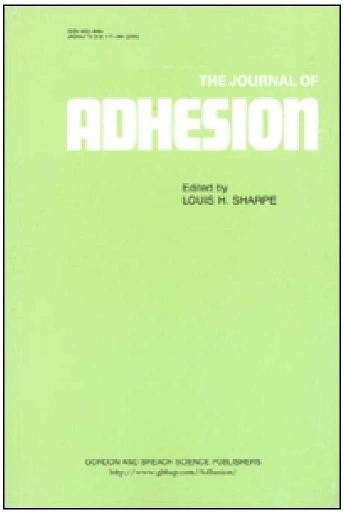

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Watts, John F. and Chehimi, Mohamed M.(1993) 'X-ray Photoelectron Spectroscopy Investigations of Acid-Base Interactions in Adhesion', The Journal of Adhesion, 41: 1, 81 — 91
To link to this Article: DOI: 10.1080/00218469308026555
URL: http://dx.doi.org/10.1080/00218469308026555

J. Adhesion, 1993, Vol. 41, pp. 81–91
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Printed in the United States of America.

X-ray Photoelectron Spectroscopy Investigations of Acid-Base Interactions in Adhesion*

Part 2: The Determination of a Scale of Polymer Basicity by a Solid State Acid-Base Titration Method

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(Received February 29, 1992; in final form September 1, 1992)

A qualitative scale of polymer basicity has been obtained using X-ray photoelectron spectroscopy (XPS). The method is based on the uptake of sodium cations (Na^+) by polymeric films cast onto glass slides containing sodium oxide. The diffusion of Na^+ from the glass substrate to the polymers is interpreted in terms of acid-base interactions between Na^+ (Lewis acid) and a series of basic polymers; poly(styrene) (PS), poly(methylmethacrylate) (PMMA), and poly(ethylene oxide) (PEO), and a series of acidic polymers; poly(vinyl butyral) (PVB), poly(vinyl chloride) (PVC), and poly(vinylidene fluoride) (PVdF). The Na^+ concentration determined by XPS is consistently higher in the basic polymers. By comparing the Na^+ uptake by different polymers we have determined the following decreasing order of basicity: PS>PMMA>PEO>PVB>PVC>PVdF. An extension of this approach, to relate the relative uptakes of Na^+ to the hardness or softness of the polymers, is also considered.

KEY WORDS polymers; XPS; glass; sodium diffusion; acid-base interactions.

INTRODUCTION

It is now well known that the non-dispersive term of the heat of adsorption of two materials describes mainly acid-base interaction rather than a dipole-dipole

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*One of a Collection of papers honoring A. J. Kinloch, the recipient in February 1992 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M*.

interaction as it has been hitherto believed. Fowkes *et al.*[1-3] have shown that acid-base interactions play a major role in many fields such as adhesion of polymers to inorganic substrates, mechanical properties of polymer composites, polymer solubility, and the swelling of polymers by solvents.

The heat of acid-base mixing ($-\Delta H^{ab}$) can be estimated readily using the Drago four-parameter equation:[4]

$$-\Delta H^{ab} = E_A E_B + C_A C_B$$

where E_A and E_B are, respectively, the tendency of the acid and the base to form an electrostatic bond; whereas C_A and C_B are, respectively, their tendencies to develop a covalent bond. Fowkes *et al.*[1-3,6,7] developed a protocol based on infrared spectroscopy (IRS) and calorimetry, bulk techniques, to determine Drago's parameters for polymers and substrates. Inverse gas chromatography (IGC) is also widely used to study the surface characteristics of solids and to determine the heat of adsorption of materials.[8-10] The exothermic term of acid-base interaction can also be determined using Gutmann's donor and acceptor numbers, DN and AN.[5] However, Fowkes[3] pointed out that the AN parameter may include an appreciable contribution from van der Waals interactions (*i.e.* dispersive interactions).

Bolger[11] suggested another model to predict the adhesion of a polymer to an inorganic solid substrate. In this model, the inorganic substrate is described by the iso-electric point of the solid surface (IEPS) and the polymer by the ionisation constant (pK_a). These parameters not only predict the stability of the adduct, but describe the acid-base characteristics of the subtrate and the polymer. Recently, Watts and Gibson[12] determined the IEPS for hydrated iron surfaces using XPS. Part of an ongoing research project in this laboratory is the use of XPS in the study of acid-base interactions of polymers and inorganic substrates. XPS is used routinely in laboratories throughout the world to determine changes to the surface composition of substrate materials following pretreatment,[9] and to study the locus of failure.[13] However, the technique has not been widely recognised as a method for the determination of acid-base properties of polymer surfaces. Paynter *et al.*[14] have determined the pK_a of acrylic copolymers using XPS. However, this work was carried out using polymers that had been dipped into saline solutions to effect surface ion exchange to evaluate pK_a.

