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Surface Structure of Low-Density Polyethylene Film Exposed to Air Plasma

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ABSTRACT

The surface structures of low-density polyethylene (LDPE) film exposed to plasma or γ-ray in air were characterized by ESCA, IR, and EMS. The formation of trans C=C bond on the LDPE film surface was observed by the exposure to ac air plasma (2×10^{-2} torr, 19 W plasma power). Large amounts of O and N atoms as an amide structure were incorporated into the polymer surface by the plasma treatment. These plasma reactions occurred mainly in the amorphous region, and the polymer surface became rough enough to have a microdomain structure upon increasing the plasma treatment time up to 3 h. γ-Irradiation of LDPE in air only brought about O-atom incorporation as ketone and ether linkages. The polymer surface did not undergo etching under γ-irradiation as it did in plasma treatment.

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INTRODUCTION

Modification of the surface structure of organic polymers is of basic importance in the fields of industrial, biomedical, and technological applications. Plasma treatment is one of the most promising methods for such surface modifications [1]. Polyolefins, in particular polyethylene, have been used as base polymers to be modified by plasma treatment. Recently Everhart et al. [2] reported an ESCA study of the surface structure of low-density polyethylene (LDPE) film exposed to radiofrequency inductively coupled N_2 and Ar plasmas. They observed that functional groups, such as C=C, C–NH_2, C–OH, C=O, CO_2H were introduced to the polymer surface by plasma treatment in the presence of oxygen and nitrogen.

The present paper is concerned mainly with a comparative study of the surface structures of LDPE films exposed to plasma and γ-ray in air by means of ESCA, IR, and electron microscopy (EMS).

EXPERIMENTAL

LDPE film (30 μm thick) was of commercial grade and used as received.

The plasma treatment was performed with the equipment shown schematically in Fig. 1. Pressure measurements were made with a MacLeod gauge, but the line to the gauge was closed during discharge to avoid contamination with mercury vapor. The plasma reactor consisted of a Pyrex tube (3 cm in diameter and with a 40-cm discharge path). Sample films were placed along the axis of the reactor tube in the center of the discharge path. The reactor tube was evacuated by a rotary pump with a cold trap. A small amount of air was passed through the reactor tube at a constant flow rate (1-5 mL/min). Plasma excitation was created by an electric discharge (60 Hz). The electric current and the potential between the two electrodes were measured directly.

γ-Irradiation of LDPE film was performed in air at room temperature with a ^{60}Co γ-ray source. The dose rate was determined as 0.7 Mrd/h by using a standard Fricke dosimeter.

ESCA spectra of the film were recorded on a Shimadzu ESCA 750 spectrometer with an MgK_α photon source. Curve analysis of C1s Spectra were accomplished with a Shimadzu ESPAC 100 processor.

Infrared (IR) spectral measurements were made by an ATR method on a JASCO A302 infrared spectrophotometer. Electron microscopy (EMS) was performed with a Hitachi-Akashi MSM-102 scanning microscope.

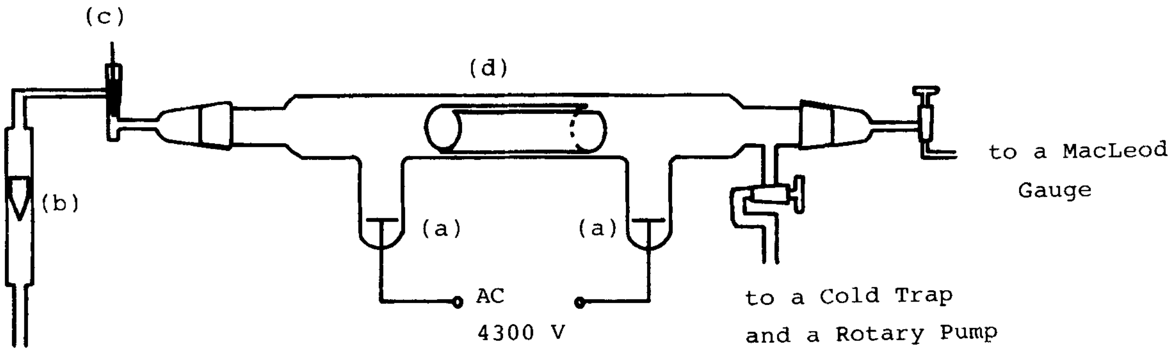


FIG. 1. Equipment for the plasma treatment of LDPE film: (a) electrode, (b) flow meter, (c) needle valve, (d) film sample.

