

# Ultraviolet Light Treatment of Thin High-Density Polyethylene Films Monitored with a Quartz Crystal Microbalance

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**ABSTRACT:** Ultraviolet (UV) treatment is an effective method for modification of the surface properties of polymeric materials. In this study, the effects of the ozone-generating UV light treatment of thin high-density polyethylene (HDPE) films were monitored with the quartz crystal microbalance (QCM) technique both in the presence of ozone and without it. The films were further characterized by X-ray photoelectron spectroscopy, optical microscopy, and atomic force microscopy. We found that the ozone not only modified the surface properties of the HDPE films but

also etched away the polymer layer. An average etching rate of 0.48 nm/min was determined. UV light exposure of the polymer film in an argon atmosphere resulted only in minor degradation of the films; the presence of ozone was needed to cause the destruction and loss of material. The QCM technique was a straightforward method for the monitoring of the kinetics of the ablation induced by the UV–ozone treatment process. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2833–2839, 2004

## INTRODUCTION

The surface modification of polymers is used in a variety of applications. Examples include treatments to increase adhesion properties, obtain better printability, remove contaminations, and improve the wettability and biocompatibility of a polymer surface. A wide range of methods have been used to achieve specific surface modifications, (e.g., flame treatment,<sup>1</sup> hot pressing against aluminum foil,<sup>2</sup> corona discharge,<sup>3</sup> ion beams,<sup>4</sup>  $\gamma$  rays,<sup>5</sup> glow discharge,<sup>6</sup> wet chemical treatment<sup>7</sup>). One interesting method is the use of ultraviolet (UV) light,<sup>8–13</sup> which is a simpler process that does not require a vacuum or chemical reagents. In addition, one avoids residual polluting byproducts and tedious posttreatments.

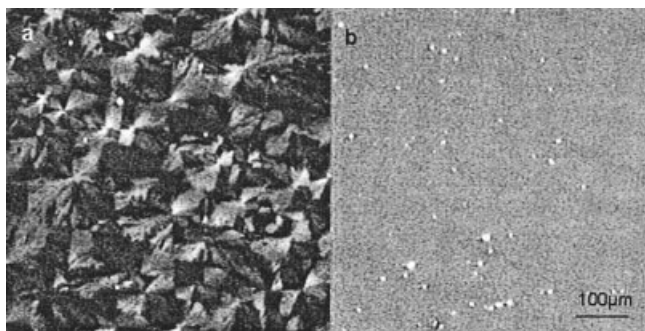
UV light can influence the polymer in at least two distinctly different ways; first, it can directly affect the bonds inside the polymer by local excitations, which introduce photocrosslinking and/or photodegradation. The second mechanism is indirect and occurs through the photochemical formation of a strong oxidant ozone [and some atomic oxygen<sup>3</sup> (AO) and oxy-

gen radicals] in the air outside the polymer. The wavelength threshold for ozone production is 181 nm. The ozone attacks and chemically modifies the top layers of the polymer, which are oxidized and/or etched primarily through the reaction  $O_3 + \text{Polymer} \rightarrow O_2 + \text{Oxidized polymer}$ . The extent of these photoinduced reactions depends on the mobility of the polymer chains, the UV absorption coefficient, the photon penetration depth into the polymer, its glass-transition temperature, and the diffusion coefficients of gases in the polymer film.<sup>14</sup> The wavelength dependence has been addressed by several researchers. For example, Andrady et al.<sup>15</sup> found that polyethylene was mostly activated at wavelengths around 330 nm. However, hydrocarbon polymers are characterized by a very strong absorption below 160 nm,<sup>16</sup> which originates from the dissociative excitation of the C—C and C—H bonds.<sup>17</sup> Torikai<sup>18</sup> claimed that the major photon absorption occurs at  $\gamma = 245$  and 310 nm. The stability of the polymer also depends on polymer density, crystallinity, the processing technique, and the size of the crystallites.<sup>18</sup> Degradation can be mitigated by the addition of antioxidants and light absorbers to the bulk polymer.

