

XPS and ESR Studies of the Photodegradation of Polyamidoimide and Polyimide in O₂, O₂ + N₂, Air, N₂, and Vacuum Atmospheres

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Synopsis

The photostability of polyamidoimide (PAI) and polyimide (PI) films has been studied. UV irradiation caused a great change in the composition and structure of the film surface. With irradiation in atmospheres such as air, oxygen, and an oxygen-nitrogen mixture, the C1s spectrum had a distinct structure at high binding energy, and the O/C and N/C ratios were considerably increased. On the other hand, in nitrogen and under vacuum, the O/C and N/C ratios remained almost unchanged during an earlier stage of irradiation, but in the latter stage for the nitrogen atmosphere these ratios decreased to a broad minimum and then increased with an increase of irradiation time. UV irradiation also produced free radicals in the polymer films; PAI gave a much stronger ESR signal intensity than PI. The signal intensity vs. irradiation time curve was strongly influenced by irradiation atmospheres. In atmospheres containing oxygen the curve exhibited a broad maximum during an initial stage of irradiation, while under vacuum and in nitrogen the signal intensity increased greatly in the latter stage. The formation of free radicals during an earlier stage of irradiation in atmospheres containing oxygen was promoted by the oxygen incorporated at the film surface, while the radical production under vacuum was considered to be due to rupturing of bonds in the bulk material. The decay of free radicals in the dark after irradiation occurred at a faster speed in oxygen atmospheres than under vacuum.

INTRODUCTION

The environmental modification of polymeric materials is of considerable industrial and technological importance. It is expected that, on photooxidation of a solid polymer surface, surface reactions are likely to begin at an earlier stage and be more extensive than bulk reactions, because at the surface the oxygen concentration remains uniformly high and the photon flux is highest.^{1,2} Recently Dilks² has reviewed studies by XPS on degradation at the surface of various polymers.

Much interest has been taken in polymers such as polyamidoimide and polyimide³ because of their unique thermal stability and dielectric properties; however, on the photostability there are only few reports available in the literature. Among these studies are the surface modification⁴ and the formation of free radicals⁵ of polyimide as a result of irradiation. Lazare et al.⁴ reported that continuous wave 185-nm irradiation of polyimide in air led to a rapid oxidation of the surface region, whereas laser (193 nm) ablation led to a surface that was depleted in oxygen. Pasal'skii et al.⁵ reported that gamma irradiation of polyimide yielded two kinds of radicals (a quintet and singlet

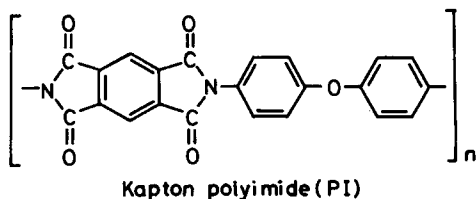
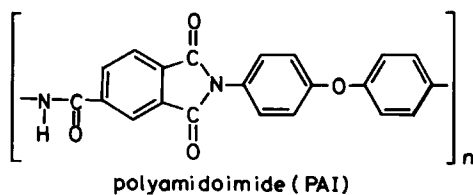


Fig. 1. Polyamidoimide and polyimide.

ESR spectrum) arising from the rupturing of polyimide ring. The interaction of a polymer surface with an irradiating atmosphere is considered to become a very important factor in changes in the surface composition and the formation of free radicals.

The purpose of our research was to examine the surface compositional and structural change of PAI and PI (poly-4,4'-oxydiphenyl pyromellitimide) (Fig. 1) films after exposure to UV radiation in various atmospheres and its relationship to the formation of free radicals.

EXPERIMENTAL

PAI (thickness, ca. 50 μm) and PI (50 μm) films used were commercial products. The C : N : O stoichiometries obtained for the PAI and PI films from C1s : N1s : O1s ratio were 78.9 : 7.0 : 14.1 (PAI) and 76.8 : 5.9 : 17.3 (PI). On the other hand, the C : N : O stoichiometries expected from the chemical formulas shown in Figure 1 were 77.78 : 7.41 : 14.81 (PAI) and 75.86 : 6.90 : 17.24 (PI). The size of a sample was 3 \times 3 mm² (XPS) and 3 \times 30 mm² (ESR). (The maximum sample size available for the XPS instrument used in the present experiments was 6 mm in diameter \times 10 mm in thickness.) The sample was exposed to a sterilization lamp (19 W; the wavelength of the most intense line, 253.7 nm) in oxygen (purity, > 99.95%; 8.5 \times 10⁴ Pa), a mixture of oxygen (3.4 \times 10⁴ Pa), and nitrogen (> 99.999%; 5.1 \times 10⁴ Pa), air (relative humidity, ca. 40%), nitrogen (8.5 \times 10⁴ Pa), and vacuum (0.3 Pa) atmospheres. The irradiation was conducted in a closed system consisting of a quartz tube (volume, ca. 37 cc) except for air atmosphere; the distance between the sample and the lamp was ca. 10 mm. A fresh sample was used for each exposure. XPS spectra were recorded on a Shimadzu ESCA 750 spectrometer with an ESCA PAC 760 data processing system. The operating conditions under which the XPS spectra were obtained were as follows: base pressure (2.5 \times 10⁻⁵ Pa >), X-ray source and power (Mg and 8 kV), resolution of the spectrometer (\pm 0.1 eV), and time to record a C1s spectrum (2.3 min). Energy referencing for the

curve resolution of C1s envelopes (Fig. 9) was achieved by assigning a carbon component with no directly bonded oxygen or nitrogen to the lowest binding energy (285 eV). Depth profiling of samples was not performed. ESR spectra were measured using a JEOL JES-3000 (Radic sensor) spectrometer. The measurements of XPS and ESR spectra were performed immediately after exposure; the XPS spectra for samples having been irradiated in atmospheres except air were measured just after the sample was taken out of the quartz tube. ESR signal intensity was expressed as the ratio to that of Mn^{2+} with $g = 1.981$ or $g = 2.034$, which was used as a standard sample. The value of the g factor for the ESR signal was determined on the basis of the Mn^{2+} signals shown in Figure 5. All the experiments were performed at 23°C.