RESULTS AND DISCUSSION

Characterization of the Structure of LDPE Film by ESCA

Figure 2 shows typical wide-scan ESCA spectra for the LDPE film before and after exposure to air plasma at a pressure of 2×10^{-2} torr and an input power of 19 W. The photoemissions from O1s (532.70 eV) and N1s (400.65 eV) levels were extremely intensified by exposure of the LDPE film to air plasma, providing a direct visual indication of the incorporation of O [3] and N atoms into the polymer surface. Smaller photoemission peaks from Si2s (154 eV) and Si2p (102 eV) were also observed. These peaks may be attributed to contamination by Si on the surface of glass-made reactor tube.

From a detailed analysis of the C1s, O1s, and N1s peaks, the relative concentrations of these components on the polymer surface were calculated (Table 1). The relative intensity coefficients for the individual peak areas are given by C1s:O1s:N1s = 1.00:2.85:1.77 [4, 5]. The concentrations of O and N atoms for the nontreated LDPE are thus evaluated as 4.6 and 3.7% (Table 1), which probably originate from a fatty amide used as the slip agent. Air plasma treatment for 1 h led to incorporation of larger amounts of O and N atoms into the polymer surface, thereby increasing the corresponding peak widths for C1s, O1s, and N1s (see also Fig. 3 and Table 2).

By reference to the monofunctional nitrogen group of nylon 6 (–CONH–R) showing 399.4 eV binding energy and 1.7 eV N1s peak width [6], the N1s peak width (2.5 eV) for the plasma-treated LDPE indicates production of a different type of functional nitrogen group. Furthermore, the binding energy for N1s (400.65 eV) suggests the structure of the nitrogen group to be nitriles, amines, or possibly imines [7] on the plasma-treated LDPE.

Lineshape analysis of the C1s peaks shows the presence of at least three types of functional carbon groups in the surface (Table 3). The peaks at 285.75 eV are assigned to –C–H or C=C [8, 9]. The peak with the highest bond energy (289.05 eV) is assigned to C=O or the amide group [8].

On the other hand, ESCA analysis of LDPE irradiated by γ-rays showed a marked increase in the O-atom content and a decrease in the N-atom content (Table 1). It is likely that γ-irradiation in the presence of O_2 brings about H elimination from the polymer surface. The resulting polymer radicals undergo either crosslinking by mutual combination or addition of O_2 to form peroxide [10].

Lineshape analysis indicates that a larger amount of –C–O– groups than of C=O groups is introduced in the γ-irradiated LDPE film. It seems that the –C–O– group is associated with the efficient formation of polymer peroxide.

