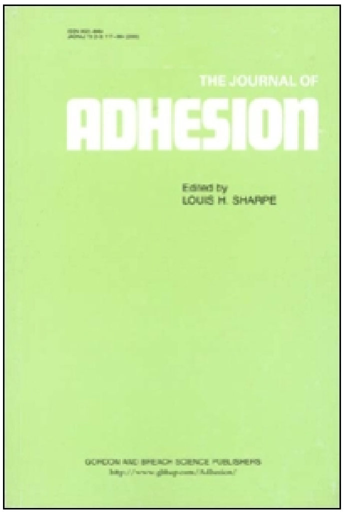

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Acid-Base Interactions in Adhesion: The Characterization of Surfaces & Interfaces by XPS

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Acid-Base Interactions in Adhesion: The Characterization of Surfaces & Interfaces by XPS#

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The consideration of acid-base interactions now plays an important role in the field of adhesion science. In this paper we describe ways in which the surface specificity of XPS can be employed to gauge the acidity or basicity of inorganic and organic surfaces, using a number of novel preparation methods. The methods described rely on the interaction of probe species, in either the gas, liquid or solid phase with the material of interest. For the determination of the properties of inorganic surfaces we describe ways in which the IEPS (isoelectric point of the solid surface) of hydroxylated iron surfaces can be determined by XPS used in conjunction with an ion exchange method. For polymer surfaces we show how the diffusion of Na^+ from a soda-lime glass substrate provides an indicator of polymer acidity and illustrate how solvent vapour uptake contains valuable information relating to polymer acidity and acid-base adduct formation. Finally we indicate the manner in which XPS can be used to identify molecular re-orientation at the polymer/inorganic interface, which is readily explained in terms of acid-base interactions.

INTRODUCTION

The role of acid-base interactions in adhesion is receiving increasing attention as a result of the pioneering work of Fowkes.[1,2] The experimental methods that have been used in such studies include microcalorimetry, infra-red spectroscopy and inverse gas chromatography. In this paper we explore the extent to which X-ray photoelectron spectroscopy (XPS) can be utilised as an analytical method for the qualitative and quantitative evaluation of the acid-base properties of inorganic/organic surfaces and interfaces.

XPS has been widely used in adhesion research over the past decade and has proved invaluable for the accurate definition of loci of failure, identification of

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*Permanent address: ITODYS, Associé au CNRS, Université Paris VII, 1 rue Guy de la Brosse, 75005 Paris, France primary interfacial bonding, and the monitoring of aggressive species at the failure interface.[3] However, it is only recently that XPS has become more widely used as a means of determining derived properties of surfaces; indeed, it now seems possible to obtain an estimation of surface free energy of polymeric material by consideration of the high resolution C1s spectrum.[4] The advantages of using such a quantitative surface specific method are clear; the adhesion process is becoming more sophisticated as a result of the use of very specific surface pretreatments or the development of very complex polymer formulations for the adhesive or organic coating. Consequently, it will no longer be acceptable to rely on measurements that probe both the bulk and surface characteristics at the same time. Pretreatments to solid surfaces may work effectively by modifying the outer few nanometres whilst, in the case of the liquid phase, complex interfacial reorientation and/or segregation effects may occur over comparable distances during application or subsequent cure.

Part of our recent research endeavour has been the evaluation of XPS as a potential method for the estimation of acid-base properties of surfaces and indeed interactions between dissimilar phases. By using XPS we have necessarily confined our analytical measurements to the outermost few atom layers, the very part of a solid involved in the adhesion process. Such surface specificity has allowed us to use planar specimens and to restrict our analysis to a few mm^2. This was a requirement of any potential technique that we considered in the early stages of our work, the eventual aim being to monitor surface (or interface) changes that occur as a result of changes in pretreatment or polymer formulation.

In this paper we describe methods that have been developed as a step toward the long term goal. The materials used are simple inorganic solids and organic homopolymers which have been well characterized by conventional methods. Thus, the experimental procedures and the results we present here are a test of the methodology that, combined with XPS, may provide novel means of probing the acid-base properties of surfaces and interfaces.