When functionalizing polymer surfaces by long-time UV–ozone treatments, we obtained some intriguing results. An experiment with a thin, 70 nm thick, high-density polyethylene (HDPE) film treated with UV–ozone for 115 min in low-pressure (ca. 4 torr)

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**Figure 1** Microscope pictures (polarization contrast imaging) of (a) a pristine HDPE film (70 nm thick) and (b) a UV-ozone modified film. The UV treatment time was carried out in low-pressure (ca. 4 torr) oxygen for 115 min.

oxygen showed a significant difference in morphology before and after the treatment (see Fig. 1). The spherulitic structure that was present in the pristine film had totally disappeared in the modified film. The effect of the UV-ozone modification on the morphology of thicker HDPE films was less severe. To investigate this further, in this study, we used the highly sensitive quartz crystal microbalance (QCM) technique to monitor the kinetics of gasification of HDPE films exposed to UV radiation with and without ozone and characterized the films by X-ray photoelectron spectroscopy (XPS), light microscopy, and atomic force microscopy (AFM).

Two studies have been reported in the literature in which the authors used the QCM technique to study the UV ablation of polymers. One of the studies dealt with the oxidation and ablation of low-density polyethylene and poly(methyl methacrylate) by vacuum ultraviolet (VUV) radiation from low-pressure plasmas.<sup>17</sup> However, only treatment times of 900 s in a low-pressure or vacuum environment were used during these experiments. The major result was that the etch rate for organic materials from reactive plasma particles increased in the following order: AO alone < VUV < VUV and AO. Another study by Lazare and Granier<sup>19</sup> used the QCM technique to measure the etch rate of polymer films [poly(ethylene terephthalate), polycarbonate, and polystyrene] under ablative photodecomposition conditions obtained by absorption of far-UV radiation of an excimer laser. The authors observed two different regimes of ablation. In order of increasing fluence, they first detected a slow ablation of a cold and solid surface and then a rapid ablation of a hot and melted surface. However, the laser pulses were highly energetic, so these results cannot be compared to polymers modified by UV light.

## EXPERIMENTAL

### QCM measurements

The QCM is a technique that is based on the piezoelectric effect.<sup>20</sup> If a mass is added to a QCM crystal

(e.g., a quartz crystal sandwiched between two electrodes), it becomes heavier, and the resonant frequency decreases. If the deposited mass is (1) rigid and (2) evenly distributed over the electrode(s) of the crystal and if (3) the frequency shift ( $\Delta f$ ) is much smaller than the oscillating frequency, there is a simple proportionality between added mass ( $\Delta m$ ) to the crystal and induced  $\Delta f$ . This relationship is described by the Sauerbrey equation:<sup>21</sup>

$$\Delta f = -\xi \Delta m \quad (1)$$

where  $\xi$  is the mass sensitivity factor, depending only on the geometry of the quartz crystal, and  $\Delta m$  is the product  $\rho_f t_f$ , where  $\rho_f$  is the density and  $t_f$  is the thickness of the added film. From the Sauerbrey equation, it is possible to calculate the thickness of a very thin film deposited onto a QCM disc. The sensitivity of the QCM allows mass changes down to 1 pg/cm<sup>2</sup> to be detected under ideal conditions *in vacuo*.<sup>22</sup> In air, the practical resolution is normally lower because of various perturbations, especially temperature fluctuations. In this study, the QCM technique was used to monitor changes in the thickness (mass) of HDPE films under the influence of UV radiation and ozone reactions. A sensitivity of about 5 ng/cm is easy to achieve and good enough for this case.

### Materials, QCM sensors, and set-up

The HDPE films we studied were prepared by hot spin coating. HDPE powder ( $\rho = 0.962$  g/cm<sup>3</sup>, MFR<sub>2</sub> = 12, number-average molecular weight = 25,000 g/mol and weight-average molecular weight = 72,000 g/mol, according to size exclusion chromatography), received from Borealis Stenungsund (Sweden), was dissolved in hot decalin (ca. 150°C; >99%, Sigma Aldrich) at various concentrations (1.5–3.0 wt %) for at least 2 h.

