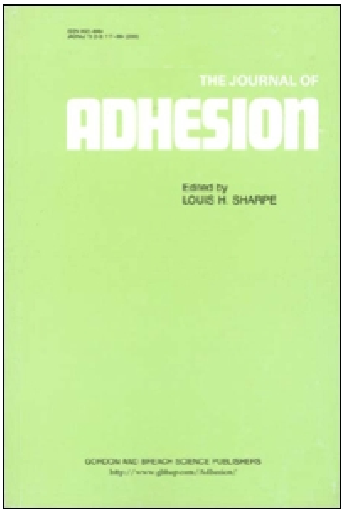

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# The Use of Monochromated XPS to Evaluate Acid-Base Interactions at the PMMA/Oxidised Metal Interface

S. R. Leadley[a]; J. F. Watts[a]
[a] Department of Materials Science and Engineering, University of Surrey, Guildford, Surrey, UK

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# The Use of Monochromated XPS to Evaluate Acid-Base Interactions at the PMMA/Oxidised Metal Interface*

S. R. LEADLEY and J. F. WATTS

*Department of Materials Science and Engineering, University of Surrey, Guildford, Surrey, GU2 5XH, UK*

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Recent studies have proposed that a near-interface conformation of PMMA in PMMA/metal substrate systems is different from the bulk polymer. High-resolution XPS analysis using monochromated X-ray sources has shown that PMMA interactions with metal oxide substrates are determined by the acido-basic nature of the substrate. It has also been shown that PMMA interacts with acidic sites on oxidised silicon *via* the carbonyl oxygen, and strongly basic sties on oxidised copper and nickel will react with the carboxyl carbon *via* nucleophilic attack. On amphoteric substrates, such as oxidised iron and aluminium, it is proposed that hydrolysis of the methyl ester occurs at weak basic sites to form a carboxylate, resulting in complexes being formed with the metal substrate. Such acid-base interactions would result in the orientation of PMMA at the interface to be dependent on the acido-basic nature of the substrate. This study also shows the resolution of a microfocussed monochromated X-ray source retrofitted to an older XPS spectrometer to be close to that of the Scienta ESCA 300 instrument.

KEY WORDS: Poly(methyl methacrylate); acid-base interactions; monochromated XPS; silicon; iron; aluminium; nickel; copper.

## INTRODUCTION

One of the most important properties of polymers, which has enabled them to be used widely in adhesion and coatings applications, is their ability to become readily adsorbed on to solid surfaces.[1] This is due to polymers having large surface areas which produce correspondingly high values of surface activity and thus, facilitating adsorption as a means of reducing the surface activity, (*i.e.* the surface free energy) of the solid.[2] In the adhesion of organic coatings or adhesives to inorganic substrates various chemical and/or configurational changes may occur in the interphase region.[3] One manner in which the performance of such systems can be improved is by a more complete understanding of such interactions; it may then become possible to engineer the exact characteristics of the interphase to provide superior properties.

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The work reported in this paper is part of an ongoing programme to understand the interactions that occur at an organic/inorganic interface, and to develop methodologies for their study.

Poly(methyl methacrylate) (PMMA) has been widely used in studies of polymer/substrate interactions.[4–8] In recent theoretical studies using a kinetic Ising model, Chakaraborty and co-workers have studied the PMMA/aluminium system.[4,5] These simulation studies have shown a near–interface conformation in which the polymer chains tend to lie in a relatively flat orientation parallel to the metallic substrate. This gives a net result in which there appears to be a thin, diffuse, layer of PMMA between the bulk polymer and the substrate, which is shown conceptually in Figure 1.

Chakaraborty *et al.* also showed that the aluminium substrate interacts with PMMA *via* the carboxyl oxygen. The interaction of aluminium with carboxyl oxygen has also been shown experimentally in XPS studies of vapour deposited aluminium on poly(ethyleneterephthalate).[9]

However, it should be noted that both the model of PMMA on aluminium and the PET study used pure aluminium, and did not include a native oxide. When a clean metal surface is exposed to the atmosphere an oxide layer is grown rapidly. Therefore, when considering polymers cast from solution on to metal substrates under laboratory conditions, the interfacial interactions under investigation will be between the polymer and the metal oxide.

It has also been shown in another study, using internal reflection infra-red spectroscopy, that the carboxyl oxygen of PMMA is hydrogen bonded to silanol sites on a silicon substrate.[6] Evidence for the interaction of PMMA at the interface of PMMA/silicon systems has also be proposed from results of X-ray photoelectron (XPS) studies.[7,8] Chehimi and Watts used XPS to study PMMA films peeled from silicon and soda glass substrates. The observation was made by angular resolved XPS that acid or alkali treatment of glass and silicon substrates can lead to the reorientation of the carboxyl group of PMMA at the PMMA/inorganic interface.[7] Such orientation was found to be most pronounced at low pH; *i.e.* when acid-base interactions between the acidic substrate and oxygen atoms of the basic carboxyl group of PMMA would be at a maximum, as shown in Figure 2.

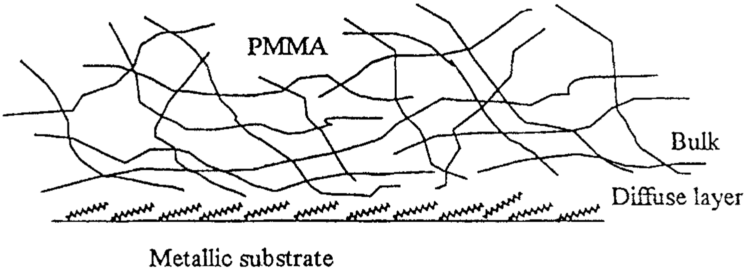


FIGURE 1 Schematic model indicating the formation of a diffuse interphase between aluminium and bulk PMMA, from the work of Chakaraborty *et al.*[4,5]

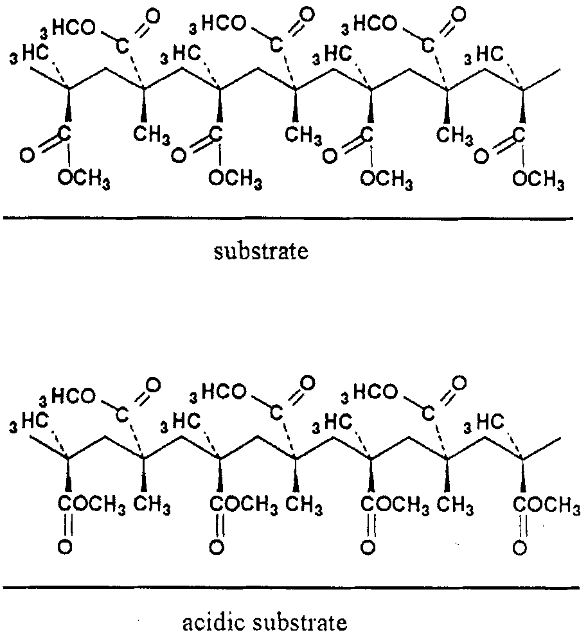


FIGURE 2 Schematic representation of PMMA interaction with a solid surface. The upper diagram represents the situation that is thought to exist when acid-base interactions are weak or non-existent. The lower sketch shows the reorientation of the carboxyl group which occurs in the case of stronger acid-base interactions that are present when PMMA is applied to an acid substrate.[7]