For hydrated metals a method of determining the isoelectric point of the solid surface (IEPS) by making use of anion and cation exchange in a series of aqueous solutions covering a range of solution pH is used. For polymer surfaces gas phase swelling by solvent molecules or the solid state diffusion of Na^+ ions can be interpreted in a meaningful manner to estimate the acid-base properties of the material.

Although the characteristics of the solid surface prior to its interaction with the other side of the adhesion couple is of prime importance, it is also beneficial to examine the way in which XPS can probe specific interactions that can be explained in terms of the acid-base properties of the two phases. Examples are provided of this aspect of the use of XPS for poly(methylmethacrylate) cast onto silicon dioxide.

EXPERIMENTAL

All materials used were of high purity grade (*i.e.*, Specpure or Analar) obtained from the usual manufacturers. All analytical measurements were taken as soon after treatment as possible. XPS spectra were recorded using a VG Scientific ESCALAB Mk II system, using AlKα X-rays and analyser pass energies of 50 eV (survey spectra) or 20 eV (high resolution spectra). The spectrometer was controlled by a VGS 5000S data system based on a DEC PDP 11/73 computer, quantification and other data processing was achieved using the manufacturer's standard software.

METAL SURFACES
AN AQUEOUS SOLUTION ION EXCHANGE METHOD

This method is based on the pioneering work of Simmons and Beard[5] who carried out cation exchange experiments. Full details of the experimental method are given elsewhere[6] but, briefly, hydroxylated ion surfaces were treated in 0.03M KOH and 0.1M Na_2HPO_4 solutions of the required pH in the range pH = 7 to pH = 12. By plotting the uptake of anion (PO_4^{3-}) and cation (K^+) as a function of pH, as shown in Figure 1, it is possible to establish the equilibrium constants for the situations in which the hydrated metal oxide behaves as an acid or a base.[6]

The IEPS is simply the mean of the equilibrium constants for these two reactions observed as the inflection points of the two curves of Figure 1. Thus for the equilibrium:

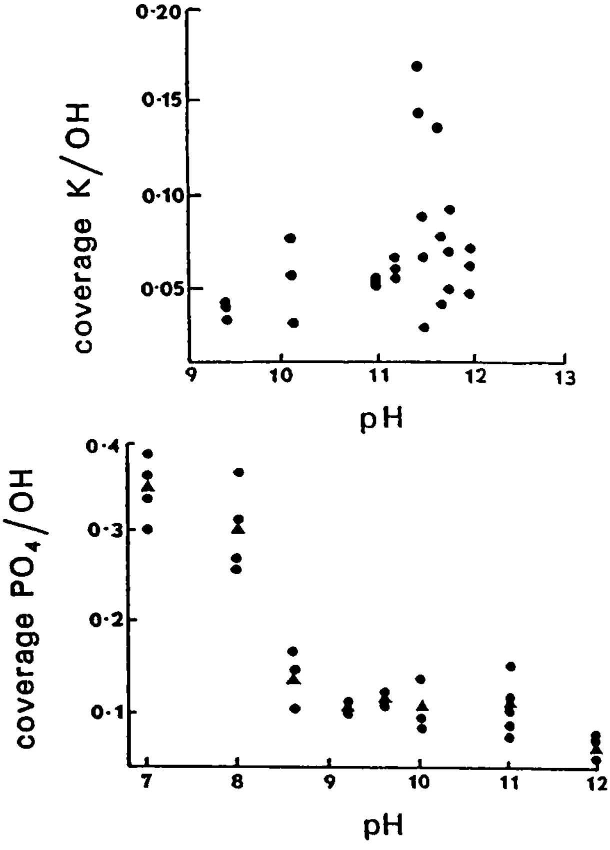

FIGURE 1 Potassium (a) and phosphate (b) coverage relative to surface hydroxyls on the oxidised iron surface as a function of pH.

$$FeOH + H^+ = FeOH_2{}^+; \qquad pK_1 = 8.4$$

and for

$$FeOH = FeO^- + H^+; \qquad pK_2 = 11.5$$

This gives a mean value, equivalent to the IEPS, of 10, a value in good agreement with that obtained from the more usual method of electrophoretic mobility, but obtained from the native oxide in place on planar coupons of the metal substrate rather than from the finely-divided oxide removed from the parent metal.