QCM discs (standard QCMD wafers from Maxtek, Inc., Torrance, CA) were cleaned in an 80°C solution of 25% NH<sub>3</sub>, 30% H<sub>2</sub>O<sub>2</sub>, and MilliQ water (1:1:5) for 10 min. They were treated twice with UV-ozone for 10 min, washed with MilliQ water, and blown dry with nitrogen.

Before the polymer solution was applied, all of the necessary equipment (QCM discs, chucks, and pipettes) was preheated to 120–150°C in an oven close to the spin coater. The transfer of the hot substrate, from oven to spin start, took about 10 s. Immediately after the substrate was completely wetted with the polymer solution, the spin coater was started, and it ran for 1 min at 2000 rpm. The spin-coating process and characterization of the films are described in detail elsewhere.<sup>23</sup>

The QCM used was a Q-Sense instrument. The QCM measurements were done with the polymer-

coated quartz crystal mounted in a stainless steel cell ( $6 \times 6$  cm) with a circular hole (diameter = 2 cm) on top, which allowed the UV radiation to illuminate the surface. The UV–ozone treatments were performed in an stainless steel UV chamber built on site and equipped with an ozone-generating mercury grid lamp (main  $\lambda = 254$  nm, ozone producing  $\lambda = 185$  nm, 12–15 mW/cm<sup>2</sup> at a distance of 2.5 cm). The oven was placed in a fume hood and was operated in ambient air. No additional gas flow was supplied, except in some experiments where argon was fed into the oven at a flow rate of 310 sccm. The QCM measurement cell was placed at the bottom of the UV chamber with a distance of about 3.5 cm between the UV lamp and the substrate. The coaxial cable to drive and record the oscillatory motion of the QCM sensor is connected to an oscilloscope, a frequency generator, and a computer through a small hole in the wall of the UV oven. The hole was sealed with aluminum foil.

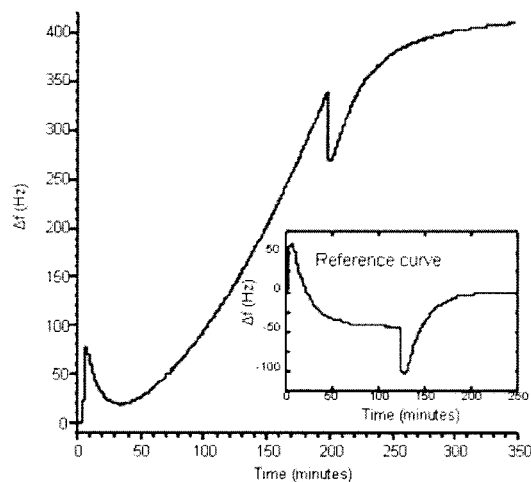
The mass constant used in the Sauerbrey equation<sup>21</sup> in this study was  $\xi = 1.8 \times 10^{-8}$  g cm<sup>-2</sup> Hz<sup>-1</sup>). A measured  $\Delta f$  of 10 Hz corresponded to a polymer thickness change of 1.9 nm (with an assumed constant polymer density of 0.962 g/cm<sup>3</sup>).

### Sample characterization

Some of the HDPE films were characterized by XPS before and after the UV treatment to obtain information about the chemical composition of the polymer. Spectra were recorded with a PerkinElmer PHI 5000C ESCA system. It consisted of an ultrahigh vacuum chamber (base pressure  $< 10^{-8}$  Pa), a monochromatic and a nonmonochromatic X-ray source, a hemispherical electron energy analyzer, a sputter ion gun, an external electron gun, a sample charge neutralizer, and a sample holder. Most of the spectra were recorded with a monochromatic Al K $\alpha$  (1486.6 eV) source without charge neutralization and at a 45° take-off angle. The relative atomic concentrations were calculated by the Physical Electronics software PC-ACCESS ESCA 7.2b with PHI sensitivity factors. Curve fits for the calculation of the relative amounts of different oxygen-containing groups were done by PHI MultiPak Software, version 6.0A.

