

Degradation of Poly(ethylene terephthalate) Film Under Proton Irradiation

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ABSTRACT: The effects of proton irradiation on the properties and structure of poly(ethylene terephthalate) films were investigated. The results showed that mass loss was rapid with fluence and then tended to level off at higher fluence. The transmittance decreased obviously in the visible range. The relative intensity of C_{1s} with a binding energy of 284.6 eV increased with the dose and then tended to level off. O_{1s} decreased with the dose and more rapidly at 533.5 eV. All this indicated that decarbonylation occurred on the surface. The Fourier transform infrared and X-ray photoelectron

spectroscopy results demonstrated that the change in the substitution of phenyl was due to the enrichment of the phenyl group on the surface; in other words, carbonification took place (in which C_{1s} was usually situated at 284.6–285 eV). The change in transmittance was considered to result from the change in the surface structure and morphology. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3625–3629, 2008

Key words: degradation; ESCA/XPS; polyesters, radiation; transparency

INTRODUCTION

With an increase in the application of polymer materials in spacecraft, more and more investigations are focusing on the effects of protons on polymer materials. Poly(ethylene terephthalate) (PET) with aluminum plate as a kind of heat-proof material is used widely on outer surfaces of parts of spacecraft. Because it is a heat-proof material, the stabilization of its optical properties is very important and has been studied widely. Different opinions have been presented on the polymer's optical properties.^{1–8} According to Darraud-Taupiac et al.¹ the change in the refractive index could not be considered to result from the formation of radicals. However, Iwata et al.⁸ reported that the formation and annihilation of radicals constitute the major factor that affects the optical properties for the polymer irradiated with charged particles. Others attribute the change in the optical properties to the formation of the polyring structure on the surface.^{4–8} Moreover, most of these published results about the effects of protons on polymers are acquired with simulators with the energy of

a few hundred megaelectronvolts, although protons with the energy of tens to hundreds of kiloelectronvolts exist in most of the space orbit environment. Study on the effects of protons with the energy of a few tens to hundreds of kiloelectronvolts is limited. Thus, with X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR), the effects of protons with energy ranging from 60 to 170 keV on the optical properties and surface structure of PET films are investigated in the paper.

EXPERIMENTAL

The thickness of the PET film was 60 μm. The specimens were dried at 75°C and then rinsed with analytically pure acetone and ethanol in turn. The specimen was cut (70 × 10 mm²) and fixed on the test bed by the binding of the ends with copper line. The specimens were kept for approximately 12 h *in vacuo* after irradiation. Once they were taken out from the vacuum chamber, the optical property measurement was carried out at once, and then XPS and electron spin resonance analysis were carried out.

The proton irradiation test was performed in a simulator with an energy of 30–200 keV. Specimens were placed in a work chamber with a vacuum of 10⁻⁴ Pa. The proton beam was perpendicular to the specimen surface. To suppress secondary electron emission, a metal plate with a voltage of -250 V was placed in front of the specimens. The energy of

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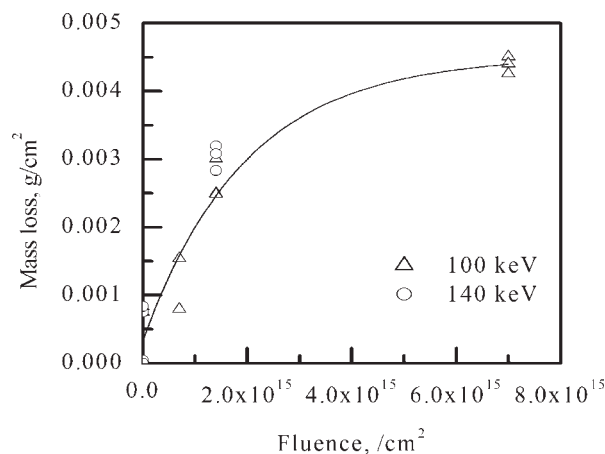


Figure 1 Mass loss of PET films versus the fluence of protons.

protons ranged from 60 to 170 keV, and the flux was $1.25 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. The fluence was varied in the range of 10^{13} to $2 \times 10^{16} \text{ cm}^{-2}$. The temperature in the vacuum chamber was lower than 0°C .

