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Scanning secondary ion mass spectroscopic studies of the micromechanics and chemical structure in the region of the interface in carbon fibre–epoxy composites

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As part of a study of the interfacial bond in epoxy resin–carbon fibre composites, scanning secondary ion mass spectrometry (Scanning SIMS) was used to study fracture surfaces parallel to the fibre direction in unidirectional composites and the way in which these surfaces varied with an increasing level of fibre surface treatment (electrolytic oxidation). Interlaminar shear strength (ILSS) and tensile strength of the composites was also measured. Chemical maps obtained, using Scanning SIMS from the transverse fracture surfaces showed that at low levels of fibre surface treatment failure occurred at the fibre-resin interface or within the fibre, whilst at the higher levels of surface treatment failure took place largely within the resin leaving a thin overlayer adhering to the fibre. It is proposed that this failure within the resin explains the presence of the plateau observed in the ILSS against surface treatment curve at higher levels of treatment. Over the range of fibre surface treatments in the study, variations in the level had little effect on the tensile strength of the composites.

1. Introduction

Fractography of fibre–polymer composites gives a valuable insight into the mechanics of failure, enabling for example, the crack initiation and growth mechanism to be identified. The application of conventional optical and electron microscopy in this context is well known [1] but has limited applicability where features such as thin resin overlayers are of interest. Secondary ion mass spectrometry (SIMS) has been shown to be sufficiently surface sensitive for this purpose. In particular, an extensive study by Briggs [2] has demonstrated the suitability of this technique in the analysis of polymers and carbon fibre–thermoplastic fracture surfaces.

In SIMS the surface is bombarded in ultra high vacuum conditions, with a focused ion beam e.g. Ga^+ at 10 keV and the material which is sputtered from the sample surface can be identified by a mass spectrometer. Thus the mass spectrum consists of a series of peaks due to ions of different mass number and is characteristic of the chemical composition within the top few nanometres of the sample material. Negative or positive ion spectra can be acquired and depending on the primary beam intensity a 'static' or 'dynamic' analysis is obtained. In the latter mode a relatively rapid erosion of the surface occurs and a depth profile of composition emerges. When analysing insulating materials, such as polymers, the use of a compensating electron flood substantially reduces charge accumulation on the specimen surface. If the beam is rastered over the sample, as in a Scanning SIMS instrument, appropriate ions may be selected for imaging and a "chemical map" of the sample surface obtained. The resolution available, down to 0.2 μm, makes the technique particularly suitable for examining fracture surfaces in carbon fibre composites where the fibre diameter is $\sim 7\,\mu$m.

In this paper we report the application of Scanning SIMS to fracture surfaces in carbon fibre reinforced plastic (CFRP) and demonstrate how a careful choice of ions used to form the image enables a correlation to be made with the interlaminar shear strength of the material.

2. Materials, fibre surface treatment and test specimen preparation

2.1. Carbon fibre

The carbon fibre used in these experiments was

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Courtaulds Grafil XA grade in the form of 10 000 filament tows (Grafil Ltd, PO Box 16, Coventry CV6 5AE, UK). According to manufacturer's data the tensile modulus of the fibre was 235 GPa and its density 1.8 g cm^{-3}. The mass/unit length of the tow was found to be 0.73 g m^{-1}, whence assuming the fibres were uniform smooth cylinders, the fibre diameter was calculated to be 7.2 μm. Measurements described later gave a fibre tensile strength of about 3.3 GPa.

2.2. Surface treatment

The carbon fibres were surface treated by passing the tow through an electrolyte (an aqueous solution of ammonium bicarbonate) and making the fibre anodic with respect to carbon rod cathodes (cf. [3]). The charge/unit area (C m^{-2}) passing to the fibre during its passage through the electrolyte was used as a measure of the level of the fibre surface treatment as shown in Table I.

2.3. Interlaminar shear strength tests

The standard ILSS test [4] is by means of a short-beam three-point bend test applied to a unidirectional composite with a span–to–depth ratio of 5.