POLYMER SURFACES
A SOLID STATE ACID-BASE TITRATION METHOD

A series of five polymers were investigated; poly(styrene) [PS], poly(methylmethacrylate) [PMMA], poly(vinyl butyral) [PVB], poly(vinyl chloride) [PVC], and poly(vinylidene fluoride) [PVdF]. These polymers were cast onto soda-lime glass microscope slides, (prepared by swabbing with a solvent-soaked tissue and air drying), either from solutions or from the melt. The diffusion of sodium into the polymer film is estimated by XPS, after peeling the polymer film from the substrate, and the extent of Na^+ uptake by the polymer film can be interpreted in terms of acid-base interactions. XPS survey spectra for three of the polymers (PVdF, PMMA, and PS) cast from the melt onto glass are presented in Figure 2. XPS analysis was carried out on both sides of the failure interface which indicated no transfer of silica to the polymer failure surface and no residue of the polymer on the glass substrate.

The sodium ion is a Lewis acid and the data of Figure 2 show quite clearly that the uptake for an acidic polymer (PVdF) is negligible, whilst for basic, or strongly basic, polymers the sodium concentration is finite and ranks with the basicity of the polymer. From the data for the five polymers we determine the following decreasing order of basicity from careful experiments of polymer pairs or triplets cast onto the same glass substrate;[7]

$$PS > PMMA > PVB > PVC > PVdF$$

It should be noted that although the ranking order is the same irrespective of the method of preparation, (solution or melt cast), the concentration of sodium detected is higher for the cast specimens. This results from the increased mobility of the Na^+ when the temperature is increased by the application of the molten polymer.

This ranking order is only qualitative at this stage of our work, although it does present a consistent scale from the basic polymers in our series through to the acidic ones. At present we see the utility of the method as one equivalent in concept to that of the Mohs scale of hardness. Candidate polymers can be cast as one of a triplet set together with two from our series; it will then be possible to assess the interfacial acid-base properties of the unknown (which may be a complex blend or formulation) against the standard homopolymers.