RESULTS

XPS for PAI and PI Films

Figures 2(a) and (b) show XPS spectra for PAI and PI samples, respectively, which were irradiated in various atmospheres for 24 h. In the case of atmospheres such as air, oxygen, and the oxygen–nitrogen mixture, the C1s spectrum exhibited a distinct fine structure with an increase in intensity at high binding energy; this structure is indicative of oxidation. The O1s and N1s bands increased highly in intensity relative to those of the starting materials. On the other hand, in nitrogen and under vacuum the O1s and N1s bands decreased remarkably, being accompanied by the disappearance of the high binding energy components in the C1s band. Particularly, it is interesting to note that in both types of films the N1s band vanished completely in nitrogen for this exposure time. After more than 72 h of irradiation in air and in

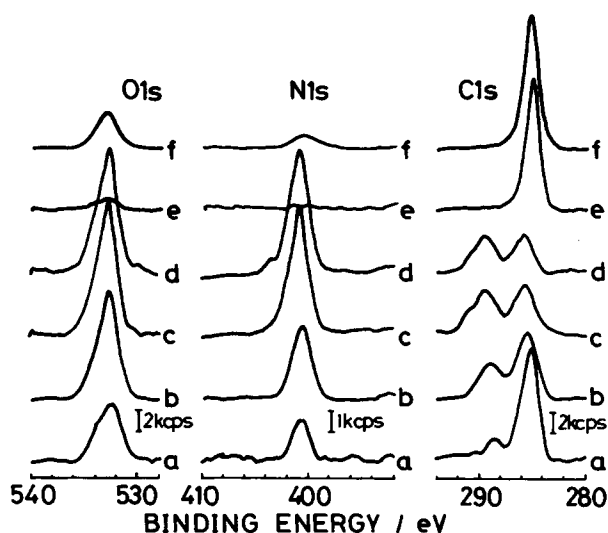


Fig. 2(a). XPS spectra for PAI samples exposed to UV radiation in various atmospheres for 24 h: (a) control; (b) air; (c) oxygen (8.5×10^4 Pa); (d) oxygen (3.4×10^4 Pa)–nitrogen (5.1×10^4 Pa) mixture; (e) nitrogen (8.5×10^4 Pa); (f) vacuum (0.3 Pa).

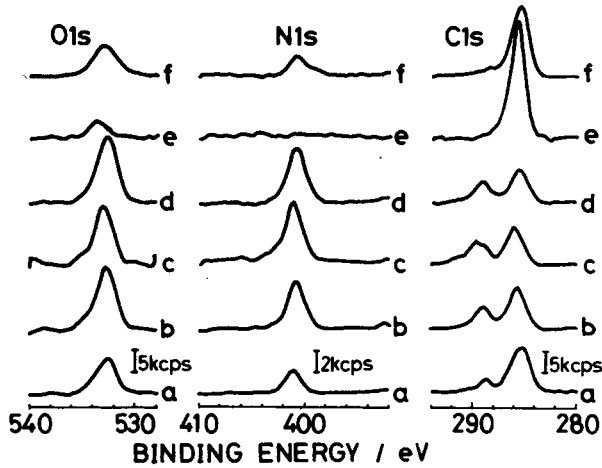


Fig. 2(b). XPS spectra for PI samples exposed to UV radiation in various atmospheres for 24 h: (a) control; (b) air; (c) oxygen (8.5×10^4 Pa); (d) oxygen (3.4×10^4 Pa)–nitrogen (5.1×10^4 Pa) mixture; (e) nitrogen (8.5×10^4 Pa); (f) vacuum (0.3 Pa).

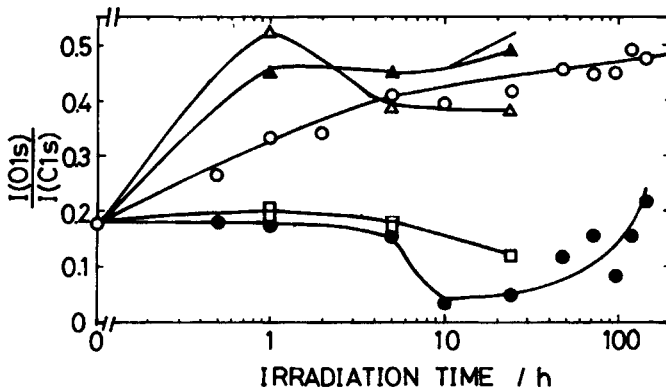


Fig. 3(a). Plots of O1s/C1s intensity ratio for PAI samples exposed to UV radiation in various atmospheres vs. irradiation time: (Δ) O₂; (▲) O₂ + N₂; (○) Air; (□) Vacuum; (●) N₂.