In the course of our XPS investigations of acid-base interactions between PMMA and soda-lime glass, we detected small amounts of the sodium cation, (Na^+), at the polymeric interface after peeling from the substrate. Since Na^+ was not a contaminant of the polymer powder we concluded that Na^+ had been transferred from the glass substrate into the polymer. As Na^+ is a Lewis acid and PMMA a Lewis base it can be suggested that the driving force for the sodium diffusion is an acid-base interaction between the polymer and the cation.

Sodium is known to be very mobile in glasses, unlike the other major constituent of the soda-lime glass employed in this study, calcium, whose ions are bound tightly within the silicate network.[15] The diffusion of Na^+ is indirectly responsible for glass corrosion, and can be readily exchanged with Cs^+.[15] A standard test of durability of glasses is to monitor the leachability of Na^+ in a strong acid, *i.e.* Na^+ is exchanged with H^+.[16]

Bearing in mind the results described above relating to the uptake of sodium from the glass substrate by PMMA, the mobility of the sodium cations, and the previous work of Paynter *et al.*,[14] we propose the use of the diffusion of Na^+ from the glass substrates to the polymer film as a novel method of "solid state acid-base titration" based on XPS measurements. Sodium has previously been employed in an acidity determination by Herlem and Popov,[17] who studied the NMR shift of ^{23}Na when solvated by a variety of basic solvents.

In this paper we present preliminary, qualitative, results which indicate the utility of this method in the estimation of the acid-base properties of polymers.

EXPERIMENTAL

XPS analyses were carried out in a V.G. Scientific ESCALAB Mk II electron spectrometer operated at a vacuum of 10^{-9} mbar. Aluminium Kα X-rays ($h\nu = 1486.6$ eV) were employed and the analyser pass energy was set at 50 eV. For each specimen a survey spectrum was recorded, together with high resolution spectra of the regions of interest (*i.e.* C1s, O1s, N1s, Na1s etc.), at an electron take-off angle relative to the sample surface of 90°. For charge referencing purposes the carbon 1s line was set to a binding energy of 285.0 eV. Quantification of the photoelectron spectra was achieved using peak areas and the appropriate sensitivity factors included in the manufacturer's standard software of the datasystem supplied with the spectrometer, which was a VGS-5000S system based on a DEC PDP11/73 computer.

Polymer powders were supplied by Aldrich except for PEO (BDH) and PVC (Fluka), and were used as supplied without further purification. The solvents used were xylene, dichloromethane, tetrahydrofuran (BDH) and chloroform (FSA). Saturated solutions were prepared using the following solvent/polymer combinations: PS in xylene (61 gdm^{-3}), PMMA in dichloromethane (12.5 gdm^{-3}), PEO in chloroform and PVC, PVB and PVdF in tetra hydrofuran (50, 28 and 550 gdm^{-3}, respectively). The glass substrates were in the form of standard microscope slides supplied by Chance Propper Ltd (Warley, UK). These were carefully ultrasonically cleaned, first in isopropanol and then in deionised water, and then dried before application of the polymer. Following cleaning no inorganic contaminants such as chloride ions or sulphate ions were detected. Such a cleaning protocol produced a clean glass surface that could be reproduced quite readily. A typical surface analysis, by XPS, of a glass substrate prepared in such a manner is as follows: C-12.6, O-54.5, Si-27.8, Na-2.9, Mg-1.7, Ca-0.6, (data in atomic percent).

The polymer solutions were cast onto the freshly cleaned substrates and stored in a dust-free environment for 24 hours, to allow for solvent evaporation, prior to peeling the polymer film. There is, of course, the possibility of the retention of solvent as a result of acid-base interaction between polymer and solvent. This, in itself, provides a potential route to the characterisation of acid-base properties of polymers and is a phenomenon we have discussed at length elsewhere.[18] However, the levels of retained solvent are extremely low and will not influence the results of the present study.

