The application of static secondary ion mass spectrometry to the study of epoxy adhesive constituents

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The application of fast atom bombardment secondary ion mass spectrometry (FAB-SIMS) with quadrupole mass analysis to the study of some of the common constituents present in epoxy adhesive formulations is described and the potential of the technique evaluated. The compounds investigated were Epikote 828 (mainly diglycidyl ether of bisphenol-A) and the cross-linking agent dicyandiamide. The characteristic secondary ion spectra recorded for both materials exhibited a number of identifiable and uniquely diagnostic signals, which should be of use in the study of surface and interface adhesive chemistry.

Key words: adhesives; surface analysis; secondary ion mass spectrometry; characteristic spectra; epoxy resin

Although the application of epoxy-based resins in composites and adhesively bonded structures continues to increase, relatively little is known concerning the surface and interfacial chemistry of the adhesives, despite the fact that it has a significant effect on adhesive properties and interfacial stability in moist or corrosive environments[1].

In the last few years, surface analysis techniques such as X-ray photoelectron spectroscopy (XPS or ESCA) and Auger electron spectroscopy (AES) have made a major impact in the field of adhesion science[2]. More recently, the various forms of secondary ion mass spectrometry (SIMS) have provided additional insight into adhesion[3,4]. Most forms of SIMS involve the bombardment of a sample with a primary ion beam and the subsequent mass analysis of the positively or negatively charged secondary ions emitted from the surface. The resultant surface mass spectra generally contain detailed and highly specific information about the chemical structure of the sample under analysis. The technique is particularly suitable for the analysis of polymer surfaces, as fragments corresponding to the characteristic functional groups that comprise the backbone and side chains of each polymer molecule are obtained. Characteristic fingerprint spectra have already been recorded for numerous reference materials[5,6]. In general, however, SIMS spectra are not as readily quantifiable as XPS or AES data.

Most work on polymer systems has been carried out in the *static* SIMS mode (SSIMS) where the primary ion dose is sufficiently low to allow secondary ion spectra to be obtained that are characteristic of the undamaged polymer. Above a threshold dose (10^{13} ions cm^{-2})[7], however, polymeric materials are degraded and as a result the spectra are no longer characteristic of the undamaged material. A recent modification of SSIMS is fast atom bombardment SIMS (FAB-SIMS) where the primary ion source is replaced by an atom source. For non-conducting samples, FAB-SIMS reduces the problems of sample charging and damage[8,9].

In the investigation to be described here, FAB-SIMS was used to study the epoxy resin Epikote 828 (mainly the diglycidyl ether of bisphenol-A, DGEBA) and a cross-linking agent (dicyandiamide). Analysis of each material is an essential first step in the detailed study of both general adhesive chemistry and the factors which affect the composition of the adhesive at interfaces.

Experimental

Instrumentation

FAB-SIMS analysis was carried out in a VG SIMSLAB instrument equipped with a 2 keV argon primary atom source and a VG MM12-12 quadrupole

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mass analyser[8,9]. Both positive and negative ion spectra were collected using a total primary ion dose of 5×10^{12} ions cm^{-2}. Charge compensation was not required for the acquisition of either the positive or negative ion spectra.

A DEC PDP11 computer was used for instrument control, data acquisition and processing of spectra.

Materials

The Epikote 828 used was the standard resin supplied by Shell Ltd. Standard purity dicyandiamide was obtained from BDH Chemicals.

Sample preparation

Epikote 828 was analysed as a thin film deposited in neat form on to aluminium foil. The sample of dicyandiamide was prepared by pressing the powdered compound into indium foil. Both foils were analysed independently so that peaks associated with the substrates could be identified and eliminated from further consideration.

Results

Epikote 828 resin

Epikote 828 contains a number of oligomers based on the structure shown in Fig. 1. Approximately 75% of the resin comprises the $n = 0$ compound (DGEBA) and 25% of higher molecular weight oligomers[10]. The positive ion spectrum (Fig. 2) contained small peaks at $m/z = 340$ and 341 corresponding to the molecular and protonated molecular ions of DGEBA, respectively. No peaks of significant intensity occurred above mass 341 and the most intense peak in this region of the spectrum was observed at $m/z = 325$, the mass of the DGEBA parent ion less one of the methyl groups. Below this mass, a number of other highly characteristic ions were detected at m/z values of 269, 191, 135, 91, 77, 57 and 31.

