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XPS O 1s Binding Energies for Polymers Containing Hydroxyl, Ether, Ketone and Ester Groups

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XPS spectra of nine model polymers containing oxygen functional groups are studied. The measured O 1s binding energies were 532.8 eV for ether and alcohol oxygens, 532.2 eV for ketone oxygens and 532.2 and 533.7 eV for the carbonyl- and ether-type oxygens in ester groups, respectively. Comparison with previous experimental and theoretical O 1s binding energies for these groups is also presented. Absolute O 1s binding energies of polymers are not in agreement with those published by other groups. However, with the exception of ketone oxygens, binding energy shifts observed for the various functional groups are comparable.

INTRODUCTION

Our interest in the surface analysis of complex polymeric systems, (e.g. random and block copolymers, biopolymers and plasma-deposited polymers) has led to a re-examination of binding energy (BE) shifts observed in the core-level binding energies of atoms in different organic functional groups.[1,2] The subject of this investigation is the measurement of oxygen 1s (O 1s) core-level BEs in several well-defined model polymer systems using x-ray photoelectron spectroscopy (XPS). Accurate determination of BEs and compositions are essential for identifying the types and amounts of functional groups present on the surface of polymeric samples.

Although O 1s BEs for the common oxygen-containing polymers have been tabulated and published, inconsistencies have been common and both experimental and calculated BE shifts have failed to lead to unambiguous BE assignments.[3–10] Furthermore, some of the studies used BEs measured from small organic molecules as models for polymers.[3,8] Although BEs from small molecules and polymers should be similar, the differences in size and molecular environments may produce some differences in the measured BEs due to oxygen-induced secondary chemical shifts[4,7,11] and relaxation effects.[9,10,12,13]

Dilks, reviewing the work of Clark *et al.* on polymethacrylates,[14] polycarbonates,[15] polyacrylates and model organic compounds,[3] summarized the O 1s BEs as shown in Table 1. The ketone oxygen BE was stated to be equal to that of the BEs for alcohols and ethers.[16] These results differ from O 1s BEs (both in absolute and relative BE) obtained in our laboratory and in other laboratories using gas-phase XPS.[10] These results also differ from theoretical O 1s BE shifts calculated by Clark *et al.*[5] for a variety of small molecules.

This background establishes the need for the examination of appropriate model polymers to distinguish the BEs of oxygen functional groups. The realization of the importance of oxygen inductive effects on neighboring atoms[2,4,7,11] (which can influence BE referencing) supports the need for accurate, contemporary data on this subject. This study demonstrates that information from high-resolution O 1s spectra can enhance the analytical capabilities of XPS. The ongoing development of more accurate BE calibration procedures and higher resolution spectrometers provides additional impetus for this study.

EXPERIMENTAL

Nine polymers were used in this study: poly(vinyl alcohol) (PVA, MW 86000); poly(ethylene glycol) (PEG, MW 4000); poly(propylene glycol) (PPG, MW 2000); poly(tetramethylene glycol) (PTMG, MW 2000); poly(vinyl methyl ketone) (PVMK, MW 50000); poly(methyl isopropenyl ketone) (PMIPK, MW 750000); poly(ethyl methacrylate) (PEMA); poly(2-hydroxyethyl methacrylate) (PHEMA); poly(acetoacetoxyethyl methacrylate) (PAAEM). 1,10-Decanediol (10-DIOL) was also analyzed. The sources of these compounds are listed in Table 2. With the exception of PEG and 10-DIOL, which were analyzed in flake form as received, purified polymer samples for XPS analysis were dissolved in an appropriate solvent and cast centrifugally at 4000 rpm onto clean 9 mm glass disks (see Table 2). The glass disks were cleaned by sonication in 4% Isopanasol™ (C.R. Callen Corp.) solution (30 min)

Table 1. O 1s binding energies for common functional groups (adapted from Dilks[16])