Beamson and co-workers observed that the peak fitting of the C 1s spectrum of thin PMMA films spin-cast on to silicon wafers varied with the thickness of the polymer overlayer, and that the thicker layers yielded spectra identical to those taken from bulk PMMA.[8] They reported that the binding energy shift of the carboxyl carbon component of PMMA was 0.1 eV greater in the thinnest film than the binding energy of the carboxyl carbon in the thicker film of PMMA, indicative of the bulk polymer. This small increase in the binding energy shift of the carboxyl carbon component was attributed to interaction between PMMA and the substrate. This correlates with the IR spectroscopic study of PMMA/silicon systems,[6] which indicates that interaction occurs *via* hydrogen bonding between the carboxyl oxygen of the polymer and silanol groups of the substrate. Hydrogen bonding is, of course, an excellent example of a donor-acceptor or acid-base interaction. When PMMA is bound to the silicon substrate, the acidity of the silanol groups causes the electropositivity of the carboxyl carbon to increase due to electron withdrawal from the carboxyl oxygen. This would result in an increase in the binding energy of the carboxyl carbon of PMMA, as observed by Beamson and Briggs.[8] This indicates that XPS can be used to investigate the acid-base interactions between polymers and substrates, and is consistent with previous work from this laboratory, in which it has proved possible to estimate the exothermic enthalpy of acid-base interactions between solid polymer and organic chemical vapour from the XPS chemical shift.[10]

The differences in binding energy shifts between thin polymer films and bulk polymer provides a futher indication that there is an interphase between bulk PMMA and the substrate on which it is cast, which is different in configuration from bulk PMMA.

The surface of naturally–acidic silicon can be rendered basic if the silanol groups are deprotonated, through treatment with sodium hydroxide. Chehimi and Watts indicated that basic silicon interacts with PMMA in such a way that the orientation of PMMA would be different from that on the naturally-acidic silicon[6]. Due to changes in the surface chemistry of the modified silicon substrate, it would be expected that the carboxyl oxygen of the PMMA would not be able to form hydrogen bonds with surface sites of the substrate.

In this work we describe the use of monochromatic Al $K_\alpha$ XPS in conjunction with a thin film approach for the direct study of interphase chemistry. Beamson and co-workers have shown that high resolution XPS can distinguish a binding energy difference of 0.1 eV between the C 1s spectra of PMMA thin films and the bulk polymer.[8] In an extension of this work we report on the use of the Scienta ESCA 300 instrument to probe the interaction of PMMA with naturally-acidic silicon and silicon modified through treatment with sodium hydroxide. We also report on the use of a VG Scientific ESCALAB MkII instrument with an upgraded X-ray monochromator to investigate the interaction of PMMA with a series of oxidised substrates. As this work discusses data acquired using two different X-ray photoelectron spectrometers, we have also reported a comparison of the resolution of these two instruments using monochromated Al $K_\alpha$ X-rays.

## EXPERIMENTAL

### Spectroscopy

XPS spectra were acquired from modified silicon substrates using a Scienta ESCA 300 spectrometer. This spectrometer combines a high-power, rotating-anode X-ray source ($AlK_\alpha$), a monochromator consisting of seven $\alpha$-quartz crystals, high transmission electron optics and a multichannel detector. The design and the performance of the spectrometer have been described in detail elsewhere.[11,12] Spectra were recorded at 150 eV pass energy, 0.5 mm slit width, 3.15 kW X-ray source power, and a take-off angle of 90°. After peak fitting the C 1s spectra, all spectra were charge referenced so that the unfunctionalised aliphatic C 1s component occurs at 285 eV binding energy. Curve fittig of the C 1s spectra was performed using the Scienta ESCA 300 data system software. This describes each of the components of a complex envelope as a Gaussian-Lorentzian sum function.[13]

The bulk of the XPS spectra presented in this paper were acquired using a VG Scientific ESCALAB Mk II electron spectrometer with an upgraded X-ray monochromator. This monochromator is of a 1/2 metre, single crystal assembly, fitted with a microfocussed electron gun. This produces monochromatised Al $K_\alpha$ X-radiation with X-ray spot sizes selectable to provide a nominal irradiated area at the specimen of 150, 300, 600, or 1000 μm diameter. Monochromated X-rays were used with the 1000 μm spot selected, and the sample placed relative to the analyser electron optics to give a 45° take-off angle. The analyser slit width was 6 mm and the electron transfer lens operated at a magnification of 3. The analyser was operated in the fixed analyser transmission mode with a pass energy of 50 eV for survey spectra, or 20 eV for core level spectra. Data acquisition, analysis, and curve fitting were performed by a VGS 5000S data system based on a DEC PDP 11/73 computer.

### Sample Preparation

The substrates used in the study utilising the Scienta ESCA 300 spectrometer included silicon as received and silicon treated in 0.1 M sodium hydroxide solution at pH 13.4, which were mounted on VG ESCALAB MkII type sample stubs. The sample stubs were then mounted on a simple low speed rotor (approximately 100 Hz), and thin films prepared by spin casting from a 0.025%*W*/*W* PMMA (medium molecular weight [MW = 120, 000, atactic], Aldrich Chemical Company) solution in chloroform.

The substrates used in the study utilising the VG ESCALAB MkII spectrometer included silicon, iron (Marz grade, Materials Research Corporation), aluminium (99.0%, Goodfellows Metals), copper (99.9%, BDH Chemicals Ltd), and nickel (99.7%, Koch-Light Laboratories), mounted on VG ESCALAB MkII type sample stubs. The gold substrate was prepared by sputter coating onto a VG ESCALAB MkII type sample stub that had been polished to a 1 μm finish. The substrates were then placed in the spectrometer and etched, using arogon ion bombardment, to remove any oxide and surface contamination. They were then removed from the spectrometer and mounted in the spin coater. On removal of the substrates from the spectrometer natural oxide growth occurred, typically of the order 1–2 nm thick. Thin polymer films were prepared by spin casting PMMA solutions in chloroform on to the rotating substrates (*ca.*, 2770 r.p.m). The thickness of the thin polymer films was measured using a Beer-Lambert approach based on the attenuation of the substrate signal compared with that from a clean *i.e.*, contamination-free) oxidised metal. The values obtained for all PMMA films were in the region of 2.5–3.0 nm with the exception of gold, which showed no evidence of PMMA deposition.

## RESULTS

### Comparison of Monochromatic X-Ray Sources

To compare the resolution of the microfocussed monochromator on the VG ESCALAB MkII spectrometer with the monochromated X-ray source of the Scienta ESCA 300 spectrometer, the C 1s spectrum of highly oriented pyrolytic graphite (HOPG) on silicon was acquired using the new single crystal monochromator fitted to the VG ESCALAB MkII, and is shown in Figure 3. At an analyser pass energy of 20 eV, the carbon spectrum had a full width half maximum (FWHM) of 0.60 eV and at an analyser pass energy of 10 eV, a FWHM of 0.55 eV. The C 1s spectrum of

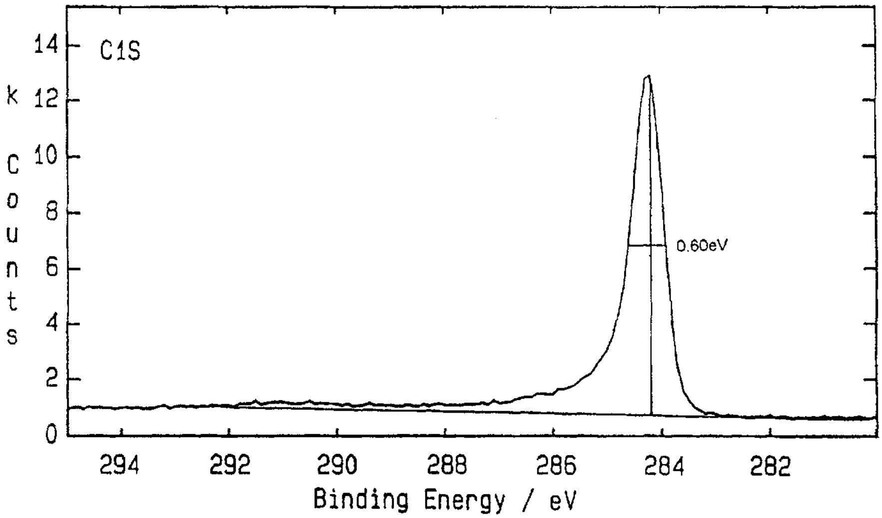


FIGURE 3 The C 1s spectrum of highly-orientated pyrolytic graphite on silicon using a microfocussed monochromatic X-ray source and 20 eV analyser pass energy.