Optical microscopy was used to study the morphology of the films before and after the UV treatment. The microscope used for the examination of the films was a Zeiss Axiotech 100 HD DIC reflective light microscope with a bright–dark field mode and differential interference contrast. The latter mode allowed polarization contrast imaging that permitted identification of birefringent structures (crystals). Micrographs were recorded by a Sanyo CCD camera attached to the microscope.

The surface microtopography of the films was measured with a Digital Instruments Nanoscope III A



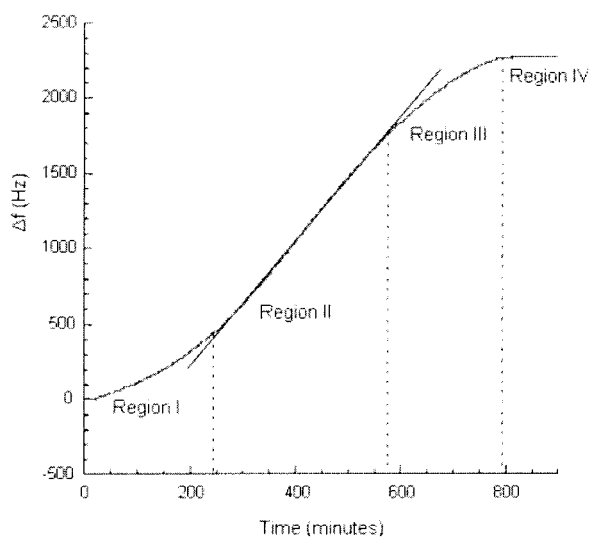
**Figure 2** Control measurement of temperature effects on QCM frequency:  $\Delta f$  versus time of a 360 nm thick HDPE-coated QCM disc treated by UV–ozone. The UV light was turned on at  $t = 4$  min and turned off at  $t = 198$  min. The insert is a QCM graph of  $\Delta f$  versus time of an uncoated QCM disc. The UV light was turned on at  $t = 2$  min and turned off at  $t = 124$  min.

atomic force microscope, with a Dimension 3000 large-sample type G scanner in the tapping mode with a standard silicon tip.

### Reference measurements

To study the influence of radiation heat from the lamp on the  $\Delta f$  in the QCM measurements, control experiments with QCM discs without polymer coatings were performed. The results are shown as an insert in Figure 2. The UV lamp was turned on at time ( $t$ ) = 2 min, and immediately, the frequency increased steeply for about 2 min. The signal then went through a maximum at about 60 Hz before it started to decrease. After 100 min, the frequency reached an equilibrium value at around  $-45$  Hz. The opposite pattern was observed when the UV lamp was turned off.

This behavior was reproducible and was attributed to two combined effects, both due to the temperature rise of the crystal, caused by radiation from the lamp. Temperature measurements in the cell close to the sensor crystal indicated an almost logarithmic temperature rise ( $\Delta T = 21$  K) to a steady state at 53°C after 100 min of UV irradiation. The fast initial rise–decline by about 60 Hz, shown in Figure 2, on heating–cooling was due to these temperature gradients established in the sensor crystal. It is well known<sup>24</sup> that such transient temperature perturbations cause transient frequency responses in QCM crystals. The second effect had a much longer timescale and was due to the inherent temperature coefficient of the AT-cut sensor crystals, which for the actual temperature range was



**Figure 3** Temperature-compensated picture of  $\Delta f$  versus time of a HDPE-coated QCM disc treated by UV-ozone (polymer film thickness = 430 nm). The UV light was turned on at  $t = 0$  min. The data for this curve was obtained by the subtraction of the data from a reference measurement of an uncoated QCM disc from the actual data of a UV-ozone treated polymer film.

typically a few hertz per degree (negative temperature coefficient).

