

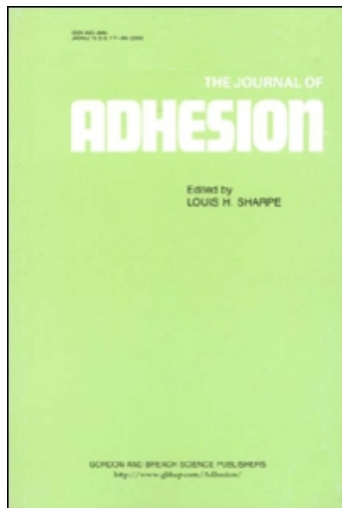
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D. Briggs^a

^a ICI PLC, Petrochemicals and Plastics Division, Middlesbrough, Cleveland, UK

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Application of Secondary Ion Mass Spectrometry to Adhesion Studies†

D. BRIGGS

*ICI PLC, Petrochemicals and Plastics Division, PO Box 90, Wilton,
Middlesbrough, Cleveland TS6 8JE, UK*

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The present paper firstly describes developments in the technique of static secondary ion mass spectrometry. Secondly, the power of this advanced surface analytical technique is illustrated by discussing the locus of failure of epoxide/polyethylene substrate joints.

KEY WORDS Adhesion studies; epoxide/polyethylene adhesion; instrumentation; locus of failure; static SIMS; weak boundary layer.

1 GENERAL INTRODUCTION

There is no doubt that, over the last ten years or so, surface analytical techniques have had a major impact on the study of adhesion.¹⁻⁴ In particular, two techniques have achieved prominence. X-ray photoelectron spectroscopy (XPS or ESCA) has been used almost exclusively to study polymer surfaces and organic layers because of the lack of problems with sample charging and radiation damage. In the case of non-organic systems, *e.g.* studies of metal oxide structures, Auger electron spectroscopy (AES) has also been applied, especially in combination with argon-ion etching to construct composition depth profiles. AES also has the facility for

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microanalysis and surface composition imaging (production of element distribution maps). Unfortunately AES cannot be applied to organic systems because of beam damage and charging problems, whereas XPS lacks spatial resolution. For adhesion studies in general, but for polymer related studies in particular, the requirement is for a technique which combines, or even exceeds, the attributes of both XPS and AES. Static SIMS has the potential to fulfil this demanding role. This technique has been developed rapidly for polymer surface analysis⁵ since about 1981 and the instrumentation is currently undergoing a major revolution with significant implications for adhesion science.⁶

1.1 Static SIMS for polymer surface analysis

1.1.1 *General considerations* The experiment, in essence, consists of sample irradiation by a beam of low energy (typically 2–4 keV) noble gas ions (Ar^+ , Xe^+) with simultaneous irradiation by relatively low energy electrons (several hundred eV) to provide charge neutralisation of the insulator surface. Ejected secondary ions are mass analysed to provide, sequentially, the positive and negative ion mass spectra. "Static" SIMS means that the primary ion dose acquired during spectral acquisition is so low that the spectra are characteristic of the unperturbed surface. Above a threshold dose (material dependent but for many polymers as low as 10^{13} ions cm^{-2})⁷ the spectra change with dose and represent beam damaged surfaces. Good signal/noise spectra can routinely be obtained for doses $< 2 \times 10^{12}$ ions cm^{-2} . Surface potential control is a key experimental issue and requires significantly different parameters for optimisation of positive and negative SIMS.^{8–10} The spectra are typical of organic mass spectra in general with high mass cluster ions representative of major structural units of polymers (*i.e.* multiple repeat unit fragments, intact side chain fragments) and their daughter fragments. Small molecules, *e.g.* additives, often give quasi-molecular ions (*e.g.* MH^+ where M is the molecular weight) and fragmentation patterns similar to those encountered in conventional mass spectrometry. Many fingerprint spectra of polymers have been reported.^{3,5,11–15} Quantification of SIMS intensity data has been demonstrated for methacrylate¹⁴ and

nylon¹⁵ copolymers and has been used to investigate the surface composition of segmented polyurethanes.¹⁶ The sampling depth in typical static SIMS appears to be $\leq 10\text{\AA}$.¹⁶

