*Macromolecules* 1994, *27*, 2893-2895

# Vacuum-Ultraviolet-Induced Oxidation of Polyethylene

**A. Holländer,**[†] **J. E. Klemberg-Sapieha, and M. R. Wertheimer***

*Groupe des Couches Minces and Department of Engineering Physics, École Polytechnique, Box 6079, Succ. Centre-Ville, Montréal, Quebec H3C 3A7, Canada*

*Received November 12, 1993*
*Revised Manuscript Received February 22, 1994*

## I. Introduction

Low-pressure glow discharge plasmas can be used for the surface treatment of polymers in order to improve their surface properties (adhesion, wettability), essentially without affecting the bulk properties of the material. Though this technology is applied in industry, the processes involved in the interaction of the polymer with the plasma are not yet well understood. Low-pressure plasmas generally comprise a complex mixture of charged particles (electrons and ions) and neutrals (ground- and excited-state molecules, free radicals), but they can also be efficient sources of electromagnetic radiation ranging from soft X-rays to the infrared. Furthermore, the concentration and the energy distribution of all these species can vary locally within a given plasma source.

The treatment of a polymer results in complex changes in the chemical structure of the polymer surface. Because changes occur in a very shallow surface layer (on the order of 10 nm) and owing to their complexity, the analysis of the chemical structures formed during plasma treatment is very difficult. Besides more detailed chemical analysis and plasma diagnostic studies, research in this area calls for the ability to separate effects on a polymer surface when it interacts with the different plasma constituents mentioned above. Short-wavelength (vacuum-ultraviolet, VUV, $\lambda < 200$ nm) radiation is generally believed to be important for the treatment of polymers, though there are only a few investigations reported in the literature on this subject.[1-5] All technically important low-pressure plasmas emit VUV radiation.[6] Organic polymers display a very strong absorption band below 160 nm, with a peak at about 80 nm,[7] originating from the dissociative excitation of the carbon–carbon and carbon–hydrogen $\sigma$-bonds. VUV radiation can evidently initiate reactions in a near-surface layer of the polymer, but the relative yield of these reactions compared to particle-initiated reactions is not known.

In this paper we report our investigations regarding the influence of VUV radiation on polyethylene in an oxygen atmosphere, and we discuss the relative yields of chemical changes initiated by radiation and by active particles from the plasma.

## II. Experimental Methodology

The experimental setup, described in detail elsewhere,[8] comprises a light source and a sample compartment which are separated by a magnesium fluoride window (cutoff wavelength $\lambda_c = 112$ nm). The light source is a microwave (MW; 2.45 GHz) plasma of selected gases or gas mixtures, confined within a quartz tube which traverses a resonant MW cavity. The emission spectra of plasmas used for the irradiation experiments and the corresponding plasma conditions are shown in Figure 1. Prior to the experiment, the sample chamber is pumped to a residual pressure of less than $10^{-4}$ Torr ($10^{-2}$ Pa) and then filled with pure oxygen to 0.1 or 1 Torr (13 or 133 Pa). Following the irradiation, the sample chamber is flooded with oxygen at atmospheric pressure. The surface oxygen concentration [O] is determined by XPS not later than 24 h after the experiment.

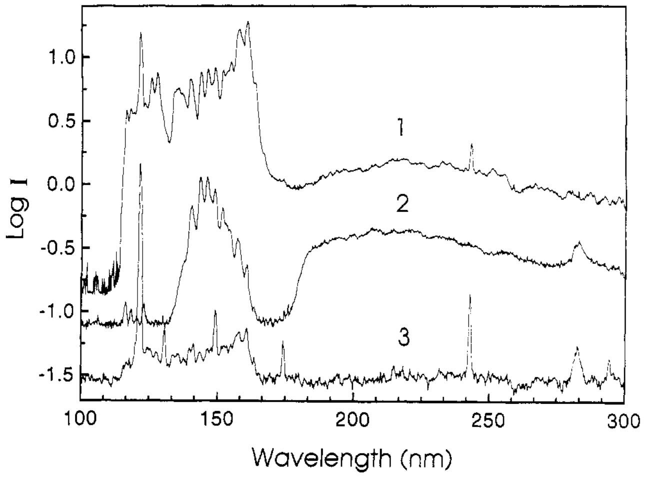

**Figure 1.** Emission spectra of MW plasmas used for PE irradiation: (1) hydrogen (100 sccm; 1 Torr, 500 W); (2) hydrogen–oxygen (10 sccm $O_2$ + 90 sccm $H_2$; 3 Torr, 500 W, spectrum shifted vertically by −0.25); (3) helium–hydrogen (98 sccm He + 2 sccm $H_2$; 1 Torr, 500 W, spectrum shifted vertically by −0.7).