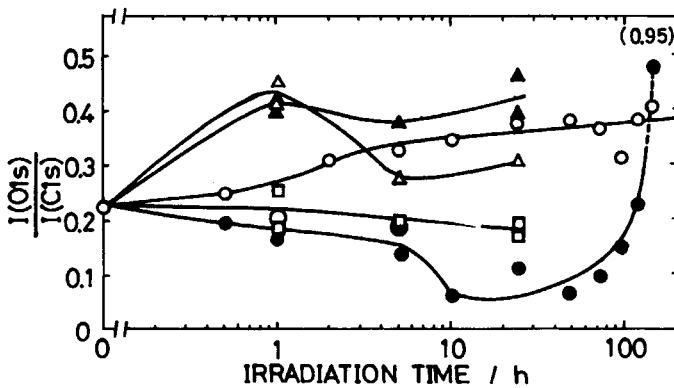


Fig. 3(b). Plots of O1s/C1s intensity ratio for PI samples exposed to UV radiation in various atmospheres vs. irradiation time: (Δ) O₂; (▲) O₂ + N₂; (○) Air; (□) Vacuum; (●) N₂.

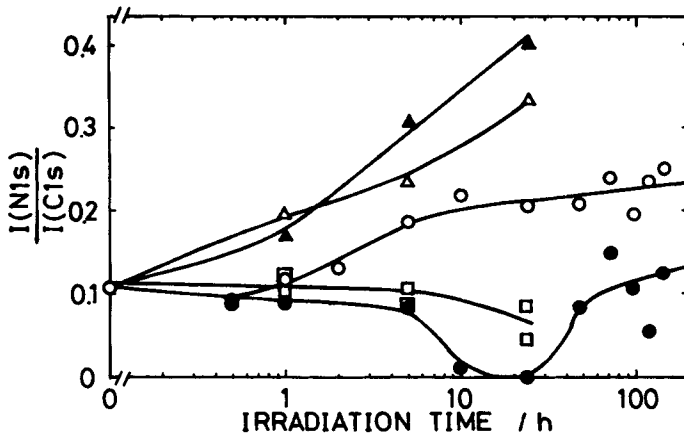


Fig. 4(a). Plots of N1s/C1s intensity ratio for PAI samples exposed to UV radiation in various atmospheres vs. irradiation time: (Δ)O₂; (\blacktriangle)O₂ + N₂; (\circ) Air; (\square) Vacuum; (\bullet)N₂.

nitrogen the PI sample produced a white-colored powder at the surface; this material was easily detached.

Figures 3(a) and (b) show the variations of the O1s/C1s intensity ratio for PAI and PI samples, respectively, as a function of time of irradiation in various atmospheres. Here, it should be noted that the intensity ratios of O1s/C1s and N1s/C1s are quoted for the altered surface layer rather than stoichiometries derived from C1s:N1s:O1s ratio, because the density of atoms at the surface changes with an increase of irradiation time due to incorporation or elimination of atoms such as oxygen and nitrogen. In the case of atmospheres containing oxygen, the O1s/C1s ratio became evidently higher than that of an unirradiated sample. Interestingly, the intensity ratio in oxygen increased rapidly to a maximum and then decreased during an earlier stage of irradiation. The change in the intensity ratio under vacuum and in nitrogen was small during an initial stage of irradiation; but in the latter stage for the nitrogen atmosphere the intensity ratio decreased to a broad minimum

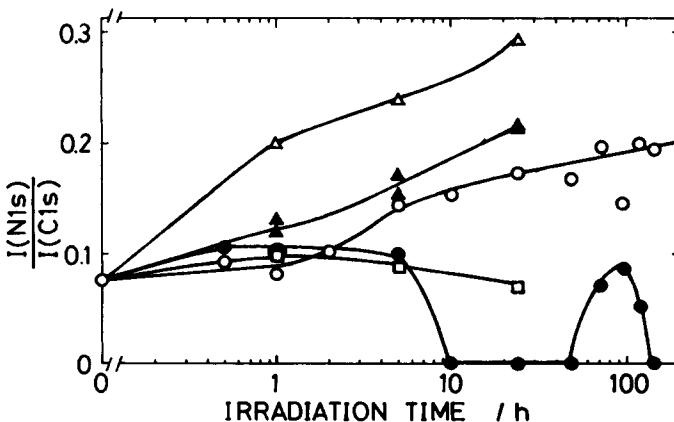


Fig. 4(b). Plots of N1s/C1s intensity ratio for PI samples exposed to UV radiation in various atmospheres vs. irradiation time: (Δ)O₂; (\blacktriangle)O₂ + N₂; (\circ) Air; (\square) Vacuum; (\bullet)N₂.

and then increased sharply. Surprisingly, in spite of this pronounced increase in O content, the C1s spectra gave no fine structure at high binding energy; this is indicative of the absence of highly oxygenated carbon components.

Figures 4(a) and (b) show the variations of the N1s/C1s intensity ratio for PAI and PI samples, respectively. The trend of the variation for each atmosphere was similar to that in Figures 3(a) and (b), but, noticeably, the N1s/C1s ratio in oxygen and in the oxygen–nitrogen mixture rose more slowly with irradiation time, and gave no maximum during an initial stage, compared with the O1s/C1s ratio shown in Figures 3(a) and (b). As can be seen from Figures 4(a) and (b), the N1s band in the nitrogen atmosphere disappeared once with PAI, and four times with PI with an increase of irradiation time.

ESR for PAI and PI Films

Typical ESR spectra for PAI and PI samples irradiated in air for 1 h are illustrated in Figure 5, together with two signals of Mn^{2+} used as a standard. An unirradiated sample had already contained free radicals, but the ESR signal intensity was greatly enhanced as a result of irradiation (Fig. 6). In all the experiments the signal was a symmetrical singlet with a g value between 2.004 and 2.005 with the exception of a slightly asymmetrical singlet for PI samples under vacuum. It should be noted that the g -value for both PAI and PI remained almost constant under the present experimental conditions.

