Plasma-catalysed Surface Rearrangement of Poly(ethylene) to a Poly(propylene) Type Structure

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Exposure of a poly(ethylene) substrate to an oxygen glow discharge, followed by ageing, results in the formation of a poly(propylene)-type structure at the polymer surface.

We describe here the discovery of a plasma-catalysed surface rearrangement reaction involving the conversion of poly(ethylene) to a poly(propylene) type structure. This is the first example of such a highly selective and efficient process occurring at the glow discharge–polymer interface.

A plasma consists of ions, atoms, metastable atomic and molecular species, as well as electrons and a broad electromagnetic spectrum.[1] It is this 'soup' of reactive species which is capable of altering the physicochemical properties of a polymer surface at room temperature. Plasma modification of polymeric materials is exploited in industry for obtaining desirable adhesion and wettability characteristics.[2,3] This mode of surface engineering has many benefits, and applications include use as a non-solvent based method for surface activation, and the possibility of recycling substrates by plasma etching away any overlayers.

It is widely accepted that the nature of a glow discharge makes it virtually impossible to attain high selectivities for specific functionalities at a given polymeric surface. For instance, plasma oxidation of a hydrocarbon material leads to a variety of oxygenated carbon environments (*e.g.* C–O, C=O, O–C=O *etc.*).[4] The extent and stability of such treatments have been widely studied by surface-sensitive techniques such as X-ray photoelectron spectroscopy (XPS)[2] and secondary ion mass spectrometry (SIMS).[5] However, our understanding of what actually occurs during the exposure of a polymer substrate to an oxygen glow discharge, and how the surface subsequently behaves on ageing,[6] remains limited.

In this work, a strip of poly(ethylene) film was positioned in the glow region of an oxygen plasma, and then subsequently aged in air.[7] The surface chemistry of interest was monitored by X-ray photoelectron spectroscopy measurements obtained on a high-resolution, high-sensitivity Kratos AXIS HS spectrometer, equipped with a monochromatic Al-Kα X-ray source and a novel magnetic immersion lens system. Significant quantities of oxidized functionalities were detected at the poly(ethylene) surface immediately after exposure to an oxygen plasma. However, careful analysis of the O(1s) and C(1s) core-level spectra revealed that plasma-oxidized poly(ethylene) suffers a gradual loss of oxygen from the surface on storing in air (Fig. 1). Additional information was obtained by examining the XPS valence band region, from which the electronic structure of a polymeric system may be determined. The photo-ionization cross-section for molecular orbitals with a major 2s character is much greater than for molecular orbitals with dominant 2p character;[8] this is of a considerable benefit, since the 2s bands are reported to be significantly easier to interpret than the 2p ones.[9] Typically, the C(2s)–C(2s) band is unique for a given polymer, and can therefore serve as a fingerprint.[10] In the case of poly(ethylene), overlap of the C(2s) orbitals along the hydrocarbon backbone yields bonding (*ca.* 19 eV) and anti-bonding (*ca.* 13 eV) molecular orbitals[11] [Fig. 2(*a*)]. The C(2p) and H(1s) orbitals involved in the C–H bond contribute towards the weak broad structure seen below *ca.* 10 eV. The relative intensities are dependent upon the ionization cross-sections of the various molecular orbitals. XPS valence band spectra of extensively aged samples are remarkably different in appearance from the

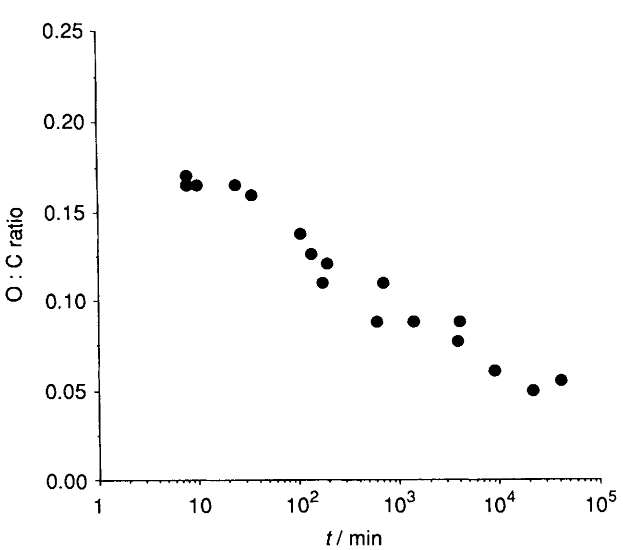


Fig. 1 Dependence of the O : C ratio on the length of time following a 1 W plasma oxidation treatment [determined by measuring the O(1s) and C(1s) peak areas]