After radiation, transmittance of the irradiated specimens in the wavelength range of 200–3200 nm was measured with an ultraviolet-visible/near-infrared scanning spectrophotometer of the UV-3101PC type (Shimadzu, Japan). The XPS analysis was carried out with a V.G. Escalab (VG Scientific Ltd., England) 220i-XL photoelectron spectrometer with a source of MgK α .

RESULTS AND DISCUSSION

The mass loss was measured in one test. That is, all samples were put into the vacuum chamber at one time and irradiated with different fluence and energy levels separately. As shown in Figure 1, after 100 and 140 keV of proton irradiation for PET films, the mass loss was weighed. The mass loss increased significantly with fluence and changed a little but insignificantly with the energy of protons.

Figure 2 shows the spectral transmittance and change in the absorbance of PET films irradiated with 150 keV of protons. The transmittance decreased obviously in the visible range, and the change in the absorbance increased obviously in the ultraviolet and visible region.

Figure 3 presents the C_{1s} and O_{1s} spectra versus the fluence for PET films irradiated with 150 keV of protons. The C_{1s} spectrum can be considered to be composed of three symmetric peaks with the binding energies of 284.6, 286.3, and 288.4 eV, which can be attributed to the phenyl group and the carbon singly bonded to oxygen and carbonyl groups separately. The O_{1s} spectrum could be fitted to two Gauss peaks with the binding energy at 531.8 and 533.3 eV. The former could be attributed to the oxy-

gen in carbonyl, and latter could be attributed to the oxygen singly bound to carbon.⁹

The corresponding area ratios for PET films irradiated with 150 keV of protons is shown in Tables I and II. The relative intensity of C_{1s} with a binding energy of 284.6 eV increased, whereas that with the higher one decreased with the increase in the dose first and then tended to level off; O_{1s} more rapidly decreased with the dose at 533.5 eV and then tended to level off.

Quasi-quantitative analysis results (in Table III) show that O_{1s} decreased slightly and changed insignificantly with the proton fluence, and C_{1s} increased a little but not significantly with the proton fluence; this indicates that the carbon with C_{1s} of 284.6 eV increased more rapidly on the surface of the sample after irradiation with protons. The results demonstrate that protons deleted the carbonyl group, and the phenyl group settled down on the surface (giving an increase in the C_{1s} spectra at 284.5 eV); the rapid decrease of O_{1s} at 533.5 eV indicates that first the bridge oxygen bond might have been broken off, and then the carbonyl group broke away

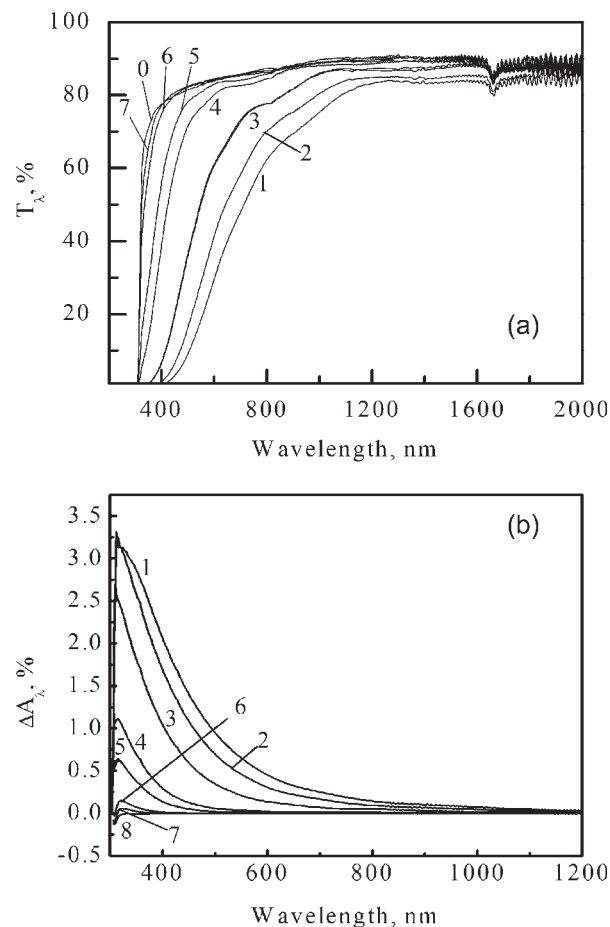


Figure 2 (a) Spectral transmittance (T_λ) and (b) change in absorbance (ΔA_λ) versus the fluence for PET films irradiated with 150 keV of protons.

