

## Applications Note

# A Multi-Technique Characterization of Polymer Materials with XPS, UPS and REELS

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### Overview

Using a combination of surface analysis tools, different polymer materials were analysed using the Kratos AXIS Supra<sup>†</sup>. A common issue with XPS analysis is that the C 1s envelope can look relatively similar for different polymer materials, making them difficult to distinguish using XPS alone. Plasmon features, such as the  $\pi$ - $\pi^*$  transition, which give information related to the  $sp^2$  content of a material are also concealed by shifts between different C chemical states. Here, a combination of XPS, UPS and REELS are used as complimentary tools to help understand the chemistry of several polymer materials.

### Introduction

Polymers are macromolecules built from a series of small repeating units. As their simple building blocks have a different nature, they have a broad range of properties and therefore have use in a wide variety of applications. Structural surface analysis of insulating polymers is difficult as a consequence of the similarities observed within the C 1s envelope of these different materials. There is also the complexity of chemical state shifts which need to be considered as these can overlap useful features of the spectrum, such as the  $\pi$ - $\pi^*$  transition. This limits the information which can be obtained from X-ray Photoelectron Spectroscopy (XPS) alone and one will need to utilise other surface analysis techniques to gain a wider insight into the structural information of these insulating materials.

Ultraviolet Photoelectron Spectroscopy (UPS) is a desirable tool which is used alongside XPS to examine the valence band structure and bonding electrons of a material in more detail. Reflected Electron Energy Loss Spectroscopy (REELS) is another complimentary tool used to understand and quantify hydrogen content within a material and gain an insight into the band gap structure, information which is not typically accessible from XPS alone.

In this study, different polymer materials were analysed using XPS, REELS and UPS. Four different polymers were chosen for structural comparison having a very different hydrogen content and valence band structure; high density polyethylene (HDPE), polycarbonate (PC), polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF).

## Experimental

Surface analysis of different polymer materials was performed using the state-of-the-art, Kratos AXIS Supra<sup>+</sup> spectrometer, fitted with a Gas Cluster Ion Source (GCIS), UPS lamp and REELS electron source. Each sample was gently cleaned to remove adventitious carbon before characterization using the 5 keV Ar<sub>2000</sub><sup>+</sup> GCIS mode, which caused no damage to the surface.

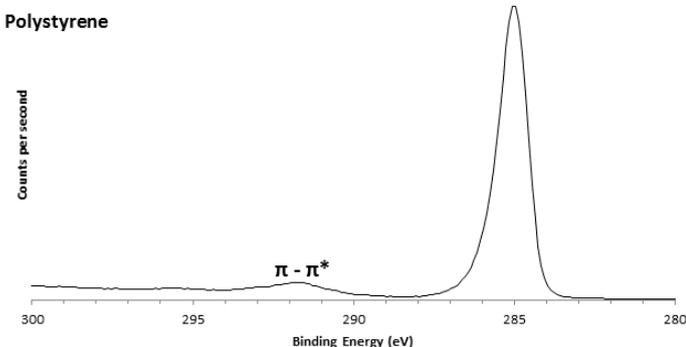
High resolution XPS spectra were acquired over a small energy range for each particular element. The co-axial charge neutraliser was used to mitigate against surface charging as a consequence of the photoemission process.

He II UPS data was acquired with a photon energy of 44.8 eV to analyse the low binding energy electrons. This makes UPS a more surface sensitive technique than XPS with an information depth of up to 3 nm (the sampling depth of XPS is typically quoted as 10 nm) and allows the valence structure of a material to be examined.

The electron source used for REELS operates up to 2 keV allowing variable energy analysis to sample different depths through a material. The surface is irradiated with a focused electron beam and the energy distribution of the reflected electrons is measured. This gives rise to a large elastically scattered peak in the spectrum, but also features that result from discrete energy loss which provide information regarding the surface electronic structure.

## Results and Discussion

Polystyrene, (C<sub>8</sub>H<sub>8</sub>)<sub>n</sub>, is an interesting polymer material for structural analysis because it displays the typical  $\pi$ - $\pi^*$  transition clearly in the C 1s spectrum (Figure 1), without being concealed by shifts of different C chemical states.

