

Ultralow Energy Ion Beam Surface Modification of Low Density Polyethylene

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Received: August 23, 2005; In Final Form: October 24, 2005

Ultralow energy Ar⁺ and O⁺ ion beam irradiation of low density polyethylene has been carried out under controlled dose and monoenergetic conditions. XPS of Ar⁺-treated surfaces exposed to ambient atmosphere show that the bombardment of 50 eV Ar⁺ ions at a total dose of 10¹⁶ cm⁻² gives rise to very reactive surfaces with oxygen incorporation at about 50% of the species present in the upper surface layer. Using pure O⁺ beam irradiation, comparatively low O incorporation is achieved without exposure to atmosphere (~13% O in the upper surface). However, if the surface is activated by Ar⁺ pretreatment, then large oxygen contents can be achieved under subsequent O⁺ irradiation (up to 48% O). The results show that for very low energy (20 eV) oxygen ions there is a dose threshold of about 5 × 10¹⁵ cm⁻² before surface oxygen incorporation is observed. It appears that, for both Ar⁺ and O⁺ ions in this regime, the degree of surface modification is only very weakly dependent on the ion energy. The results suggest that in the nonequilibrium plasma treatment of polymers, where the ion flux is typically 10¹⁸ m⁻² s⁻¹, low energy ions (<50 eV) may be responsible for surface chemical modification.

1. Introduction

Treating polymeric materials with nonequilibrium plasmas can affect the surface properties in a number of beneficial ways, for instance, by enhancing wettability, printability, adhesion, and biocompatibility, etc.^{1–4} The compatibility of both vacuum and atmospheric nonequilibrium plasma reactors with the scale and throughput requirements of industrial processing has led to increasing interest in their use for modifying such surfaces.² Despite the burgeoning literature on plasma treatment,³ there is little agreement on the relative importance of the different mechanisms involved in the plasma–polymer surface interaction. For instance, the relative role of ions (Ar⁺, O⁺, O₂⁺, etc.) and VUV photons in plasma treatment has been “hotly” debated. Some studies in which treatment was carried out under VUV irradiation only^{4–6} showed that the VUV had a significant effect in the formation of surface free radicals, and it has been argued that this effect was comparable to that from plasma treatment.⁷ Indeed it is argued that the VUV component has a key, if not dominating, effect on modification in many plasma treatments.⁸ However, a lack of knowledge of the absolute power densities of the components in plasma (the ions, neutrals, excited species, radicals, and photons) and in VUV treatment hinders true comparison of their individual effect. Despite this, the energy flux of both the ionic and VUV fluxes arriving at a substrate in an RF barrel reactor at low-pressure⁹ has been determined, but

their individual roles in the creation of free-radical sites in the surface treatment could not be determined.

There have been attempts to model the ionic component in a plasma using ion beams with prescribed energy. These techniques have the advantage of removing the VUV component. In most reported ion beam work; however, ion energies are usually rather high, e.g., N⁺ ions of >100 eV in ref 10, and Ar⁺ ions in the range 0.5–5 keV.^{11,12} This is in contrast to ion and electron energies in nonequilibrium plasmas that are typically in the 1 to 100 eV range.¹³ However, by extracting ions from a plasma, Groning et al.¹⁴ used low-energy ion beams at energies <10 eV (together with separate VUV lamp irradiation) to the chemical modification of poly(methyl methacrylate) (PMMA). They concluded that low energy ion–surface interactions are significant if not key in the modification process. In another study,¹⁵ O⁺ ion beams from a specially developed beam source were used down to 100 eV to bombard polyimide films, and this work showed that O incorporation takes place at low energy. However, for energies 1.5 keV and above, O levels were found to decrease due to sputtering.

In this paper, we use ultralow energy ion beams of well-defined energy and flux to treat polyethylene surfaces in vacuum and relate the level of surface modification (i.e., oxygen incorporation during ion beam exposure and post-exposure to atmosphere) to the dose (and energy). Since we have chosen energies and doses consistent with those encountered in non-equilibrium plasma treatment, the results provide evidence on the importance of ion bombardment in such plasma processes.