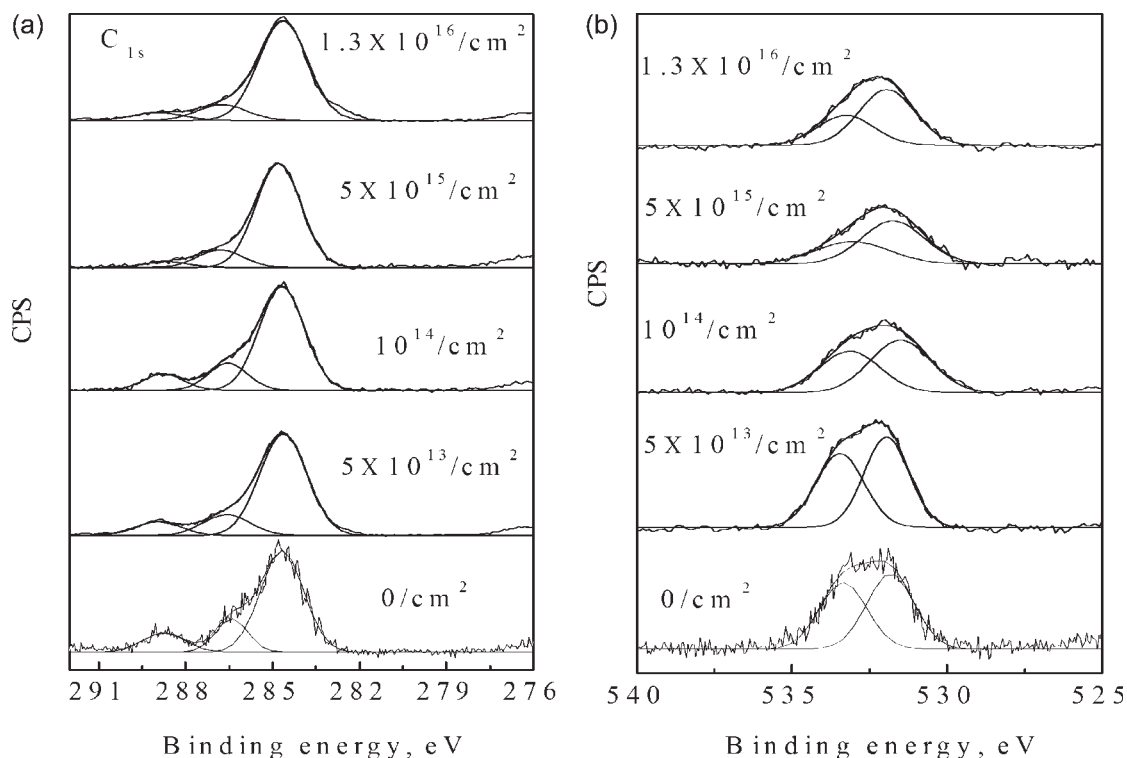


Figure 3 (a) C_{1s} and (b) O_{1s} spectra versus the fluence for PET films irradiated with 150 keV of protons.

under proton irradiation. In other words, decarbonylation occurred on the surface.

Figure 4 shows the change in the FTIR spectra for PET films before and after proton irradiation. If normalized with the intensity at 2971 cm^{-1} , the relative intensity at 3630 and 3550 cm^{-1} increased, whereas that at 3430 cm^{-1} decreased a little after proton irradiation; this indicates that the relative concentration of the associated hydroxyl group decreased a little and the dissociated hydroxyl group increased. New peaks at 1539 , 1558 , and 1636 cm^{-1} could be considered to result from the change in the substitution of phenyl groups, but no new C_{1s} peak was observed. The results demonstrate that the change in the substitution of phenyl might be due to the enrichment of the phenyl group on the surface; in other words, carbonification might have taken place (in which C_{1s}

was usually situated at $284.6\text{--}285\text{ eV}$), so it could not give a new C_{1s} component. Some changes around 632 cm^{-1} and between 1800 and 2000 cm^{-1} further demonstrate the change in the substitution of the phenyl group and formation of unsaturated groups,^{10,11} whereas the peaks at 1652 cm^{-1} is very weak, corresponding to unsaturated groups. All of the changes are summarized in Table IV.

