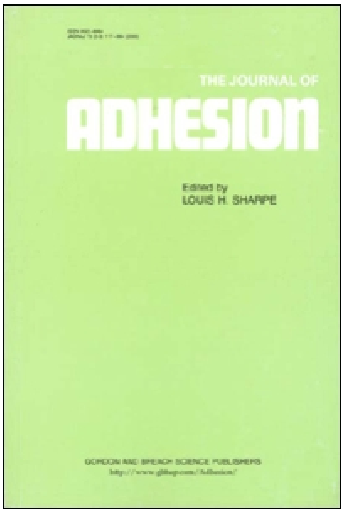

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The Definition of the Locus of Failure on Ceramic Substrates: The Benefit of Monochromated XPS*

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The use of X-ray photoelectron spectroscopy (XPS) to assess the locus of failure of a photo-cured resin on an alumina substrate is reported. It is shown that the carbon 1s spectra obtained with conventional (achromatic) and monochromatic photon sources are markedly different. The spectrum obtained with the monochromatic source reveals the fine structure associated with the polymer whilst the spectrum recorded with the conventional source is distorted by differential charging. This observation has important ramifications when XPS is used for the definition of the locus of failure of organic coatings, or adhesives, applied to insulating substrates such as ceramics.

KEY WORDS monochromated AlKα XPS; XPS; locus of failure; photo-cured resins; charge compensation in XPS; alumina substrates.

INTRODUCTION

In a recent paper the failure mode of a photo-cured resin applied to a commercial alumina substrate has been described.[1] XPS was used as the primary spectroscopic technique in an effort to identify the amount and nature of a thin organic overlayer remaining on the alumina substrate following tensile testing of a simple butt joint. The tensile test was carried out within the UHV chamber of the spectrometer and consequently the authors felt confident in the assignment of the source of the organic material by the inspection of the high resolution carbon 1s spectrum. The C1s spectrum was a symmetrical peak with no apparent fine structure, in contrast to the spectrum recorded from the bulk resin[1], and failure was ascribed to the presence of a pre-existent contaminant layer. This result was in contrast to the spectrum recorded from the bulk polymer, which showed fine structure to the higher binding energy side of the main C1s component, consistent with the functional groups present within the material.

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The opportunity has recently arisen to re-examine similar samples using a very high resolution spectrometer, equipped with monochromatic AlKα radiation, of a type not generally available. The results obtained in this study have made it necessary to review the original conclusions based on standard XPS analysis methods. The purpose of this communication is twofold: firstly, to draw attention to the additional information that may be available in locus of failure studies on insulating substrates, by using a monochromatic radiation source and secondly, to urge caution in the interpretation of XPS spectra from thin polymer films deposited onto insulating substrates, particularly if the management of surface charge is not fully and properly defined.

CARBON 1s XPS SPECTRA

The spectra to be discussed in this communication were acquired using two spectrometers. A VG Scientific ESCALAB MkII, using achromatic MgKα photons from a VG Scientific XR2 twin anode X-ray source, operated at a power of 100 W. The use of MgKα was necessary as the alumina substrate contained a small amount of silica, and the Si2p photoelectron peak (100 eV) is exactly coincident with the Bremsstrahlung-induced AlKLL Auger peak in AlKα radiation. In the case of monochromatic AlKα radiation the Bremsstrahlung component of the radiation is removed by the crystal monochromator. The spectrometer was operated in the CAE mode at an analyser pass energy of 20 eV and an entrance aperture of 6 mm. As is usual in this form of analysis no efforts were made to compensate for electrostatic charging of the specimen, although electrons generated at the aluminium window of the source will partially achieve this. The other spectrometer was a Scienta ESCA300, located at SERC Daresbury Laboratory, equipped with a high power rotating anode monochromator (1 KW for this experiment), together with auxiliary flood guns for charge compensation. The geometry of the system is described elsewhere[2]. The flood gun used (VSW EG2) was operated at a potential of 7 eV with a filament current of 2.3 A and a focus potential of approximately 17 V. The ESCA300 spectrometer was also operated in the CAE mode, using a pass energy of 150 eV with a slit width of 1.1 mm. The Scienta ESCA300 spectrometer also has a sensitivity far higher than that of the ESCALAB instrument. This ensures that the spectra can be recorded at very high resolution within a time window during which no damage is observed. This aspect of the XPS analysis of photo-cured polymers is addressed in detail elsewhere[3].

As outlined above the ESCALAB data has been published previously, and the comparison with the ESCA300 data is striking, as shown in Figure 1. Both spectra were recorded at an electron take-off angle of 45° and are reproduced with the major C1s component set at a binding energy of 285.0 eV. In practice the ESCALAB data exhibited around 2.0 eV electrostatic charge, whilst the successful management of surface charge on the ESCA300 leads to a slight negative shift of approximately 1.5 eV.