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TABLE 1: XPS Spectral Data from the Fitting of the C (1s) for Samples 1, 2, and 3 Together with the Ion Beam Conditions

sample	condition	C (1s) fitted data Atomic % C				Atomic % O
		CH _n	C–O	C=O/O–C–O	O–C=O	O
1	virgin LDPE	93.2	6.8	0	0	3
1a	10 ¹⁶ 50 eV Ar ⁺	78.1	17.3	3.5	1.2	8
1b	1a overnight in lab	69.0	19.1	8.3	3.6	51
2	virgin LDPE	95.9	4.1	0	0	3
2a	10 ¹⁶ 50 eV Ar ⁺	82.2	15.0	2.6	0.2	9
2b	2a plus 10 ¹⁶ 20 eV O ⁺	66.4	22.2	6.6	4.8	48
3	virgin LDPE	94.3	5.7	0	0	3
3a	10 ¹⁶ 20 eV O ⁺	74.9	18.2	4.9	2.0	13

2. Experimental Methods

The low density polyethylene (LDPE) surfaces were irradiated in the Salford ultralow energy ion beam system, which is capable of delivering precise doses of mass selected and charge selected monoenergetic ions with energies down to 10 eV in an ultrahigh vacuum (UHV) environment. Details of the system have been published elsewhere.¹⁶ Briefly, the system is equipped with twin, universal Bernas-type ion sources. Efficient transport of ion beams at low energies, e.g., less than 2 keV, is obtained through the use of an acceleration–deceleration technique in which the ions extracted from the source are transported at high energy, i.e., 10 or 15 keV, and are decelerated in a UHV environment just in front of the target, which itself is at earth potential. During transport the ion beam passes in sequence through two magnets, in the first of which the ion beam is mass analyzed while in the second any neutral component in the beam is filtered out. Any neutral component remaining in the beam, which would not undergo retardation in the subsequent deceleration stage, is estimated to be less than 0.01% of the ion beam current. The UHV implant chamber is equipped with an X-ray photoelectron spectrometer (XPS) system (VG CLAM 200) to enable surface chemical changes to be studied and to assess changes in the chemical bonding of surface atoms due to irradiation with different ion species (e.g., Ar⁺ or O⁺ ions), without breaking vacuum. The availability of in-situ XPS is important since atmospheric exposure following plasma treatment is expected to mask some of the immediate ion bombardment effects. Such post-exposure reactions are well known in the plasma treatment of polymers.¹⁷

In this study, the ion beam system is used specifically in an attempt to model the ionic surface interactions present in low-pressure nonequilibrium plasma polymer treatment, with the advantage that the role of ions can be isolated from other species (VUV photons, metastables, etc) present in plasmas.

Five additive-free LDPE sample film sections of 0.05 mm thickness (supplied by Goodfellow, Cambridge Ltd.), were cut to a size of approximately 1 cm² and then surface cleaned with 2-propanol prior to insertion into the UHV chamber. These samples remained in high vacuum for approximately 20 min prior to ion beam exposure with low energy ions in UHV at the following energies and dose levels: (1) 50 eV Ar⁺ at 10¹⁶ cm^{−2}, (2) 50 eV Ar⁺ at 10¹⁶ cm^{−2} followed by 20 eV O⁺ at 10¹⁶ cm^{−2}, (3) 20 eV O⁺ at 10¹⁶ cm^{−2}, (4) 20 eV Ar⁺ at 10¹⁶ cm^{−2} followed by 20 eV O⁺ at 10¹⁶ cm^{−2} (O⁺ in 2 stages), (5) 50 eV O⁺ at 10¹⁴–10¹⁶ cm^{−2} in steps of increasing dose levels to represent different exposure conditions that might be experienced in nonequilibrium plasma surface treatments.