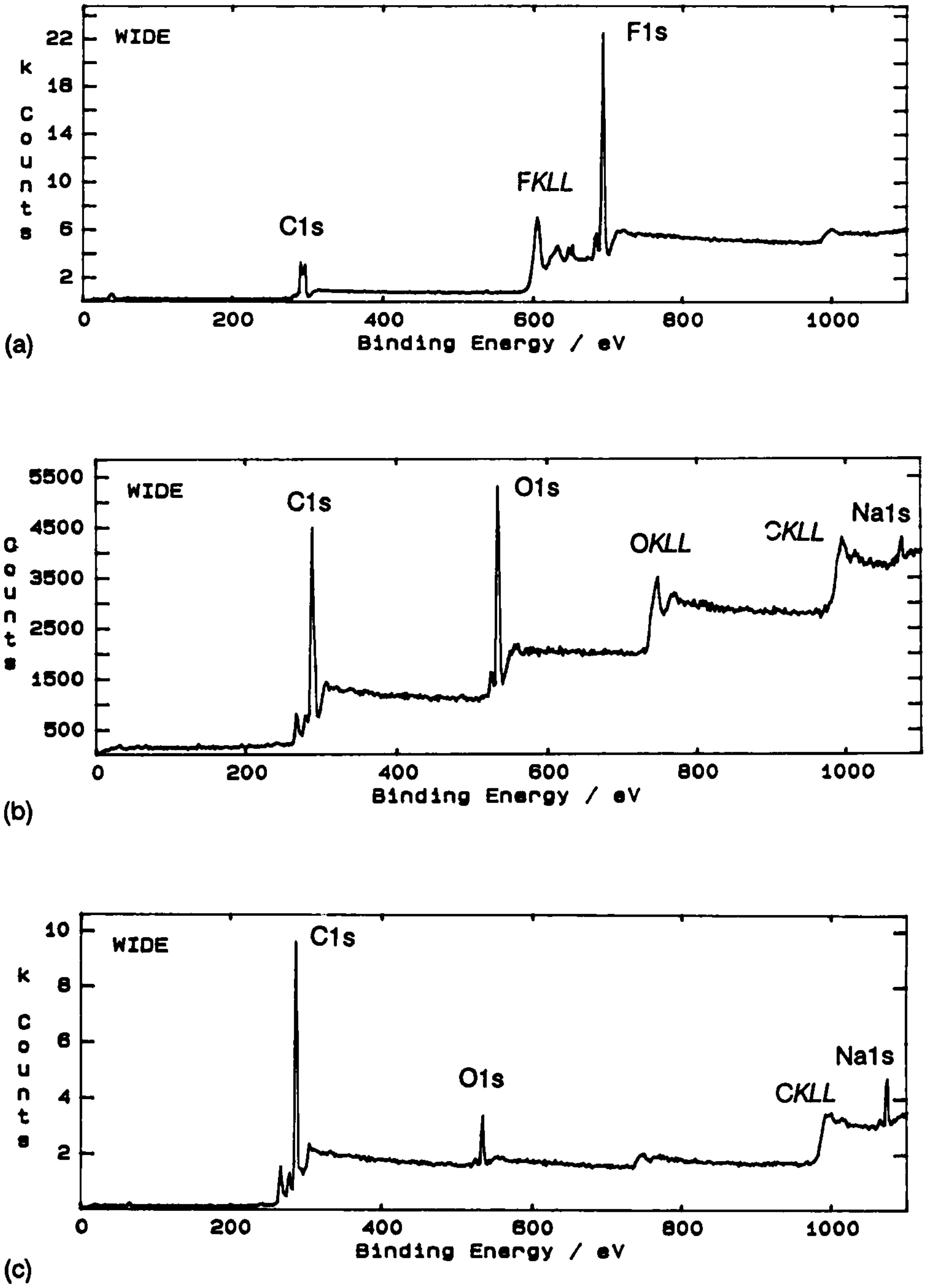

FIGURE 2 XPS survey spectra of polymers cast onto soda-lime glass showing the interfacial uptake of Na$^+$ by (a) PVdF, (b) PMMA, (c) PS.

POLYMER SURFACES

A GAS PHASE POLYMER SWELLING METHOD

Fowkes *et al.*[8] have shown that the swelling of polymers by solvent vapours is strongly dependent on the acid-base properties of the two phases. In the present work, films of a basic polymer (PMMA) were exposed to a range of solvents of different acidity and basicity; in the scaling of the solvents we made use of Gutman's acceptor and donor number concept (AN and DN), and the AN values have been corrected for dispersive interactions in line with the recommendations of Riddle and Fowkes.[9] The solvents used are described in Table I.

After a normalised exposure period (10 atms.mins) the residual solvent was estimated by XPS using the Cl2p or N1s signal as appropriate. The uptake of solvent molecules as a function of solvent acidity is shown in Figure 3. There is an inflection

TABLE I
Acid-base properties of solvents employed

Solvent	AN	DN	Acronym
CCl_4	2.3	0	CTC
$CHCl_3$	18.7	0	TCM
CH_2Cl_2	13.5	0	DCM
CF_3COOH	111.0	0	TFAA
$C_6H_5NO_2$	8.1	4.4	NB
C_5H_5N	0.5	33.1	PY