Unidirectional composite bars, 125 mm × 12.5 mm × 2 mm, with a fibre volume fraction of 60% were made by a wet lay-up technique using an epoxy resin, di glycidyl ether of bisphenol A (DGEBA) cured with nadic methylene anhydride (NMA) and a proprietary amine hardner, Shell Epikure K61B (Shell Chemicals Ltd, UK) in the ratio by weight of DGEBA : NMA : K61I/100 : 115 : 4. The cure cycle was 2 h at 120° C followed by 16 h at 180° C. Each of these composite bars were cut into eight ILSS test specimens and thus the ILSS values shown in Fig. 1 are the mean of eight tests.

2.4. Impregnated tow strength tests

The tensile strength of unidirectional composites in the form of tows impregnated with the DGEBA resin mix, described above, was determined. Impregnation was carried out (W. Johnson, personal communication) by pulling the tow at about 300 mm min^{-1} through a dish containing the resin mix diluted with an equal volume of butanone as solvent and then upwards through a small hole in a carbon disc to remove excess resin. In each case a sufficient length of two was impregnated to make, subsequently, nine impregnated tow samples for tensile testing. This length of tow was attached to a frame where it was held under slight tension and, after standing in air for 0.5 h to allow most of the butanone to evaporate, was transferred to an oven to cure the resin. The cured tow was cut into nine lengths before attaching end fittings of braided glass fibre with quick setting epoxy resin. Tensile testing of the tows was carried out on a conventional tensile test machine. By making allowance for the amount of resin in the tow the average tensile strength of the fibres could be determined.

TABLE I Surface treatments for fibres and composite interlaminar shear strengths

XA Fibre surface treatment		Composite ILSS (MPa)
Parameter*	Notation	
0	UT	77
25	IT	82
230	HT	>93

*Level of treatment per m^2 of surface area.

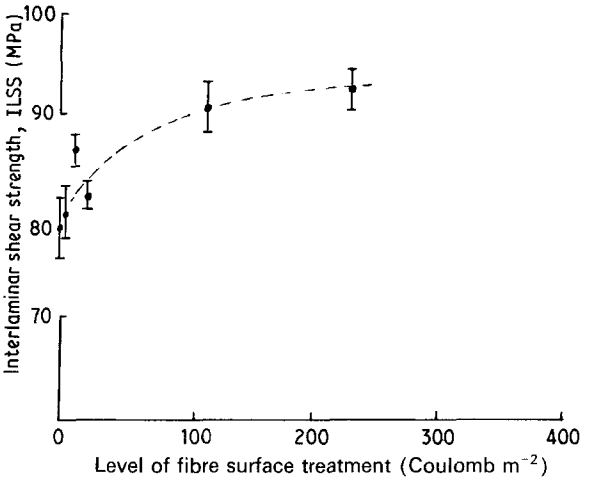


Figure 1 Composite ILSS as a function of level of fibre surface treatment.