RESULTS AND DISCUSSION

The soda-lime glass contains sodium oxide, the Na^+ ion rendering the surface weakly acidic. This enabled us to peel off the basic polymers with ease in order to analyse the glass/polymer interface by XPS. Most specimens, when examined by XPS, showed a true interfacial failure with no evidence of any polymer remaining on the glass substrate. In the case of PMMA there was sometimes evidence of a residual polymer layer in which reorientation of the carbonyl group had taken place to effect more intimate acid-base interaction between substrate and overlayer.[19] The original observation of the uptake of sodium cations by PMMA was interpreted as a result of diffusion of Na^+ into the polymer governed by acid-base interaction between the substrate and the polymer. This hypothesis was examined in more detail by casting a PVC film from solution. Since PVC is an acidic polymer, a very small uptake of Na^+, if any at all, is expected. The XPS results were in full agreement with this assumption. This striking result confirming our interpretations led us to propose the diffusion of Na^+ as a new method to determine the relative acidity of polymers in the solid state. This feature is clearly seen in Figure 1, which contrasts the survey spectra recorded from (a) PVdF, (b) PMMA and (c) PS, following peeling from the glass substrate. The presence of sodium is confirmed by the Na1s line at a binding energy of 1072 eV.

The percentage of Na^+ per repeat unit was calculated for each polymer from the quantitative XPS data. To achieve this the sodium concentration (in atomic percent calculated from the Na1s intensity) was combined with the concentration determined from the C1s, Cl2p and F1s peak intensities for PS, PVC and PVdF, respectively; and with the O1s for PEO, PMMA, and PVB. For example, in the case of poly(vinylidene fluoride), which has a repeat unit of $-(CH_2-CF_2)-$ the concentration of sodium ions (per repeat unit) is simply given by:

$$\%Na^+ \text{ (per repeat unit)} = (\text{at}\%Na/\text{at}\%F) \times 2 \times 100$$

For all sample preparation methods, the XPS results indicate a large degree of scatter within each data set of $\%Na^+$ uptake. The range of values of $\%Na^+$ obtained for experiments repeated in triplicate or quadruplicate is indicated in Table I for polymers prepared by casting from solution.

From Table I one can easily see that the $\%Na^+$ range for all polymers might overlap because of the use of different glass slides. This may be due to unknown factors associated with the preparation of the glass surface, the level of hydration for example. However, the surface composition as determined by XPS was remarkably reproducible and it is unlikely that variations in the surface concentration of sodium is responsible for this spread of results. Consequently, it is not possible to compare quantitatively the $\%Na^+$ in one polymer with that in another polymer cast onto a different glass slide. As the preparation of the glass slides is an important variable,