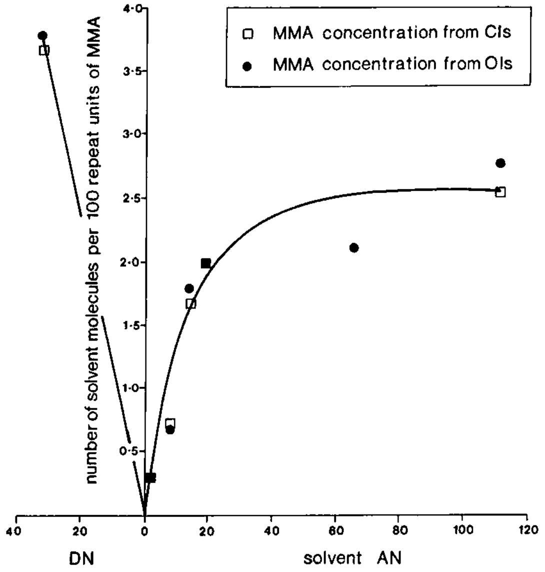

FIGURE 3 Swelling of PMMA by solvent molecules; the solvent concentration as a function of Gutman's AN and DN values.

point at an AN value of approximately 10, this we term the acceptor number equivalent (ANE) of the polymer. This parameter provides an indication of polymer basicity. The lower the ANE the higher the basic character of the polymer. In associated studies[10] we have investigated a commercial aromatic moisture-cured urethane[11] in this way and found an ANE value in the region of 20–30.

Additional information on the nature of the formation of intermolecular bonds is available in the XPS chemical shift observed on all core lines. For example, PMMA behaviour is dominated by its basic properties; however, its interaction with pyridine, a classical organic base, is extensive as seen from the data of Figure 3. This suggests that the carbonyl carbon of PMMA is acting as an acidic site for interaction with the base. Inspection of the N1s binding energy following the swelling of PMMA by pyridine indicates an increase of 1 eV, equivalent to an increase in nitrogen atomic charge from -0.30 to -0.04 unit charge.[10] This chemical shift experienced by the characteristic atom of the gas-phase probe molecule (*i.e.*, nitrogen) is indicative of the magnitude of the acid-base interaction, *i.e.* its exothermic enthalpy ($-\Delta H_{ab}$). It has been suggested by Chehimi,[12] on the basis of the studies of Burger and Fluck[13] and Joyner and Roberts,[14] and confirmed by recent work from this laboratory,[15] that this is indeed the case. By using solvents of known acid-base properties to probe a particular polymer it is conceptually possible to determine the E and C constants for the polymer in Drago's Equation:

$$-\Delta H_{ab} = E_p E_s + C_p C_s$$

where E and C are constants representing the propensity of the species to form electrostatic and covalent bonds, and the subscripts p and s refer to polymer and solvent. This method has been used to good effect by Fowkes,[1] although in his work the thermochemical parameter was determined by microcalorimetry or the shift of a characteristic infra-red absorbance line.

INTERFACIAL ORIENTATION OF FUNCTIONAL GROUPS

Angular resolved XPS of specimens produced as part of the Na^+ diffusion study indicated that there was a well-defined orientation of the basic carbonyl component of the ester group towards the acidic substrate. To confirm this observation the experiment was repeated using SiO_2 thermally grown on a silicon wafer, which provides a more acidic substrate; the acidic character of this substrate was also conditioned by treating in hydrochloric acid of pH = 0.4. The O1s spectra obtained are presented in Figure 4 and the C=O component is clearly enhanced at low take-off angles (relative to the sample surface), *i.e.* by the more surface-specific analysis; this observation is confirmed on inspection of the C1s spectra of Figure 5, but the trend is not as clear as that seen in the O1s spectra. The variation of O1s $C{=}O/O{-}CH_3$ ratio as a function of take-off angle for glass, thermally grown SiO_2, and acid conditioned SiO_2 substrates is presented in Figure 6. It is clear from these data that the $C{=}O/O{-}CH_3$ ratio increases with the acidity of the substrate for all take-off angles; this indicates that the carbonyl groups develop an increasing affinity for the acidic sites as substrate acidity increases. The orientation is still apparent