1.1.2 Imaging The obvious application for molecular imaging in adhesion studies is the investigation of failure surfaces. Static SIMS imaging of molecular species in all-polymeric systems has been demonstrated with a spatial resolution of $\sim 50\ \mu\text{m}$.^{13,17} In this experiment the focussed ion beam is rastered over the surface with the mass spectrometer tuned to detect a chosen ion (m/z) and the intensity of the signal fed to an oscilloscope scanning synchronously (entirely equivalent to SEM). As the probe diameter decreases (increased spatial resolution) and the irradiated area decreases (higher magnification), two problems occur. Firstly, charge neutralisation becomes more difficult and secondly, the static SIMS threshold is rapidly exceeded producing unacceptable sample damage. To overcome these problems requires more sensitive instrumentation.³

1.1.3 Instrumentation developments A new generation of instrumentation is approaching introduction based on very high spatial resolution liquid-metal ion sources (500A probe) and time-of-flight mass spectrometry (ToF SIMS).⁶ The ToF promises several orders of magnitude improvement in sensitivity over the conventional quadrupole mass spectrometer as well as a vastly increased mass range (>5000 compared with several hundred).¹⁸ The ion source needs to be pulsed which should help overcome charging problems.

1.2 Applications of SIMS to adhesion studies

The twin-aspects of increased molecular specificity and decreased sampling depth, relative to XPS, are of enormous benefit in the study of organic contamination/potential weak boundary layers and failure planes. The importance of small molecules at surfaces and interfaces, arising from *in situ* additives, contamination *via* the atmosphere or by contact (*e.g.* of film surfaces with each other or

with machinery) on adhesion and durability, is becoming increasingly recognised as a result of SIMS information.⁵ In the case of poly(ethylene terephthalate) surface oligomers have even been analysed.¹⁹ The classic case of poor adhesion between polyethylenes and epoxide adhesives has recently been reinvestigated and the results are now discussed as an illustrative case.

2 FAILURE OF POLYETHYLENE/EPOXIDE ADHESIVE JOINTS

2.1 Introduction

In 1976, in the first paper which used XPS to study adhesion to polyolefins,²⁰ Briggs, Brewis and Konieczko briefly reported the results of LDPE/epoxide adhesive failure surface analysis. The apparent lack of LDPE transfer to the adhesive (deduced from a comparison of the adhesive surfaces from a broken joint and from a film cured in air) has subsequently been quoted²¹ as evidence against the weak boundary layer theory for the poor adhesion properties of untreated polyolefins. Because of uncertainties about the XPS sampling depth (at that time) the authors included a caveat in their conclusions to the effect that a very thin layer of LDPE may go undetected. Today caution for this reason can reasonably be dismissed. However, SIMS has since emerged as a more powerful tool than XPS for this type of analysis on account of its greater surface sensitivity and molecular specificity.⁵ Several aspects of the early data and the fact that the experiment has never been repeated, led us to reinvestigate using both XPS and SIMS.

2.2 Experimental

Films, 0.15 mm thick, of Akathene 11 LDPE (ICI), an additive-free blown film, and Rigidex 002-55 HDPE (BP), pressed from additive-free powder between sheets of poly(ethylene terephthalate) previously Soxhlet extracted in carbon tetrachloride, were used. The LDPE was freshly cut from a reel prior to use, the HDPE film was briefly extracted with THF and diethylether.

The "Araldite" (Ceiba Geigy) adhesive used was a 1:1 mixture

of the resin AV100 (a standard bisphenol-A diglycidyl ether) and hardener HV100 (believed to be a polyamide containing a tertiary amine accelerator). Lap shear joints were prepared as described previously.²⁰ Adhesion was very poor ($\leq 0.7 \text{ MN m}^{-2}$), but it should be noted that the same adhesive gives joint strengths with the same polyethylenes, which have received a standard pretreatment, which are greater by an order of magnitude.

XPS measurements were carried out on a Kratos ES200B instrument under control of a DS800 data system which also allowed complex curve synthesis to be carried out. Surface atomic compositions were computed from peak areas using sensitivity factors appropriate to the FRR analyser mode.²² Variable "take-off" angle experiments could be performed and quoted values of θ refer to the electron exit angle with respect to the surface.