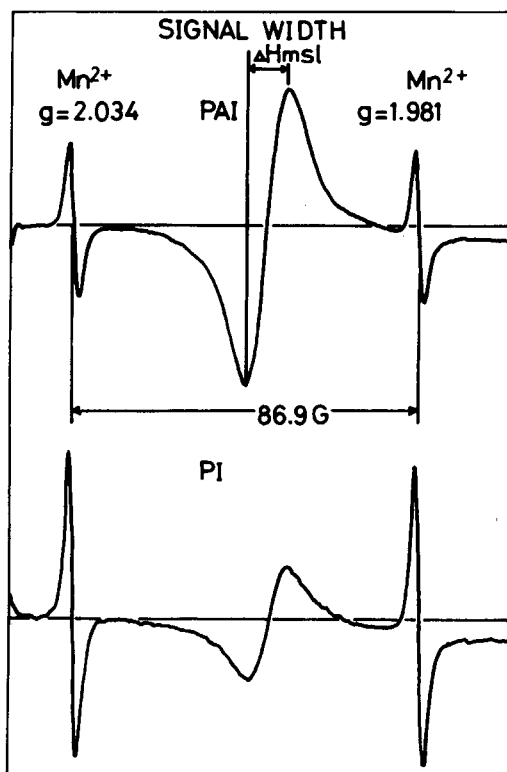


Fig. 5. ESR spectra for PAI and PI samples exposed to UV radiation in air for 1 h.

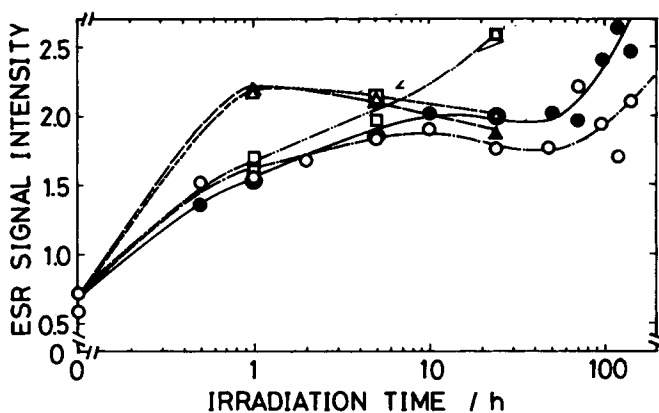


Fig. 6(a). Plots of ESR signal intensity for PAI samples exposed to UV radiation in various atmospheres vs. irradiation time: (Δ)O₂; (\blacktriangle)O₂ + N₂; (\circ) Air; (\square) Vacuum; (\bullet)N₂.

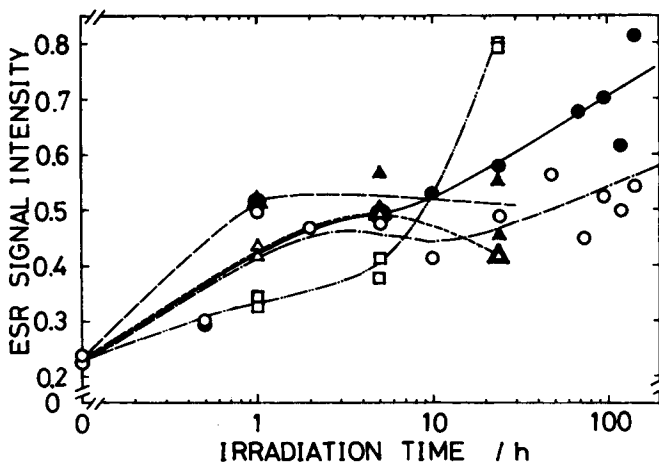


Fig. 6(b). Plots of ESR signal intensity for PI samples exposed to UV radiation in various atmospheres vs. irradiation time: (Δ)O₂; (\blacktriangle)O₂ + N₂; (\circ) Air; (\square) Vacuum; (\bullet)N₂.

Figures 6(a) and (b) show the ESR signal intensity for PAI and PI samples, respectively, plotted against time of irradiation in various atmospheres. Interestingly, the signal intensity vs. irradiation time curve was strongly affected by the atmospheres. Also, the signal intensity for PAI was much greater than that for PI. It is worth noting that, for both PAI and PI samples, the irradiation in oxygen and in the oxygen–nitrogen atmosphere gave a rapid increase and then a broad maximum in the signal intensity. Also, the irradiation in air had a tendency to cause a maximum in the signal intensity. On the other hand, the signal intensity under vacuum and in nitrogen increased continuously with an increase of time, thus resulting in the order vacuum > N₂ > air in the latter stage of irradiation.

Figures 7(a) and (b) show the ESR signal width (ΔH_{msl} denoted in Fig. 5) for PAI and PI samples, respectively, plotted against irradiation time. Apparently, the line width was significantly dependent on the atmospheres; the

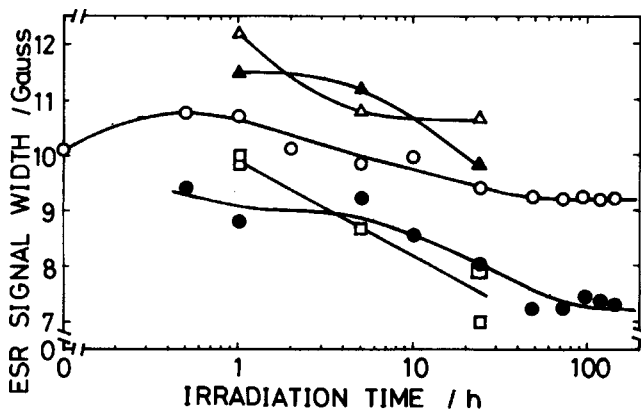


Fig. 7(a). Plots of ESR signal width for PAI samples exposed to UV radiation in various atmospheres vs. irradiation time: (Δ) O_2 ; (\blacktriangle) $O_2 + N_2$; (\circ) Air; (\square) Vacuum; (\bullet) N_2 .