The dose parameter represents the total number of ions falling on the samples per cm². These doses were chosen to be consistent with doses received in typical plasma treatment scenarios, where the ion flux is approximately 10¹⁴ cm^{−2} s^{−1} (ref 13) and is applied for typically just a few 10s of seconds up to about 100 seconds, in order to obtain saturation of the

TABLE 2: XPS Data for O Incorporation Together with the Ion Beam Conditions for Sample 4

conditions	step dose/ions	total dose/ions	atomic % O	O/C
20 eV Ar ⁺		1.0 × 10 ¹⁶	6.6	0.07
20 eV Ar ⁺ + 20 eV O ⁺	4.2 × 10 ¹⁵	1.42 × 10 ¹⁶	19.2	0.24
20 eV Ar ⁺ + 20 eV O ⁺	5.8 × 10 ¹⁵	2.0 × 10 ¹⁶	23.3	0.30

number of free radical sites;¹⁸ this corresponds to a dose of approximately 10¹⁶ cm^{−2} in ion beam exposure. Hence the modification observed here is directly comparable to that achieved in low-pressure plasma treatment.

Each LDPE sample was mounted on a silicon wafer after being cleaned with 2-propanol in an ultrasonic bath for about 15 s. Before and after each irradiation stage, in-situ XPS spectra were taken. In addition, XPS spectra were recorded on samples 1 and 2 that had been exposed to air overnight, and twice on sample 4 before treatment to investigate the degree of damage caused by XPS analysis. Using an AlK α X-ray source, spectra were recorded from 1200 to 0 eV (using 1 eV steps, 1 co-add; wide scan), and for the C (1s) and O (1s) regions of 270–300 eV and 520–550 eV, respectively, (using 0.1 eV steps, 5 co-adds). Similarly the Ar (1s) region around 242 eV was scanned, although in no case was Ar observed. Stoichiometry ratios (C:O) were calculated from the sum of the signal intensity of the high-resolution spectra with corrections for the instrument sensitivity factors. In addition, the C (1s) envelope was resolved into a series of Gaussian peaks using a computer-based peak fitting routine. Peak assignments were made to the following carbon functionalities: CH_n (285.0 eV), C–O (~286.5 eV), C=O/O–C–O (~288.0 eV), and O–C=O (~289.5 eV).¹⁹ It is noteworthy that two XPS analyses on a virgin LDPE sample over time periods commensurate with the spectral acquisition time scales indicated that the X-rays used in the XPS analysis were not causing appreciable damage to the surface, hence X-ray effects have been ignored in this study.

3. Results

The C(1s) spectrum of all of the virgin LDPE samples contained a single peak at 285 eV, as expected, indicating the presence of CH_n. A small amount of oxygen was also present, typically 3%, indicating some surface oxidation was already present in the materials as would be expected of additive free LDPE. The details of the XPS analysis for the five samples, under different bombardment conditions, ion type, dose, and energy are shown in Tables 1 and 2. A typical C(1s) peak with its Gaussian deconvoluted components is shown in Figure 1 for sample 3; this form of peak is found in all cases where oxygen has interacted with the surface. In general, the O(1s) peak appears as a singlet Gaussian with a width-at-half-height of typically 2.4 eV; this may be deconvoluted to reveal two components centered on 531.5 and 532.8 eV with a width of typically 1.8 eV, corresponding to the C–O and C=O species.

