A comparison of plasma-oxidized and photo-oxidized polystyrene surfaces

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High-resolution core-level and valence-band X-ray photoelectron spectroscopic measurements show that polystyrene surfaces become more heavily oxidized during ultraviolet photo-oxidation than under plasma oxidation. A greater proportion of $-\underline{C}O_2-$ linkages are evident following the former treatment, along with the virtual absence of any phenyl features in the valence region and an attenuated π–π^* shake-up satellite in the C(1s) spectra. This apparent paradox of the more reactive medium producing a less oxidized surface is explained in terms of the complex plasma–surface interactions associated with the exposure of a polymer surface to an oxygen glow discharge.

(Keywords: polystyrene; ultraviolet oxidation; plasma oxidation; valence band; surfaces)

INTRODUCTION

Oxidation of polymer surfaces can be used to enhance their susceptibility towards adhesion and wettability[1,2]. Although the extent and stability of such treatments have been widely studied, the precise mechanistic details remain a much debated issue[3,4]. The purpose of this study is to pinpoint the subtle differences in oxidative chemistry between photo-oxidized polystyrene surfaces and their plasma-oxidized counterparts. For a valid comparison, the experimental parameters have been optimized such that the greatest degree of oxidation is obtained for each treatment[5,6]. This is an important aspect in terms of understanding the activation of polystyrene surfaces for adhesion purposes, since it is not clear to potential end-users whether these treatments are synonymous, or if they impart different functionalities to the surface. Up till now, this choice has been commonly based on empirical rationale.

The chemical nature of modified polystyrene surfaces has been evaluated by core-level and valence-band X-ray photoelectron spectroscopies (x.p.s.). These techniques are widely recognized as being complementary tools for the analysis of polymer surfaces[7]. The former is routinely used for locating highly electronegative/positive heteroatoms within a polymeric structure[8]; however, it is incapable of distinguishing between different types of hydrocarbon segments belonging to a specific polymeric backbone. In this context, the x.p.s. valence-band region can usually provide a much better description[7]. Most polymers possess a unique set of molecular orbitals, and therefore they will exhibit their own characteristic valence-band spectra.

EXPERIMENTAL

Polystyrene (ICI) film was cleaned in an ultrasonic bath with isopropyl alcohol and subsequently dried in air. Research-grade-quality oxygen (BOC) was used without any further purification.

Plasma oxidation was carried out in a cylindrical glass reactor, which was inductively coupled to a 13.56 MHz r.f. generator via an externally wound copper coil[9]. A strip of polymer was located in the glow region (i.e. in the centre of the coil). The reaction vessel was initially evacuated by a two-stage rotary pump to a base pressure of better than 4×10^{-3} Torr. Then oxygen was passed through the chamber at a pressure of 0.2 Torr for 10 min. Subsequently the plasma was ignited and left running for 5 min (longer periods resulted in no further changes at the polymer surface, as measured by x.p.s.).

A glass reactor with a quartz port (cut-off wavelength 180–200 nm) was used for the photo-oxidation experiments. The u.v. source was an Oriel 200 W low-pressure Hg–Xe arc lamp operating at 100 W. This gave a strong line spectrum in the 240–600 nm region. Polystyrene film was positioned facing the quartz window, and a high flow of oxygen was passed through the reactor at atmospheric pressure. This was maintained before, during and after u.v. exposure. The limiting O(1s):C(1s) ratio was achieved after 80 min of u.v. irradiation.

High-resolution core-level and valence-region spectra were taken on a Kratos AXIS HS instrument. This state-of-the-art instrument was equipped with a monochromatic Al K_α (1486.6 eV) X-ray source and a novel magnetic immersion lens system—giving high resolution and high sensitivity. The X-ray power was limited to ~240 W (14 kV, 17 mA) to limit radiation damage. Uniform charge neutralization with little energy shift was

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effected with a low-energy electron source. These measurements were taken with the surface normal of the sample being aligned with the axis of the electron spectrometer. All binding energies are referenced to the hydrocarbon component $(-\underline{C}_xH_y-)$ at 285.0 eV[10], and the instrumentally determined sensitivity factors are such that, for unit stoichiometry, the C(1s):O(1s) intensity ratio is ~0.36.