In a previous study,¹² we reported the change in the FTIR spectra of PET after vacuum ultraviolet (VUV) irradiation. Comparing our current results with the results of that study, we can see that the change was similar, except that no new absorption peaks appeared in the region of $1640\text{--}1645\text{ cm}^{-1}$ in the FTIR spectra. The XPS analysis shows a similar enrichment of C_{1s} of 284.6 eV for PET irradiated with protons and VUV separately, except for the

TABLE I
Binding Energies and Corresponding Area Ratios of C_{1s} for the PET Films Irradiated with 150 keV of Protons

Fluence (cm^{-2})	Binding energy (eV) and area ratio (%)		
	C—C, C—H,	C—O	C=O
0	284.6, 69.6	286.3, 17.1	288.4, 13.3
10^{14}	284.6, 75	286.6, 15	289.0, 10
5×10^{14}	284.6, 75	286.6, 15	289.0, 10
10^{15}	284.6, 73	286.5, 17	288.7, 10
10^{16}	284.6, 82	286.4, 14	288.5, 5
1.3×10^{16}	284.6, 81	286.7, 13	289.0, 6

TABLE II
Binding Energies and Corresponding Area Ratios of O_{1s} for the PET Films Irradiated with 150 keV of Protons

Fluence (cm^{-2})	Binding energy (eV) and area ratio (%)	
	C—O	C=O
0	533.4, 47	531.7, 53
5×10^{13}	533.5, 47	531.9, 53
10^{14}	533.1, 44	531.5, 56
5×10^{15}	533.1, 38	531.7, 62
1.3×10^{16}	533.3, 39	531.9, 61

TABLE III
XPS Quasi-Quantitative Analysis Results Showing the Changes in the Skin
Composition of the PET Films Irradiated with 150 keV of Protons

Fluence (cm ²)	1.35 × 10 ¹⁶	1 × 10 ¹⁶	1 × 10 ¹⁵	1 × 10 ¹⁴	5 × 10 ¹³	1.25 × 10 ¹³	0
C _{1s} (atom %)	83	85	83	77	82	80	80
O _{1s} (atom %)	17	15	17	23	18	20	20

extent of the concentration of carbon on the surface. In addition, the change in the surface color was different under the different irradiation conditions. It was dark and dust-colored for the VUV irradiation and yellow first and then brown with the change in the fluence for proton irradiation. All this indicates a difference in the degradation mechanism. For PET films irradiated with VUV, Norrish I and II type breaking is speculated. For PET films irradiated with protons, the high-energy protons could break all weak bonds and ionize the molecule. The active protons then continue to add to the resultant radicals and cease their active by forming a single bond or add to carbonyl and result in other reactions. It has been observed in polytetrafluoroethylene films^{13,14} that C_{1s} changes from a single peak with a binding energy of 292.8 eV to five different peaks with binding energies ranging from 284.6 to 293.3 eV, and this indicates that the carbon-to-fluoride bond is broken down by the high-energy protons. Then, the active protons occupy the resultant active sites. However, for PET molecules, the bridge oxygen is easily broken and leads to Norrish II degradation mainly. However, the extent of carbonization is limited for the effects of energetic protons. The slower carbonification results in a slower increase in absorbance in a longer wavelength region, especially in the infrared region.

In addition, the mass loss of PET films under proton irradiation indicates that PET degrades to a small molecule and degasses from the surface, and this results in the change in the surface morphology and thus leads to the change in reflection. The increase in C_{1s} at 284.6 eV further indicates that carbonification takes place on the surface and leads to the overall decrease in the spectra of PET films.

CONCLUSIONS

Effects of proton irradiation on the properties and structure of PET films were investigated with FTIR and XPS. The results showed that mass loss was rapid with fluence and then tended to level off at higher fluence. The transmittance decreased obviously in the visible range. The relative intensity of C_{1s} with a binding energy of 284.6 eV increased with the dose and then tended to level off. O_{1s} decreased