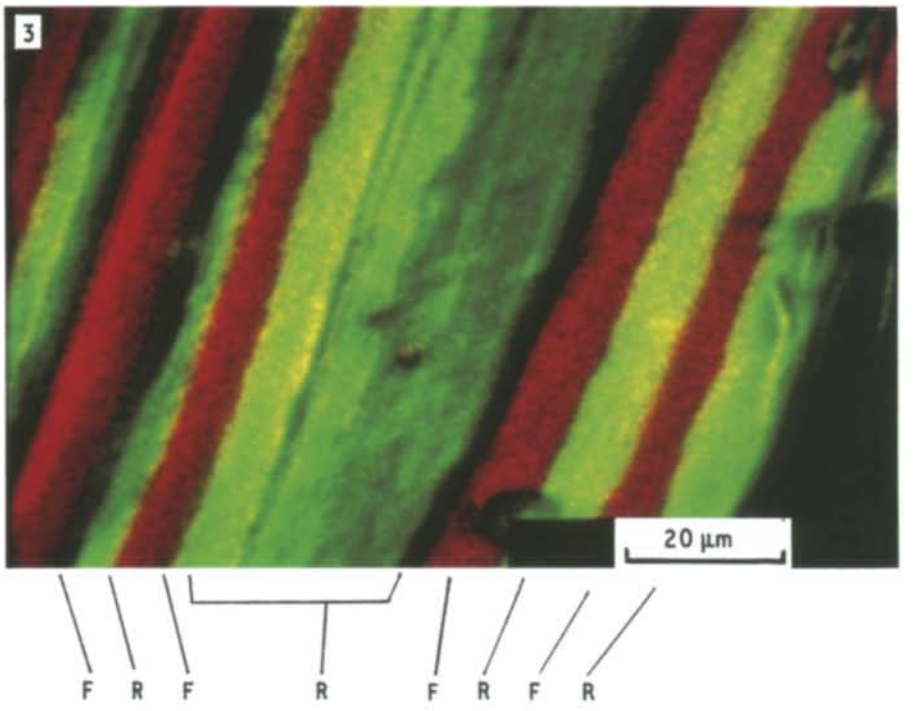
3. Scanning SIMS analysis

Analyses were conducted at the Surface Analysis Service of the Chemistry Department, University of Manchester Institute of Science and Technology, using a VG SIMS LAB instrument fitted with a MIG 100 Ga liquid metal ion gun, MM12–12 (0–1200 Dalton) quadrupole Mass Spectrometer and a charge compensating LEG 31 electron flood gun. A VG 5100 Framestore data system interfaced with the spectrometer permits acquisition, storage and processing of spectra and images. In scanning mode a lateral resolution of 0.2 μm was attained, and up to four secondary ions detected in a given acquisition sequence. Multiple overlaying of selected ion images enables positional comparisons to be made between features with contrasting surface chemistries.

A primary Ga^+ ion beam at 10 keV energy, 0.1 nA current was used together with an electron flood of 500 eV, 5 nA cm^{-2}, for charge compensation. Imaging of secondary electrons permits microscopic selection of suitable analysis areas, and on fracture surfaces, two such areas were studies, as a test for reproducibility, on a given sample.