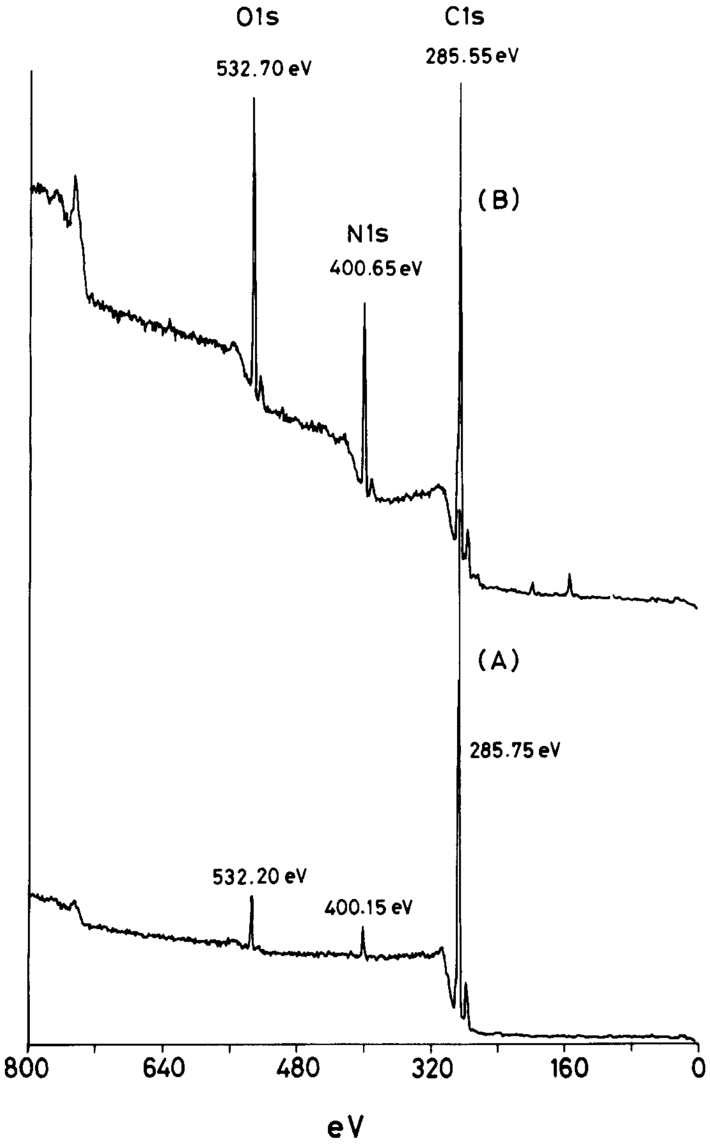


FIG. 2. ESCA spectra of LDPE film (A) before and (B) after air plasma treatment for 1 h.

TABLE 1. ESCA Analysis of Plasma- and γ-Ray-Treated Polyethylene (LDPE)[a] Surface

	Relative intensity[b]			Ratio of components	
Treatment	C	O	N	O/C	N/C
Nontreated	91.65	4.62	3.73	0.051	0.041
Air plasma[c]	88.64	6.87	4.48	0.078	0.050
Air plasma[d]	69.45	15.58	14.97	0.224	0.216
γ-Ray[e]	90.49	9.01	0.50	0.100	0.006

[a] Low-density polyethylene film with a thickness of 30 μm.

[b] Corrected using the intensity coefficients [4, 5]: C1s:O1s:N1s = 1.00:2.85:1.77.

[c] Treated for 10 min at 2 × 10^{-2} torr and 19 W input power.

[d] Treated for 1 h at 2 × 10^{-2} torr and 19 W input power.

[e] Irradiation dose of 10 Mrd in air.

TABLE 2. ESCA Data for O1s and N1s Signals of Plasma- and γ-Ray-Treated Polyethylene (LDPE)

Treatment[a]	Signal	Position, eV	Width, eV	Area, cps·eV
Nontreated	O1s	532.20	1.85	12,344
	N1s	400.15	1.75	6,194
Air plasma (10 min)	O1s	532.45	2.15	18,478
	N1s	400.35	1.90	7,483
Air plasma (1 h)	O1s	532.70	2.15	40,617
	N1s	400.65	2.50	24,232
γ-Ray (10 Mrd)	O1s	533.10	1.90	23,346
	N1s	401.05	1.10	807

[a] The conditions are the same as in Table 1.