SIMS measurements were carried out on a system described previously,⁸ based on an ESCALAB Mk 1 XPS/SIMS instrument (VG Scientific). A primary ion beam of 4 keV Xe^+ (1 nA cm^{-2}) was used with a 700 eV flood of electrons for charge neutralisation.

2.3 Results

The XPS results are collected in Table I. The "deconvolution" of the complex C1s envelope is illustrated in Figure 1, in which four components of similar width are used. For present purposes it is not important to discuss the possible interpretation of the component peaks except to note that: (a) C_1 corresponds to C atoms bound only to C or H (e.g. the position of $(-\text{CH}_2-)_n$ from polyethylene) whereas C_2 – C_4 represent C atoms in functional groups involving O and N); (b) all C1s spectra were fitted identically except for the intensities of the four components and (c) in each case an extremely

TABLE I
XPS data from epoxide adhesive surfaces

Sample (θ)	Relative intensity				atomic %		
	C_1	C_2	C_3	C_4	C	O	N
Epoxide scraped (80°)	69.9	22.0	5.7	2.4	73.4	20.7	5.8
Epoxide/LDPE (80°)	75.5	19.6	4.2	0.7	82.2	13.1	4.7
Epoxide/LDPE (15°)	80.2	14.0	4.4	1.4	82.8	14.5	2.6

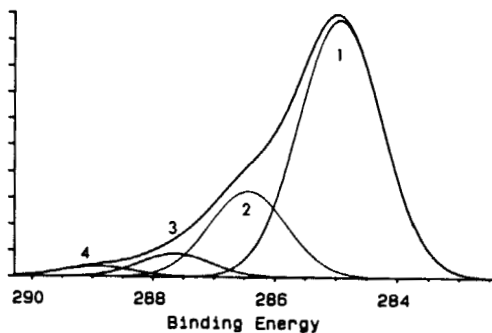


FIGURE 1 Position of components (C_1 - C_4) used to fit the experimental C1s envelope (in this case for the scraped epoxide adhesive surface).

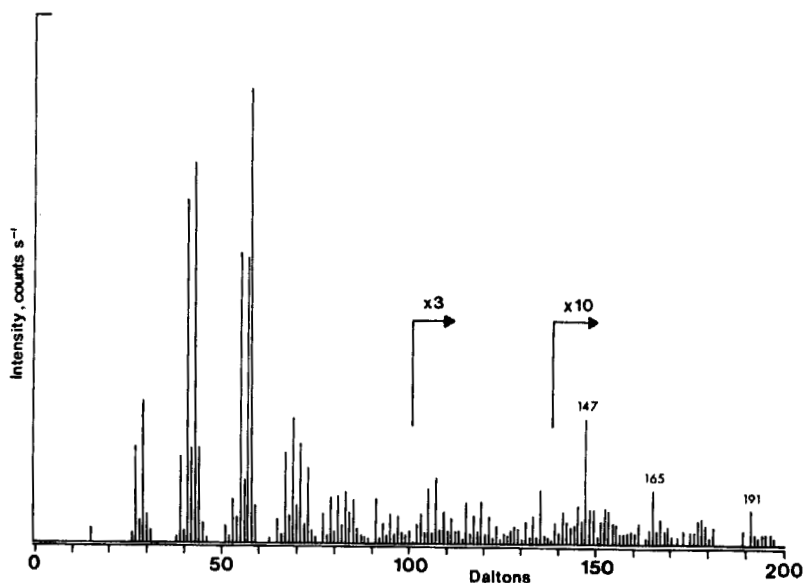


FIGURE 2(a) Positive SIMS of the epoxide adhesive surface resulting from failure of the LDPE/epoxide joint. Annotated peaks are characteristic of dimethyl silicone.