4. Results and discussion

Figs 2a and 2b show Scanning SIMS images obtained from the same area ($\sim 100\,\mu m^2$) of a fracture surface of a composite made using untreated carbon fibre. Fig. 2a was formed using negative ions of mass 26 and it is seen that carbon fibres in the fracture surface emit ions of this mass number from the intervening areas of resin. Fig. 2b, on the other hand, shows that negative ions of mass 35 are emitted almost exclusively from areas of the fracture surface consisting of resin. This point is reinforced in Fig. 3 which is a computer generated overlay, in colour, of the information used to form Figs 2a and 2b. The local signal intensities for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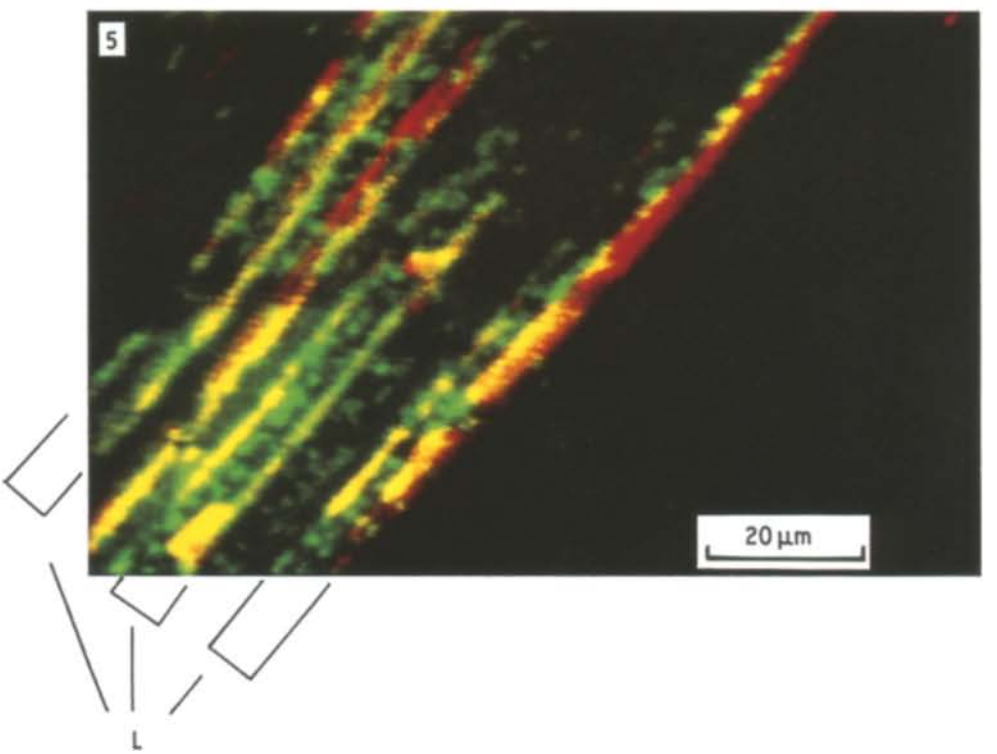
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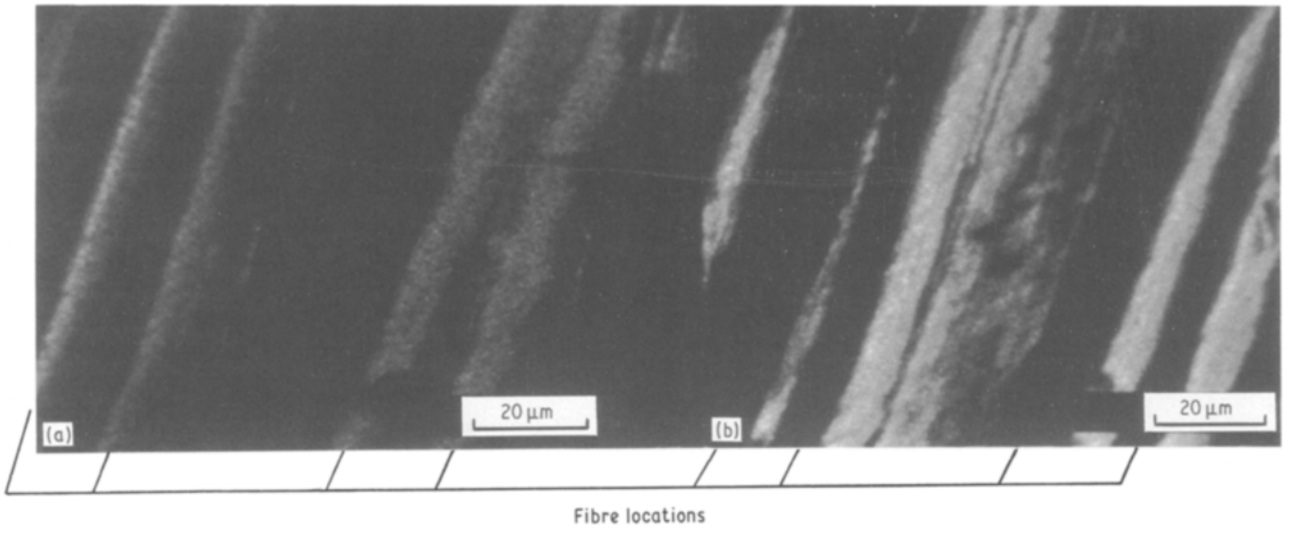

Figure 2 Scanning SIMS images formed using negative ions, of (a) mass 26 and (b) mass 35, from a fracture surface of a composite containing untreated fibres.

the respective ions are converted into scales of black to red (mass 26) and black to green (mass 35). It is immediately apparent that there are well defined red/green/red bands with little if any coincidence between the two ion signals which would be indicated as a yellow colour.

Thus the use of negative ions of mass 26 and mass 35 to form images enables a complete differentiation to be made between regions of the fracture surface consisting of 'bare' carbon fibre and those consisting or resin.

It seems likely that the negative ions of mass 26 emitted only by the fibre correspond to CN^-; the nitrogen arising due to the incomplete pyrolysis of the polyacrylonitrile used to make the fibre. The ions of mass 35 emitted only by the resin corresponds to Cl^-, present in the resin as a contaminant due to the use of epichlorhydrin in its synthesis (see Fig. 4).

