XPS VALENCE BAND ANALYSIS OF PLASMA TREATED POLYMERS

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ABSTRACT

The valence bands (VB) of remote oxygen and remote nitrogen plasma treated polyethylene and polypropylene were studied to determine changes in the basic polymer structure. Each of the polymers showed a characteristic valence band profile, which retained much of its original shape after plasma treatment. This has suggested that even though plasma treatment can cause the incorporation of a high proportion of functional groups, significant segments of the original polymer structure remain unchanged within the X-ray photoelectron (XPS) sampling depth. Angle-resolved X-ray photoelectron spectroscopy (ARXPS) suggests that near the outer surface, the polyethylene structure is modified by branching and cross-linking.

INTRODUCTION

The most commonly used surface analytical tool to study the changes in surface chemistry has been X-ray photoelectron spectroscopy (XPS or ESCA). The use of XPS core level spectra to study functional groups on the surfaces of polymeric materials has enabled some degree of understanding of the process of plasma treatment of polymers. While groups such as hydroxyls, amines and amides may be identified, changes in the hydrocarbon polymer backbone, such as unsaturation and cross-linking, can not be observed. Some alternatives are available. One is Static Secondary Ion Mass Spectroscopy (SSIMS), whose practitioners are rapidly developing a body of evidence to show that cross-linking and branching can be observed /1-3/.

Another approach to better identify the carbon functionality is to use the XPS valence band (VB) information. The XPS VB spectrum observed for a polymer represents the photoelectrons emitted from the delocalized or bonding molecular orbitals within the polymer, to a typical analysis depth of 50-60 Å. XPS valence band spectra of polymers were first recorded in the early 1970's /4-6/. The subject was carefully researched both experimentally and theoretically by Pireaux and co-workers /5,7,8/. Their results are discussed and reviewed in several articles /9,10/.

The VB spectrum (0 to about 30 eV) consists of many closely spaced energy levels which together give rise to a band structure that can potentially reveal information on the chemical of the elements and thus the molecular structure of the polymer. While a complete interpretation usually requires careful experimentation and the full support of elaborate and accurate quantum mechanical calculations /4-9/, it is possible to make useful identification of specific structures using a fingerprint approach.

The purpose of the present paper is to study the effect of remote plasma treatment on polyethylene and polypropylene, with reference to their VB spectra, in an attempt to further understand the nature of the newly formed surface. In addition, core level spectra, obtained under higher resolution conditions than previously /11-13/, are presented to complement the valence band assignments. The technique of plasma modification, as used in this work, and interpretation of the core level spectra obtained with respect to treatment time, experimental conditions and sample aging, have been discussed in detail elsewhere /11-13/.

EXPERIMENTAL

Linear low density polyethylene (LLDPE) and monoaxially oriented polypropylene (PP) were obtained from ESSO Chemicals Inc., Sarnia, Ontario, Canada in the form of thin film. The samples were plasma treated, under the conditions described below, and were transported to the UK for detailed XPS analysis approximately one to two weeks after treatment. Reference spectra were obtained using high density polyethylene and propafilm, Imperial Chemical Industries, Wilton, UK.

The plasma reactor used for the treatment of LLDPE and PP has been described previously /12/. Using a 2.45 GHz microwave generator, a gas flow rate of 1000 sccm and a working pressure of approximately 3 torr, with the samples placed approximately 3-5 cm from the lower edge of the plasma, very rapid polymer surface modification can be achieved /12-13/. The typical reactor base pressure was 10^{-5} torr. Samples were exposed to the plasma afterglow species for 5 seconds.

XPS was performed on a SCIENTA ESCA 300 spectrometer at the Wilton Materials Research Centre, U.K. This instrument employs a high power rotating anode monochromatized X-ray source (Al Kα), high transmission optics and a multichannel detector. The design and performance of the spectrometer have been described previously /14/. Charge compensation was achieved using a low energy electron flood gun (VSW EG2) with the sample mounted on a 10 mm diameter stub underneath a silver plate with a 2*8 mm slot for the X-ray beam. The silver plate is responsible for some spectral contamination, giving the Ag 4d lines in the valence band spectra at ≈ 6 eV. For the variable take-off angle studies the sample was mounted on the stub underneath a stainless steel ring. The monochromated X-ray source was used at powers of either 1.4 or 2.8 kW, a pass energy of 150 eV and slit width of 0.5 mm were used, giving an instrument resolution of approximately 0.30 eV.