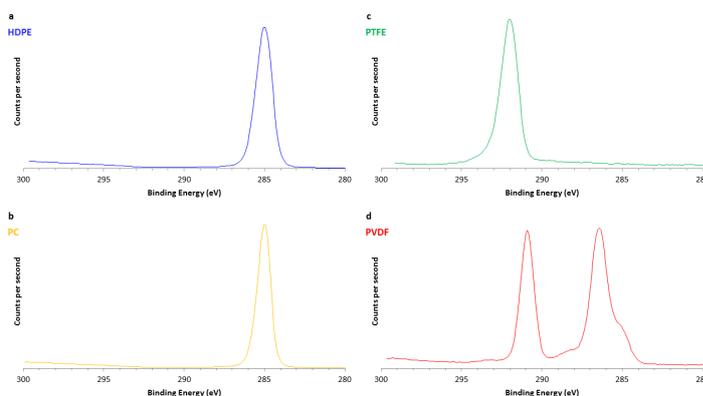


**Figure 1. XPS C 1s spectrum of polystyrene highlighting the  $\pi$ - $\pi^*$  transition.**

For other polymers, however, this bonding-antibonding transition is not so clearly seen and is often overlapped by chemically shifted C 1s photoelectrons within the C 1s envelope of the material. This can cause difficulty with the interpretation of com-

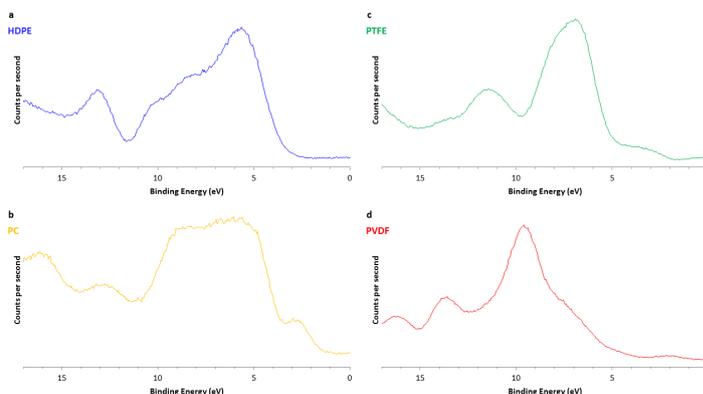
plex polymer materials and the use of other surface analysis techniques, such as UPS and REELS, becomes essential to understand their surface electronic structure.

High resolution XPS spectra were acquired for the four different polymer materials (HDPE, PC, PTFE, PVDF), where Figure 2 reveals a comparison between C 1s spectra. For HDPE and PC, the C 1s envelope is very similar in appearance for both materials, despite PC being an oxygen-containing unit repeat whilst HDPE is purely carbon and hydrogen containing. Although PTFE also displays only one C 1s peak, this is at a higher binding energy than HDPE and PC, a result of carbon bonding to electronegative fluorine. PVDF shows the most complex C 1s envelope with both C-C, C-O and C-F bonding present within the material.



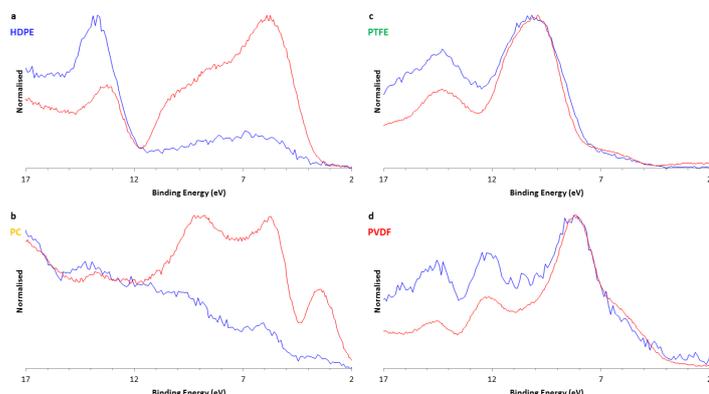
**Figure 2. XPS C 1s spectra for the four different polymer materials; HDPE (blue), PC (yellow), PTFE (green), PVDF (red).**

UPS uses a lower photon energy than the conventional Al K $\alpha$  XPS source and therefore can only excite the low binding energy valence electrons. Due to the lower kinetic energy of the photoelectrons excited with the He II radiation relative to the Al K $\alpha$  X-rays, UPS is a more surface sensitive technique. The removal of surface contamination by the gas cluster ion source is vitally important in acquiring a valence band photoemission spectrum of the polymer surface which is not compromised by surface contamination.