We did not quantify these phenomena because we could calibrate away this temperature effect by treating it as a background; that is, the frequency versus time curve shown in the inset in Figure 2 was subtracted from the measured curve in the measurements with a polymer film on the QCM sensor.

A graph of the QCM measurement during UV-ozone treatment of a 360 nm thick HDPE film is displayed in Figure 2. The first part was similar to the uncoated QCM disc, but after 40 min, another process started to dominate, and the frequency increased as long as the UV lamp was on. The total  $\Delta f$  of 410 Hz corresponded to a thickness loss of about 77 nm, which gave an average etching rate of 0.4 nm/min. After the UV light was turned off, the graph again appeared similar to the one observed for the uncoated crystal as a result of temperature effects. The shifts seen in Figure 2 are referred to as the temperature effect.

Before the UV-ozone treatment, the polymer surfaces were characterized by XPS, AFM, and optical microscopy. The relative atomic composition (excluding hydrogen) was 100% carbon, and the microscope pictures showed spherulitic features in the polarized mode [see Fig. 6(a), shown later]. AFM analysis of the pristine films confirmed the spherulitic structure and measured the surface roughness to  $R_{\text{ms}} = 30$  nm ( $80 \times 80 \mu\text{m}$ ).

## RESULTS AND DISCUSSION

### UV-ozone treatment of the HDPE films

The similarity between the temperature effects for uncoated and coated crystals in the reference measurements shown in Figure 2 allowed us to subtract the temperature effect from the  $\Delta f$  because of the mass change. Such a temperature-compensated graph from the QCM measurement of UV-ozone treatment of a 430 nm thick (as measured by QCM) HDPE film is displayed in Figure 3. The graph was sigmoid shaped with four relatively easily distinguished regions. First, there was a region where the slope of the curve increased with time; then, there was a middle part where  $\Delta f$  was almost linear versus elapsed time; and this was followed by a third region where the slope decreased with time. Finally, a zero-slope region was observed when the polymer film was completely removed.

The form of the first part most likely reflected an increase in the concentration of hydroperoxy radicals in the film caused by UV-induced chain scission, which occurred at the defect sites in the polymer chains. In this region, the rate of mass loss was limited by the rate of radical formation. XPS data (Table I) from this region (treatment time = 100 min) showed that the atomic concentration of oxygen was 14%.

A second possible factor was that the UV-ozone treatment increased the roughness of the surface, thus making a larger surface area available for the reaction. However, the AFM results showed that after 100 min of treatment, the profile was affected little compared to a pristine film.

In the linear part, region II, the oxidation process reached a steady state, and the etching rate was constant. Calculations of the slope gave values of the etching rates, which corresponded to polymer film removal rates of  $0.65 \pm 0.18$  nm/min. The film was now saturated with hydroperoxy radicals, which led to a constant etching rate, which was determined by the ozone partial pressure.

The declining slope of the graph, region III, corresponded to an etching process where the substrate was no longer fully covered by the polymer. This was confirmed by the XPS analysis, where the underlying

**TABLE I**  
Atomic Concentration Percentage as Measured by XPS

Treatment time (min)	Carbon (%)	Oxygen (%)	Gold (%)
0	100	0	0
43	89	11	0
100	86	14	0
360	87	13	0
630	85	13	2
900	39	15	46