The peak at $m/z = 269$ can be accounted for by

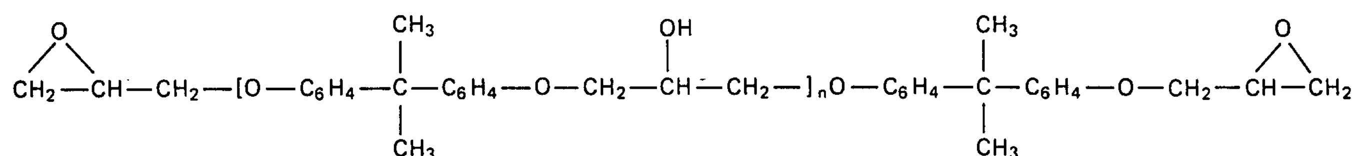
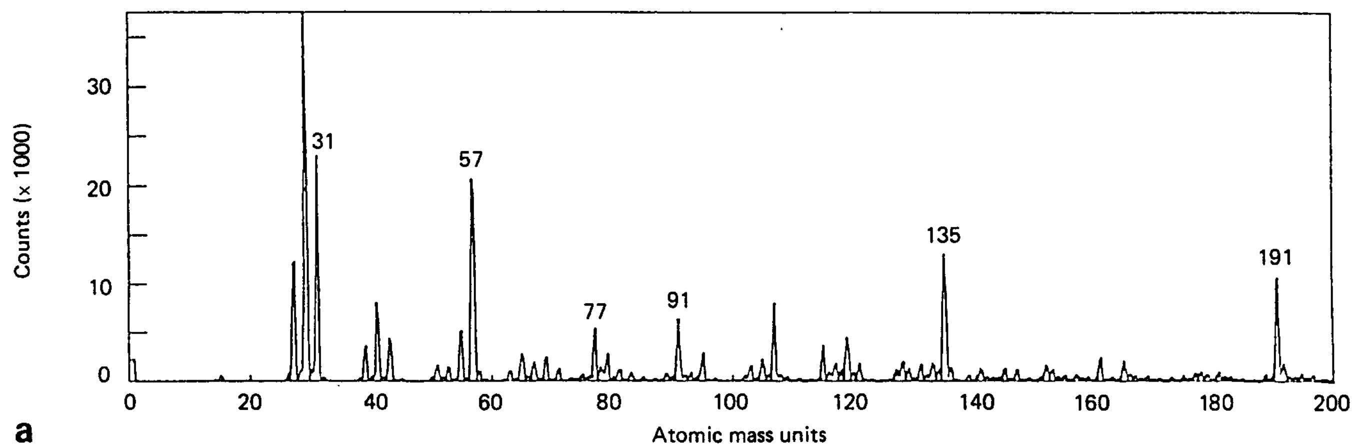