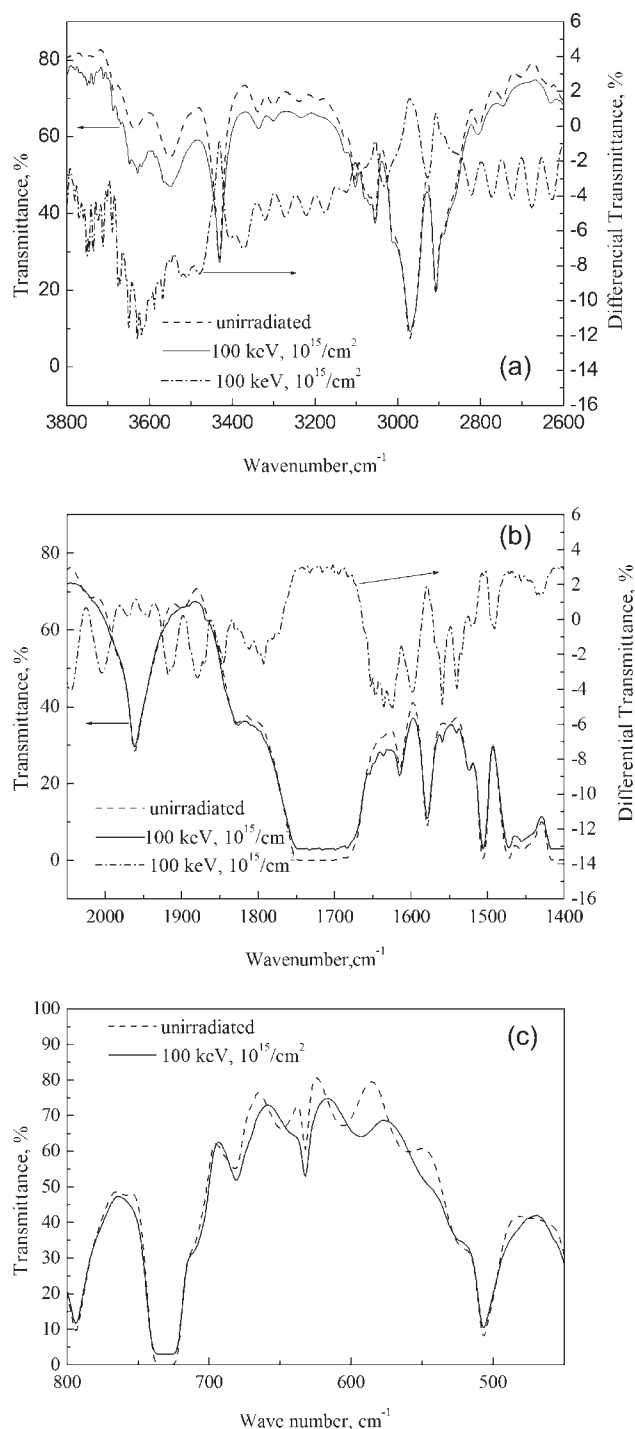
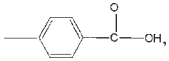
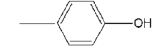
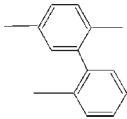
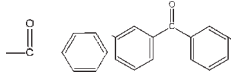
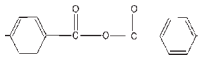


Figure 4 FTIR spectra in the wave-number ranges of (a) 2600–3800, (b) 1400–2100, and (c) 400–800 cm⁻¹ for PET films irradiated with 100 keV of protons.

TABLE IV
Newly Formed and Changed Groups in the PET Films After Proton Irradiation

Group	Change in the FTIR spectrum	Change in the C _{1s} or O _{1s} spectrum
	Increasing peak intensity at wave numbers of 3545 and 3627 cm ⁻¹ .	O _{1s} gave a more rapid decrease with a dose of 533.5 eV, whereas a dose of 531.8 eV changed little.
	Changes in the intensity and position of peaks in the wave-number region from 500 to 700 cm ⁻¹ .	C _{1s} at 288.4 eV decreased first and then tended to level off.
	New peaks appeared in the wave-number region from 1636 to 1539 cm ⁻¹ .	The intensity of the peak at 284.6 eV for C _{1s} increased.
change in the substitution of phenyl		
	Changes in the intensity and position of peaks in the wave-number regions from 500 to 700 and 2100 to 1850 cm ⁻¹ .	
	New peak appeared at a wave number of 1885 cm ⁻¹ .	O _{1s} gave a more rapid decrease with a dose of 533.5 eV, whereas a dose of 531.8 eV changed little.
-C=C-	New peaks appeared in the wave-number region from 1652 cm ⁻¹ .	C _{1s} at 288.4 eV decreased first and then tended to level off.

with the dose and more rapidly at 533.5 eV. All this indicated that decarbonylation occurred on the surface. The FTIR spectra revealed some changes in the substitution of the phenyl group, and this agreed well with the results of XPS. The change in transmittance was attributed to the changes in the surface structure and morphology.

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