**Figure 3. He II excited UPS spectra for the four different polymer materials; HDPE (blue), PC (yellow), PTFE (green), PVDF (red).**

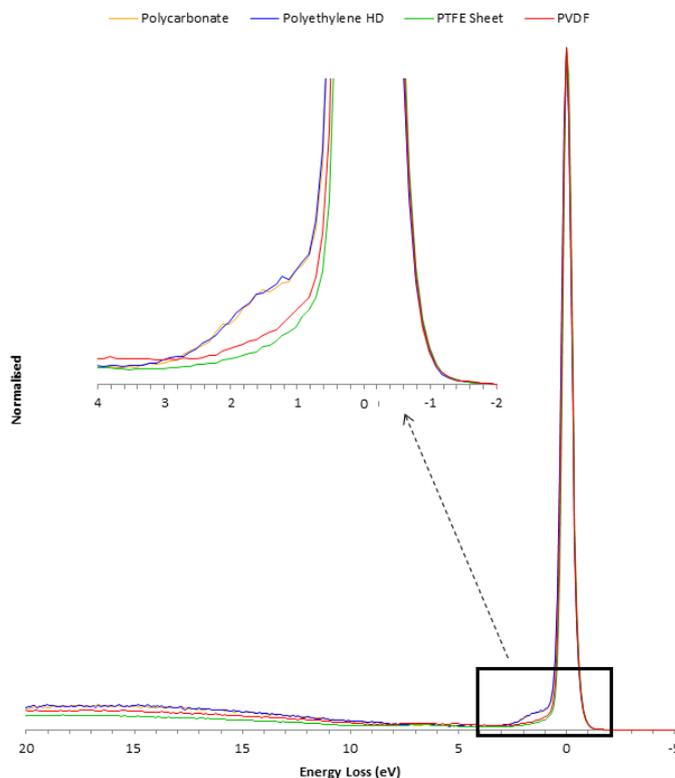
A comparison of the UPS spectra for the four different polymer materials is displayed in Figure 3. It is apparent that the valence band spectra show considerable differences, despite the C 1s spectra being similar. As expected for these insulating polymer materials the measured valence band density of states shows that there are no electronic states close to the 0 eV binding energy value, indicating that the materials are insulating.



**Figure 4. Comparison of XPS valence band spectra (blue) with UPS spectra (red) for the four different polymer materials.**

A comparison between the X-ray and UV excited Valence Band (VB) spectra is displayed in Figure 4 for all four materials. It is noted that the X-ray and UV excited spectra exhibit similar density of states. Differences in the spectral intensities are attributed to the different photoelectron cross sections for the valence electrons excited with the two different excitation sources.

REELS spectra were acquired for each of the four polymer materials using an electron source. Figure 5 shows an overlay comparison of these REELS spectra, where the characteristic elastically scattered electron loss peak appears at a peak energy of 0 eV. The Full Width Half Maximum (FWHM) for this zero loss peak is measured to be approximately 0.5 eV for all four polymer materials. The shoulder observed between energy loss of 1–2 eV is a measurement of the hydrogen content of each material. Comparing the REELS spectra in Figure 5 therefore reveals that PE displays the broadest shoulder as a consequence of having the most hydrogen, whilst PTFE has the smallest shoulder as it has no hydrogen present in the polymer structure.



**Figure 5. REELS spectra for the four different polymer materials; HDPE (blue), PC (yellow), PTFE (green), PVDF (red).**

## Conclusions

Four polymer materials with a very different hydrogen content and valence band structure have been analysed using a range of surface analysis techniques. This includes high density polyethylene (HDPE), polycarbonate (PC), polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF). A combination of XPS, UPS and REELS has allowed the characterization of the surface electronic structure and the opportunity to gain an understanding into the surface chemistry of these materials.

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