 1 cm⁻¹. The test wave numbers were in the range of 400 to 4,000 cm⁻¹. Tensile tests were carried out at room temperature on MTS, which is produced by MTS Systems Corporation of USA. The range of

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Scheme 1

sensor measure was 5 kg. The engaged surface area of the film specimens was $20 \times 5 \text{ mm}^2$. The cross-head speed was 2.4 mm/min. The data are averages of five samples.

RESULTS AND DISCUSSION

Figure 1 shows the effect of VUV radiation on the spectral transmittance of PI film. The spectral transmittance decreases dramatically especially in the visible and near infrared zones. The absorption line redshifts with the increase of VUV radiation dose. When the VUV radiation dose is higher than 1600 esh (equivalent sun hours, multiply intensity by the irradiation time in facility), an absorption peak was observed near 590 nm. Under the same irradiation dose, the transparency decreases more obviously when irradiated with VUV of higher intensity, which indicates that the optical properties do not change linearly with VUV intensity; it should be carefully considered for the ground experimental data to use in predication of lifetime in space.

Figure 2 shows the effect of VUV radiation on the tensile properties of PI film. The tensile fracture strength (σ_f) changes unobviously, while the elongation (δ) of PI film decreases gradually with the increase of VUV irradiation dose.

Figure 3 shows the C_{1s} spectra of PI film before and after VUV radiation. The C_{1s} spectra before radiation can be considered to be composed of three peaks. The C_{1s} peak at 288.5 eV comes from the carbon doubly binding to oxygen, that at 285.9 eV can be considered to result from the carbon binding to bridge oxygen and nitrogen, and that at 284.6 eV is from the carbon in benzene without oxygen and nitrogen binding to it.⁹⁻¹² After VUV radiation the relative intensity of C_{1s} peak at 288.5 eV decreases and the peak at 285.9 eV shifts to 286.6 eV with the intensity decreases, while the intensity of the peak at 284.6 eV increases. Usually the C_{1s} peak due to carbon that singly binding to oxygen is situated around 286.6 eV.⁹

Before VUV radiation the spectra of O_{1s} is asymmetrical and could be considered to include two peaks at 533.3 and 532 eV, as shown in Figure 4, which originates from the oxygen singly and doubly binding to carbon separately. After the VUV radiation the intensity of O_{1s} decreases significantly with the binding energy shifting to the higher. By fitting the spectrum

with the peaks at 533.3 and 532 eV, it can be seen that the peak at 532 eV decreases more obviously than that at 533.3 eV. After VUV irradiation, the binding energy and the spectrum intensity of N_{1s} decreased, as can be seen in Figure 5. Usually the binding energy of N_{1s} in imide is higher than that in amide.⁹⁻¹²

All of these data show that the binding of carbon to nitrogen and the bridge oxygen could be preferentially broken. But no change could be observed on the FTIR spectra of PI film before and after VUV irradiation, as seen in Figure 6. On the other hand, the change in transparency with the surface color darkening a little after irradiation for PI film indicated that carbonification maybe take place on the surface to some extent.

All of these results indicate that, after VUV irradiation, the bond of bridge oxygen and nitrogen could be easily broken, and then decarbonylation and the condensation of benzene group and further carbonification might take place to some extent sequentially. This entire process could be expressed as in Figure 7.

The significant decrease of the transparency of PI film after VUV irradiation might relate to the change of the surface carbonification to a certain extent. Comparing the color of films irradiated with different intensities, it is found that the color of PI film irradiated with 100 VUV suns changes more significantly than that irradiated with 10 VUV suns, while no obvious difference was observed in the XPS analysis. That is, the intensity of VUV could have influence on the extent of surface carbonification.

If postulating that there is only the heating effect in the work chamber and all of the radiation energy is deposited on the film, the increased rate of temperature can be calculated using the following formula:¹³

$$\Phi \times t = C_p M \Delta T \quad (3-3)$$

in which, Φ is the thermal flux of the VUV radiation, which is 2.4 W/m² for 10 VUV suns and 24 W/m² for

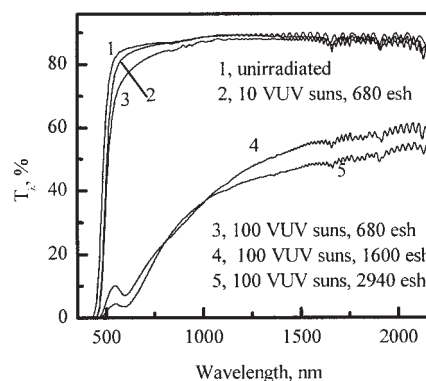


Figure 1 The spectral transmittance versus VUV dose and intensity for PI film.