Linear low-density polyethylene (LLDPE), the polymer we report here, was supplied by Dow Chemical Canada, Inc. The plasma gases (hydrogen, helium, and oxygen) were UHP quality (Canadian Liquid Air Ltd.) and were used without further purification. VUV emission spectra were recorded using a 0.2-m VUV/vis spectrophotometer (Model VM 502, Acton Research Corp.) which can be connected to the sample chamber in a line-of-sight configuration with the discharge tube. A VG-ESCALAB 3 MkII surface analytical instrument was used for the XPS measurements.

## III. Results and Discussion

The transmission characteristics of the optical path between the light source and the polymer are determined by the window cutoff $\lambda_c$ and by the absorption of the gas in the sample chamber. Molecular oxygen absorbs between 135 and 170 nm,[9] dissociating into a ground state ($O^3P$) and an excited ($O^1D$) atom.[10] Consequently, radiation of wavelengths $112 \leq \lambda \leq 135$ nm and $\lambda \geq 170$ nm can arrive at the polymer surface essentially unattenuated. By combining knowledge of the plasma emission (Figure 1) and of the transmission characteristics, we are able to carry out three types of experiments:

(i) The helium–hydrogen plasma emits very strong hydrogen Lyman $\alpha$-radiation. It dominates the spectrum, being about 40 times more intense than any other line.[11] Its wavelength, $\lambda = 121$ nm, is well below the oxygen absorption, and it can therefore be used to activate the LLDPE practically without affecting the molecular oxygen in the sample chamber.

(ii) Under certain conditions the emission of the hydrogen–oxygen plasma closely resembles the absorption of molecular oxygen. This VUV emission allows us to produce atomic oxygen in the sample chamber practically without activating the PE sample.

(iii) Finally, the "broad-band" emission of a hydrogen plasma not only produces O atoms, but it also activates the polymer. These conditions are similar to those in a remote, downstream oxygen plasma.

Exposure to any one of the three types of radiation results in the oxidation of LLDPE, but the reaction rates are quite different, as we show below. The evolution of

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* To whom correspondence should be addressed.

[†] Permanent address: Fraunhofer-Institut für Angewandte Polymerforschung, 14153 Teltow, Germany.

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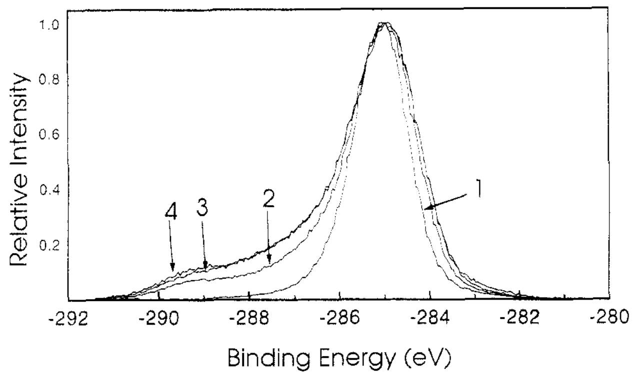

**Figure 2.** XPS C 1s peaks of PE irradiated with the emission of a hydrogen plasma (Figure 1, spectrum 1) for different durations: (1) untreated PE; (2) 20 min; (3) 40 min; (4) 60 min.