O—C in carbonate	>	O—C in acid, ester	>	O—C in alcohol, ether	~	O=C in ketone	>	O=C in acid, ester, carbonate
~535.0 eV		~534.3 eV		~533.6 eV				~532.8 eV

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Table 2. Model compound preparation

Model	Vendor	Purification	Casting solution
PVA	Aldrich	—	2.5% in H_2O
10-DIOL	Aldrich	—	Solid analyzed as received
PEG	Polysciences	—	Solid analyzed as received
PPG	Reichold	—	2% in methanol
PTMG	DuPont (Teracol)	—	5% in chloroform
PVMK	Scientific Polymer Prod.	Ppt. from chloroform into methanol	2% in chloroform
PMIPK	Polysciences	—	2% in chloroform
PEMA	[a]	Ppt. from ethanol/H_2O into petroleum ether	5% in chlorobenzene
PHEMA	[a]	Ppt. from ethanol/H_2O into petroleum ether	5% in DMF[b]
PAAEM	[a]	Ppt. from THF into methanol	2% in THF[c]

[a] Polymerized from monomer in our laboratory.
[b] DMF = dimethylformamide.
[c] THF = tetrahydrofuran.

and subsequently rinsed and sonicated (10 min) in distilled water three times.

The XPS experiments were done on an SSX-100 surface analysis system (Surface Science Instruments, Mountain View, CA) using a monochromatic Al Kα x-ray source and a detection system with a 30° solid angle acceptance lens, a hemispherical analyzer and a position-sensitive detector. All the polymers were analyzed at a take-off angle of 0°. The take-off angle is defined as the angle between the surface normal and the axis of the analyzer lens. (Note: this angle is the complement of the take-off angle defined in ASTM E673-89, 'Standard Terminology Relating to Surface Analysis', American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103, USA.) 10-DIOL was analyzed at a take-off angle of 55°. It was cooled to about −100 °C during analysis to prevent out-gassing.

The BE scale of the spectrometer was calibrated by setting the Au $4f_{7/2}$ peak equal to 83.9 eV and the difference between the Cu $2p_{3/2}$ and the Cu 3s peaks to 810.1 eV. Metallic Au and Cu samples, cleaned by ion etching, were used for this calibration. Survey scans (0–1000 eV BE) were run at an analyzer pass energy of 150 eV and an x-ray spot size of 1000 μm to determine the elemental composition of each polymer. High-resolution O 1s and C 1s spectra were obtained at a pass energy of 25 eV and various spot sizes (150, 300, 600 and 1000 μm). The high-resolution spectra were resolved into individual Gaussian peaks using a least-squares fitting program.

All samples were mounted so that they were electrically insulated from the spectrometer. Charge neutralization of the samples was done with a low-energy electron flood gun. The energy of the flood gun was adjusted to produce the narrowest C 1s and O 1s peak widths. Typical energy settings of the flood gun were between 1 and 3 eV. This resulted in the measured BEs appearing at values lower than the true BEs. Thus, an internal reference was used to linearly shift the BE scale. With the exception of PEG, all polymer (and 10-DIOL) BEs were referenced by setting the maximum of the resolved C 1s peak corresponding to carbon in a hydrocarbon environment (CH_x) to 285.0 eV. Because no hydrocarbon peak is present in the PEG C 1s spectra, the BEs for this polymer were referenced by setting the maximum of the C 1s peak corresponding to carbon in an ether environment (CH_2—O) to 286.5 eV. A further description of the charge neutralization method is given elsewhere.[17]

RESULTS AND DISCUSSION

Table 3 shows the elemental compositions for the compounds studied, as determined from XPS survey scans. With the exception of PVMK and 10-DIOL, all measured elemental compositions agree with the theoretical composition (obtained from the expected stoichiometry of the compounds) within the typical experimental error for XPS measurement (~10% of the atomic composition). In no case were elements other than carbon and oxygen detected. High-resolution C 1s spectra of the PVMK and 10-DIOL suggested that the excess carbon was probably due to hydrocarbon contamination on the samples. In these cases, the deviation of the surface composition from the theoretical composition should not affect the accurate measurement of the oxygen functionality BE.