Fig. 1 Structure of oligomers in Epikote 828



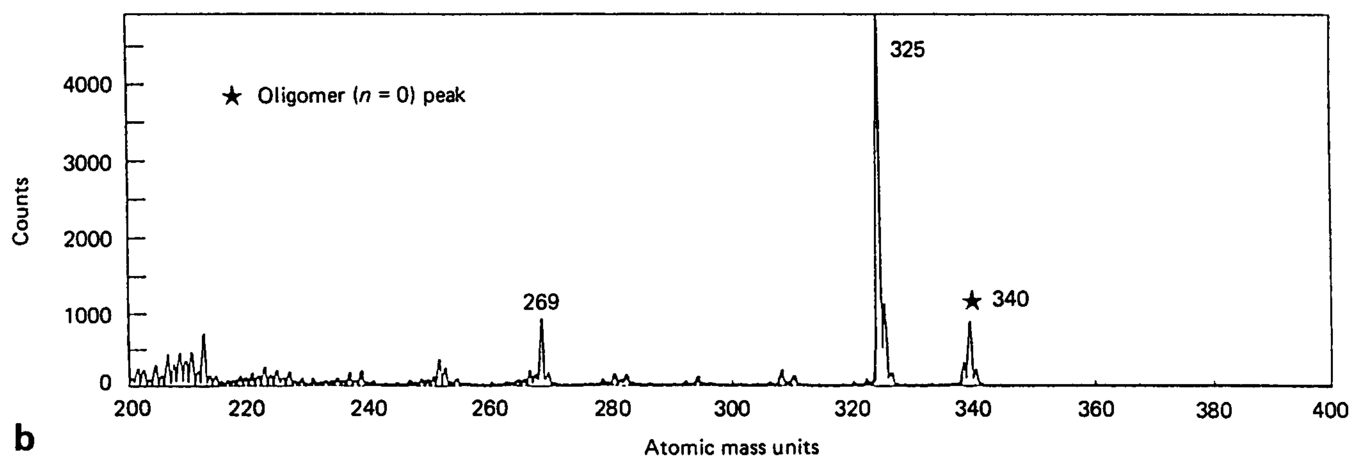
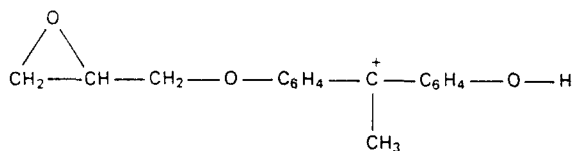
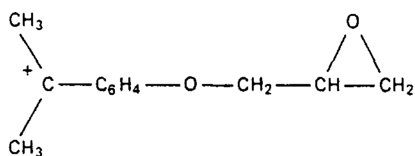


Fig. 2 Positive ion FAB-SIMS spectrum of Epikote 828 resin

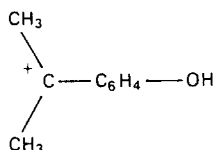
a fragment of the type:



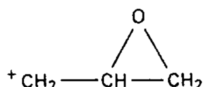
and the m/z = 191 peak corresponds to the fragment:



The most likely fragment to account for the m/z = 135 peak is:

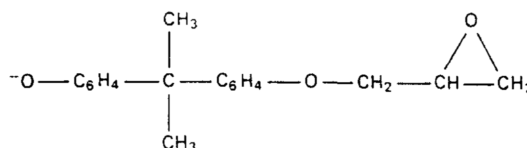


and the peak at m/z = 57 corresponds to the epoxide fragment:

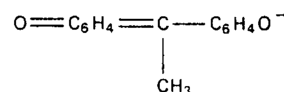


Of the remaining peaks in the spectrum, those at m/z = 91, 77 and 31 correspond to the $C_7H_7^+$, $C_6H_5^+$ and CH_2OH^+ fragments.

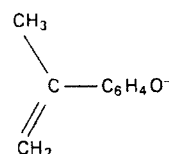
In the negative ion spectrum (Fig. 3), a very intense peak was observed at a m/z = 283 which corresponds to the bisphenol-A epoxide fragment:



Other intense peaks in the spectrum occurred at m/z = 211, 133, 117, 93 and 73, together with the normal collection of high intensity peaks below m/z = 50 corresponding to C_2OH^-, C_4H^-, C_2H^-, CH^-, O^- and OH^- fragments. Of the higher mass peaks, the one at m/z = 211 corresponds to the fragment:

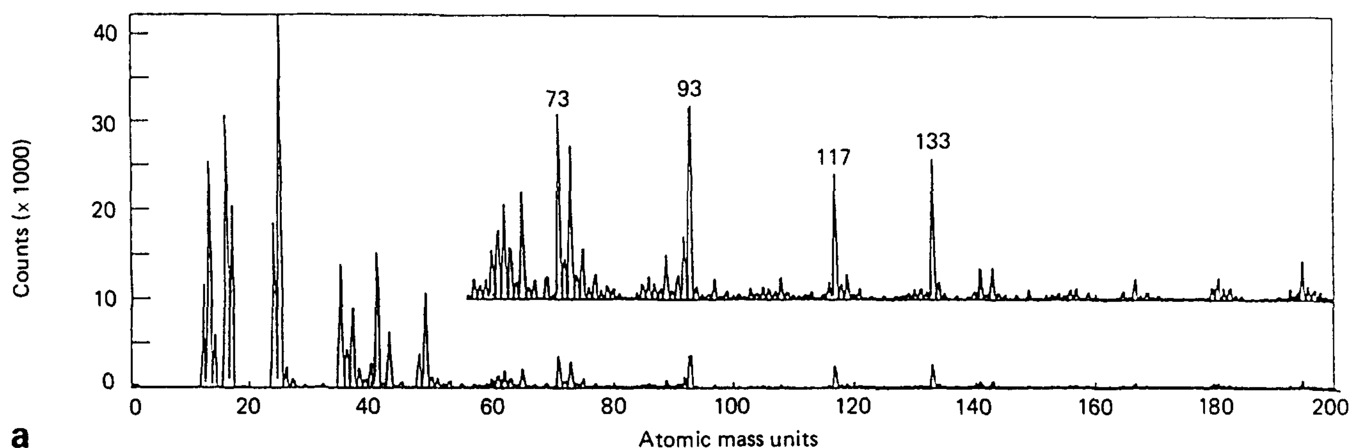


and the m/z = 133 peak to the fragment:



Peaks at m/z = 117 and 93 correspond to the $CH{\equiv}C\text{-}C_6H_4\text{-}O^-$ and $C_6H_5\text{-}O^-$, respectively.

The peak at m/z = 73 can be accounted for by the etherated epoxide fragment of the epoxide molecule:



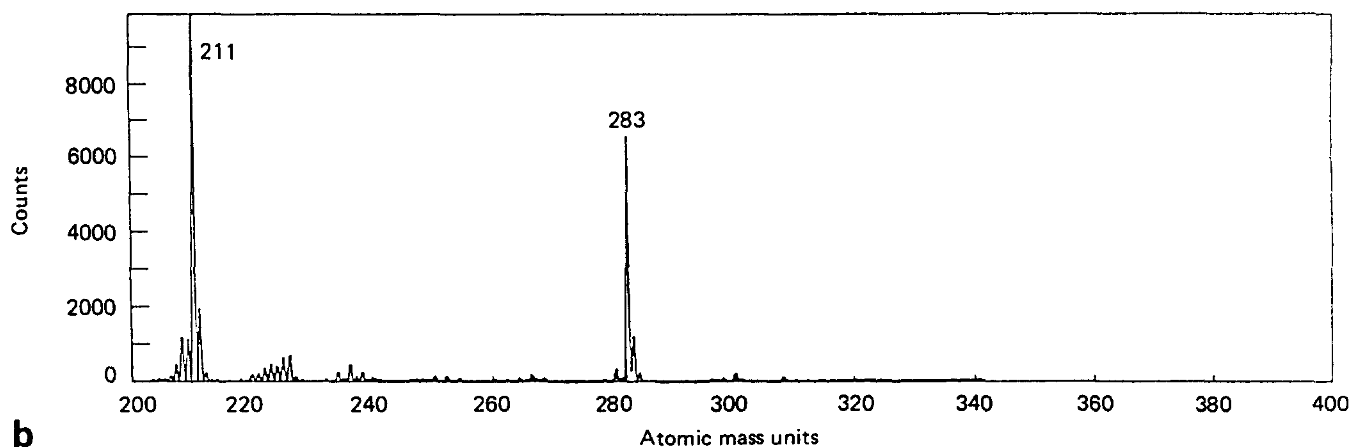
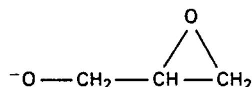


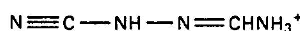
Fig. 3 Negative ion FAB-SIMS spectrum of Epikote 828 resin

Fig. 4 FAB-SIMS spectra of dicyandiamide: (a) positive ion spectrum; (b) negative ion spectrum

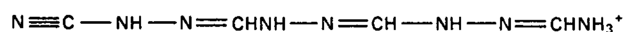


Dicyandiamide

The positive ion FAB-SIMS spectrum (Fig. 4(a)) of the crystalline compound contained an intense fragment at m/z = 85 corresponding to the protonated dicyandiamide parent ion:



Other intense peaks observed at m/z = 60 and 43 correspond to the NH_2-N=$CHNH_3^+$ and N≡C-NH_3^+ protonated fragments of the parent molecule. In addition, a relatively intense fragment was observed at m/z = 18 which can be accounted for by the NH_4^+ ion and/or the H_2O^+ species associated with water emission from the surface of the sample. Above the mass of the parent ion, peaks at m/z = 169 and 102 were observed which correspond to the dimer of dicyandiamide:



and the hydrated parent molecule:

The precise structure of the latter hydrate species is unknown. Note that a signal at m/z = 115 was derived from the indium substrate.

The negative ion spectrum (Fig. 4(b)) of this compound contained a very intense CN^- component at m/z = 26, together with smaller CN_2^- and $C_2N_3^-$ components at m/z = 40 and 66.

Discussion

In adhesive studies, the high specificity and fingerprinting ability of SIMS should allow curing chemistry and the characterization of small differences in adhesive composition at interfaces to be evaluated. It should also be possible to monitor the structural changes occurring at interfaces in adhesive joints and as a result begin to evaluate the effects of environmental degradation. Whilst curing will result in a reduction, to varying degrees, in many of the ion yields, a number of characteristic ion species are likely to remain observable. It is also likely that new ion signals derived from the cross-linked polymer network will appear in the spectra. In epoxide chemistry, the characteristic positive ion peak found in the FAB-SIMS spectrum of the bisphenol-A molecule at m/z = 135 and negative ion peaks at m/z = 93, 117, 133 and 211 have also been identified in the static SIMS spectra of polycarbonates formed from bisphenol-A and the bisphenol of acetophenone, where polymerization resulted in molecular weights in excess of M_w = 20 000[11]. This identification of common peaks in the two sets of spectra illustrates the transferability of the characteristic signals associated with a common component, from one material to another.

No other technique is currently capable of providing the same structural information concerning adhesive components. For example, in XPS, the spectra of organic compounds often contain a series of poorly resolved carbon peaks which can only be separated by the use of various deconvolution and curve synthesis techniques and this makes precise chemical state identification difficult. However, XPS data are readily quantifiable and chemical state identification can be improved by the use of monochromated X-ray sources and high resolution analysers[12]. Chemical state information can also be augmented by consideration of other signals in the spectrum (e.g., nitrogen and oxygen). Auger analysis often results in severe decomposition of the surface under analysis and whilst the technique is quantifiable and has good spatial resolution, chemical structure cannot be evaluated. Curing of epoxy resin systems has been monitored using a combination of Fourier transform infra-red (FTIR) and nuclear magnetic resonance (NMR)[13] spectroscopies but no attempt has been made to separate the surface spectra from those of the bulk polymer.

Although the FAB-SIMS with quadrupole mass analysis resulted in the identification of a range of characteristic fragments from dicyandiamide and Epikote 828 resin, the technique did not have sufficient sensitivity at high masses to allow detection of peaks which are specifically characteristic of the higher molecular weight oligomers[10] present in the resin. Epikote 828 contains approximately 25% of higher molecular weight compounds of which the majority is the $n = 1$ oligomer. It was also difficult to obtain useful spectra from thicker insulating films of Epikote 828 primarily due to decomposition by the electron beam used for charge neutralization[14]. Although charging problems are reduced in FAB-SIMS, they are not eliminated completely[15]. It should be emphasized, however, that the intensity of the electron beam used for charge neutralization in FAB-SIMS is very much less than that used in Auger electron spectroscopy. Such limitations of the quadrupole-based SIMS technique may be overcome by recent developments in time-of-flight mass analysis which have lead to the introduction of time-of-flight SIMS (ToF-SIMS)[3]. ToF-SIMS is likely to have a number of advantages in the study of adhesives[16], due primarily to its much higher mass range, sensitivity and use of lower primary ion and electron beam fluences.

Conclusion

Positive and negative ion FAB-SIMS spectra of Epikote 828 and dicyandiamide each exhibited a number of identifiable and highly characteristic signals which should be of use in future studies of adhesive surface and interface chemistry.

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