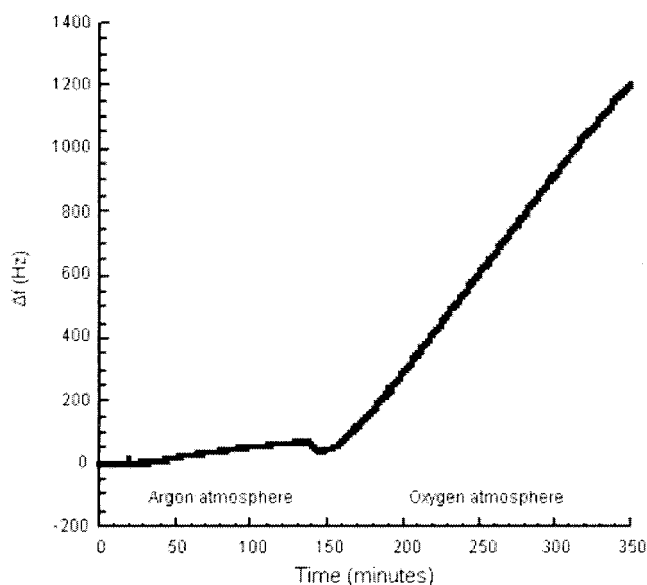
gold electrode could be detected (see Table I). The film displayed more and more pits, and thus, the available surface area decreased, which led to a decrease in etching rate. This fact was verified by optical microscopy, where craters were observed in the polymer film. Moreover, the bottom polymer layers might have been bound more tightly to the substrate and might have been less prone to oxidation, which resulted in a decreased etching rate.

The total observed  $\Delta f$  in Figure 3, 2280 Hz, corresponded to the removal of 427 nm of polymer material, which was close to the initial thickness of the film (430 nm). When the samples were examined under the optical microscope, no residues of the polymer coating were observed. XPS analysis showed a surface composition of about 15% oxygen, 39% carbon, and 46% gold. This amount of carbonaceous species was somewhat larger than for gold surfaces stored in air, possibly because the UV–ozone treatment left some graphite-like residues, which were much less readily oxidized by the UV–ozone treatment. The average etching rate of the total process was  $0.48 \text{ nm/min} \pm 0.11$ . This rate was in gross agreement with UV ablation rates for other types of polymers.<sup>9</sup>

#### UV treatment in a nearly oxygen-free ambient environment

The objective behind the experiments described next was to determine whether the UV light itself or the reactive ozone created by the UV light gave rise to the observed etching of the polymer films. In these experiments, an argon flow was connected to the UV chamber to reduce the amount of oxygen in the experimental chamber. With low levels of oxygen, only a small amount of ozone was created, and consequently, the polymer films were mainly influenced by the UV light. The oxygen deficiency also led to an increase in the UV intensity because of less absorption in the gas phase. A temperature-compensated QCM graph of this type of experiment is shown in Figure 4.

The argon flowed into the oven from the start of the measurement. At  $t = 18 \text{ min}$ , the UV light was turned on and, thereafter, followed a region where the UV light modified the polymer film. From the linear part of the curve in Figure 4, we calculated the etching rate, which was as low as  $0.12 \text{ nm/min}$ . We believe that the observed etching was due to residual oxygen still present in the chamber. The argon gas flow was stopped at  $t = 130 \text{ min}$ . The QCM signal changed as air diffused into the UV chamber and because of the pressure change when the gas flow stopped. From about  $t = 150 \text{ min}$ , a change in the frequency was observed. The frequency increased rapidly and almost linearly until the UV light was turned off. In this region, the sample was subjected to ozone because



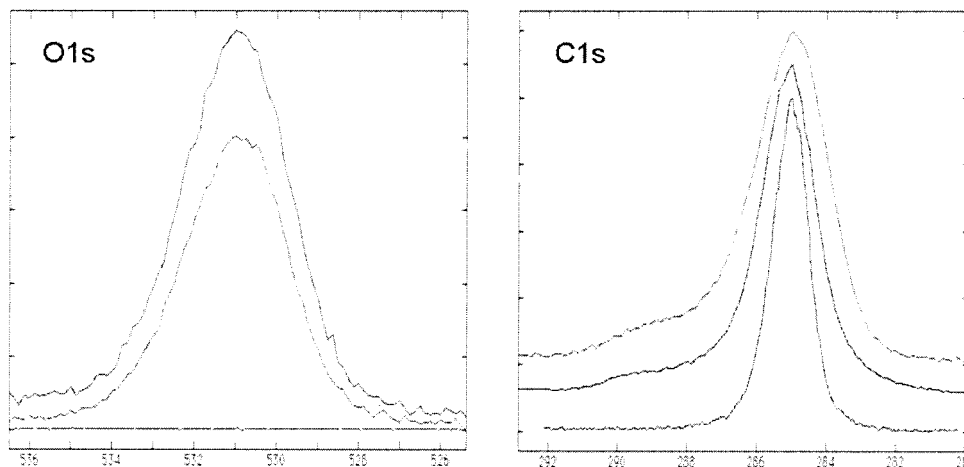
**Figure 4** Temperature-compensated QCM measurement ( $\Delta f$  versus time) of the UV treatment of a 400 nm thick HDPE film first in an argon atmosphere (the first 130 min) and then in ambient air. The UV lamp was turned on at  $t = 18 \text{ min}$  and turned off at  $t = 355 \text{ min}$ .