The peak positions for the resolved high-resolution C 1s spectra for each of the polymers are given in Table 4. Resolved peak areas agree well with areas expected

Table 3. Elemental compositions (theoretical and XPS)

Model	%C	%O	XPS C/O	Theoretical C/O
PVA	69.4	30.6	2.3	2.0
10-DIOL	87.9	13.1	6.7	5.0
PEG	67.9	32.1	2.1	2.0
PPG	74.9	25.1	3.0	3.0
PTMG	80.9	19.1	4.2	4.0
PVMK	83.0	17.0	4.9	4.0
PMIPK	83.8	16.2	5.2	5.0
PEMA	76.2	23.8	3.2	3.0
PHEMA	69.3	30.7	2.3	2.0
PAAEM	68.3	31.7	2.2	2.0

Table 4. C 1s peak positions (eV)[a]

Model	$-\underline{C}H_n$	$\underline{C}-\underset{\underset{O}{\|}}{C}=O$	$\underline{C}-O$	$-\underline{C}(=O)-$	$\underline{C}(=O)-O$
PVA	285.0	—	286.5	—	—
10-DIOL	285.0	—	286.4	—	—
PEG	—	—	286.5[b]	—	—
PPG	285.0	—	286.5	—	—
PTMG	285.0	—	286.4	—	—
PVMK	285.0	—	—	287.7	—
PMIPK	285.0	—	—	287.6	—
PEMA	285.0	285.8	286.8	—	288.8
PHEMA	285.0	285.7	286.6	—	288.9
PAAEM	285.0	285.7	286.7	287.9	289.0
Average	285.0	285.7 ± 0.1	286.6 ± 0.2	287.7 ± 0.2	288.9 ± 0.2

[a] Referenced to the hydrocarbon peak at 285.0 eV.
[b] Referenced to the average of ether carbon peaks in PPG and PTMG.

from the polymer structure. Individual peak positions obtained for carbons in different bonding environments are also consistent with those observed by other researchers.[16] Agreement of carbon BEs for the same functional groups from different polymers was also good. For instance, polymers with only alcohol- or ether-type oxygens exhibit essentially identical $\underline{C}-O$ BEs (286.5 ± 0.1 eV).

For the methacrylate polymers, peak positions are reported for a peak fit to the spectrum, which includes a separate peak for the backbone carbon that is directly bonded to the ester carbon. This carbon has been assigned to a different BE than other hydrocarbon species because of the next-nearest-neighbor effect induced by the ester oxygens (~0.7 eV BE shift). The inclusion of a separate peak for this 'beta-shifted' carbon has been justified previously for several types of methacrylate polymers.[2,4,7,11]

O 1s spectra of the ten samples are shown in Fig. 1. Peaks for different functional groups are in good agreement and are easily distinguishable. The tabulated peak positions are given in Table 5. For the more complex O 1s spectra (i.e. those for PHEMA and PAAEM), peak fitting was done so that resultant peak area ratios were consistent with the theoretical polymer structure. For example, because the HEMA repeat unit contains three oxygens (hydroxyl, ester group carbonyl and ester group ether), three distinct peaks are needed to obtain the observed symmetric O 1s spectral envelope observed (Fig. 2). Conversely, for PAAEM, which contains five oxygens (ketone, two ester group carbonyls and two ester group ethers), the inclusion of a peak at intermediate BEs to account for the ketone group (as suggested by Table 1) would not result in the observed asymmetric spectrum. A two-peak fit with the ketone oxygen having the same BE as the carbonyl oxygen in the ester group results in a reasonable peak fit and area ratios consistent with the polymer structure (Fig. 3).