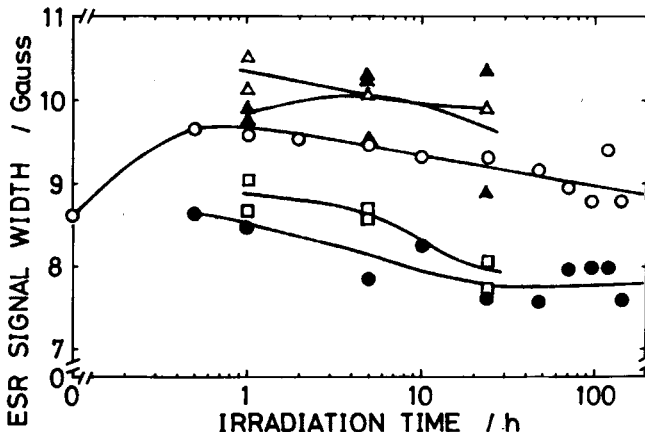


Fig. 7(b). Plots of ESR signal width for PI samples exposed to UV radiation in various atmospheres vs. irradiation time: (Δ) O_2 ; (\blacktriangle) $O_2 + N_2$; (\circ) Air; (\square) Vacuum; (\bullet) N_2 .

value at 1 h of irradiation for both PAI and PI decreased in the order $O_2 > O_2 + N_2 > \text{air} > \text{vacuum} > N_2$. Also, the line width for each atmosphere decreased with an increase of time, particularly, more markedly in the case of PAI samples. Interestingly, the width of PAI samples was much greater than that for PI samples during an earlier stage of irradiation.

In order to check the stability of radicals produced in PAI and PI samples, the ESR signal intensity was plotted against time of keeping in the dark after 2-h irradiation in various atmospheres [Figs. 8(a) and (b)]. These data were obtained in another series of the experiments, so that the intensity of signals just after irradiation was not in agreement with that shown in Figures 6(a) and (b). The signal intensity decreased considerably slowly at first, and then approximately linearly at a faster speed with time on the semilogarithmic scale. Evidently, the decrease of the signal intensity for PAI samples was much larger than that for PI samples; for both PAI and PI the decay rate of radicals produced in oxygen and in air was greater than that under vacuum.

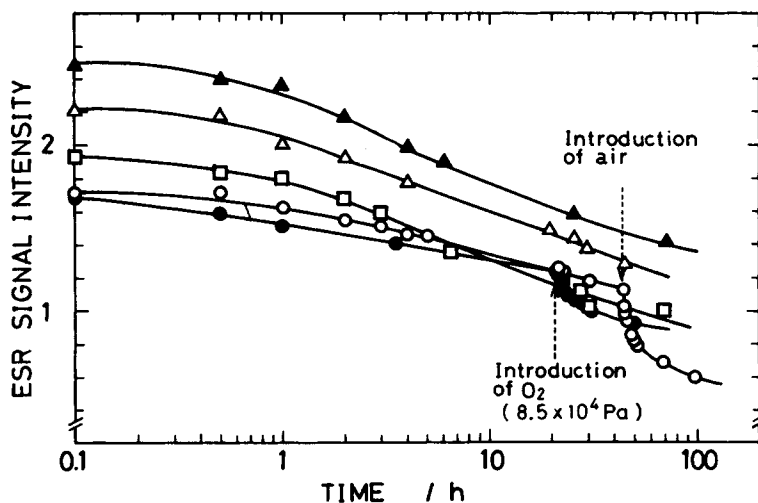


Fig. 8(a). Time dependence of ESR signal intensity for PAI samples kept in the dark after UV irradiation in various atmospheres: (▲) O_2 (8.4×10^4 Pa); (△) O_2 (4.0×10^4 Pa); (○) Vacuum (0.4 Pa); (●) Vacuum (0.4 Pa); (□) Air.

As can be seen from Figures 8(a) and (b), when the samples, having been kept in the dark after irradiation under vacuum, were exposed to oxygen or air, the signal intensity dropped suddenly and then decreased slowly with time, and at this time the signal width was broadened by ca. 2 G.

DISCUSSION

Surface Reactions in Air

In the first place the curve resolution of $C1s$ spectra was performed on the basis of the shift in binding energies due to the substituent effect of oxygen.^{2,6,7} Figure 9 illustrates a typical example of peaks resolved in the $C1s$ spectrum for a PAI sample. Thus, the $C1s$ spectrum for PAI and PI samples irradiated in air fell into six components. The structural feature and the binding energy for each component are assigned according to Clark and Dilks,^{2,6} as shown in Figure 9. It is worth noting that the most extensively oxidized carbons (carbonate groups) appeared newly at ~ 290.6 eV.

In connection with the component at ~ 286.6 eV, Leary and Campbell⁸ reported that a peak appearing at ~ 286.0 eV for polyimide [condensate of pyromellitic dianhydride (PMDA) and 4,4'-diaminodiphenyl ether (DADPE)] was due to partially oxidized carbons of unknown origin. Baise and Buchwalter,⁹ also, reported that a peak at ~ 286.1 eV for the same type of polyimide was attributed to the aromatic carbons in the PMDA ring, rendered electron-deficient by the attached carbonyl groups. Peeling and Clark¹⁰ reported that a $C1s$ component at ~ 286.0 eV observed in nylon 66 arose from carbons immediately adjacent to the amide group. Therefore, these types of carbons are considered to contribute the peak centered at ~ 286.6 eV.