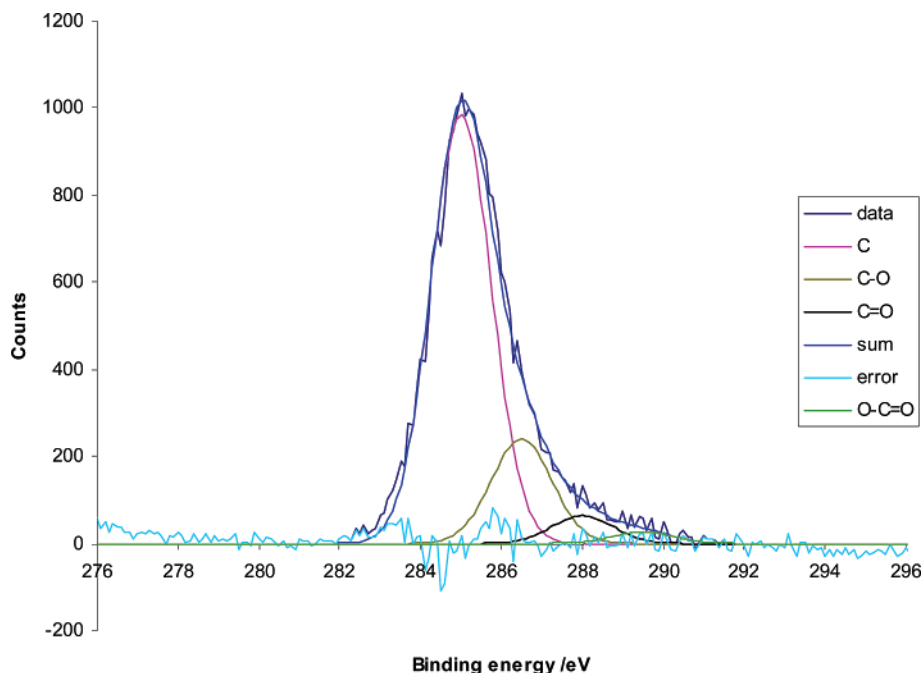


Figure 1. Original XPS C(1s) peak and its Gaussian deconvoluted components and error of fit for sample 3.

TABLE 3: XPS and Ion Beam Conditions for Incremental Irradiation with O^+ Beams for Sample 5 (the sample was not exposed to air after each treatment stage)

sample	condition (total dose after each step and ion energy)	C (1s) fitted data atomic % C				atomic % O
		CH_n	C-O	C=O/O-C-O	O-C=O	O
5	virgin LDPE	93.3	6.7	0	0	3
5a	1.2×10^{14} 50 eV O^+	93.5	6.5	0	0	5
5b	2.1×10^{14} 50 eV O^+	94.0	6.0	0	0	2
5c	6.8×10^{14} 50 eV O^+	94.2	5.8	0	0	4
5d	3.3×10^{15} 50 eV O^+	95.1	4.2	0.7	0	3
5e	7.4×10^{15} 50 eV O^+					10
5f	1.1×10^{16} 50 eV O^+	86.7	11.9	1.4	0	6

Typical irradiation times ranged from 10 to 30 min, depending on the required dose. After Ar^+ ion beam bombardment (samples 1 and 2), the hydrocarbon CH_n peak had broadened and a reduction in intensity was noted, see Table 1. This broadening and accompanying drop in intensity is probably due to the presence of carbon radicals. Under vacuum conditions after Ar^+ irradiation, a slight increase in the amount of surface oxygen was noted ($O \sim 8\%$), which we associate with the reaction of residual oxygen in the chamber and from the polyethylene. However, once sample 1 was removed and aged overnight in the lab, large amounts of oxygen were incorporated into the sample surface, with $O \sim 51\%$. This supports the idea/hypothesis that active radical sites are readily created by Ar^+ ion beam bombardment, and these then react with oxygen in the air to form surface oxygen functionalities.

In the case of sample 2, oxygen was incorporated onto the surface of the LDPE by treating the activated surface with 20 eV O^+ ions after Ar^+ bombardment. The percentage of oxygen in the upper surface was observed to be about 48%. However if no Ar^+ pretreatment is carried out, oxygen incorporation in the film due to O^+ irradiation is much smaller. This is demonstrated by sample 3, which was virgin LDPE treated with 20 eV O^+ ions only, i.e., without prior surface activation with Ar^+ ions. The results show that surface oxygen incorporation is significantly lower (13% O) than for sample 2, as shown in Table 1. The data for samples 2 and 3 indicate that the LDPE surface requires activating if larger amounts of O^+ ions at 20 eV energy are to be incorporated. It also suggests that the low

energy oxygen alone may not be energetic enough to activate the surface (and then react), in contrast to 50 eV Ar^+ ions.

Sample 4 was activated with an Ar^+ ion beam of 20 eV energy and analyzed in-situ by XPS without breaking vacuum conditions. At these reduced energies there was a similar level of oxygen (7%) in the film to that observed when samples were irradiated with 50 eV beams at the same dose (i.e., 9% as seen with samples 1 and 2). The observed broadening of the C(1s) envelope indicated probable radical formation. The sample was then treated with 20 eV O^+ ions at a dose of $4.2 \times 10^{15} \text{ cm}^{-2}$ and the oxygen incorporation was observed to be about 19%; this increased to 23% on further irradiation up to a total O^+ ion dose of 10^{16} cm^{-2} . The significance of this result is that it indicates that in this dose range incremental surface change is occurring on increasing dose. To investigate this further, another LDPE sample was treated sequentially with doses of 10^{14} to 10^{16} cm^{-2} of 50 eV O^+ ions. The XPS data from each stage of this analysis is presented in Table 3.