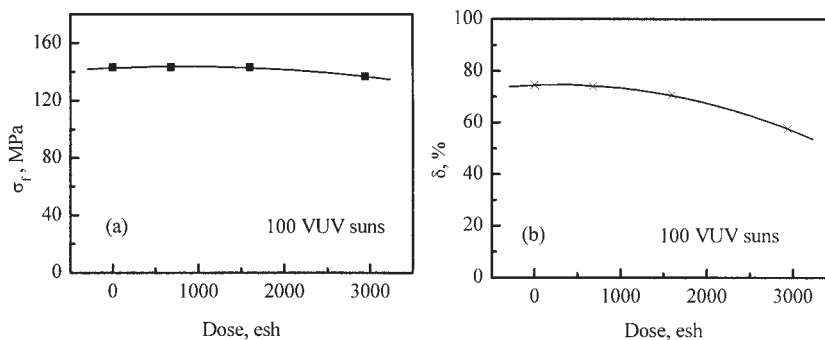


Figure 2 The tensile fracture strength σ_f (a) and elongation δ (b) versus VUV dose for PI film.

100 VUV suns. C_p is the specific heat capacity, M is the mass of the layer that the radiation energy is deposited on, and ΔT is the increase of temperature. From the formula, the heating rate for 100 VUV suns would be nearly ten times higher than that for 10 VUV suns. For the cooling effects of the vacuum chamber wall, the balance of the temperature on the surface of film is 1–2°C higher than that of the ambient temperature under the irradiation of 10 VUV suns. When the radiation intensity increased to 100 VUV suns, the thermal flux Φ increased 10 times. But cooling effects of the vacuum chamber wall would be not changed, therefore, the local heating effect might exist in the surface, which would be more significant and contribute to the serious carbonification for that irradiated with 100 VUV suns, which is not so obvious under the radiation of UV with lower intensity or longer wavelength. Previous studies have shown that, for PTFE film, VUV led to serious degradation of tensile properties and a little carbon richening on the surface.^{8,14} The carbon richening was observed also on the surface of PTFE film under 100 VUV suns, although not as obviously

as that for PI films. That is, inferior processing under lower intensity and longer wavelength would be much more obvious when the intensity increased from 10 to 100 VUV suns, which might distort the prediction of the service life of materials in space from this ground simulating data.

Skurat¹⁵ and Wilken et al.¹⁶ also indicated that the photochemistry of VUV is different from classical photochemistry, which is more similar to that of the ionizing radiation. In their work, the wavelength of the VUV source is longer than 100 nm. The VUV source in this work gives lots of photons with wavelengths less than 100 nm, which could act more like ionizing irradiation, that is, most of the bonds could be ionized and most of the inferior process could occur more obviously.

From the change of the PI film after VUV irradiation, it can be considered that, although the high energy of VUV photon could break any of the bonds in the polymer, the π conjugate system in the macromolecule could transfer and dissipate the absorbed energy and stabilize the molecule structure to some extent. The final effect is the superposition of the stabilizing effect of the π conjugate group and

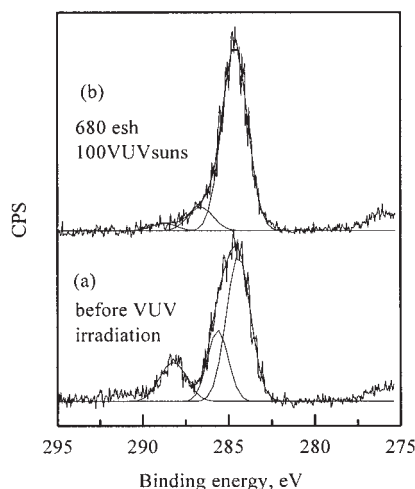


Figure 3 The C_{1s} spectra of PI film before (a) and after (b) VUV irradiation.

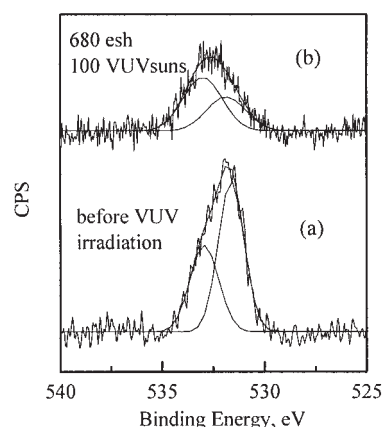


Figure 4 O_{1s} spectra of PI film before (a) and after (b) VUV irradiation.