RESULTS AND DISCUSSION

Untreated LLDPE and OPP:

The VB spectrum of untreated (Figure 1A) is in agreement with previously documented spectra /4-9/. The molecular structure of PE consists of repeating (-CH_2-) units, the C 2s contribution of which is seen as the two intense bands at binding energies of ≈ 11 eV and 17 eV. The higher binding energy band represents the bonding molecular orbital and the lower binding energy band the antibonding analogue /6-8/. C 2p contributions are seen as the broad structure below 10 eV. Detailed theoretical interpretations of the spectrum can be found elsewhere /4-9/.

When substituting one of the hydrogen atoms in the basic polyethylene unit for a methyl group to give polypropylene the VB changes considerably (Figure 1B) with the appearance of a third intense peak within the C 2s feature at ≈ 14.5 eV representing the methyl side chain /7-9/.

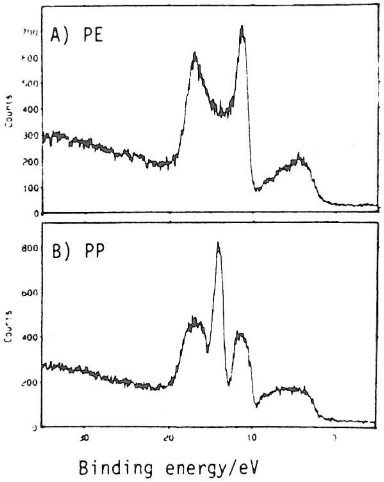

FIGURE 1 - Valence band spectra of untreated PE (A) and PP (B)

Remote oxygen plasma treatment:

LLDPE and PP were treated in a remote oxygen plasma for 5 seconds using a power of 40 W, a gas flow rate of 1000 sccm with the samples placed at 10 cm from the lower edge of the plasma. A greater distance was chosen in order to allow more control over the reaction with the oxygen plasma and to avoid sample damage. XPS elemental analyses of remote oxygen plasma treated LLDPE and PP two weeks after treatment indicated an O/C ratio of 21.9% and 24.1% respectively.

The VB spectra of both LLDPE and PP (Figure 2) changed with the appearance of a broad band around 25 eV, indicating O 2s character. The intensity increase of the band below 10 eV reflects O 2p character and some contribution due to Ag 4d photoelectrons. The original C 2s features (11-17 eV) for both polymers, however, were still clearly visible. This suggests that the molecular structure of the plasma treated polymers must contain runs of original hydrocarbon units for polyethylene and polypropylene, sufficiently long that the C 2s region of the valence band still resembles that of the untreated polymer. The striking resemblance of the VB spectra of the untreated and treated polymers has led us to believe that any hydrocarbon reorganization must occur within a thin surface layer, as no evidence of it was seen in the VB spectra of these samples (see below).

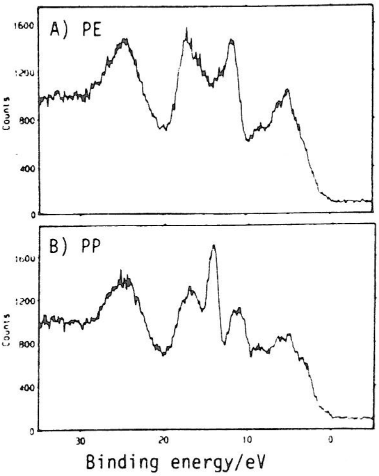

FIGURE 2 - Valence band spectra of remote oxygen plasma treated LLDPE (A) and PP (B)

The C 1s spectra of the untreated polymers (not shown) represent a single sharp line representing the hydrocarbon units. After treatment, the spectra of both polymers (Figure 3) are seen to change with the appearance of several high energy components. The peak at the lowest binding energy represents the remaining hydrocarbon units. A peak at a small shift of ≈ 0.6 eV represents ($\underline{C}$-CO_2) groups. The peak at a binding energy shift of ≈ 1.5 eV represents hydroxyl (C-OH) or ether groups (C-O-C) formed as a result of the treatment. The latter two peaks, at binding energy separations of 3 eV and 4.5 eV, represent carbonyls (C=O) and carboxyl groups (O-C=O) on the surface. Even though differences may be seen in the C 1s spectra and the component relative intensities, the two surfaces appear to be very similar.