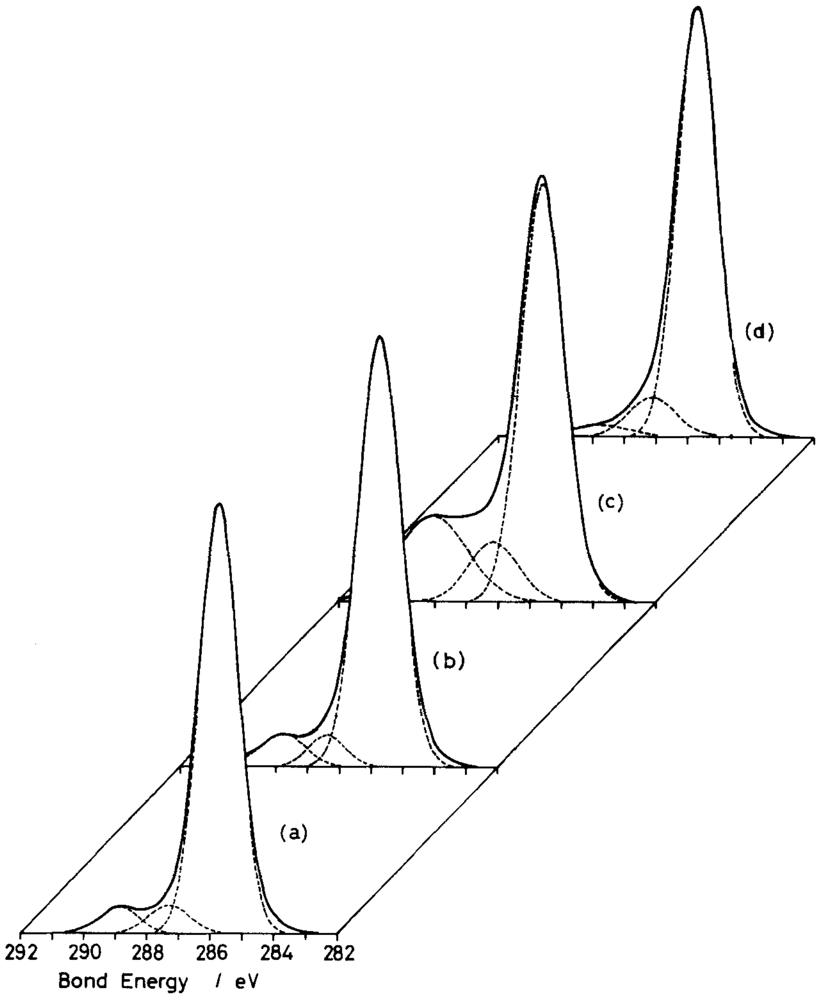


FIG. 3. Lineshape analysis of C1s peaks for LDPE: (a) nontreated and exposed to air plasma for (b) 10 min and (c) 1 h, and (d) γ-irradiated in air with a total dose of 10 Mrd.

TABLE 3. Lineshape Analysis of C1s Signals of Plasma- and γ-Ray-Treated Polyethylene (LDPE)

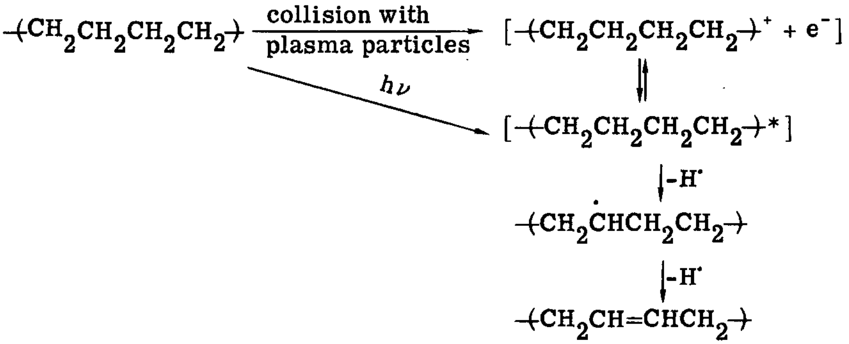
Treatment	Peak	Position, eV	Width, eV	Area, cps·eV	Possible assignment	Total carbon, %
Nontreated	1	285.75	1.40	37,860	CH_2; C=C	88
	2	287.30	1.50	2,741	C–O	6
	3	288.90	1.40	2,368	C=O	6
Air plasma (10 min)	1	285.75	1.50	36,524	CH_2; C=C	87
	2	287.40	1.30	2,337	C–O	6
	3	288.80	1.60	2,938	C=O	7
Air plasma (1 h)	1	285.55	1.60	21,525	CH_2; C=C	68
	2	287.15	1.80	3,433	C–O	11
	3	289.05	2.50	6,799	C=O	21
γ-Ray (10 Mrd)	1	285.70	1.40	35,917	CH_2; C=C	87
	2	287.10	1.70	3,900	C–O	10
	3	288.75	2.00	1,316	C=O	3

[a] The conditions are the same as in Table 1.

IR Spectral Characteristics of LDPE Surface Exposed to Air Plasma

The time dependence of the IR spectral change of LDPE by exposure to air plasma is shown in Fig. 4. In the spectrum for the nontreated LDPE surface, absorption bands were observed at 1640 cm^{-1} (amide I band) as well as at 3450 and 3230 cm^{-1} because the polymer film contained a fatty amide as the slip agent. A marked spectral change was observed in the 960 cm^{-1} range (trans C=C) over the initial exposure time of 5 min, but the intensity no longer increased upon further exposures. In contrast, IR absorptions in the 1640 and 3400-3200 cm^{-1} regions increased almost linearly with exposure time.

Changes in optical densities at 960 cm^{-1} (trans C=C) and 1640 cm^{-1} (amide I band), relative to the virtually invariant $-CH_2-$ band, as a function of exposure time are shown in Fig. 5. The ratio of $O.D._{960}/O.D._{2850}$ increased and reached an ultimate value of about 0.1 upon increasing the exposure time up to 1 h. Further exposures, however, resulted in no change of the ratio. This result suggests that H_2 elimination from the polymer surface took place, forming trans C=C bond which disappears by successive reactions with plasma species. It is possible that such a H_2 elimination proceeds not only by direct reactions with plasma particles but also by a photochemical process under the illumination effect of electronically excited plasma species (i.e., reaction with a photon) [11, 12].