oxygen from the air was present in the chamber. The etching rate in this part was about  $1.15 \text{ nm/min}$ , notably higher than the rates seen for ozone treatment of samples not subject to UV light pretreatment in an argon atmosphere.

The dramatic change in frequency between the UV light treatments in an argon atmosphere compared to those in air supported the view that the presence of ozone was the main reason for the etching away of the HDPE film. However, some modifications of the polymer film had taken place during the inert UV treatment, most likely chain scission and bond breakage, but the reactive oxygen was needed for the formation of volatile products. This would explain why the etching rate was higher when the UV-illuminated films were subjected to UV light in the presence of air. In this case, the surface of the polymer already consisted of smaller chemical species, which were more easily oxidized and removed from the surface. The absence of an induction period (the linearity of the graph right from the start of the ozone treatment) also verified that the initial part of the destruction process (see region I in Fig. 3) had already taken place during the inert UV treatment.

#### Characterization results

The XPS data showed that pristine HDPE films did not contain any oxygen (see Fig. 5 and Table I). The UV–ozone treatment introduced oxygen species to the polymer, and after 50 min of UV–ozone exposure, the relative atomic concentration of the polymer surface



**Figure 5** High-resolution XPS spectra of the oxygen and carbon peaks for HDPE films treated by UV-ozone for different time periods (0, 360, and 630 min displayed from bottom to top). The graphs were offset in the  $y$  direction for clarity.

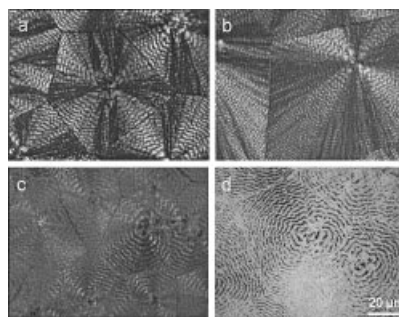
reached a steady state around 13–14%. Although the oxygen content was stable, the amount of different oxygen-containing groups changed, for example, the relative amount of the C—O groups increased with time (see Table II), which is shown as a broadening of the left-hand side of the C1s peak in Figure 5. These results could be compared with other studies where the surface oxidation products of UV-ozone treated polyethylene were, according to several XPS studies, mainly carboxyl, carbonyl, and ether groups at fully oxidized surfaces.<sup>11,12</sup> Hoekstra et al. found that after long treatment times (up to 30 days) in a climate chamber, the rate at which carbonyl groups were formed accelerated with exposure time.<sup>13</sup>

A sequence of optical microscope pictures (Fig. 6) shows the change in appearance of the polymer film occurring from the UV-ozone treatment. The pictures correspond to a pristine film and samples subjected to different treatment times (regions I–III, as seen in Fig. 3), respectively. The sharp spherulite boundaries, as seen in the pristine film, disappeared more and more with treatment time. This observation was confirmed by AFM measurements (Fig. 7), where the large scale profile of the films flattened out with treatment time.