Concerning the component at ~ 289.0 eV, it was reported that carbons in imide and amide carbonyl groups of PMDA-DADPE polyimide gave rise to

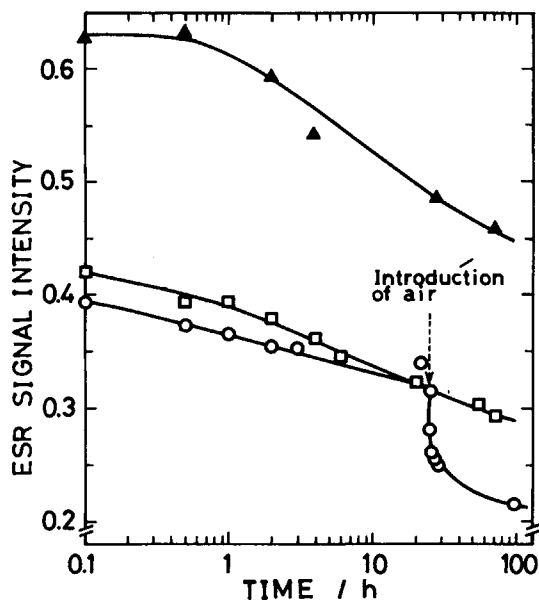


Fig. 8(b). Time dependence of ESR signal intensity for PI samples kept in the dark after UV irradiation in various atmospheres: (▲) O_2 (8.3×10^4 Pa); (○) Vacuum (0.4 Pa); (□) Air.

peaks at ~ 289.0 and ~ 288.4 eV, respectively.⁸ Therefore, these types of carbons in PAI and PI samples, also, appear at ~ 289.0 eV. The peak at ~ 290.6 eV is considered to originate from imide and amide carbonyl carbons bonded to one oxygen as a result of the photooxidation as well as the carbonate carbons. The $\pi-\pi^*$ shake-up component indicative of the presence of aromatic groups in the polymer films⁷ appears at ~ 291.7 eV.

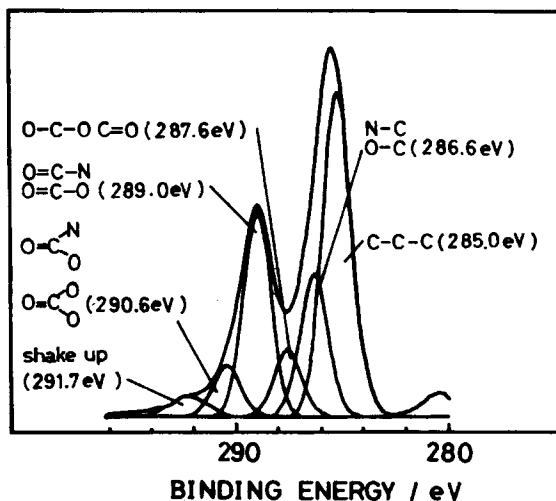


Fig. 9. Component peaks in the C_{1s} spectrum for a PAI sample exposed to UV radiation in air for 24 h.

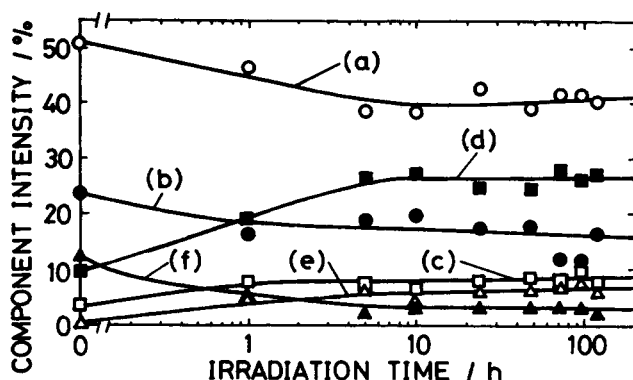


Fig. 10(a). Plots of the intensity of components in the C1s spectrum for PAI samples exposed to UV radiation in air vs. irradiation time: (a) 285.0 eV; (b) 286.6 eV; (c) 287.6 eV; (d) 289.0 eV; (e) 290.6 eV; (f) 291.7 eV.

Figures 10(a) and (b) illustrate the component analysis of C1s spectra for PAI and PI samples, respectively, as a function of time of irradiation in air. The component intensity was expressed as a percent of the total band intensity. The oxidative functionalization as a result of the irradiation in air becomes clear from the buildup of more highly oxygenated carbon components appearing at ~ 287.6 , ~ 289.0 , and ~ 290.6 eV. Particularly, a much more pronounced increase of the component at ~ 289.0 eV for both types of the films suggests that C—N bond in the imide and amide carbonyl groups is subject to oxidative attack. On the other hand, a decrease in the components at ~ 285.0 and ~ 291.7 eV indicates loss of aromaticity, resulting from oxidation of the aromatic rings. A difference in the distribution behavior of the components at ~ 285.0 and ~ 286.6 eV between PAI and PI samples may be attributed to the stability of the aromatic ring system of PAI and PI on the photooxidation. In connection with photooxidation, Peeling and Clark¹⁰ suggested that in the case of polystyrene and poly(methyl methacrylate), the oxidation continues at carbons subjected to initial oxidative attack, producing