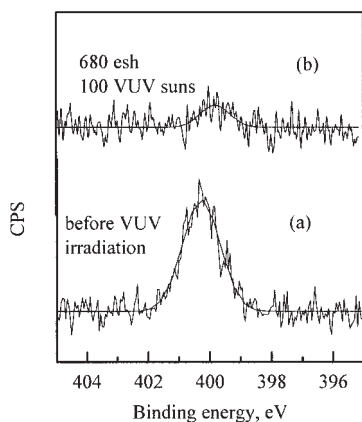


Figure 5 N_{1s} spectra of PI film before (a) and after (b) VUV irradiation.

the carbonification, which may only be a trend of carbonification.

CONCLUSION

The degradation of PI film irradiated with VUV of 5 to 200 nm is investigated on a gas-jet VUV source. The results show that the transparency of PI film decreases obviously after irradiation and the optical properties degrade more obviously for the films

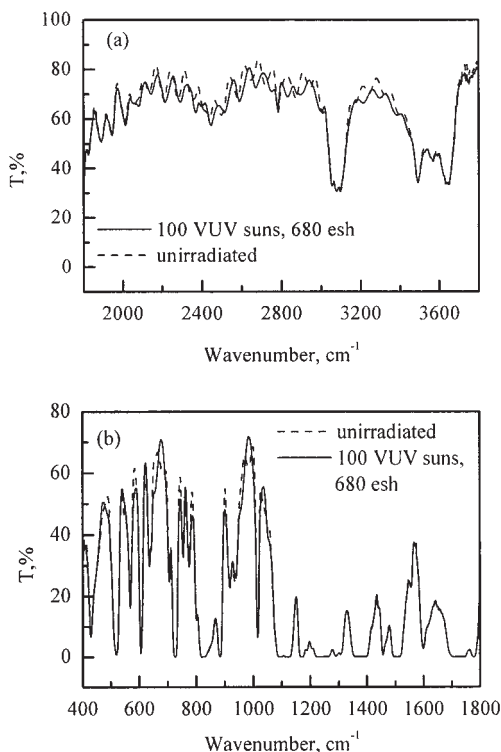


Figure 6 FTIR spectra of PI film in $1,800 \sim 3,800 \text{ cm}^{-1}$ (a) and $400 \sim 1,800 \text{ cm}^{-1}$ (b) regions before and after VUV irradiation.

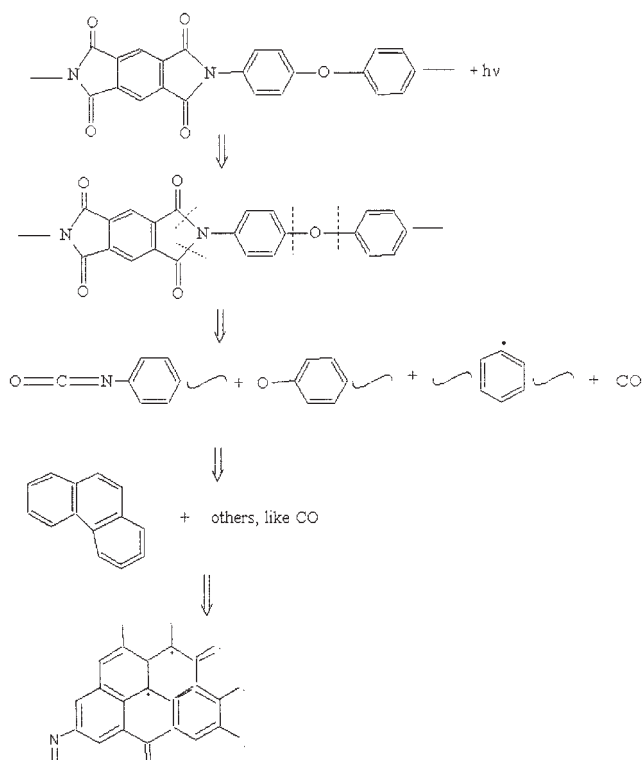


Figure 7 The change in PI molecule structure under VUV irradiation.

irradiated with VUV of higher intensity. In addition, the absorption line red-shifts for the PI film. The significant decrease of the transparency of PI film after VUV irradiation might relate to the stabilizing effect of the π conjugate group, as well as to the change of the surface structure to a certain extent. With the help of the literature, the degradation mechanism of VUV on polymer films is discussed.

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