On the other hand, the ratio of $\Delta O.D._{1640}/O.D._{2850}$ increased linearly with an increase of the exposure time except in the early stage. Such IR data concerning amide formation agree with the corresponding ESCA spectral data listed in Table 1. In view of the fact that the extinction coefficient for C=O in amide is about ten times larger than that for

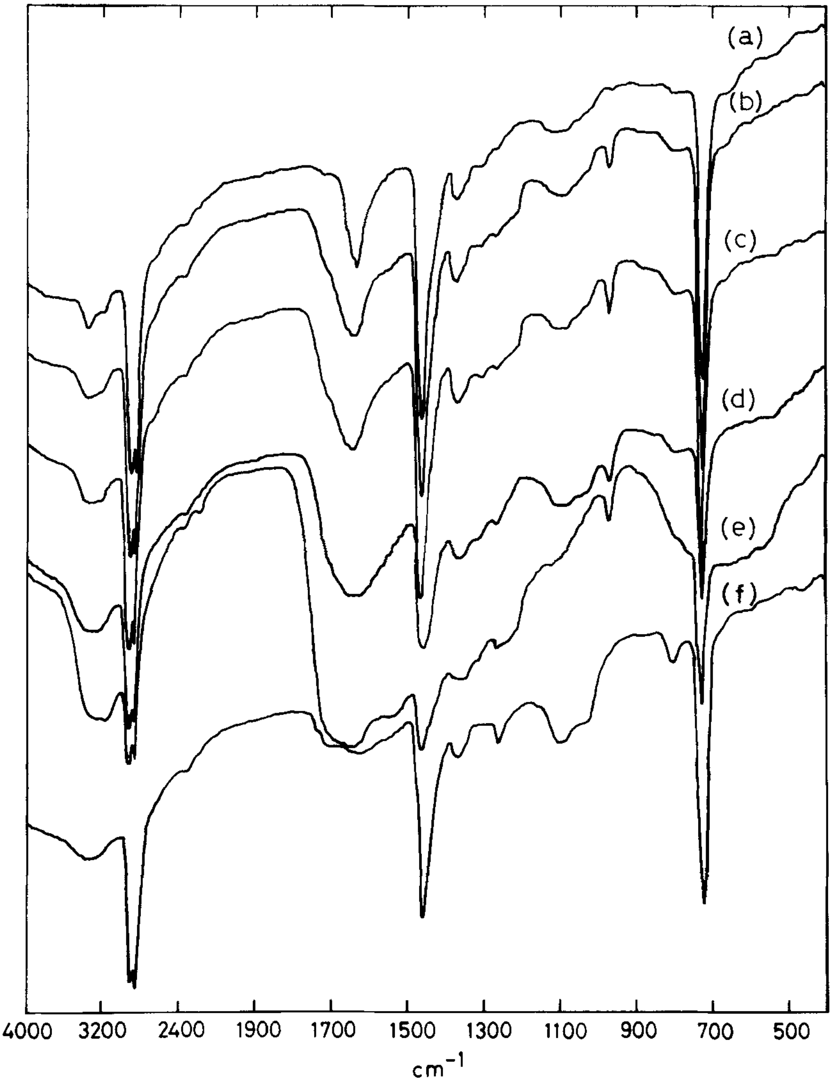


FIG. 4. IR spectra of LDPE film: (a) nontreated, exposed to air plasma for (b) 5 min, (c) 10 min, (d) 1 h, and (e) 3 h; and (f) γ-irradiated in air with a total dose of 10 Mrd.

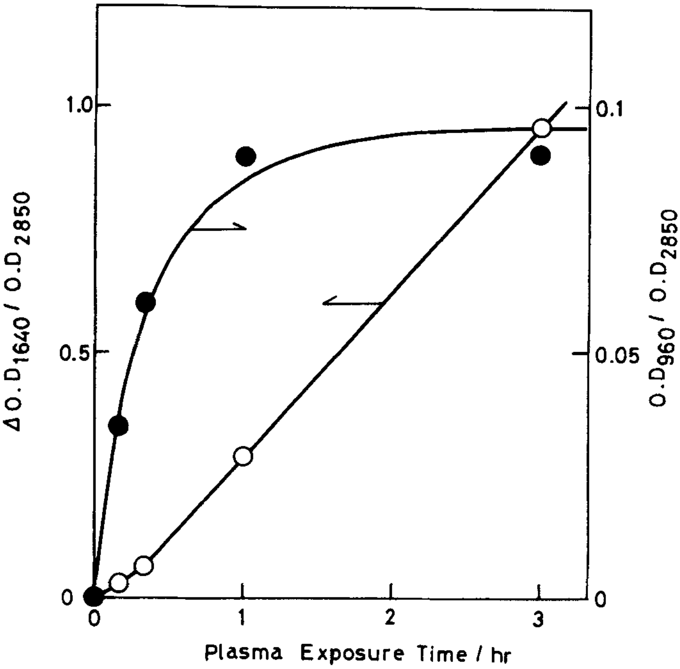


FIG. 5. Changes in optical densities at (●) 960 cm^{-1} (O.D.$_{960}$) and (○) 1640 cm^{-1} (ΔO.D.$_{1640}$) relative to that at 2850 cm^{-1} as a function of plasma exposure time.

trans C=C [13], the concentration of the C=C bond produced at the polymer surface under these conditions is nearly equal to the amide concentration. Therefore, we presume that the amide formation is attributable to the secondary reaction of the C=C bond with an N atom or a related species generated by plasma extinction.