HOPG on silicon acquired with the Scienta ESCA 300 spectrometer has been shown to have a FWHM of 0.54 eV with a pass energy of 150 eV and a slit width of 0.5 mm, and a FWHM 0.45 eV with a pass energy of 75 eV and a slit width of 0.2 mm.[14] All C 1s spectra acquired by the VG ESCALAB MkII spectrometer presented in this paper used a 20 eV analyser pass energy, and C 1s spectra acquired by the Scienta ESCA 300 spectrometer shown in this paper used a slit width of 0.5 mm with a pass energy of 150 eV. Therefore, it can be seen that, under the operating conditions used in the acquisition of data discussed in this paper, the resolution of the microfocussed monochromator was close to the resolution of Scienta ESCA 300 spectrometer. However, it should be noted that the X-ray source of the Scienta ESCA 300 spectrometer has a greater power than the microfocussed monochromator on the VG ESCALAB MkII spectrometer, in addition to a much larger analyser. As a result, the transmission (sensitivity) of the Scienta ESCA 300 spectrometer was far superior to that of the VG ESCALAB MkII spectrometer fitted with a microfocussed monochromator.

## Modified Silicon Substrate

Polymer films were spin-cast from a PMMA solution onto silicon substrates, as received and treated with 0.1 M sodium hydroxide. The survey spectra of these samples clearly show the presence of the silicon substrate and, thus, the C 1s spectra can be considered indicative of PMMA at the polymer-substrate interface. Figure 4 shows a comparison of the C 1s spectra of PMMA on the two silicon substrates. It can be seen that the binding energy of the carboxyl carbon at approximately 289 eV was greater on the modified silicon than on the naturally-acidic silicon substrate,

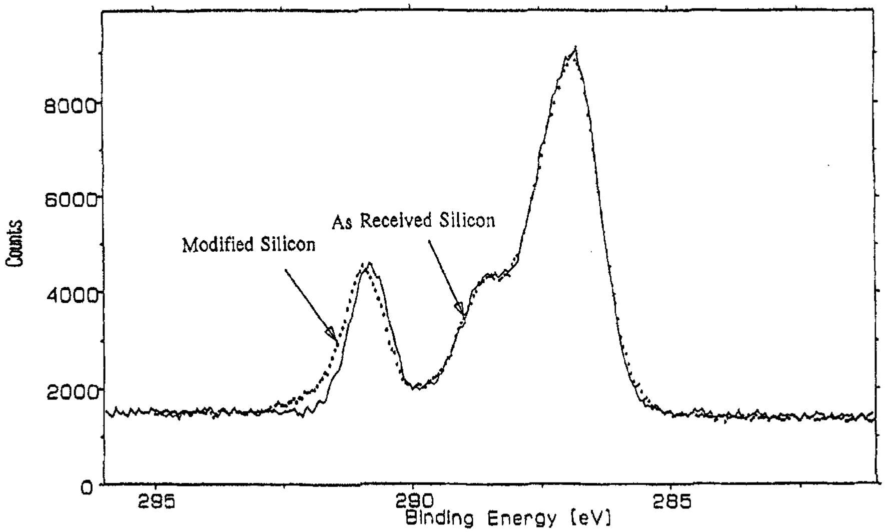


FIGURE 4 A comparison of the C 1s spectra of PMMA on silicon as received and PMMA on silicon modified with 1M sodium hydroxide at pH 13.4.

while the rest of the spectra show extremely good agreement. This change in the C 1s spectra of PMMA clearly shows that the treatment of the silicon substrate with sodium hydroxide altered the polymer/substrate interface.

## Substrates of Differing IEPS Values

Polymer films were spin-cast from a PMMA solution onto a series of substrates which had an increasing level of natural basicity, as indicated by the iso-electric point of the solid surfaces (IEPS). Figure 5 shows the XPS survey spectrum of the PMMA film spin-cast on to oxidised iron. The survey spectrum clearly shows the presence of the iron substrate and, thus, the spectra can be considered indicative of PMMA at the polymer-substrate interface.

Although it was originally accepted that the peak synthesis of the C 1s spectrum of PMMA should involve a three-peak fit, Pjipers and Donners proposed that a better fit to the experimental data could be obtained by using a four-peak fit, with the fourth peak being due to a beta-shift induced by ester oxygens.[15] Beamson and co-workers have also shown, using high resolution XPS, that a three-peak fitting scheme is not an adequate description of the PMMA C 1s spectrum, although they were not able to distinguish as to whether a four-peak or five-peak fitting scheme gave the best description.[8] Therefore, when curve fitting the high resolution C 1s spectra of PMMA in this study a four-peak fit was applied to experimental data; *i.e.* the four peaks, aliphatic hydrocarbon ($\underline{C}_1$—C/$\underline{C}_1$—H) (assumed to have a binding energy of 285.0 eV[13]), an ester oxygen induced beta-shifted carbon ($\underline{C}_2$—C=O), the methyl ester ($\underline{C}_3$—O), and the carboxyl carbon ($\underline{C}_4$=O). Examples of this peak-

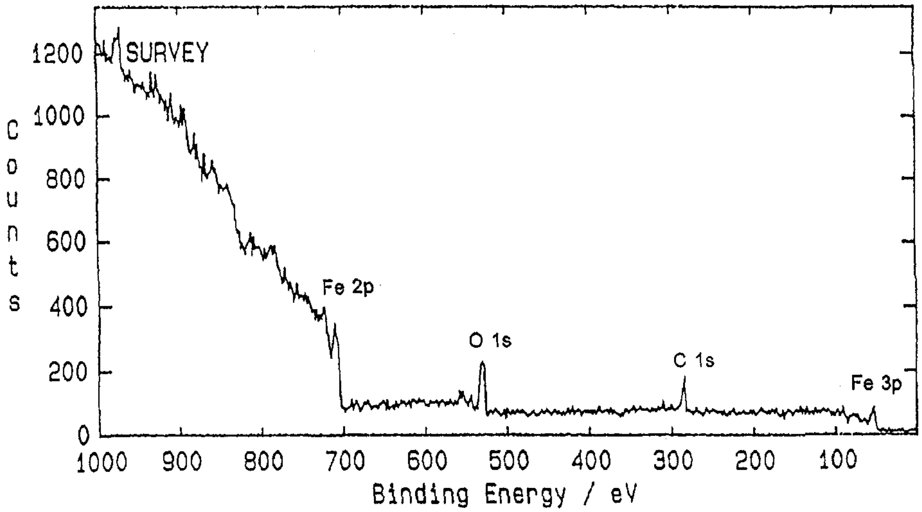


FIGURE 5 XPS survey spectrum of 0.025% *w/w* PMMA in $CHCl_3$ on an oxidised iron substrate.

fitting protocol are shown below for PMMA spin-cast onto oxidised silicon (acidic) and oxidised iron (basic) substrates.