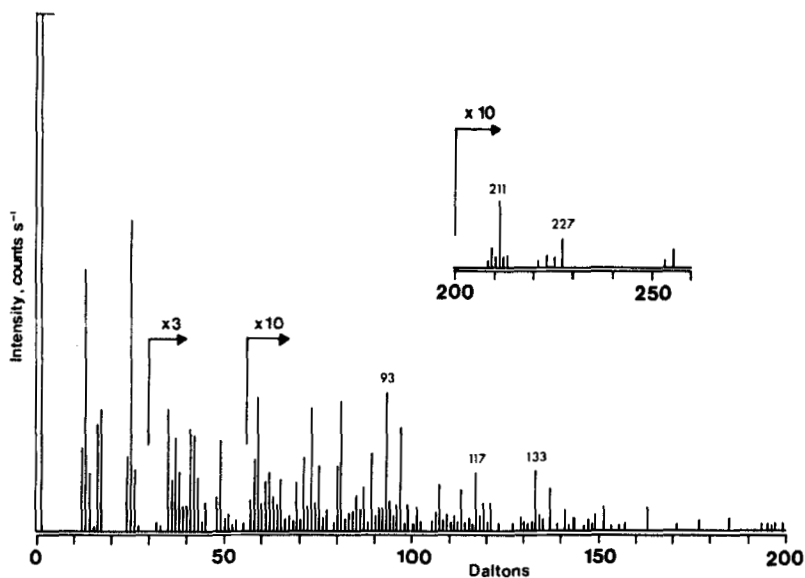


FIGURE 2(b) Negative SIMS of the epoxide adhesive surface resulting from failure of the LDPE/epoxide joint. Annotated peaks are characteristic of the bisphenol-A part of the structure (see Ref. 3 for an interpretation of the polycarbonate spectrum, also derived from bisphenol A).

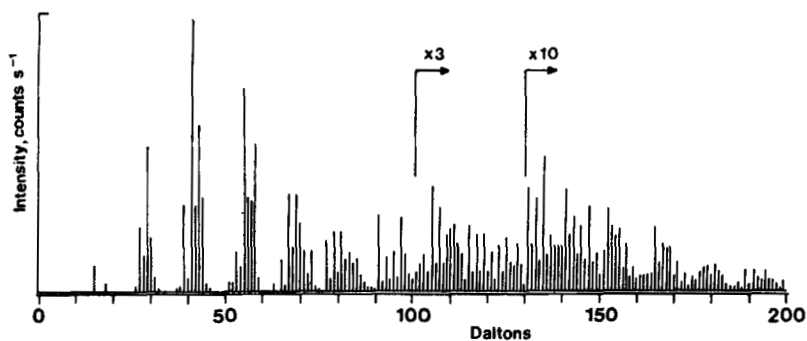


FIGURE 3 Positive SIMS of the epoxide adhesive surface resulting from failure of the HDPE/epoxide joint.

good match between the experimental and synthetic envelope was achieved.

SIMS spectra from the polyethylene film surfaces which had been in contact with the adhesive were identical to those from the original film surfaces (previously reported^{5,23}). Figure 2 shows the spectra from the adhesive surface of the failed LDPE/epoxide joint. The equivalent positive ion spectrum from the HDPE/epoxide joint is shown in Figure 3, the negative ion spectrum being very similar to Figure 2(b). Spectra from the epoxide adhesive after curing in air (with precautions to avoid contamination from the atmosphere) and after scraping this surface with a razor blade are qualitatively similar to Figures 3 and 2(b) (positive and negative ions respectively).

2.4 Discussion

It is quite clear from the SIMS data that failure of the HDPE/epoxide joint is purely interfacial; this can be asserted simply on the basis of the fingerprint nature of the spectra of all the materials involved. In the case of LDPE/epoxide, comparison of Figure 2(a) and Figure 3 reveals a significant contribution from hydrocarbon species ($C_xH_y^+$, e.g. 27, 29, 41, 43, 55, 57D etc) with a relative intensity pattern characteristic of the polyolefin, thus indicating some transfer of LDPE to the adhesive surface. However, the negative ion spectrum (Figure 2(b)) is still characteristic of the adhesive which strongly suggests that the LDPE is very patchy (the negative ion spectrum of LDPE is featureless beyond 30D). The positive ion spectrum also reveals a trace of silicone contamination (peaks at 147, 165, 191D).⁵ The origin of this material is unknown. It is not seen on the original film surfaces, nor is it present in the adhesive. It may have migrated from the aluminium used to make the lap shear joint or have been picked up from the atmosphere during joint preparation. Its presence is not material to the discussion, but its detection reveals another facet of SIMS analytical capability.