IR data of γ-irradiated LDPE showed no marked changes in the absorption regions for the trans C=C bond and amide, although relatively weak absorption at 1720 and 1100 cm^{-1} could be observed. These data are consistent with incorporation of O atoms as ketone and ether linkages to the polymer surface, as is also indicated by the ESCA measurement (see Table 1). It is likely that γ-ray energy is initially absorbed by the polymer to form polymer radicals which undergo not only crosslinking by mutual combination, but also O_2 addition, leading to ketone and ether structures [14].

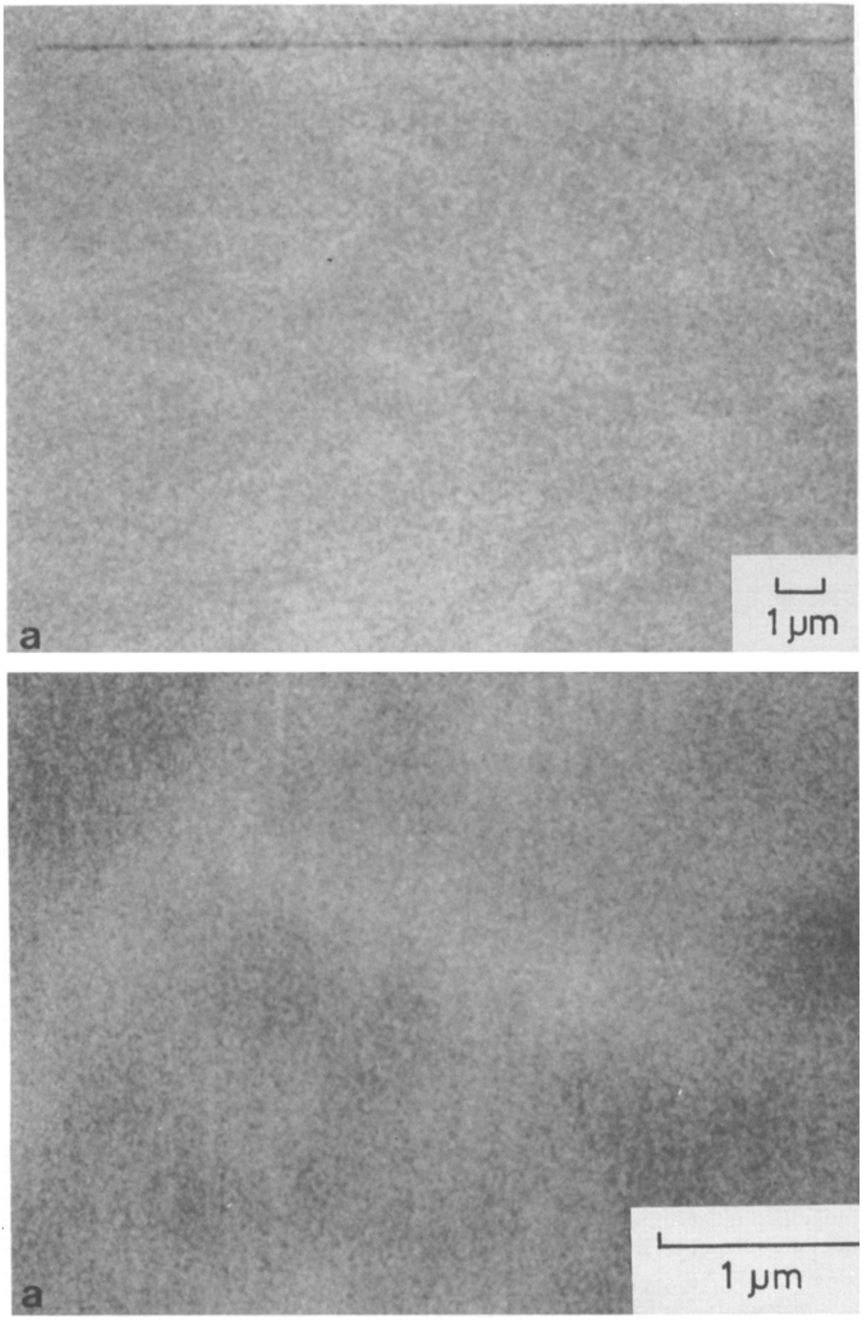


FIG. 6a. Electron micrographs of nontreated LDPE.