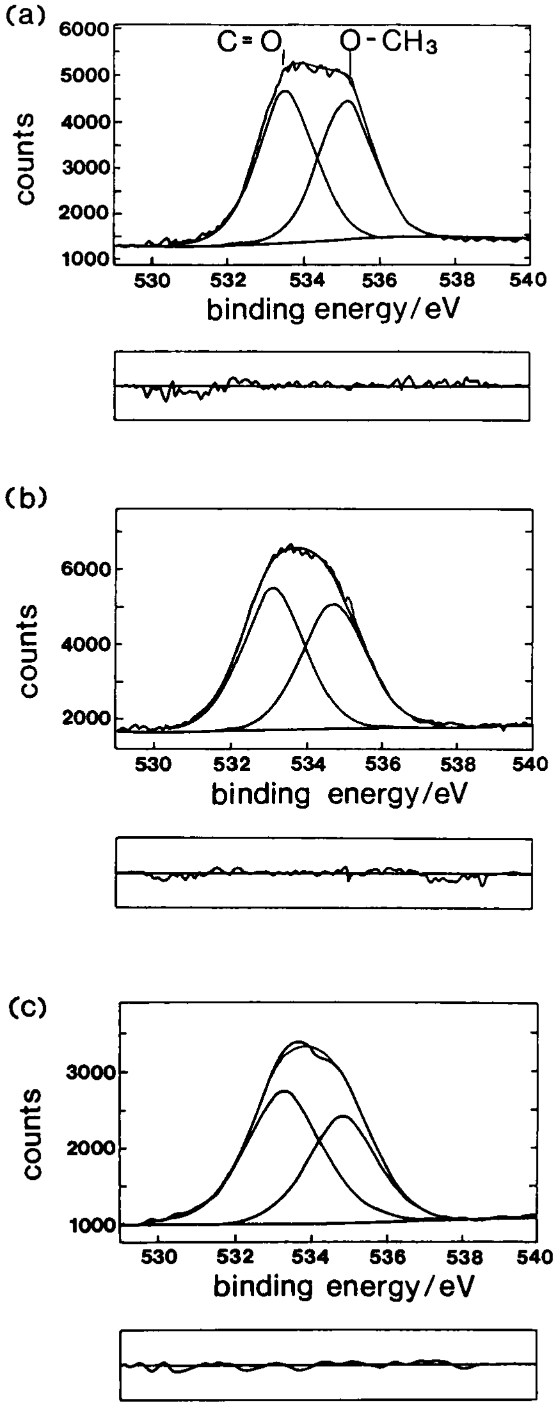

FIGURE 4 PMMA O1s spectra following peeling from SiO_2. Take-off angles are (a) 90°, (b) 45°, (c) 15°, relative to the sample surface.