The polymers analyzed show consistent O 1s BEs for the various oxygen functional groups. Alcohol and ether oxygen BEs range from 532.7 to 533.1 eV. The ether-type oxygen and carbonyl oxygen in the ester groups range from 533.5 to 533.9 eV and 532.0 to 532.3 eV, respectively. Contrary to previously published experimental results, the ketone oxygen (532.1–532.3 eV) is closer in BE to carbonyl-type oxygens in ester groups than to alcohol or ether oxygens.

It should be noted that, with the exception of this final result, the BE shifts observed for the different

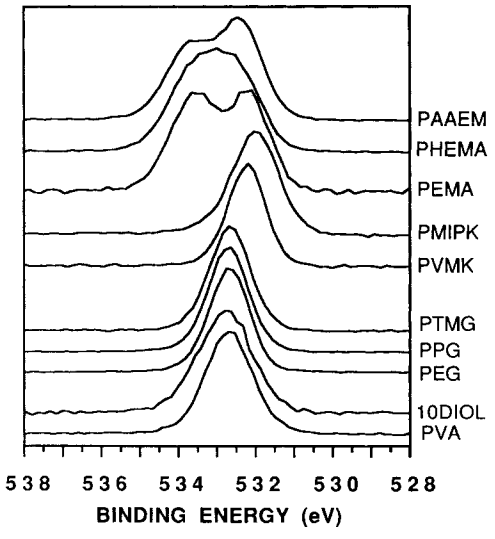

Figure 1. The XPS O 1s spectra for the nine model polymers and 10-DIOL. All BEs have been referenced as described in Table 5.

Table 5. O 1s peak positions (eV)[a]

Model	$\underline{O}=C$	$\underline{O}-C-O$	$C-\underline{O}-C$ $H-\underline{O}-C$	$O-C-\underline{O}-C$
PVA	—	—	532.7	—
10-DIOL	—	—	532.8	—
PEG	—	—	532.7[b]	—
PPG	—	—	532.7	—
PTMG	—	—	532.7	—
PVMK	532.2	—	—	—
PMIPK	532.1	—	—	—
PEMA	—	532.0	—	533.5
PHEMA	—	532.3	533.1	533.9
PAAEM	532.3	532.3	—	533.7
Average	532.2 ± 0.1	532.2 ± 0.2	532.8 ± 0.2	533.7 ± 0.2

[a] Referenced to the hydrocarbon peak at 285.0 eV.
[b] Referenced to the ether carbon peak at 286.5 eV.