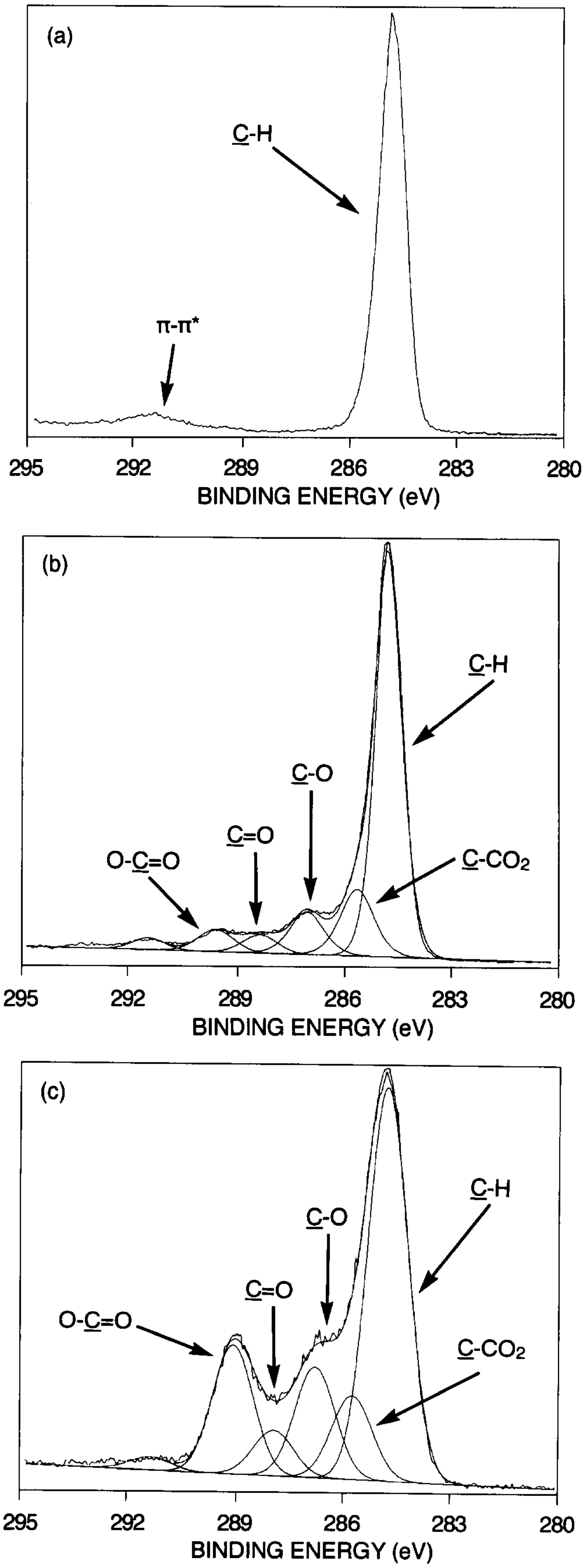

Figure 1 X.p.s. C(1s) region of (a) clean polystyrene, (b) 1 W plasma-oxidized polystyrene and (c) photo-oxidized polystyrene

RESULTS

Figures 1a and *2a* show the x.p.s. C(1s) core-level and valence-band spectra of clean polystyrene, respectively. The major feature in the C(1s) core-level region is the hydrocarbon component at 285.0 eV; an additional satellite structure at ~291.6 eV is also apparent, which arises from low-energy π–π^* shake-up transitions accompanying core-level ionization[3]. The alkyl backbone in polystyrene makes only a minor contribution to the x.p.s. valence-band region, since the density of states for these levels spans a rather broad structure, and the number of such levels is much lower in comparison to those associated with the phenyl groups. As a result, the sharp features of the benzene spectrum predominate[11,12].

Polystyrene readily undergoes oxidation, and this reactivity may be attributed to the fact that this polymer contains phenyl centres; for instance, these aromatic rings can act as chromophores leading to photo-oxidation[13]. Detailed chemical information about the modified polymer surfaces was obtained by fitting the C(1s) x.p.s. spectra to a range of carbon functionalities (*Figure 1b*): carbon adjacent to a carboxylate group ($\underline{C}$–CO_2 ~ 285.7 eV), carbon singly bonded to one oxygen atom ($\underline{C}$–O ~ 286.6 eV), carbon singly bonded to two oxygen atoms or carbon doubly bonded to one oxygen atom (O–$\underline{C}$–O or $\underline{C}$=O ~ 287.9 eV), carboxylate groups (O–$\underline{C}$=O ~ 289.0 eV) and carbonate carbons (O–$\underline{C}$O–O ~ 290.4 eV)[14]. Loss of aromaticity at the polystyrene surface could be monitored by the attenuation in intensity of the π–π^* shake-up satellite. On comparing the C(1s) spectra of photo-oxidized and plasma-oxidized polystyrene, it is evident that the