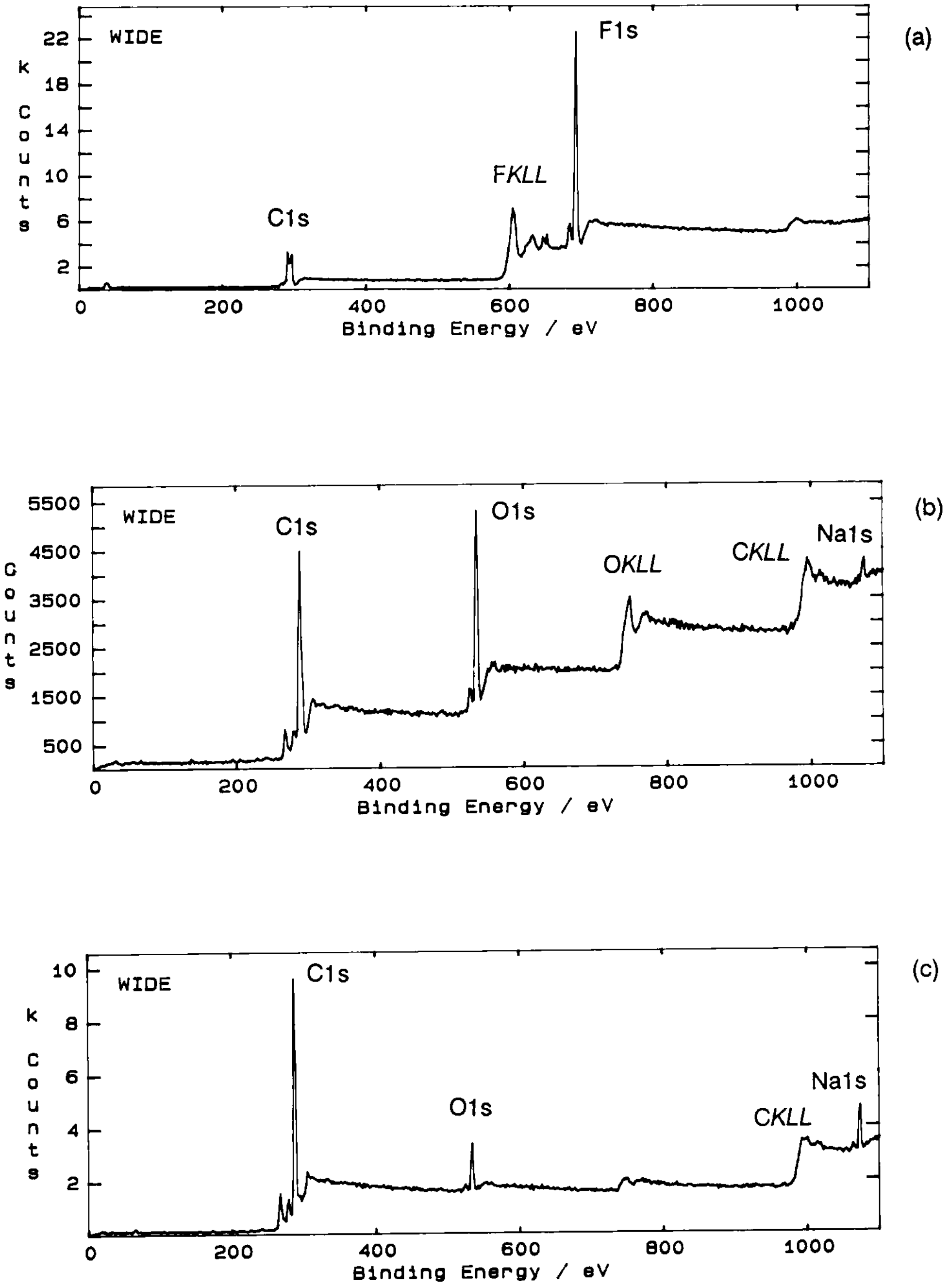

FIGURE 1 XPS survey spectra of polymers cast onto soda-lime glass showing the uptake of Na^+ by (a) PVdF, (b) PMMA, (c) PS.

TABLE I
Concentration of sodium per polymer repeat unit for polymers cast from solutions

Polymer	%Na^+
PVdF	0–0.08
PVC	0–0.4
PVB	0.8–1.5
PMMA	0.5–4.0
PS	0.8–6.45
PEO	0–0.64

the method was modified slightly to cast two or three different polymers on the same glass slide. This mitigates the uncertainty described above and allows direct comparison of Na^+ uptake by different polymers. For a set of two or three polymers cast on the same glass, the decreasing order of Na% indicates the decreasing order of basicity of the polymers used as shown in Table II.

Combining all these trends of basicity we determined the following decreasing order of basicity:

PS>PMMA>PEO>PVB>PVC>PVdF

The lack of data from a PVB/PEO couple means that the relative positions of these two materials is not clear from our experiments. The positions may, indeed, be reversed and, as we have shown elsewhere,[18] polymers such as PMMA, which are traditionally regarded as basic, may possess acidic properties or vice versa.

Although the aim of this study was to monitor the concentration of Na^+ at the polymer/glass interface, the modified Auger parameter (α^*) was recorded routinely and showed much scatter. However, a gradual change was observed from that of the

TABLE II
Ranking of basicity for polymer pairs and triplets cast on the same slides

		Basic . . . Acidic		
	PMMA	>	PVC*	
	PMMA	>	PVdF	
	PVC	>	PVdF	
	PMMA	>	PVB	
	PS	>	PMMA*	
	PMMA	≈	PVB	
	PVB	>	PVdF	
	PEO	>	PVC†	
PS	>	PMMA	>	PVC*
PS	>	PMMA	>	PVB
PMMA	>>	PEO	>	PVC

*Indicates experiment carried out in duplicate.
†Indicates experiment carried out in triplicate.