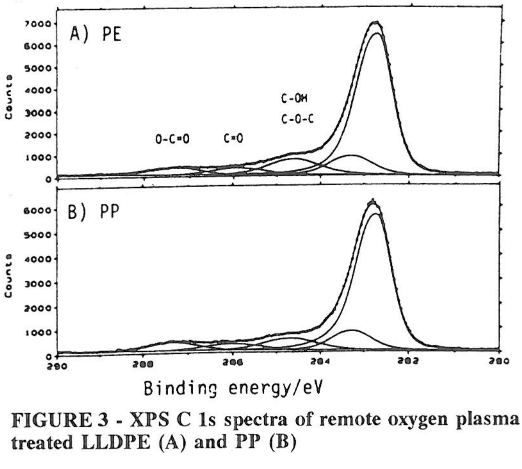

FIGURE 3 - XPS C 1s spectra of remote oxygen plasma treated LLDPE (A) and PP (B)

Remote nitrogen plasma treatment:

For remote nitrogen plasma treatment, the samples were placed approximately 3-5 cm from the nitrogen plasma, using the experimental conditions mentioned above. XPS analysis of the

LLDPE after two weeks indicated an N/C ratio of 25.2% (O/C =17.2%). For PP an N/C ratio 9% (O/C=8.6%) was observed.

Even at such high treatment levels the valence band spectra for LLDPE and PP (Figure 4) have retained enough of their original fingerprint character that identification of the polymers is still possible. The higher binding energy portion of the C 2s feature was seen to overlap with the N 2s contribution at ≈ 17-20 eV. Further broadening of the O 2s (≈ 25 eV) and N 2s features causes the formation of one broad structure ranging from ≈ 17 eV to 27 eV.

For nitrogen plasma treated LLDPE, evidence for a weak additional band at ≈ 14.5 eV is seen (see arrow). This is believed to result from the creation of some polymeric side chains by cross-linking. The cross-linking effect seems to be more evident for nitrogen plasma treatment than for oxygen plasma treatment. The valence band spectrum of remote nitrogen plasma treated LLDPE, however, still suggests the presence of significant concentrations of its original structure. Within the VB spectrum of PP the characteristic structure at ≈ 14.5 eV and the characteristic peak at ≈ 11 eV are still clearly visible.

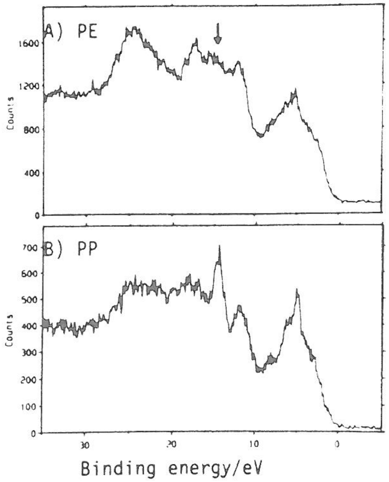

FIGURE 4 - Valence band spectra of remote nitrogen plasma treated LLDPE (A) and PP (B)

The C 1s peak profiles (Figure 5) for both polymers after remote nitrogen plasma treatment suggest the formation of a number of functional groups on the surface. Since both oxygen and nitrogen are incorporated during the treatment, precise identification is more difficult than for the oxygen plasma treated polymers. The C 1s spectrum of remote nitrogen plasma treated PP suggests the presence of a peak at a binding energy separation of 0.8 eV suggesting the formation of amines. Higher binding energy components suggest the formation of imines, nitriles at 1.7 - 2.2 eV, amides at ≈ 3 eV and even urea-type linkages at ≈ 4-4.3 eV. Since the concentration of oxygen on the surface is low in comparison to that of nitrogen, it can be assumed that most of the intensity observed is due to nitrogen containing functional groups.