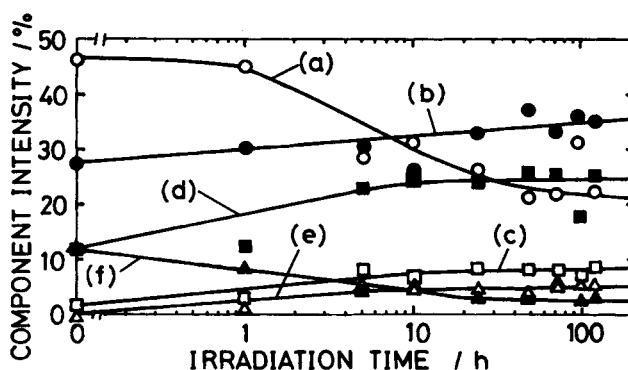


Fig. 10(b). Plots of the intensity of components in the C1s spectrum for PI samples exposed to UV radiation in air vs. irradiation time: (a) 285.0 eV; (b) 286.6 eV; (c) 287.6 eV; (d) 289.0 eV; (e) 290.6 eV; (f) 291.7 eV.

extensively oxidized carbon sites. Therefore, the same situation is considered to have occurred in the PAI and PI films.

In the case of unirradiated PAI and PI samples, in addition to the expected components at ~ 285.0 , ~ 286.6 , ~ 289.0 , and ~ 291.7 eV, a small peak at ~ 287.6 eV was observed [Figs. 10(a) and (b)]. This suggests the presence of a low concentration of O—C—O and C=O functionalities in the starting materials, although there are no these components in the structural formulas (Fig. 1).

The O1s spectrum for PAI and PI samples irradiated in air was composed of two components centered at ~ 532.5 and ~ 534.2 eV. According to Leary and Campbell⁸ and Clark and Dilks⁶, the lower and higher binding energy components can be attributed to doubly bonded and singly bonded oxygens, respectively. The intensity of the lower binding energy component increased with an increase of irradiation time. The relative amount of doubly bonded to singly bonded oxygens for unirradiated PAI and PI samples was 78:22% and 73:27%, respectively. After 120-h irradiation in air these values became 84:16% (PAI) and 87:13% (PI); this suggests that the production of doubly bonded oxygens became more predominant as the oxidation proceeded.

The N1s spectrum for PAI and PI samples irradiated in air had a main component at ~ 401.0 eV, and this relative amount remained almost unchanged. This indicates that oxidized nitrogens were not formed on the photooxidation, because these would have a binding energy considerably higher than the imide and amide nitrogens (Fig. 1).¹⁰

Effect of Irradiation Atmospheres on Surface Reactions

It is clear from Figures 2, 3, and 4 that the surface composition and structure of PAI and PI samples differed widely due to the irradiation atmospheres. The C1s spectrum in oxygen and in the oxygen–nitrogen mixture was quite similar to that in air (Fig. 2); therefore, the oxidative functionalization in these atmospheres is considered to resemble that in air. It is known that oxygen and UV radiation with wavelengths shorter than 300 nm play a role in the depolymerization of photoresist polymers, giving rise to major products such as H₂O and CO₂.¹¹ Therefore, simpler volatile molecules may have been produced in the present experiments.

As can be seen from Figures 3 and 4, the O1s/C1s and N1s/C1s ratios for PAI and PI samples irradiated in atmospheres containing oxygen increased clearly relative to those for unirradiated samples, and the O1s/C1s ratio increased more rapidly with an increase of irradiation time than the N1s/C1s ratio; however, the N1s/C1s ratio under vacuum and in nitrogen did not increase. Therefore, the increase in N content in atmospheres containing oxygen is closely associated with the incorporation of oxygen at the surface. It is not clear at present whether the concentration of nitrogen at the surface for the oxygen atmosphere was caused by a post-irradiation reaction of the surface with atmospheric N₂ or by a change in the surface composition of the polymer material itself.

For each atmosphere the O1s/C1s ratio vs. irradiation time curve showed a close similarity to the N1s/C1s ratio vs. irradiation time curve (Figs. 3 and 4). The situation becomes more apparent in the case of the nitrogen atmosphere;

that is, the decrease or disappearance of O1s and N1s bands occurred at the same time, being accompanied by the vanishment of high binding energy components in the C1s spectra (Fig. 2). This can be attributed to the desorption of some volatile oxygen–nitrogen type photoproducts. In the latter stage of irradiation in the nitrogen atmosphere, the O1s and N1s bands appeared again and, interestingly, the O1s/C1s ratio continued to increase with an increase of irradiation time (Fig. 3), while the N1s/C1s ratio increased and then leveled off [Fig. 4(a)] or declined through a maximum [Fig. 4(b)]. The C1s spectrum for PAI and PI samples after 144-h irradiation in nitrogen had two major components at ~ 285.1 and ~ 286.2 eV without giving a distinct fine structure at high binding energy. This increase in O content may be attributed to oxygen uptake brought about by a post-irradiation reaction of the substantially damaged polymer surface with atmospheric O_2 .^{12,13} In this connection it was reported in a previous paper¹³ that in the case of poly(vinylidene fluoride) and ethylene–propylene copolymer, oxygen incorporation took place onto the polymer surface after Ar-plasma treatment, being due to post-plasma surface reaction with atmospheric O_2 .

On the other hand, the surface composition for PAI and PI samples, having been irradiated in air for 2 h, remained almost constant with an increase of time of keeping in the dark after irradiation. Also, in the case of PAI and PI samples irradiated in oxygen for 2 h, the surface composition was maintained nearly constant even after keeping in the atmosphere and subsequent exposure to air in the dark. Therefore, these findings suggest that the production of more highly oxidized carbon components in atmospheres containing oxygen (Figs. 10 and 2) was brought about only under UV irradiation.