TABLE III
Concentration of sodium per repeat unit for polymers fused against the glass substrate

Polymer	%Na$^+$
PVdF	1.0
PMMA	8.0–19.1%
PS	9.6–18.5%

glass ($\alpha^* = 2060.3$–2060.9 eV) to that recorded from the underside of the polymer ($\alpha^* = 2060.8$–2061.3 eV), where the Na$^+$ is conjugated with the polymer. Both these values are substantially lower than that for Na_2O and, although the poor quality of the data precludes a rigorous analysis, it seems likely that there may be a correlation between XPS data and the extent of acid-base interaction. Such a relationship appears to exist for the interaction of organic polymers with organic solvents.[18]

A limited set of experiments using molten polymers was carried out because of the problems described in the previous section. The specimens were prepared by melting the polymer against the glass slides at 130–140°C for two hours. The level of sodium detected is much higher, as would be expected from the higher temperature employed, although the general ranking order is the same as for the cast polymers. Table III shows the magnitude of the %Na$^+$ parameter for these specimens. The higher temperature would bring about a higher concentration of Na$^+$ at the glass surface. The observation that more sodium is taken up by the polymer is a result of this increased concentration of Na$^+$ available at the glass/polymer interface.

The ranking of the polymer pairs for the molten polymer preparation method is given in Table IV.

From these comparisons the following decreasing order of basicity can be deduced:

$$\text{PS} > \text{PMMA} > \text{PVdF}$$

This trend is consistent with the previous one determined for polymers cast from solutions.

For future work at elevated temperatures heat treatment in a vacuum or inert environment should be used to obviate the potential difficulties of sample degradation. By using the short times described above such degradation was avoided; but

TABLE IV
Ranking of basicity for polymer pairs from molten polymer experiments

Basic . . . Acidic		
PS	>	PMMA
PMMA	>	PVdF

heat treatment at extended times (24 hours at 90°C) shows a much higher uptake of Na^+ by PMMA (46 at%) than by PS (19 at%). The advantages of such sodium concentrations include the ability to determine the sodium Auger parameter with improved confidence, but the precautions outlined above should be employed. The supply of Na^+ to the polymer/glass interface increases, as one would expect, with increasing temperature. However, the supply of the cation to the interface will be constant for any particular set of conditions. The parameter that is monitored in this work, the uptake of Na^+ by the polymer, is the result of chemical interactions of the polymer with the source of sodium ions at the interface. The concentration of ions in the source will be constant for constant conditions but, of course, the amount determined by XPS will depend on the extent of chemical interaction. Angular resolved XPS indicates that the Na^+ penetrates the polymer to a depth of several nanometres, and the composition is uniform within the XPS analysis depth. The penetration of the polymer by the cations will be time dependent, but this will not affect the XPS results, as the concentration of titrant will remain constant in the near-interface region.

In our analyses of the sodium levels present at the polymer/glass interface we have assumed that the soda-lime glass is the only source of the Na^+ ion. This is not necessarily the case and in complementary work undertaken using silicon wafers as the substrate material we have also detected sodium but at a much reduced level. The source of such sodium is unclear, but it seems likely that it is present both as a contaminant at the silicon wafer surface (where it is detected by XPS) and at very low levels within the polymer source material.

Thus it would seem that although the soda-lime glass provides the greater proportion of the Lewis acid, this is superimposed on that already present in the polymer. Although it is possible to speculate that the concentration will be higher in the more basic polymers for the very reason of enhanced acid-base interactions, it clearly means that the integral concentration of Na^+ does not provide a direct, quantitative, measure of polymer basicity.

Thus, although the scale is only qualitative at this stage of our work, it is encouraging that this simple method does show a consistent ranking order from the basic polymers through to the acidic ones. This result in itself lends credence to the idea that a scale of polymer acidity can now be obtained on the basis of the uptake of sodium from a glass slide by a polymeric film. A first step to producing a quantitative method would be to use a simple glass system and to develop surface preparation procedures, with a view to reducing the spread of analytical data reported in Tables I and III. A larger series of acidic and basic polymers could then be tested. The scale could be universal since the "titration" is carried out in the solid state, in the absence of solvent. Only the nature of the solvent used can change a given scale of acidity. A titration by lithium-containing glass is envisaged, or perhaps Cs^+ if it can be exchanged with Na^+. These scales would help to confirm the one that has been determined in the present work. It is, however, potentially more advantageous to use a binary glass, Na_2O-SiO_2, because in the absence of Ca^{++} the Na^+ becomes very mobile and we might obtain greater diffusion at room temperature, which will enable a more precise determination of Na^+ uptake by XPS.