The surface of remote nitrogen plasma treated LLDPE, however, indicated sufficiently high oxygen concentrations to make differentiation between oxygen and nitrogen functional groups difficult. Thus, the peak at a binding energy separation of ≈ 0.5 eV represents C-CO_2, while that at a separation of ≈ 1.6 eV represents an overlap of C-O and C=N species. Higher binding energy peaks represent groups such as imines/carbonyls and amides/carboxyl groups. From the C 1s peak structures, it appears

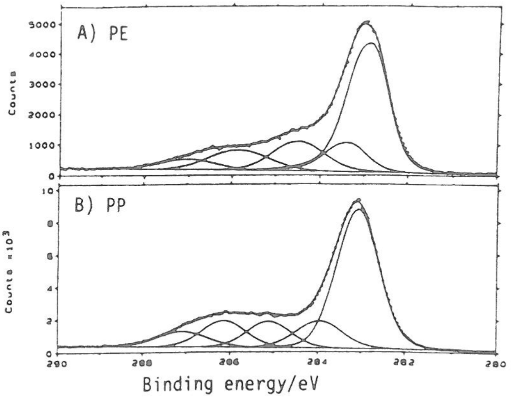

FIGURE 5 - XPS C 1s spectra of remote nitrogen plasma treated LLDPE (A) and PP (B)

that the lower N/O ratio of remote nitrogen plasma treated LLDPE leads to a surface with a greater quantity of groups such as C-O, C=N and C-N. That of PP, however, with a much higher N/O ratio, suggests a greater quantity of more highly functionalized carbons such as amide groups.

Angle-resolved depth profiling of nitrogen plasma treated LLDPE:

ARXPS was performed on remote nitrogen plasma treated LLDPE to investigate changes in the C 2s structure with depth. The ETO angle was increased from 20° to 70° which, assuming an electron mean free path of 3 nm, corresponds to a sampling depth of ≈ 15 nm to 40 nm. The concentration of nitrogen and oxygen did not change appreciably with depth; at 20° O/C=10.6, N/C=13.5; at 70° O/C=9.0%, N/C=14.7%. O/C ratios obtained for lower angles may include a small contribution due to contaminating hydrocarbon on the stainless steel ring used to hold the sample in place.

The valence band spectra observed at 20° and 70° (Figure 6) indicate that the hydrocarbon structure of the modified polymer does vary with analysis depth. The VB spectrum recorded at 70° shows a C 2s structure which more closely resembles that of the unmodified polymer by the two distinct C 2s peaks at 11 and 17 eV. By decreasing the ETO angle to 20° this structure was seen to change with an increase of the additional feature at ≈ 14.5 eV. Thus, the C 2s structure within the uppermost monolayers of nitrogen plasma treated polyethylene bears more resemblance to that of polypropylene, than it does to polyethylene. It is believed that this provides the first XPS evidence for cross-linking within the uppermost surface layers as a result of plasma treatment.

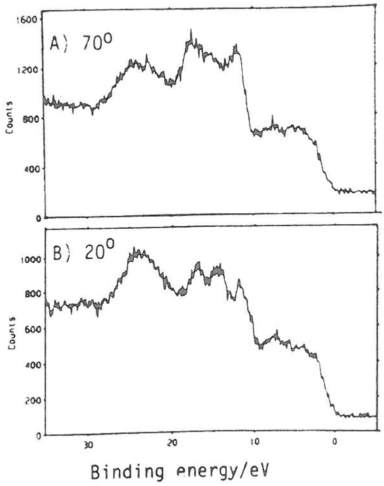

FIGURE 6 - Valence band spectra of remote nitrogen plasma treated polyethylene at ETO angles of (A) 70° and (B) 20°

CONCLUSIONS

There is considerable spectroscopic evidence suggesting that with plasma treatment, nitrogen and/or oxygen add to the polymers leaving intermittent "chains" of the original hydrocarbon units of polyethylene and polypropylene. Further, the uppermost monolayers of the nitrogen plasma treated LLDPE, show evidence of cross-linking of these intermittent chains by the appearance of a polypropylene-like feature within the C 2s valence band structure.

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