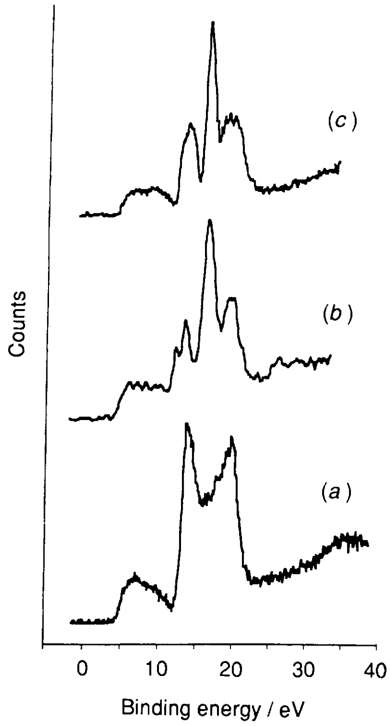
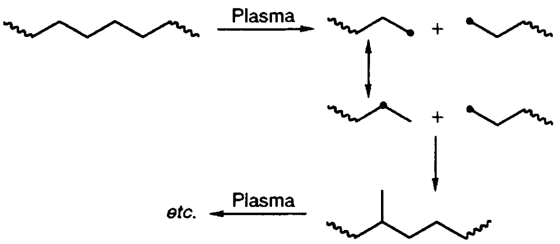


Fig. 2 XPS valence band spectra of: (*a*) clean poly(ethylene); (*b*) 1 W plasma oxidized–aged poly(ethylene); and (*c*) clean poly(propylene)

characteristic spectrum of a clean poly(ethylene) surface [Fig. 2(*b*)]. The major new feature in the C(2s) vicinity happens to overlap exactly with the extra peak reported for poly(propylene), and the relative intensities of the two outer C(2s) features are also consistent with a poly(propylene) type of structure [*i.e.* the attachment of a methyl side chain to the main poly(ethylene) backbone introduces an extra feature in the middle of the C(2s)–C(2s) region at *ca.* 16 eV,[10] Fig. 2(*c*)]. A slight splitting is evident in the poly(ethylene) band at *ca.* 13 eV, which could be a manifestation of either head-to-head and head-to-tail linkages in the poly(propylene) structure,[11] or a mixture of iso- and syndio-tactic poly(propylene).[12] A small amount of O(2s) is still observable for the plasma oxidized–aged surface. The loss of oxygen from the surface with ageing may be a direct consequence of the creation of this new extended structure, or due to the gradual desorption of low molecular weight species.

The degree of poly(ethylene) surface modification is greater and much more selective in these experiments (where the polymer substrate was positioned within the glow region) than in repeated studies in which a remote oxygen plasma was employed.[13] The striking resemblance of the valence band spectral features observed for plasma oxidized–aged poly(ethylene) with those known for clean poly(propylene) can be attributed to a rearrangement reaction taking place at the surface to create a poly(propylene) type structure (Scheme 1). Extensive rupture of the poly(ethylene) chains occurs during plasma exposure, to form primary hydrocarbon carbocations and free radicals which are energetically unstable with respect to their secondary isomers,[14] and will therefore undergo rearrangement, followed by recombination with a neighbouring poly(ethylene) chain which has just undergone fragmentation. This sequence of steps results in the generation of a poly(ethylene) backbone to which methyl groups have become attached at random. To a first approximation the valence band (VB) spectrum of a polymer based upon a poly(ethylene) backbone to which a short chain is fixed can be considered as being a simple summation of the individual constituents, *i.e.* VB[poly(ethylene)] + VB(attached group).[10] Therefore the XPS valence band spectrum of a poly(ethylene) chain with randomly attached methyl side groups would be expected to bear a strong resemblance to the valence region spectra reported for poly(propylene). Examination of the valence band spectra of a whole range of other hydrocarbon polymers supports this view[15] [the closest is found to be a poly(ethylene) backbone with two methyl side groups on each carbon centre, *i.e.* poly(isobutylene); however the peak binding energies differ significantly, but this could explain the origins of the slight splitting seen in the *ca.* 13 eV band]. The only other possible interpretation is that the plasma causes isopropyl groups to become attached to the chain ends of fragmented poly(ethylene) moieties; these bulky propyl heads could then preferentially migrate through the poly(ethylene) subsurface towards the surface on ageing. However, the latter explanation can be ruled out since one would expect to observe some perturbation in the molecular orbitals compared to poly(propylene) in order to account for the poly(ethylene) tails.



Scheme 1

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