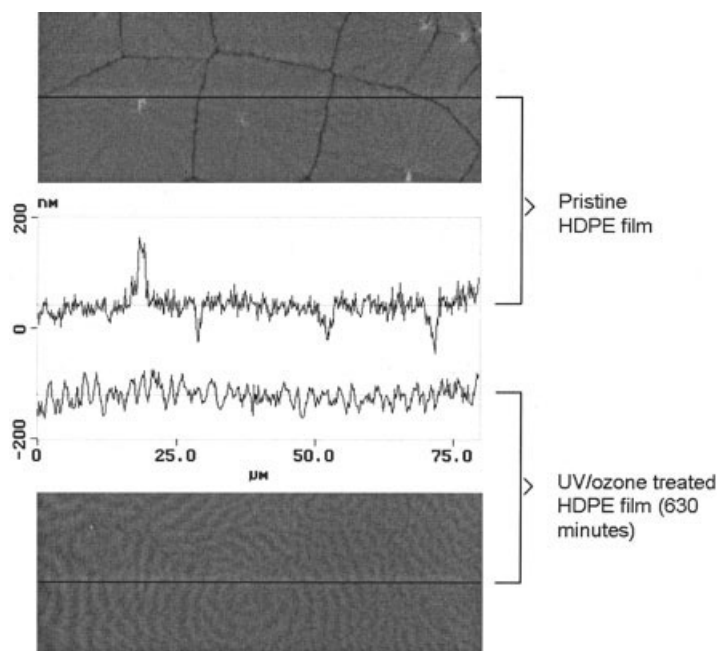
**TABLE II**  
Quantification (%) of the Different Components of the Carbon 1s Peak

Treatment time (min)	C—C 285.0 eV	C—O 286.5 eV	C=O 288.0 eV	O—C=O 289.5 eV
0	100	0	0	0
43	87	5	7	1
100	87	6	4	3
360	86	6	6	2
630	81	10	6	3
900	84	1	14	1

Surface roughness values (Rms  $80 \times 80 \mu\text{m}$ ) of 18 nm were recorded after 630 min of UV treatment compared to 30 nm for a pristine film. The valleys at the boundaries of the spherulites were about 50 nm deep, whereas the middle of the spherulites rose to around 100 nm above the average pristine film surface. However, no major topographic features were observed with AFM after 630 min of UV-ozone treatment. However, as seen in Figure 6, the banding of the spherulites stayed intact until the film was more or less completely removed. The banding occurred from the twisting of lamellae in the crystalline structure where the darker parts corresponded to lamellae oriented edge-on. These lamellae seemed harder to etch away. The banding was also observed as undulations in the AFM profiles. A crater was seen in the last optical microscope picture [Fig. 6(d)] where the UV treatment etched a hole in the polymer.



**Figure 6** Light microscope pictures (polarization contrast imaging) of UV-treated HDPE films. The picture sequence shows how the appearance of the polymer film was changed by the UV ozone treatment: (a) a pristine film and films treated for (b) 100, (c) 360, and (d) 630 min. Note the lack of contrast in part (d) because of a substantial loss of polymer material.



**Figure 7** AFM roughness analysis. The top AFM picture shows a pristine HDPE film with spherulites with sharp boundaries, and the bottom picture shows a HDPE film that was treated with UV–ozone for 630 min. The boundaries disappeared, but the banding is clearly visible. In the middle are the respective roughness profiles of the films.

## CONCLUSIONS

In this study, the influence of UV treatment of thin HDPE films was monitored in real time by the QCM technique. From this investigation, we concluded that

- The QCM technique was a straightforward and sensitive method for monitoring the kinetics of the etching process.
- The maximum etching rate of the HDPE films was  $0.65 \pm 0.18$  nm/min after an initial period of about 200 min where slower oxidation occurred. The average etching rate of the HDPE films was  $0.48 \pm 0.11$  nm/min.
- UV light in the absence of oxygen broke bonds and cut polymer chains but was not reactive enough to remove any mass from the film. Ozone was needed to cause severe damage and a loss of material.
- The QCM technique could be a useful additional tool to already existing techniques for testing the UV protection of polymers.

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