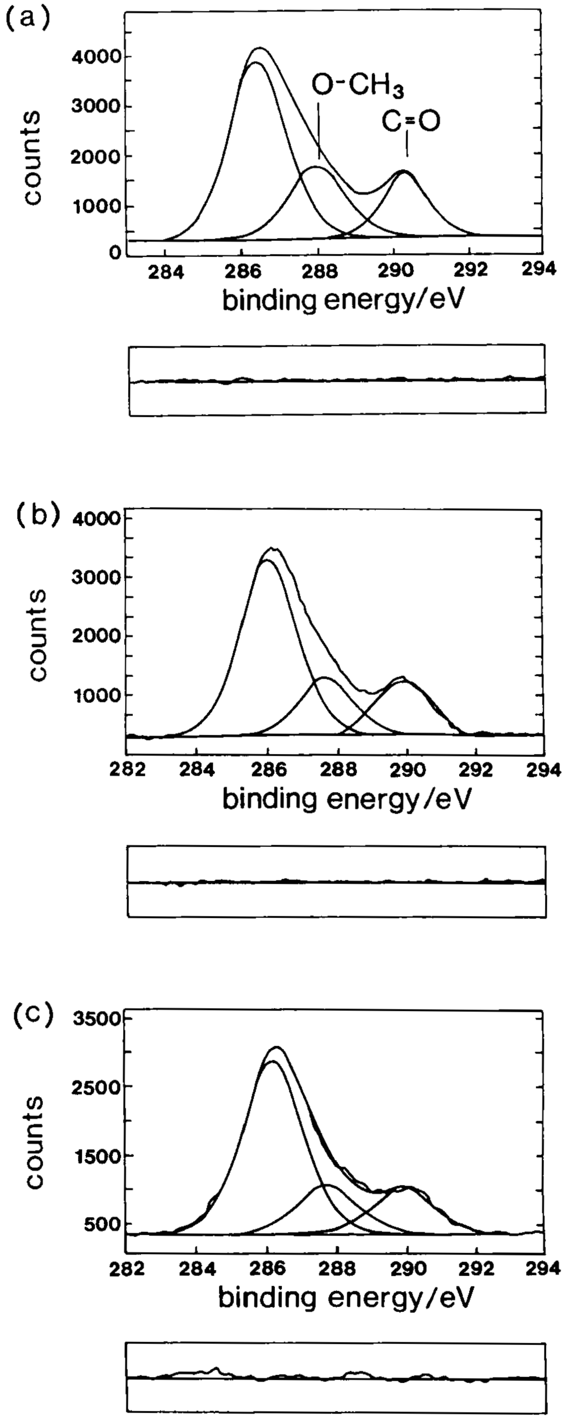

FIGURE 5 PMMA C1s spectra following peeling. Other details as in Figure 4.

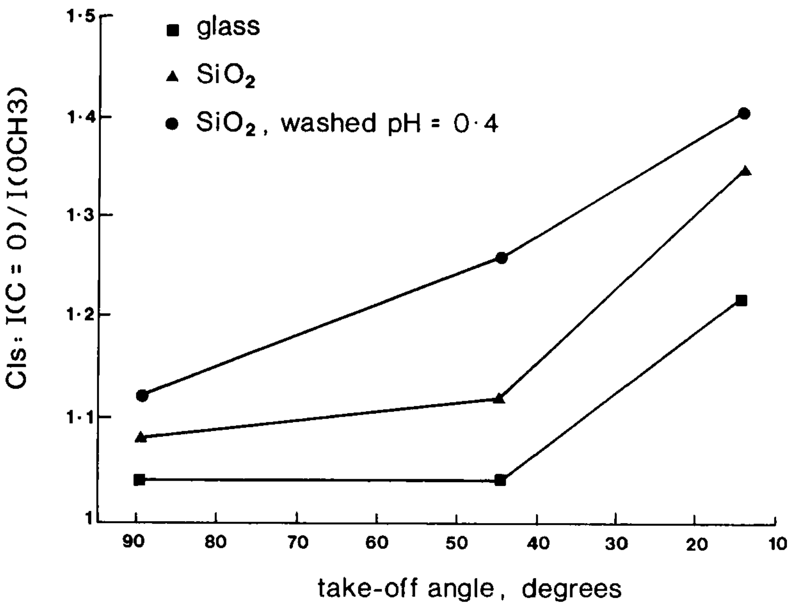

FIGURE 6 PMMA O1s C=O/O—CH_3 intensity ratios as a function of take-off angles for different substrates.

after peeling because, although the acid-base bond has been broken, the temperature (20°C) is not high enough to allow the ester group to rotate in such a way that it will recover its "equilibrium" position, which would yield C=O and O—CH_3 components of the oxygen 1s spectrum having equal intensities.

The results presented above all indicate the reorientation of the PMMA carbonyl group, to a lesser or greater extent, towards the inorganic substrate. This phenomenon is shown schematically in Figure 7 and is a result of acid-base interactions between the basic polymeric phase (in which the functional groups are initially mobile) and the acidic inorganic substrate. The data of Figure 6 scale very well with the substrate acidity; the glass employed has an IEPS of 7 while SiO_2 has a value of approximately 2.