When deciding whether the peak-fitting of an XPS spectrum is acceptable, the reduced chi-squared value incorporated in most commercial software might be considered, which is generally related to chi-squared in the following manner:

$$\text{reduced}\chi^2 = \frac{\chi^2}{\text{NormalisationFactor}}$$

The normalisation factor used in the VGS5000S software is related to the number of peaks fitted and the number of degrees of freedom, $N$ (this includes the usual peak-fitting variables of peak width, position, intensity, shape and so on).

$$\text{Normalisation Factor} = N + 4 \times (\text{Number of Peaks})$$

Thus, reduced chi-squared should only be used for assessing acceptability of peak-fitting of spectra if the number of peaks used in fitting each spectrum are the same. A sensitive and flexible test of goodness of fit is the human eye and a plot of the residuals (the difference between experimental and calculated data plotted on a horizontal axis) will also be very informative.[16] Thus, all the peak-fitting discussed in this paper has been assessed by the plot of the residuals and visual assessment of the quality of fit. In this manner, a self-consistent protocol for peak-fitting of the C 1s spectra considered in this work was eventually developed. This is described below.

Figure 6a shows the C 1s spectrum of PMMA spin cast on to a naturally-acidic oxidised silicon substrate, which has an IEPS of pH 2.2.[17] It can be seen that the four-peak fit strategy fitted the experimental data well, with baseline separation of the carboxyl carbon ($\underline{C}_4{=}O$) from the rest of the spectrum. The beta-shifted carbon

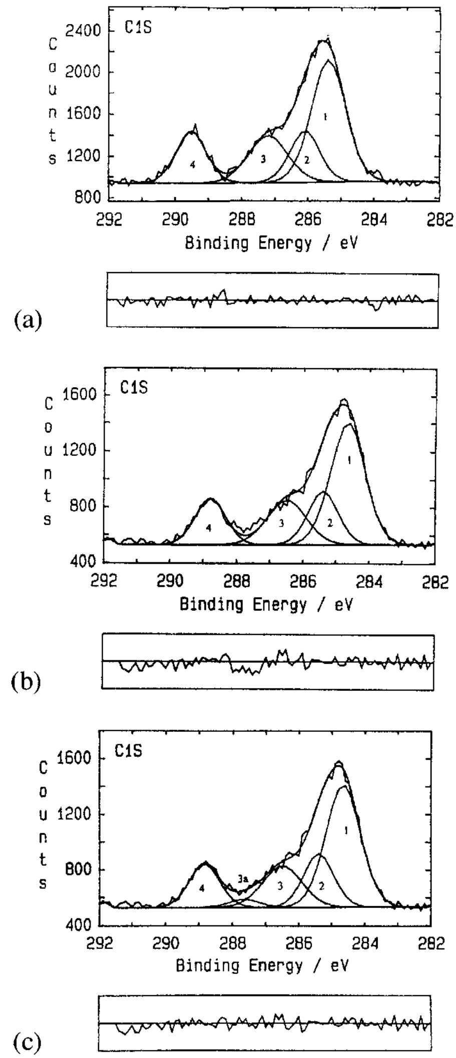


FIGURE 6 HIgh-resolution XPS spectra showing: a) four-peak fit of PMMA on an oxidised silicon substrate, b) four-peak fit of PMMA on an oxidised iron substrate, c) five-peak fit of PMMA on an oxidised iron substrate.

($\underline{C}_2$—C=O) had a binding energy shift of 0.7 eV, the methyl ester carbon ($\underline{C}_3$—O) a binding energy shift of 1.8 eV and the carboxyl carbon ($\underline{C}_4$=O) having the binding energy shift of 4.1 eV, as shown in Table I. From the area ratios shown in Table I, it can be seen that the methyl ester peak ($\underline{C}_3$—O) is larger than would be expected from the stoichiometry, but this might also be due to its FWHM being slightly larger than the other three peaks fitted. A slight increase in the FWHM of the methyl ester peak ($\underline{C}_3$—O) has been attributed to some form of interaction between the ester side chains.[7]

TABLE I

Four-Peak Fitting Data From the C 1s Spectra of PMMA on Substrates of Differing IEPS

| | | ($\underline{C}_2$—C=O) | | | ($\underline{C}_3$—O) | | | ($\underline{C}_4$—O) | | | ($\underline{C}_4$—O) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Substrate | IEPS[17] | BE Shift (eV) | FWHM (eV) | % Area | BE Shift (eV) | FWHM (eV) | % Area | BE Shift (eV) | FWHM (eV) | | BE Shift (eV) | FWHM (eV) | % Area |
| Silicon | 2.2 | 285.0 | 1.27 | 46 | 285.7 | 1.10 | 17 | 286.8 | 1.44 | 20 | 289.1 | 1.10 | 17 |
| Iron | 7.0 | 285.0 | 1.27 | 47 | 285.7 | 1.10 | 18 | 286.8 | 1.44 | 20 | 289.1 | 1.10 | 16 |
| Aluminium | 9.0 | 285.0 | 1.25 | 46 | 285.7 | 1.08 | 16 | 286.8 | 1.42 | 20 | 289.1 | 1.08 | 18 |
| Copper | 9.5 | 285.0 | 1.27 | 49 | 285.7 | 1.10 | 17 | 286.8 | 1.44 | 19 | 289.1 | 1.10 | 15 |
| Nickel | 10.3 | 285.0 | 1.27 | 44 | 285.7 | 1.10 | 19 | 286.8 | 1.44 | 21 | 289.2 | 1.10 | 16 |

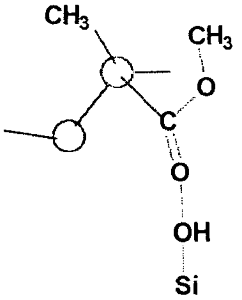
Having shown that a four-peak fitting strategy shows good agreement with the experimental data acquired from PMMA spin-cast on to the silicon substrate, four peaks of the same shape as those used in Figure 6a were fitted to the C 1s spectrum of PMMA spin-cast onto an oxidised iron substrate, as shown in Figure 6b. It can be seen in Table I that the binding energy shifts of the four peaks fitted to the C 1s spectrum of PMMA spin-cast on to oxidised iron were similar to those used in the peak synthesis of PMMA on oxidised silicon. However, it can be seen in Figure 6b that the C 1s spectrum of PMMA spin-cast onto oxidised iron did not show baseline resolution between the carboxyl carbon ($\underline{C}_4{=}O$) and the rest of the spectrum as seen in Figure 6a. In addition to the lack of baseline resolution, the plot of the residuals in Figure 6b also shows that the four-peak fitting strategy was inadequate for PMMA spin-cast onto oxidised iron. Therefore, a fifth peak ($\underline{C}_{3a}$) was fitted to the C 1s spectrum which resulted in better agreement with the experimental results, as shown by the plot of the residuals in Figure 6c. The lack of baseline resolution between the carboxyl carbon ($\underline{C}_4{=}O$) and the rest of the spectrum and the necessity of a five-peak fitting strategy was also observed in the C 1s spectra of PMMA spin-cast on to substrates of oxidised aluminium, copper and nickel.