The XPS data from the Table are entirely consistent with this conclusion and also with the previously reported results.²⁰ Taking the scraped epoxide data as representative of the bulk adhesive composition (80° giving the maximum sampling depth for our

instrument), comparison with the data from the failed joint reveals a little hydrocarbon transfer (greater % of carbon, but particularly of type C_1). However, the enhancement of this component at $\theta = 15^\circ$ (minimum sampling depth) is very small and definitely not consistent with there being a continuous overlayer of polyolefin, even of only monolayer thickness; *i.e.* transfer is patchy and sub-monolayer.

The variation in composition of the epoxide adhesive surface between the air-cured sample and the failed joint noted previously²⁰ is seen more clearly from the Table, the angular variation data suggesting a significant composition gradient below the surface. This is mirrored by the SIMS data. Relative intensity differences between peaks representing the epoxide resin and others characteristic of the cross-linked (nitrogen-containing) polymer can be observed when comparing air-cured adhesive before and after scraping and the failed joint surfaces. A detailed interpretation of the adhesive spectra is not appropriate in this note, but will be given in a future paper which follows the curing process.

In a recent paper²⁴ concerned with adhesion to polyethylenes we demonstrated that lack of chemical functionality was the key reason for the poor adhesive properties. The presence of mobile low molecular weight material, in the case of LDPE, complicated the situation relative to HDPE, but there could be no doubt that arguments based purely on weak boundary layers are entirely inadequate.

The present results from direct interrogation of the interfacial situation in polyethylene/epoxide joints bears this out. Adhesion is negligible for both HDPE and LDPE. In the former case there is no evidence for cohesive failure whereas in the latter case, where no attempt was made to minimise weak boundary layer effects, only sub-monolayer transfer to the adhesive was observed.

References

1. D. M. Brewis, Ed., *Surface Analysis and Pretreatments of Plastics and Metals* (Applied Science Publishers, London, 1982).
2. D. M. Brewis and D. Briggs, Eds., *Industrial Adhesion Problems* (Orbital Press, Oxford, 1985).
3. D. M. Brewis and D. Briggs, *Polymer* **22**, 7 (1981).

4. D. M. Brewis, *Prog. Rubber Plast. Tech.* **1** (4), 1 (1985).
5. D. Briggs, *Surf. Interface Anal.* **9**, 391 (1986).
6. VG Scientific Ltd, East Grinstead, UK have recently constructed a ToF SIMS microprobe for high resolution (1000 Å) imaging and high mass secondary ion detection.
7. D. Briggs and M. J. Hearn, *Vacuum*, in press.
8. D. Briggs and A. B. Wootton, *Surf. Interface Anal.* **4**, 109 (1982).
9. A. Brown and J. C. Vickerman, *ibid.* **8**, 75 (1986).
10. D. Briggs and M. J. Hearn, in preparation.
11. D. Briggs, *Polymer* **25**, 1379 (1984).
12. D. Briggs, *Surf. Interface Anal.* **4**, 151 (1982).
13. D. Briggs, *ibid.* **5**, 113 (1983).
14. D. Briggs, M. J. Hearn and B. D. Ratner, *ibid.* **6**, 184 (1984).
15. D. Briggs, *Org. Mass Spec.*, in press.
16. M. J. Hearn, D. Briggs, S. C. Yoon and B. D. Ratner, in preparation.
17. D. Briggs and M. J. Hearn, *Spectrochim. Acta* **40B**, 707 (1985).
18. D. M. Hercules and I. V. Bletsos, *Polym. Mat. Sci. Eng.* **54**, 302 (1986).
19. D. Briggs, *Surf. Interface Anal.* **8**, 133 (1986).
20. D. Briggs, D. M. Brewis and M. B. Konieczko, *J. Mater. Sci.* **11**, 1270 (1976).
21. See, for example, A. J. Kinloch, *ibid.* **15**, 2141 (1980).
22. D. T. Clark and H. R. Thomas, *J. Polym. Sci., Polym. Chem. Ed.* **16**, 791 (1978).
23. D. Briggs and M. J. Hearn, *Int. J. Mass Spec. Ion Processes* **67**, 47 (1985).
24. A. Chew, *et al.*, *J. Coll. Interface Sci.* **110**, 88 (1986).