Thus, by using angular-resolved XPS it is possible to identify subtle, near-surface concentration gradients, which can be interpreted in terms of the orientation of functional groups in response to acid-base forces. In a recent paper Allara *et al.*[16] reported broadening of the C=O stretch mode in the infra-red spectrum of PMMA cast on silica, compared with simulated spectra of non surface bonding thin films of PMMA. These authors interpreted their IR spectral data as evidence for a hydrogen bonding interaction between the C=O groups of the polymer (basic) and the silica surface (acidic). To achieve such an interaction a preferential orientation of the carbonyl group at the SiO_2/PMMA interface was proposed, a hypothesis that is completely in accord with our XPS results described above. No such broadening or shift was observed in the IR spectrum when PMMA was cast onto basic alumina.

The logical extension of the XPS approach is to determine a quantitative depth profile within the polymer. This can be readily achieved using the appropriate Beer-

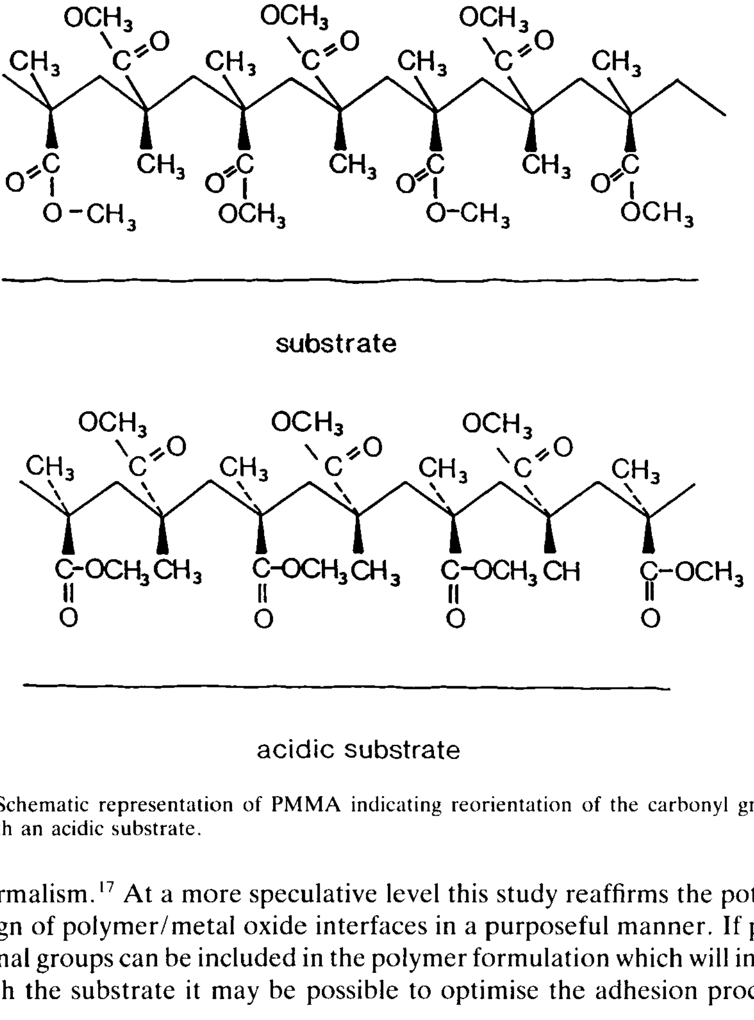

FIGURE 7 Schematic representation of PMMA indicating reorientation of the carbonyl group on interaction with an acidic substrate.

Lambert formalism.[17] At a more speculative level this study reaffirms the potential for the design of polymer/metal oxide interfaces in a purposeful manner. If particular functional groups can be included in the polymer formulation which will interact strongly with the substrate it may be possible to optimise the adhesion process.

CONCLUSIONS

The work described in this paper indicates the utility of XPS in the determination of acid-base properties of organic and inorganic materials. Although we have yet to appraise fully the range of applicability of the different methods described, the hope is that they will be useful for a wide range of technologically-important materials. The proviso for such an achievement seems to be the careful characterization of the systems, in terms of surface chemistry, at each stage of sample preparation.

Acknowledgements

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