## DISCUSSION

The results reported above have shown that monochromated Al $K_\alpha$ X-ray sources can be used successfully to observe changes in high resolution C 1s XPS spectra of PMMA interacting with substrates of differing acido-basic character. For the sake of clarity, the results relating to PMMA spin-cast on to silicon substrates will be considered first.

Through a four-peak fitting strategy, the binding energy shift of the carboxyl carbon ($\underline{C}_4{=}O$) in bulk PMMA on a silicon substrate has been shown to be 4.0 eV.[14] However, when a similar four-peak fitting strategy was applied to an ultra-thin layer of PMMA on a silicon substrate, as shown in Figure 6a, the binding energy shift of the carboxyl carbon ($\underline{C}_4{=}O$) was found to be 4.1 eV, as shown in Table I. When a four-peak fitting strategy was applied to the C 1s spectrum of PMMA spin-cast onto the as received silicon substrate acquired using the Scienta ESCA 300 spectrometer, 4.1 eV binding energy shift of the carboxyl carbon was also observed. It should be noted that the fitting of four peaks to the C 1s spectrum of PMMA on silicon acquired using the ESCA 300 spectrometer was entirely consistent with data acquired using the VG ESCALAB MkII spectrometer.

A study by Beamson and co-workers, using a Scienta ESCA 300 spectrometer,[8] has shown that the carboxyl carbon in an ultra-thin film of PMMA on silicon had a binding energy shift 0.1 eV greater than that observed in thicker polymer films. IR spectroscopic data has shown that PMMA interacts with silanol groups *via* hydrogen bonding with the carbonyl oxygen.[6] Thus, the increase in binding energy shift of the carboxyl carbon of 0.1 eV between ultra-thin films and bulk PMMA can be attributed to hydrogen bonding between the carbonyl oxygen of PMMA and silanol groups on the substrate. This is consistent with the orientation of PMMA at the interface as shown below.



It can be seen in Figure 4 that the binding energy of the carboxyl carbon at approximately 289 eV was greater on the modified silicon than on the naturally-acidic silicon substrate, while the rest of the spectra show extremely good agreement. It was assumed, from a previous study,[7] that the treatment of silicon with sodium hydroxide would deprotonate the naturally-acidic silanol groups present at the surface of silicon and, thus, prevent hydrogen bonding between the carbonyl oxygen of PMMA and silanol groups. It has been discussed above that hydrogen bonding at the PMMA/silicon interface results in the carboxyl carbon of PMMA having a binding energy shift 0.1 eV greater than that observed in thicker polymer films. Therefore, it would be expected that if hydrogen bonding was prevented, the carboxyl carbon of PMMA on the sodium-hydroxide-treated silicon would have a binding energy shift lower than that observed in the C 1s spectrum of PMMA on as received silicon; however, as observed in Figure 4, this is not the case.

When applying a four-peak fitting strategy to the C 1s spectrum of PMMA spin-cast onto the sodium-hydroxide-treated silicon substrate an accurate fit was not achieved, due to asymmetry of the carboxyl carbon. A more accurate fit was achieved by fitting a fifth peak to the carboxyl carbon component, as shown in Figure 7. This indicates that the carboxyl carbon interacts with the sodium-hydroxide-treated substrate in such a way that it becomes more electropositive. The binding energy shift, relative to the aliphatic hydrocarbon ($\underline{C}_1$—C/$\underline{C}_1$—H) of this additional peak was 4.5 eV, *i.e.* some 0.4 eV greater than the other carboxyl component. This is equivalent to a binding energy shift associated with carbon bound to three oxygen atoms, as observed in poly(ortho esters).[14]

In acyl nucleophilic substitution, the trigonal planar acyl carbon is stoichiometrically open to attack from a nucleophile, which is, sterically, relatively unhindered. Through the breaking of a weak $\pi$ bond, and the oxygen atom gaining a negative charge, a stable intermediate may be formed, as shown in Figure 8.[18] As the carboxyl carbon in PMMA is acyl, it can be assumed that it is open to nucleophilic attack from the sodium-hydroxide-treated silicon substrate, possibly leading to the interaction shown in Figure 9. If this is the manner in which the PMMA interacts with the sodium-hydroxide-treated substrate, inductive effects will make this carboxyl carbon more electropositive than when the carbonyl oxygen is hydrogen bonded to the substrate, leading to a much higher binding energy shift. This would

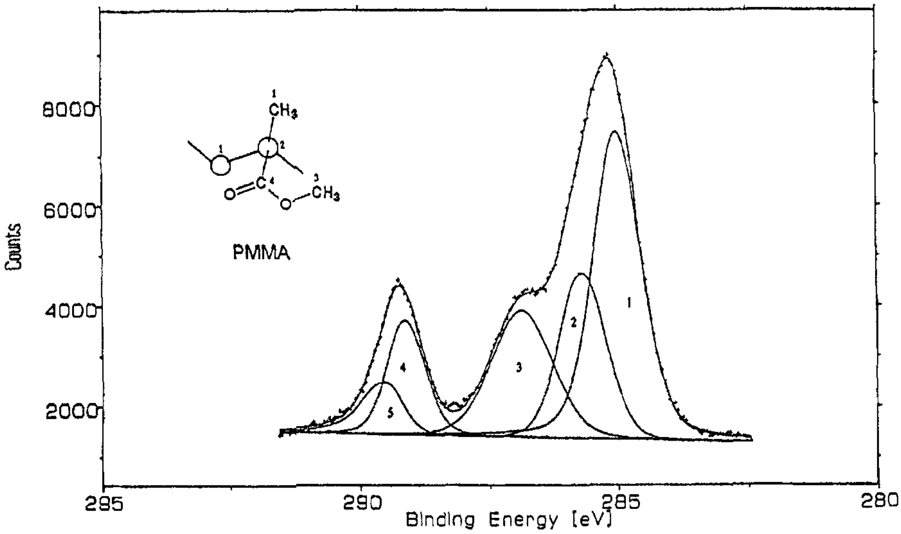


FIGURE 7 Curve fitting of the C 1s spectrum of PMMA on silicon modified with 1M sodium hydroxide at pH 13.4.

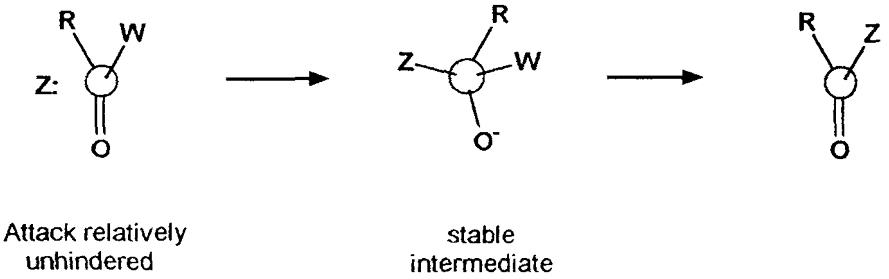


FIGURE 8 Acyl nucleophilic substitution.[14]

explain the necessity of fitting a fifth peak to the C 1s spectrum shown in Figure 7, which had the binding energy shift of 4.5 eV.

The fitting of two peaks to the carboxyl component of the C 1s spectrum of PMMA on the sodium-hydroxide-treated silicon indicates that a number of silanol groups were not deprotonated. This is shown by the lower binding energy component having a binding energy shift of 4.1 eV, which is indicative of hydrogen bonding between the carbonyl oxygen of PMMA and silanol groups at the polymer substrate interface.