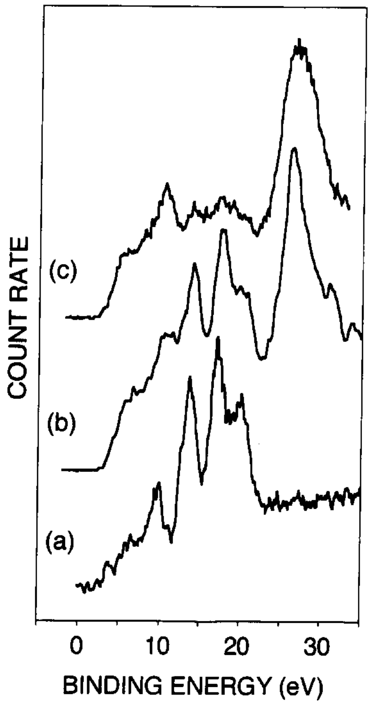

Figure 2 X.p.s. valence-band spectra of (a) clean polystyrene, (b) 1 W plasma-oxidized polystyrene and (c) photo-oxidized polystyrene

former treatment leaves a much greater proportion of $-\underline{C}O_2-$ functionalities at the surface. Furthermore the O(1s):C(1s) ratio was found to be 0.38 after photo-oxidation, whereas it was only 0.27 following exposure to an oxygen glow discharge.

The valence-band spectra offer a deeper insight into the extent of disruption of the polystyrene structure following surface oxidation. Virtually no polystyrene valence-band features are evident for the photo-oxidized surface. This implies that all the phenyl centres have undergone some mode of fragmentation during u.v. irradiation in the presence of oxygen. In marked contrast to this behaviour, the characteristic phenyl-ring features are clearly visible for the plasma-oxidized surface. The C(1s) π–π^* shake-up satellite mirrors the aforementioned trends; however, these signal intensities are much weaker in comparison, and also overlap to some extent with the C(1s) binding energy for carbonate species ($O-\underline{C}O-O \sim 290.4$ eV). O(2s) photoelectrons usually appear at a binding energy of around 25–27 eV, whereas O(2p) electrons from oxygen lone pairs in π and non-bonding molecular orbitals, and O(2p)–H(1s) and O(2p)–C(2p) bonds occur below 10 eV[11]. A significant amount of O(2s) is clearly evident for both types of oxidized surface.

DISCUSSION

One of the merits of studying x.p.s. rather than u.p.s. (ultraviolet photoelectron spectroscopy) valence-band spectra is that the relative photoionization cross-sections of molecular orbitals with major 2s character are greater than their 2p counterparts[15]. This is of significant benefit, since the 2s bands are much easier to interpret than the corresponding 2p features[15]. The C(2s)–C(2s) region can be used as a fingerprint for the molecular orbitals of a specific polymer.

In the case of polystyrene, reaction at the phenyl centres can cause an extensive breakdown of the parent polymer and a high degree of oxidation[16]. This is clearly evident from the valence-band spectra of the treated surfaces. In these studies, photo-oxidation has been measured to be more disruptive towards the polystyrene surface than is plasma oxidation. In the former case, it is the phenyl centres that strongly absorb in the u.v. region and therefore subsequently undergo reaction[17]. Consecutive oxidation steps will all converge on the eventual desorption of CO_2 gas, which is consistent with the intense $-\underline{C}O_2$ C(1s) component observed.

A pure oxygen plasma is known to comprise ions, atoms, ozone and metastables of atomic and molecular oxygen, as well as electrons and a broad electromagnetic spectrum[18]. Therefore, in addition to photo-oxidation taking place at the surface, there will also be a variety of concurrent ablative processes occurring. The net outcome of these competing degradation pathways is a less oxidized surface.

Photo-oxidation:

$$\mathrm{PS} \rightarrow \text{oxidation} \rightarrow CO_2(g)$$

Plasma oxidation:

$$\begin{tikzcd}[column sep=small] & & \text{ablation} \\ \mathrm{PS} \arrow[r] & \text{oxidation} \arrow[ur] \arrow[dr] & \\ & & CO_2(g) \end{tikzcd}$$

CONCLUSIONS

The apparent paradox of a more reactive oxygen glow discharge generating a less oxidized surface can be attributed to the inherent sputtering characteristic of a plasma, which continuously unveils fresh polystyrene substrate. On the other hand, during straightforward short-wavelength u.v. photo-oxidation, all reaction pathways culminate in the eventual desorption of carbon dioxide.

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