HARD AND SOFT ACIDS AND BASES

According to Pearson,[20] a "hard" acid is a Lewis acid of small size, high positive charge and with no valence electrons that are easily distorted or removed. A "soft" acid is one in which the acceptor atom is of large size, small or zero positive charge or has several electrons which are easily removed or whose orbitals are easily distorted. A "soft" base is a Lewis base in which the valence electrons are easily distorted (polarized) or removed. A "hard" base has the opposite properties, holding onto its valence electrons much more tightly. Using this classification sodium may be considered as a hard acid. A general rule states that the stability of acid-base complexes depend upon the softness or hardness of both acidic and basic species in a way that "a hard acid prefers to bind to a hard base, and a soft acid prefers to bind to a soft base." Pearson suggested[20,21] that the C/E ratio is a measure of the softness of the Lewis acids and bases since this ratio increases (roughly) with the softness. This suggestion has been rejected by Drago[22,23] for the simple reason that a large C divided by a large E gives the same ratio as a small C divided by a small E. Drago explains that the magnitudes of C and E are lost in the ratio. For this reason, many examples of acids or bases (*e.g.* benzene) show a violation of Pearson's classification of hard and soft acids and bases. Despite the remarks made by Drago the C/E ratios are still used in the literature, often without sufficient care, for estimating the relative softness of species.

In our work we need to correlate the diffusion of sodium with the hardness (or softness) of the species involved: Na^+ and polymers. The polymers' relative softnesses are once again determined using Drago's parameters, but we took great care in the sense that not only are the C/E ratios of polymers (here PMMA and PEO) compared, but also the respective C and E values to avoid the difficulties concerning the C/E ratios and Pearson's scale of softness (or hardness). Table V reports C_b and E_b parameters for PMMA and PEO, taken from Valia's Ph.D. thesis,[24] as well as their respective C/E ratios. From Table V one can notice that although the E_b values are very close, C_b and the C/E ratios are quite different, and larger, for PEO. In this case we can argue with confidence that PEO is softer than PMMA (or the latter harder than the former). If we now rely on Pearson's rule we might expect a stronger diffusion of Na^+ (hard acid) toward PMMA (harder base) rather than toward PEO. Our XPS results are in full agreement with these expectations.

This result, however, is unique and we cannot, at the present time, predict that diffusion of Na^+ is in part or totally governed by the hardness of the polymers studied by this method. The concept of HSAB, although controversial in some cases, must not be ignored by adhesion scientists at a time when acid-base interac-

TABLE V
Comparison of Drago's parameters with %Na^+ for PEO and PMMA

Polymer	C_b	E_b	C_b/E_b	%Na^+
PEO	5.64 ± 0.27	0.77 ± 0.03	6.71–7.99	0.1–0.51
PMMA	1.18 ± 0.2	0.59 ± 0.01	1.63–2.38	0.8–1.6

tions at polymer-metal oxide interfaces are increasingly being considered. However, we would like to reiterate that it is not as easy as it appears on first sight in the literature to relate Pearson's concept of softness to Drago's C/E ratio. We strongly recommend, for this purpose, further reading of Reference 20.

CONCLUSIONS

A qualitative method for the evaluation of polymer surface acidity and basicity has been described. This is based on the monitoring, by XPS, of the diffusion of a Lewis acid (Na^+) from a soda-lime glass substrate to a polymeric overlayer cast onto it. The abundance of sodium detected at the polymer interfacial surface reflects the strength of the acid-base interaction but this parameter also depends on the temperature at which the experiment is carried out; this is assumed to be related to the degree of mobility of the sodium ion in the silicate network. The diffusion of cations in polymer films is not well documented, although recent advances have been made using Rutherford Backscattering Spectrometry (RBS) to establish diffusion coefficients of monovalent cations in organic coatings.[25,26] Future work will explore the effect that such parameters have on the experimental data. It is also hoped to expand this work to devise a universal quantitative scale of polymer surface acidity in the near future.

At present we see the utility of the method as one equivalent in concept to that of Mohs scale of hardness; candidate polymers can be assessed and placed within a scale of six well characterised homopolymers. Further development of substrate material, and perhaps conditioning procedure, will enable the development of a quantitative method.

Acknowledgements

The authors thank the SERC and British Gas plc for the financial support of adhesion research at the University of Surrey, and Mr. S. J. Greaves for experimental assistance. MMC thanks the CNRS for partial support during his time at Guildford. We also thank Professors J. E. Castle and M. Delamar for invaluable advice and discussions.

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