At very low doses, effectively no oxygen is incorporated onto the LDPE surface. It is not until the dose approaches 5×10^{15} to 10^{16} cm^{-2} that noticeable amounts of surface oxygen are seen. The findings also suggest that if the energy of the oxygen ions is very low (i.e., below 50 eV), then they do not have the ability to react with the LDPE in large quantities unless the surface has been previously activated (i.e., with Ar^+ ions). As the dose increases, the chances of an O^+ ion impinging on a region already activated by an earlier O^+ ion increases. This is highlighted in Figure 2 where the data for the O^+ treated LDPE

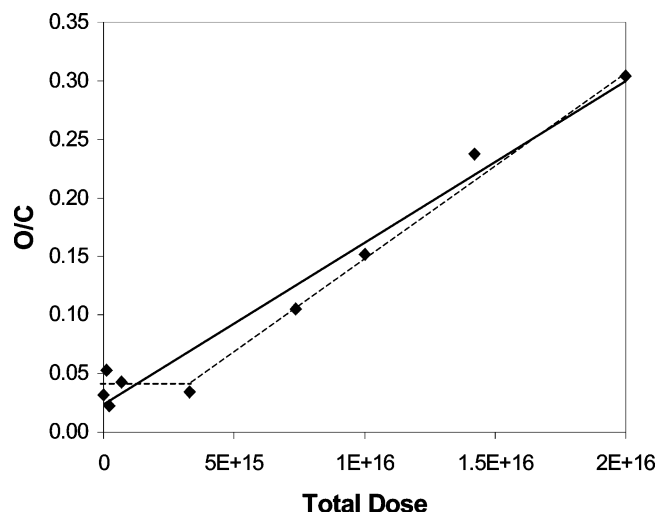


Figure 2. Variation of the O/C ratio with O^+ dose for ion beam irradiation of LDPE. The O^+ energies used were 20 and 50 eV. Full line is the linear regression of all data points, and the dotted line that for a threshold effect with linear regression for data points above the threshold.

samples from Tables 1, 2, and 3 have been combined. Figure 1 shows two plots for the data obtained — the full line is a linear regression of all of the points and the dotted line illustrates the strong linear correlation between dose and O/C ratio with a surface activation dose threshold of about $5 \times 10^{15} \text{ cm}^{-2}$ for O^+ ions.

4. Conclusions

Using an ultralow energy ion beam system, Ar^+ and O^+ ions have been delivered at controlled doses and energies to an LDPE polymeric sample under vacuum conditions. XPS analysis of treated samples exposed to atmosphere has shown clearly that the surface can be made very reactive (radical sites generated) by treatment with 50 eV Ar^+ ions. The levels of treatment, ($> 25\%$ O/C ratio in the upper 5 nm surface) are similar to that observed in nonequilibrium plasma treatment for equivalent doses (i.e., 10^{16} ions per 1 cm^2 sample). Furthermore, if this activated surface is then exposed to low energy oxygen ions, greatly enhanced surface oxygenation is observed (48% O). However, for the treatment of the surface with 20 eV O^+ ions

only, there is little more incorporation of O than from Ar^+ with the take-up of ambient oxygen. It also appears that for O^+ ions there is a dose threshold of about $5 \times 10^{15} \text{ cm}^{-2}$ before O incorporation takes place. For both Ar^+ and O^+ ion beams in this regime, the degree of surface modification is only weakly dependent on ion energy. The results from this study indicate strongly that in low-pressure nonequilibrium plasma treatment of polymers, low-energy plasma ions ($< 50 \text{ eV}$) may be responsible for surface chemical modification as observed in polymer surfaces undergoing typical plasma treatment times.

Acknowledgment. The authors thank the UK EPSRC for funding this work.

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