Electron Microscopic Analysis of LDPE Surface Exposed to Air Plasma

As shown in Fig. 6a, nontreated LDPE film had a very smooth surface which became rougher as exposure time to air plasma increased (Figs. 6b and 6c). A microdomain structure with about 0.5 μm diameter (Fig. 6c) was observable in the film after plasma treatment for 3 h. This observation shows etching of the amorphous region of a polymer surface.

On the other hand, the surface of γ-irradiated film was still smooth (similar to the nontreated film surface), indicating that γ-rays are not responsible for surface etching.

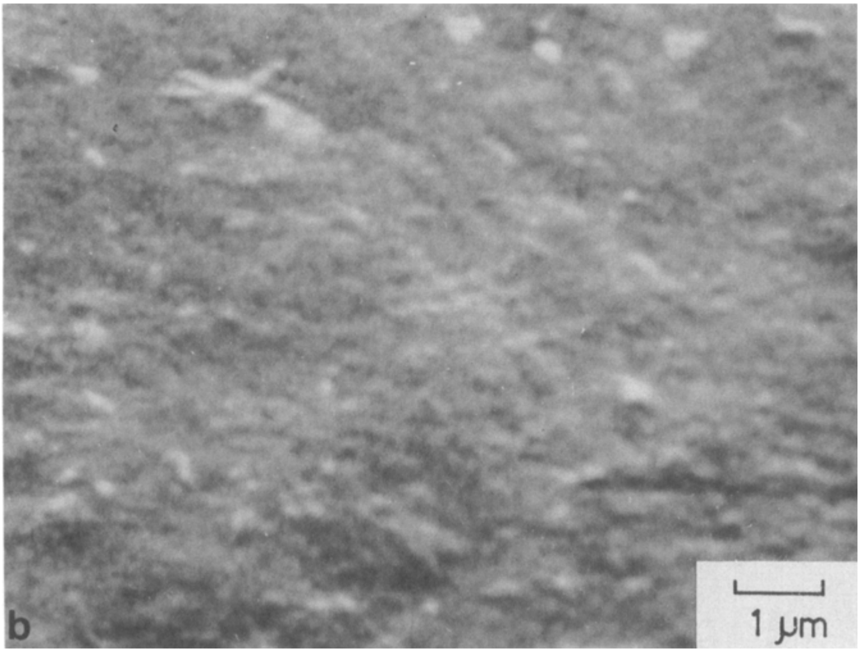


FIG. 6b. Electron micrograph of LDPE exposed to air plasma for 1 h.