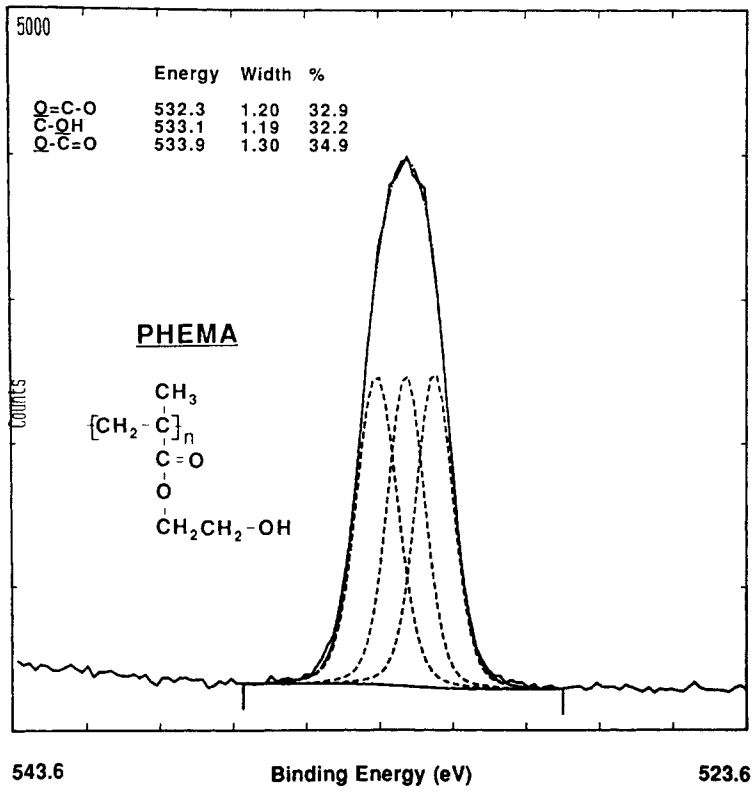

Figure 2. The resolved XPS O 1s spectrum of PHEMA, showing peaks arising from the O—C=O, C—OH and O—C=O oxygens present in PHEMA.

oxygen functional groups (~0.7 eV between ethers and either ester oxygen) agree with those observed by Clark *et al.* (see Table 1). The absolute BEs reported, however, vary substantially between the two groups. This may be related to differences in the BE scale calibration procedures used.

It is interesting to consider the implications of the observed O 1s BE shifts. Assuming that the shifts are

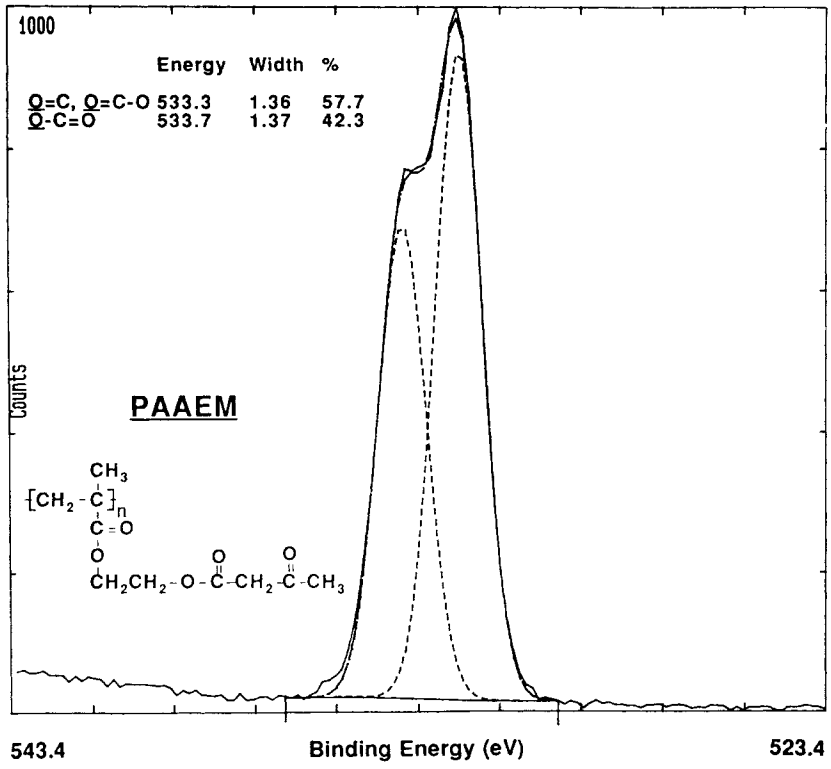

Figure 3. The resolved XPS O 1s spectrum of PAAEM, showing peaks arising from the C=O, O—C=O, and O—C=O oxygens present in PAAEM.

caused by initial state effects (i.e. the shifts are related to the electron density on each oxygen functional group), the following statements can be made. First, for the functional groups in this study, the carbonyl oxygen is the most effective electron-withdrawing group since it has the lowest O 1s BE. Second, the presence of another oxygen two atoms away does not significantly decrease or enhance the ability of the carbonyl oxygen to withdraw electron density from the carbonyl carbon, i.e. C=O (ketone) and O—C=O (ester) groups have approximately the same carbonyl O 1s BE. Third, the electron-withdrawing power of a singly bonded oxygen is affected by the presence of a carbonyl group. In an ester group, a portion of the electron density of the ester carbon is withdrawn by the carbonyl oxygen, resulting in a more electropositive carbon bound to the ester-linked oxygen. This results in the higher BE observed for O=C—O—C (ester) compared to C—O—C (ether). Finally, C—O—C (ether) and C—O—H (hydroxyl) oxygens have similar BEs. This is reasonable since carbon and hydrogen have similar electronegativities. Similar arguments rationalizing initial state contributions to oxygen core ionization energies of esters, carboxyls, alcohols and ethers have been made previously by Siggel and Thomas.[13]