The C1s spectrum recorded on the ESCALAB is a broad featureless peak of the type that is to be expected from adventitious carbon contamination that frequently bedevils analysis by XPS. The ESCA300 spectrum on the other hand shows the fine structure that is expected from the photo-cured polymer[1]. Clearly the situation that exists is that the organic residue is a thin (of the order of 1–2 nm) layer of the polymer remaining on

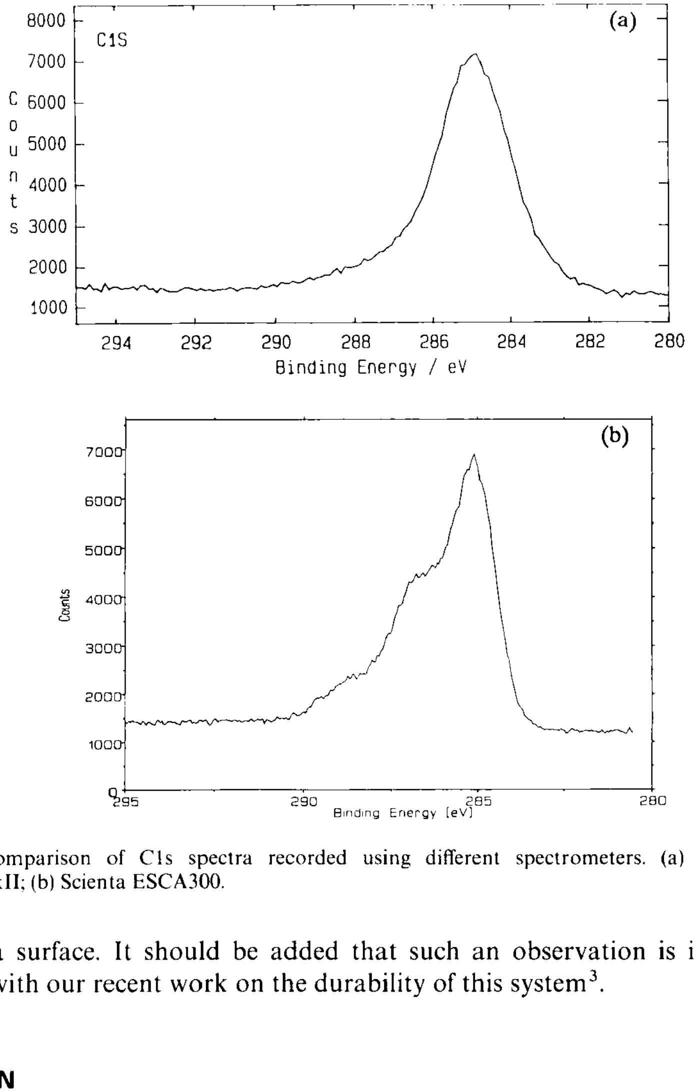

FIGURE 1 Comparison of C1s spectra recorded using different spectrometers. (a) VG Scientific ESCALAB MkII; (b) Scienta ESCA300.

the alumina surface. It should be added that such an observation is in complete agreement with our recent work on the durability of this system[3].

DISCUSSION

The above observation indicates the additional information that can be obtained by using the ESCA300 spectrometer. In attempting to understand this apparent anomaly it is necessary to consider the electrostatic surface charge situation of the individual experiments. On irradiating the specimen with (either) X-ray source photoelectrons will be generated from both the substrate and the polymer overlayer, giving rise to a slight positive potential. In the case of the ESCALAB experiment this is partially neutralised by the flood electrons from the source window; however, there is still the possibility that there is a variation of electrostatic potential with depth. This phenomenon is known as vertical differential charging (VDC)[4]. The experimental manifestation of the process is a slight relative movement on the binding energy scale of the spectra produced as a function of depth. This yields the type of spectrum illustrated in Figure 1a. The alternative to VDC, lateral differential charging, is discounted as angular resolved XPS shows the polymeric residue to be present as a uniform overlyer of approximately 2 nm in thickness[3].

In the case of the ESCA300 experiment the application of a well-defined flux of flood electrons from an explicit source (the electron flood gun) ensures that the VDC phenomenon is absent. Thus, the spectra produced are of a much higher resolution and enable the fine structure to be identified quite readily, as shown in Figure 1b.

CONCLUSIONS

The above data indicate the care that must be taken in the definition of the locus of failure of polymer layers on insulating substrates such as ceramics. The use of monochromatic X-rays and an electron flood gun enable data of much higher quality to be produced. In some cases this will ensure a more accurate definition of the organic residue.

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