Having shown that PMMA interacts at the interface with sodium-hydroxide-treated silicon in a different manner from that of "as-received" silicon, it is proposed that this is due to changes in the acido-basic nature of the substrate. This indicates that high-resolution XPS analysis using monochromated X-rays can be used to investigate acido-basic interactions at the polymer/substrate interface. The remainder

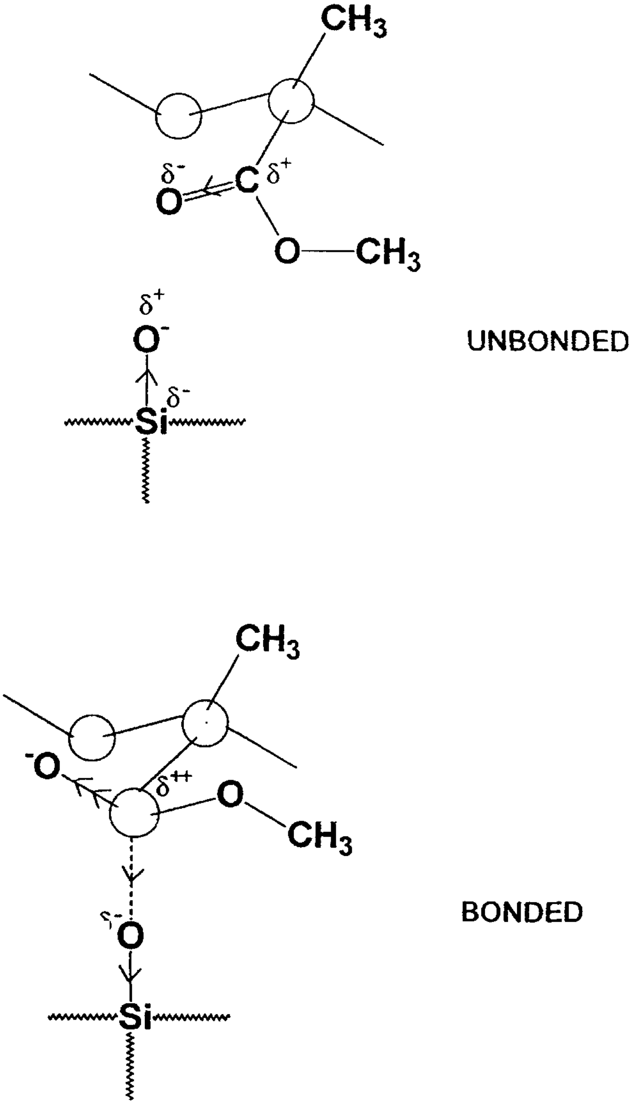


FIGURE 9 Schematic showing possible inductive effects in PMMA and silicon modified with 1M sodium hydroxide at pH 13.4.

of this discussion will concentrate on the interactions of PMMA with substrates which have IEPS more basic than naturally-occurring silicon oxide.

It was shown that although a four-peak fitting strategy was applicable to the C 1s spectrum of PMMA spin-cast onto oxidised silicon, four-peak fits of the C 1s spectra of PMMA spin-cast onto oxidised iron, aluminium, copper and nickel did not accurately represent the experimental data. Thus, it was necessary for a fifth peak to be added to the C1s spectra of PMMA spin-cast onto substrates more basic than silicon, as shown in Figure 6c. It can be seen in Table II that the binding

TABLE II

Five-Peak Fitting Data From the C 1s Spectra of PMMA on Substrates of Differing IEPS

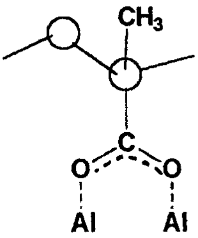
| | | ($\underline{C}_1$—C/$\underline{C}_1$—H) | | | ($\underline{C}_2$=C=O) | | | ($\underline{C}_3$—O) | | | ($\underline{C}_{3a}$) | | | ($\underline{C}_4$=O) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Substrate | IEPS[17] (pH) | BE Shift (eV) | FWHM (eV) | % Area | BE Shift (eV) | FWHM (eV) | % Area | BE Shift (eV) | FWHM (eV) | % Area | BE Shift (eV) | FWHM (eV) | % Area | BE Shift (eV) | FWHM (eV) | % Area |
| Iron | 7.0 | 285.0 | 1.27 | 47 | 285.7 | 1.10 | 18 | 286.8 | 1.44 | 18 | 288.0 | 1.12 | 3 | 289.1 | 1.10 | 15 |
| Aluminium | 9.0 | 285.0 | 1.24 | 46 | 285.7 | 1.07 | 16 | 286.8 | 1.41 | 19 | 288.0 | 1.07 | 2 | 289.1 | 1.07 | 17 |
| Copper | 9.5 | 285.0 | 1.27 | 48 | 285.7 | 1.10 | 18 | 286.8 | 1.44 | 17 | 288.7 | 1.10 | 3 | 289.1 | 1.10 | 14 |
| Nickel | 10.3 | 285.0 | 1.27 | 44 | 285.7 | 1.10 | 19 | 286.8 | 1.44 | 19 | 287.8 | 1.10 | 4 | 289.2 | 1.10 | 15 |

energy shifts of the five peaks fitted to the C 1s spectra of PMMA spin-cast onto oxidised iron and aluminium were very similar and, thus, it can be assumed that the interactions at the PMMA/substrate interface were similar for oxidised iron and aluminium.

The use of inelastic tunnelling spectroscopy (IETS) to study PMMA adsorbed on aluminium oxide suggested that acid or base catalysed hydrolysis occurred, generating carboxylate groups.[19] IETS studies of Hall and Hansma[20] propose that carboxylic acids dissociate on the aluminium oxide surface due to the presence of adsorbed water, *i.e.*

$$(\mathrm{OH}^-)_{\mathrm{ad}} + \mathrm{RCOOH} \rightarrow (\mathrm{RCO_2})_{\mathrm{ad}} + \mathrm{H_2O}$$

The carboxylate anions are then thought to adsorb *via* a symmetrical bidentate complex with the aluminium ions in the oxide. Therefore, it can be proposed that PMMA is converted to poly(methacrylic acid) (PMAA) at basic sites interacting with the oxidised aluminium substrate as shown below.



If this interaction was occurring through carboxylate anions generated by hydrolysis, the C 1s spectra of PMMA would be expected to change in three ways: loss of intensity from the ($\underline{C}_3$—O) component, an equivalent loss from the ($\underline{C}_4$=O) component and the appearance of a new peak due to COO; having an intensity equal to that lost by ($\underline{C}_3$—O) or ($\underline{C}_4$=O). As it was necessary for a fifth peak to be fitted to the C 1s spectra of PMMA on iron and aluminium oxides, this peak can be assigned to a carboxylate ($\underline{C}_{3a}$OO). By comparing Tables I and II it can be seen that the peak areas of both the ($\underline{C}_3$—O) and ($\underline{C}_4$=O) components of PMMA on oxidised iron and aluminium were reduced in the five-peak fit, and that the peak area of the ($\underline{C}_{3a}$OO) component was equal to the reduction in the peak areas of the ($\underline{C}_3$—O) and ($\underline{C}_4$=O) components. Thus, both the fitting of the fifth peak and the experimental stoichiometry give evidence for PMMA interacting with oxidised iron and aluminium *via* a carboxylate anion as a result of hydrolysis. The binding energy of the ($\underline{C}_{3a}$OO) peak was found to be 288.0 eV, and it is expected that future experimental results will show that a binding energy shift of 3.0eV is indicative of a carboxylate anion (COO).