However, the differences in molecular environments of the various oxygen functional groups may have a significant influence on the relative magnitudes of final state contributions (e.g. relaxation effects) to the respective O 1s BEs. Demonstration of the importance of the final state contribution to O 1s BEs requires either a systematic variation of the molecular structure around the functional group or detailed theoretical analysis of the photoionization and the ensuing electronic relaxation of the molecule. Mills *et al.*[10] used the former methodology to study a series of gas-phase alcohols, ethers and esters. Jolly and Schaaf[9] also investigated carbonyl-containing compounds. Clark *et al.*,[5] using molecular orbital calculations which included relaxation energy, determined O 1s BEs for a variety of small molecules containing oxygen functional groups. A few other theoretical studies of O 1s BEs have been published,[3,7,11,13] but these have dealt mainly with ester functional groups.

Despite the limited number of theoretical studies addressing alcohol-, ether- and ketone-containing compounds, we can make some comparisons of relative O 1s BEs. Using relative BEs for the different oxygen functional groups in similar molecular environments (i.e. structure, molecular size, etc.) for small molecules to minimize relaxation effects, BE shifts should be comparable with data obtained from the model polymers (which are assumed to have similar relaxation energies). For example, Table 6 compares the O 1s BE shifts for the various oxygen functional groups in polymers with BE shifts obtained from gas-phase XPS[10] and molecular orbital calculations[5] for simple molecules. Table 6 shows that the O 1s BE shifts obtained from the model polymers are in good agreement with those from the model compounds.

Table 6. Experimental and theoretical XPS O 1s BE shifts, relative to the ester group carbonyl, O—C=O

	BE shift (eV)		
	Model polymers	Gas phase[a]	Calculated[b]
O—C=O	0	0 ($CH_3CO_2CH_3$)	0 ($CH_3CO_2CH_3$)
C=O	0.0	0.02 (CH_3COCH_3)	−0.1 (CH_3COCH_3)
C—O—H	0.6	0.86 (CH_3CH_2OH)	0.7 (CH_3CH_2OH)
C—O—C	0.6	0.65 (CH_3OCH_3)	0.4 (CH_3OCH_3)
O—C=O	1.5	1.53 ($CH_3CO_2CH_3$)	1.4 ($CH_3CO_2CH_3$)

[a] Experimental gas-phase O 1s BE shifts derived from gas-phase molecules (from Ref. 10).
[b] Theoretical O 1s BE shifts for small molecules (from Ref. 5).

CONCLUSIONS

Although disagreement in the absolute O 1s BEs (~1 eV) was found, results presented here confirm BE shifts previously published for alcohol-, ether- and ester-containing polymers. Contrary to previous studies, however, the ketone oxygen was found to exhibit a BE shift much closer to that of the carbonyl oxygen in esters than to alcohol or ether oxygens. The polymer O 1s BEs measured in this study are

C=O ~ O—C=O (532.2 eV)
< C—OH ~ C—O—C (532.8 eV)
< O=C—O (533.7 eV)

For polymers that contain a mixture of ester and alcohol or ketone groups (e.g. PHEMA or PAAEM), the O 1s spectrum provides a means of distinguishing the three different types of oxygen present in those groups. As line widths in XPS spectra of polymers continue to decrease, the utility of O 1s spectral information from polymers will undoubtedly add analytical power to XPS functional group determination.

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