Formation of Free Radicals

It is known that radicals trapped in solid polymer materials give the following g values (isotropic term): alkyl radical (ca. 2.002–2.003), alkoxy radical (ca. 2.004), peroxide radical (ca. 2.014), and acyl radical (ca. 2.001).¹⁴ Therefore the g value (2.004–2.005) obtained in the present experiments suggests that the ESR signal was due to alkoxy and alkyl type radicals, not peroxide radicals. Also, Ledneva *et al.*¹⁵ reported that radicals produced in the thermal and thermooxidative degradation of polyamidoimide pertained to radicals of polyconjugated systems where the unpaired electron was delocalized along a sufficiently long portion of the conjugated chain.

The fact that PAI samples gave much greater amounts of radicals than PI samples with all the irradiation atmospheres (Fig. 6) can be associated with the presence of not only the imide bonds, but also the amide bonds in PAI (Fig. 1). Also, this difference in the radical amount corresponds to the fact that the O1s/C1s and N1s/C1s ratios for PAI samples in atmospheres containing oxygen were greater than those for PI samples (Figs. 3 and 4); this reflects that PAI is subject to oxidative attack compared with PI.

To explain the effect of irradiation atmospheres on the formation of radicals (Fig. 6), two types of radical formation processes can be considered; that is, one is associated with the incorporation of oxygen at the surface, and the other is involved in the rupturing of bonds in the bulk material. As can be seen from Figures 3 and 6, the radical accumulation behavior in oxygen and in

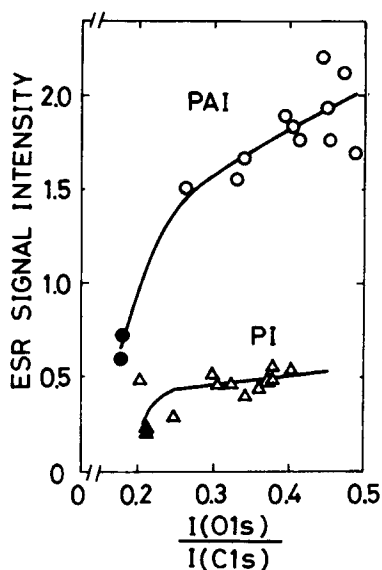


Fig. 11. Plots of ESR signal intensity vs. O1s/C1s intensity ratio for PAI and PI samples exposed to UV radiation in air: (●,▲) control samples.

the oxygen–nitrogen atmosphere showed a close similarity to the change of the O1s/C1s ratio. This suggests that the formation of radicals was promoted by the oxygen incorporated at the surface, giving rise to a maximum in the radical amount. Figure 11 shows the ESR signal intensity plotted against O1s/C1s ratio in the case of air, using the data in Figures 3 and 6. Apparently, the amount of radicals increased with an increase of O1s/C1s ratio. This suggests that the incorporated oxygen played a role of favoring the formation of radicals. In connection with the effect of oxygen on radical formation, it was reported that the rate of accumulation and the limit concentration of radicals produced in polyamidoimide were significantly higher in thermal oxidation as compared with thermal degradation processes.¹⁵ On the other hand, the decreasing order of radical amount in the latter stage of irradiation, that is vacuum > N₂ > air, differed completely from that of the O1s/C1s and N1s/C1s ratios in these atmospheres (Figs. 3 and 4). This fact suggests strongly that the radicals, particularly in the case of vacuum atmosphere, pertained to the rupturing of bonds in the bulk, not the surface reactions, and in the case of air the oxygen in air seems to have played a role of suppressing the production of radicals.

It is clear from Figures 7(a) and (b) that atmospheres containing oxygen gave larger line widths; also, as described in Figure 8, the width under vacuum was broadened by exposure to oxygen or air. This suggests that the oxygen incorporated or contacted at the surface had a strong interaction with the unpaired electrons. It is known that oxygen contained in a radical causes widening of the signal.¹⁶ The increase in line width in the present experiments is considered to be due to an effect of lifetime broadening and a result of the number of different radical environments arising from differences in chemical species, crystallinity, and atom density. The narrowing of the line width with

an increase of irradiation time in atmospheres containing oxygen (Fig. 7) may be attributed to an increase in the relative amount of radicals due to the rupturing of bonds in the bulk, and the narrowing under vacuum and in nitrogen may be associated with an increase in the radical concentration (so-called spin-spin exchange narrowing) as well as the depletion in oxygen at the surface (Fig. 2).

The fact that the decay of radicals was accelerated in oxygen and in air (Fig. 8) suggests that the radicals were subject to destruction by the oxygen in these atmospheres. Also, the sudden reduction of the radical amount under vacuum by exposure to oxygen or air (Fig. 8) suggests that a large amount of radicals was localized in the vicinity of the surface. Here, it is worth noting that when PAI and PI samples, having been irradiated under vacuum for 2 h, were kept in the dark, the surface composition remained almost unchanged after keeping and subsequent exposure to air; that is, the incorporation of oxygen did not occur. Therefore, this radical reduction can be attributed to a recombination process assisted by the introduced oxygen or air.

The authors wish to acknowledge T. Nanba and H. Eriguchi for assistance in the experimental work, Mr. M. Kohno of JEOL Ltd., for the measurement of more accurate ESR spectra, and Professor J. Sohma of Hokkaido University for interesting discussions. The authors also wish to thank Yamazaki Works, Hitachi Chemical Co. for providing a chance to start this study.

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Received February 25, 1986

Accepted September 5, 1986