It can be seen from Table II that, although the five-peak fit of PMMA on oxidised iron and aluminium gives evidence for interaction *via* a carboxylate anion, the binding energy shift of the carboxyl ($\underline{C}_4$=O) component has a value of 4.1 eV, which is indicative of hydrogen bonding. Although oxidised iron and aluminium can be considered neutral or slightly basic, with IEPS of pH 7 and 9, respectively, there will be both acidic and basic sites present. Thus, it is not unexpected that hydrogen bonding, indicated by the binding energy shift of the ($\underline{C}_4$=O) component, was observed in the C 1s spectra of PMMA on oxidised iron and aluminium substrates.

It can be seen from Table II that the binding energy shifts of the fifth ($\underline{C}_{3a}$) peak fitted to the C 1s spectra of PMMA on oxidised copper and nickel were very similar. Thus, it can be assumed that the interactions at the PMMA/substrate interface were similar for oxidised copper and nickel. Due it being necessary to fit a fifth peak, with an area equal to the reduction in intensity of the ($\underline{C}_3$—O) and ($\underline{C}_4$=O) components of PMMA on oxidised copper and nickel, it is assumed that PMMA-interacts with oxidised copper and nickel *via* a carboxylate anion. However, the exact nature of the interaction is not known. Oxidised copper and nickel substrates are more basic than oxidised iron and aluminium; therefore, interactions of PMMA with more basic sites on the substrate would result in a greater degree of electron donation from the substrate. This causes the carbon component of PMMA at the point of interaction to be less electropositive and would account for the binding energies of the ($\underline{C}_{3a}$) peak fitted to the C 1s spectra of PMMA on oxidised copper and nickel being less than the binding energies observed in the five-peak fit of PMMA on oxidised iron and aluminium.

It can be seen from Table II that the carboxyl carbon ($\underline{C}_4$=O) in the C 1s spectrum of PMMA on oxidised nickel has a binding energy shift of 4.2 eV. This indicates that interactions occur at the PMMA/oxidised nickel interface that result in the carboxyl carbon becoming more electropositive. This was also observed in the C 1s spectrum of PMMA on the sodium-hydroxide treated silicon substrate, as shown in Figure 7. It was also observed that there was asymmetry on the high-binding-energy side of the carboxyl carbon ($\underline{C}_4$=O) in the C 1s spectrum of PMMA on oxidised copper. Therefore, a sixth peak was fitted to the carboxyl carbon ($\underline{C}_4$=O) in the C 1s spectra of PMMA on oxidised copper and nickel. It can be seen from Table III that the binding energy shifts of these additional peaks were 4.6 and 4.5 eV on oxidised copper and nickel, respectively. Thus, it can be proposed that PMMA is subjected to nucleophilic attack of the acyl carboxyl carbon from strong basic sites on the copper and nickel substrates, as proposed for PMMA on sodium-hydroxide-treated silicon. The necessity of a six-peak fitting strategy indicates that there are at least two different sites of different basic strength in the copper and nickel oxide substrates. It can be seen from Table III that the carboxyl carbon ($\underline{C}_4$=O) component has a binding energy shift of 4.0 eV, indicating that no hydrogen bonding with acidic sites is occurring, and that some of the C 1s signal will be associated with PMMA above the interface. It is most likely that some of the C 1s signal of PMMA on the oxidised silicon, iron and aluminium substrates will also be associated with bulk PMMA above the interface. However, the C 1s spectra of PMMA on the oxidised silicon, iron and aluminium substrates do not show evidence of bulk PMMA as clearly as shown in the C 1s spectra of PMMA on oxidised copper and nickel, in spite of the similarities in overlayer thickness.

Therefore, it can be proposed from the XPS data that the acido-basic nature of the substrate influences the interaction of PMMA with an oxidised metal in three ways; *i.e. via* hydrogen bonding of the carboxyl group at acidic sites, *via* hydrolysis to a carboxylate adsorbate at weak basic sites, and *via* nucleophilic attack of the

TABLE III

Six-Peak Fitting Data From the C 1s Spectra of PMMA on Copper and Nickel Substrates

| | ($\underline{C}_1$—C/$\underline{C}_1$—H) | | | ($\underline{C}_2$—C=O) | | | ($\underline{C}_3$—O) | | | ($\underline{C}_{3a}$) | | | ($\underline{C}_4$=O) | | | ($\underline{C}_{4a}$) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Substrate | BE Shift (eV) | FWHM (eV) | % Area | BE Shift (eV) | FWHM (eV) | % Area | BE Shift (eV) | FWHM (eV) | % Area | BE Shift (eV) | FWHM (eV) | % Area | BE Shift (eV) | FWHM (eV) | % Area | BE Shift (eV) | FWHM (eV) | % Area |
| Copper | 285.0 | 1.27 | 47 | 285.7 | 1.10 | 18 | 286.9 | 1.44 | 17 | 287.8 | 1.10 | 3 | 289.0 | 1.10 | 11 | 298.6 | 1.10 | 4 |
| Nickel | 285.0 | 1.27 | 44 | 285.7 | 1.10 | 19 | 286.8 | 1.44 | 18 | 287.8 | 1.10 | 3 | 289.0 | 1.10 | 9 | 289.5 | 1.10 | 7 |

carboxyl carbon at strong basic sites. Thus, it can be assumed that changes will be seen in the conformation of PMMA as a result of reorientation at the interface with one, or a combination, of the proposed orientations shown in Figure 10.

If one considers a thin film of PMMA cast onto an intert (noble) metal substrate, the resultant C 1s spectrum should be identical to that of bulk PMMA. Figure 11 shows the XPS survey spectrum of PMMA spin-cast, in the manner previously described for ESCALAB studies, on to a gold substrate (Fig. 11b), compared with the XPS survey spectrum of the clean gold-coated specimen stub (Fig. 11a). It can be observed that there is only trace amount of carbon present following PMMA deposition. This indicates that, due to lack of acido-basic, or other, interaction between PMMA and the gold substrate, only physisorption has occurred resulting in either the loss of polymer in the ultra high vacuum of the spectrometer or, more likely, the complete dewetting of the substrate by the polymer solution at the spin-coating stage. In order to deposit a thicker film of PMMA, a sessile drop of the polymer solution was deposited on the gold substrate, and the solvent allowed to evaporate. The resulting spectrum indicated a thick layer of PMMA had been deposited, with only weak Au 4f features being apparent in the survey spectrum, along with C 1s and O 1s lines. The curve fitting of the high-resolution C 1s spectrum showed a slight, uniform broadening of the individual components indicative of charge-induced broadening. However, the binding energies of the peaks fitted were characteristic of bulk PMMA and showed none of the features seen in the thin film studies.