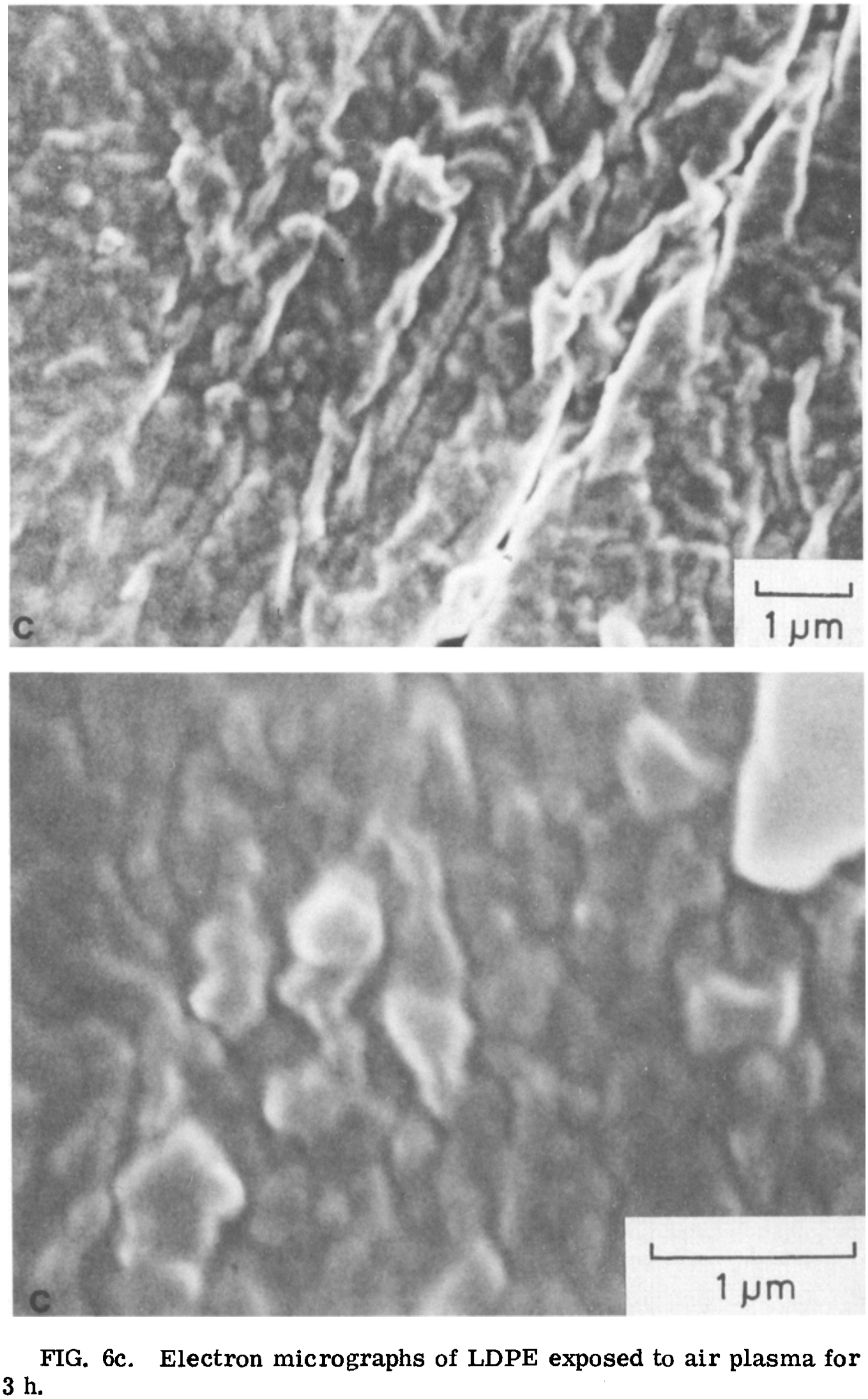


FIG. 6c. Electron micrographs of LDPE exposed to air plasma for 3 h.

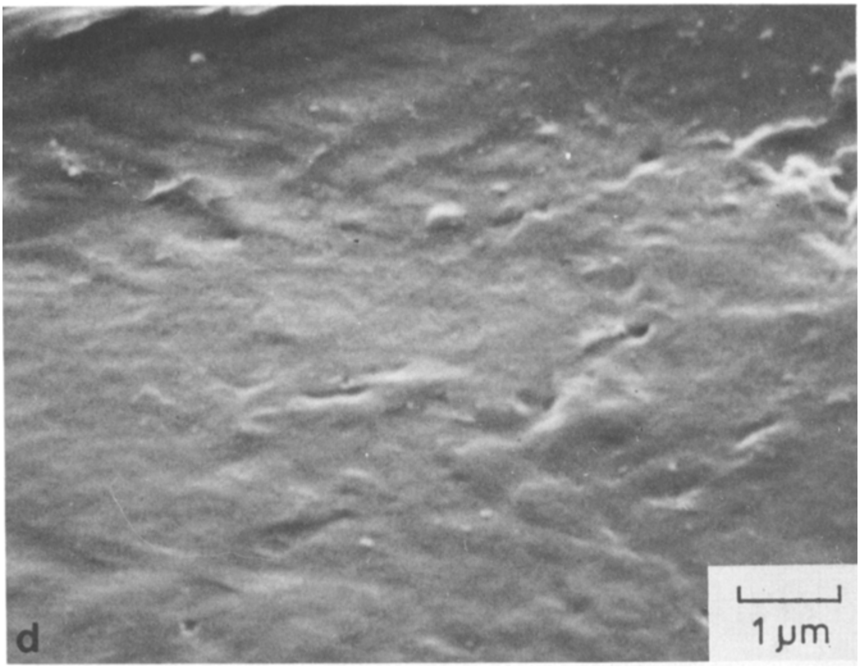


FIG. 6d. Electron micrograph of LDPE γ-irradiated with a total dose of 10 Mrd.

CONCLUSION

We have shown that exposure to air plasma leads to incorporation of O and N atoms on the film surface together with the formation of trans C=C bonds. These plasma reactions occur in the amorphous region of the polymer surface, producing a microdomain structure of about 0.5 μm diameter. γ-Irradiation in air caused incorporation of only O atoms into the LDPE film surface without formation of a microdomain structure.

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