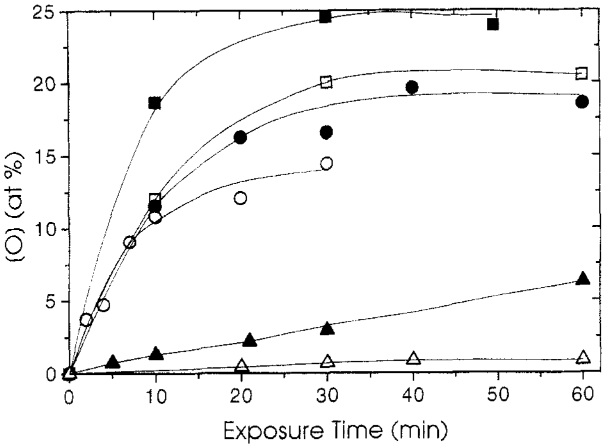

**Figure 3.** Surface oxygen concentration (XPS) as a function of irradiation time for various plasma emission sources and treatment conditions. Full symbols: 0.1 Torr. Open symbols: 1 Torr $O_2$ pressure in the sample chamber. (■,□) Hydrogen plasma; (●,○) helium–hydrogen plasma; (▲,△) hydrogen–oxygen plasma.

the C 1s peak in the X-ray photoelectron spectrum (XPS) following the irradiation with hydrogen plasma emission is shown in Figure 2. The peak shape and the final oxygen concentration are very similar to those observed on samples treated directly in oxygen plasma, but the reaction rate is much lower.

In Figure 3, the surface oxygen concentration determined by XPS is shown as a function of the treatment duration under various irradiation conditions. The rate of oxidation and the maximum oxygen concentration are highest following the experiment with the hydrogen plasma emission. Both quantities are slightly lower when the LLDPE is activated by the Lyman $\alpha$-radiation from the helium–hydrogen plasma, while the emission from a hydrogen–oxygen plasma results in a much lower oxidation. The order of the oxidation rates in these three experiments suggests that the radiative excitation of LLDPE is more important for the oxidation reaction than attack of unactivated polymer by atomic oxygen. This is confirmed by experiments with different oxygen pressures in the sample chamber, where Figure 3 shows the oxidation rate to be lower at the higher $O_2$ pressure for all three types of irradiation: The radiation intensity at the polymer surface in the $O_2$ absorption region is about 10 times higher at 0.1 Torr than at 1 Torr, while the absolute concentration of atomic oxygen is higher at 1 Torr. We conclude that the higher oxidation rate at 0.1 Torr is due to the relatively higher intensity of radiation in the $O_2$ absorption region.

These data are consistent with reports[12-14] that thermal oxygen atoms oxidize polyolefins at a rather slow rate. The reaction is substantially accelerated by simultaneous VUV irradiation, as demonstrated above and in ref 1, or if the oxygen atoms possess a high kinetic energy.[16] However, while these results are reasonable for ground-state $O^3$ P, excited-state $O^1$ D could be expected to be much more reactive.[17] We therefore surmise that $O^1$ D is present only in small concentrations.

Because the products of the VUV action (O functionalities, unsaturation, etc.) absorb radiation at $\lambda > 160$ nm[18] and can therefore be initiation sites for further reactions, the overall oxidation is expected to be autoaccelerating. This has not been observed; however, the overall reaction may well comprise an equilibrium between reactions which incorporate oxygen, on the one hand, and others involving chain scission and desorption of low molecular weight oxidation products, on the other hand. The existence of such an equilibrium is supported by the apparent decrease of the oxidation rate at longer exposure times, independent of the actual oxygen concentration.

## IV. Conclusions

Using different plasma light sources, we have been able to expose LLDPE selectively to VUV radiation or to atomic oxygen, and we can compare the results of these experiments with those of broad-band irradiation, which both activates the LLDPE and also simultaneously produces atomic oxygen. The oxidation rate and the maximum oxygen concentration in the activation experiment is close to the values obtained following the broad-band irradiation, while the attack of the polymer by O atoms results in much slower oxidation. We conclude that O atoms play a relatively minor role in the plasma oxidation of LLDPE, while the formation of radicals at the polymer surface by VUV irradiation seems to be the most important initiation step, capable of leading to a high oxidation rate.

**Acknowledgment.** The authors are grateful to GaSonics International, San José, CA, for providing the VUV monochromator and for useful discussions with Drs. J. T. Davies and E. M. Liston of GaSonics. This work has been supported by grants from the Fonds "Formation de Chercheurs et Aide à la Recherche" of Quebec and by the Natural Sciences and Engineering Research Council of Canada, which also awarded A.H. an International Fellowship.

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