The sputter cleaning of substrates was performed to allow the formation of an air-formed native oxide for all metals. Invariably, the atmospheric exposure will lead to the deposition of a small amount of adventitious hydrocarbon. This will be bound to the oxidised metal surface by weak, non-specific bonds (for example

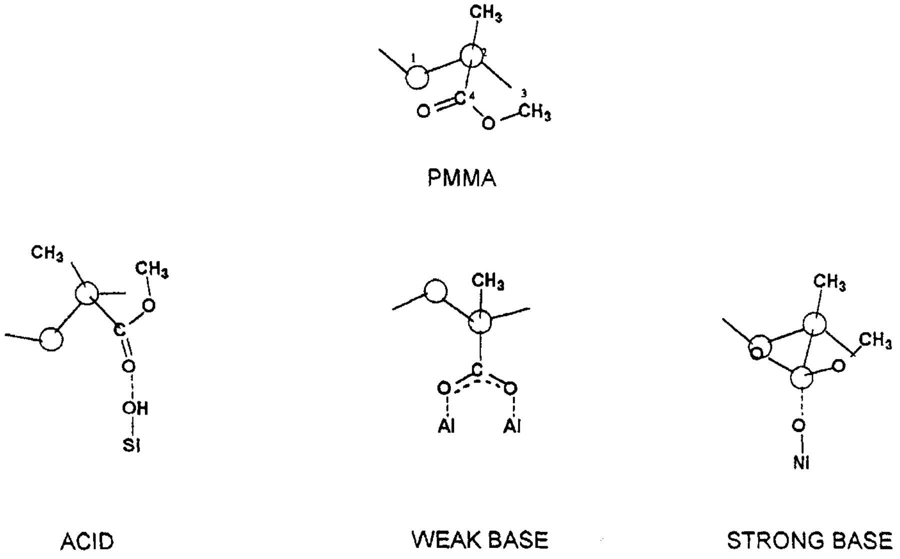


FIGURE 10 Proposed acido-basic interactions of PMMA.

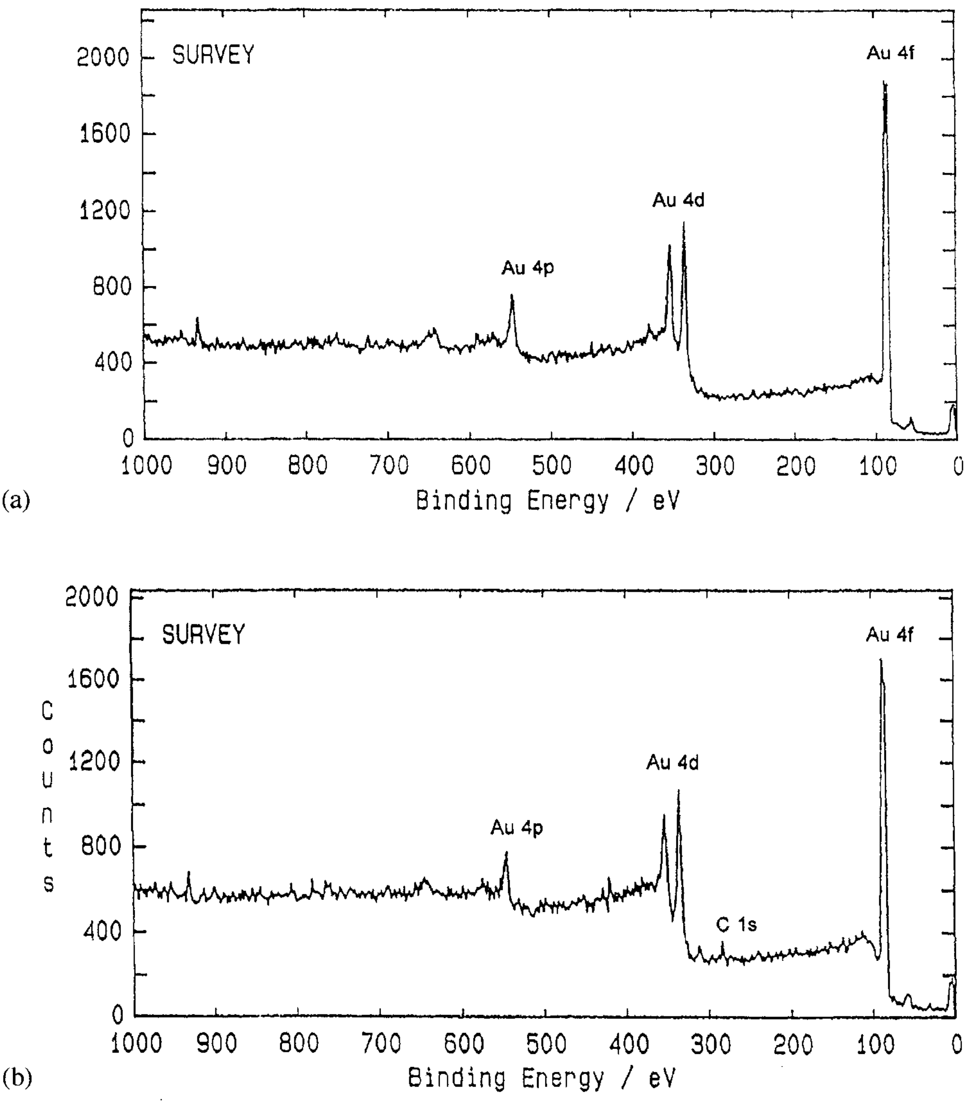


FIGURE 11 The XPS survey spectrum of:a) a clean gold substrate, b) after deposition of PMMA by spin-casting.

dispersion forces) and will, therefore, be relatively labile. Thus, on the application of PMMA by spin-coating the specific interactions between polymer and oxide will displace the weakly-bound contaminant layer. The exception to this is the gold specimen where the absence of an oxide leads to lack of specific interactions of the donor-acceptor type.

It is known that PMMA degrades under XPS analysis *via* main-chain scission.[21] It might be suggested that changes seen in the high-resolution C 1s spectra of ultra-thin layers of PMMA on oxidised metal substrates are the result of X-ray damage. However, previous studies have shown that sample degradation induced by Al $K_\alpha$ radiation goes unnoticed in XPS analysis.[21] Therefore, it is our conclusion that changes seen in the high-resolution C 1s spectra of PMMA on oxidised metal substrates are a result of acid-base interactions at the interface.

## CONCLUSIONS

This study has shown that XPS can be used for the direct examination of the acido-basic interactions of PMMA on both modified and model substrates. The XPS data indicated that the acido-basic nature of the substrate affects PMMA-substrate interactions. It was shown the PMMA interacts with acidic sites through hydrogen bonding *via* the carbonyl oxygen, as observed by a 0.1 eV binding energy shift of the carboxyl carbon in C 1s spectra. It was shown that the interaction between PMMA and strongly basic sites most probably involves nucleophilic attack of the carboxyl carbon in the polymer. This was observed as an increase in the binding energy shift of the carboxyl carbon in C 1s spectrum. It has also been proposed that weaker basic sites interact with PMMA *via* the hydrolysis of the methyl ester to a carboxylate, observed in the C 1s spectrum of PMMA by the necessity to adopt a five peak fit strategy.

Having determined that the acido-basic nature of a substrate affects the interaction PMMA at the interface, it is possible to use the C 1s spectrum of PMMA to comment on the nature of acid or basic sites present on a oxidised metal substrate. It was observed that neutral or slightly basic metal oxides, such as iron oxide and aluminium oxide, have both acidic and weak basic sites. Oxidised metals with an IEPS greater than pH 9.5 were shown to have only basic sites of interaction, as shown with oxidised copper and nickel. It was also observed that two types of basic site were present in the oxides of copper and nickel, one type being stronger than the other. Due to the acido-basic interactions that occur between a oxidised metal substrate and PMMA, it can be proposed that the orientation of PMMA at the interface would be different from that in the bulk. These conclusions are in agreement with previous theoretical studies, and with vibrational spectroscopic studies.[4–6] It has also been demonstrated that a microfocussed monochromatic X-ray source can be used to acquire XPS spectra which have comparable resolution with spectra acquired using the Scienta ESCA 300 instrument.

This direct method of observing interface chemistry is believed to have important application in the study of fully-formulated polymer systems, such as adhesives, organic coatings and polymer matrices for composite materials. Work is at present under way to establish if interface segregation of minor components in such systems can be studied by this method.

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