Consider now the micromechanics of the fracture process in the light of the above Scanning SIMS results and the composite shear strengths shown as a function of fibre surface treatment shown in Fig. 1. The composite incorporating untreated fibre has a relatively low shear strength of 79 MPa while Scanning SIMS indicates that the crack leading to failure was either at the fibre–resin interface or within the surface regions of the fibre. Thus the cohesive strength of the fibre resin interface or the fibre surface region is less than that of the resin.

Scanning SIMS examination of fracture surfaces of

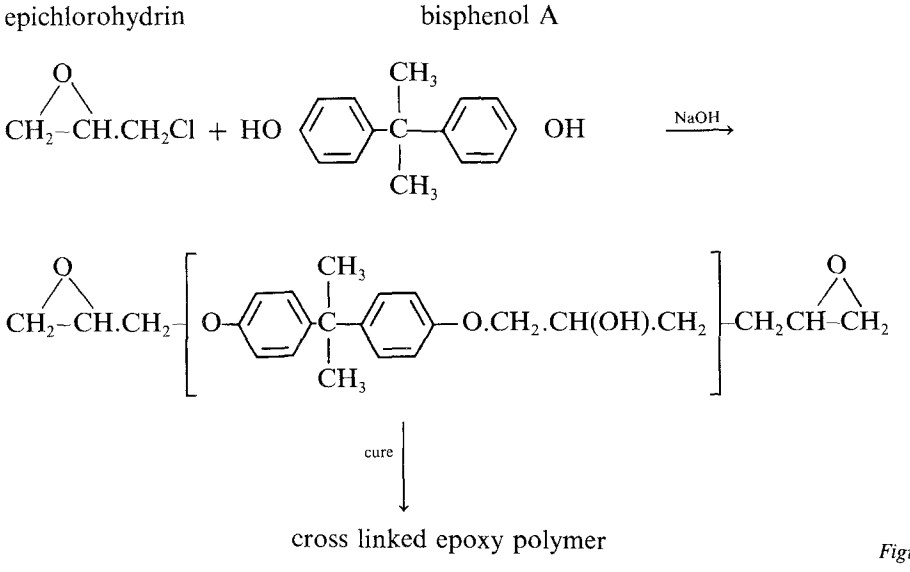

Figure 4 Molecular structure of DGEBA.

Colour plates

Figure 3 Computer generated red/green overlay of Figs 2a and b; Fibre (F), Resin (R).

Figure 5 Computer generated overlay of images formed using ion masses 26 and 35, from a fracture surface of a composite containing fibre with a high level of surface treatment. L shows the location of fibres with resin overlayers.

composities made with an intermediate level of surface treatment (23 C m^{-2}) gave results very similar to those obtained with untreated fibre although the ILSS had increased slightly to 82 MPa.

The fracture surface of a composite made from fibres with a high level of surface treatment (230 C m^{-2}; ILSS of 93 MPa) appeared quite different, however. Fig. 5 shows the computer generated overlay of the signals correspond to mass numbers 26 and 35. In places there is a considerable degree of coincidence between the two signals, shown by yellow, which indicates the presence of thin, ~ nm thick, layers of resin overlaying the fibre although there are still some portions of the fibre which are 'clean'.

Thus it appears that at this level of surface treatment the cohesive strength of the fibre and the fibre resin interface is greater than that of the resin and that failure propagates mainly through the matrix.

These results provide an explanation for the shape of the ILSS against fibre surface treatment curve, Fig. 1. Initially, as surface treatment is increased, ILSS increases and failure continues to occur at the fibre–resin interface or within the surface region of the fibre. Above a certain level of surface treatment, however, the interfacial bond strength exceeds the cohesive strength of the resin and failure occurs mainly within the latter. Hence, further increases in surface treatment do not increase the ILSS. This accounts for the plateau nature of the curve in Fig. 1 at higher levels of surface treatment.

It is, however, interesting to note (Fig. 6) that the tensile strength of unidirectional composites in the form of impregnated tows is not significantly affected over the range of fibre surface treatment studied; the apparent fibre strength remaining at about 3.3 GPa.

5. Conclusions

Scanning SIMS is clearly demonstrated to be a powerful technique for the characterization of fibre composite fracture surfaces. The 0.2 μm resolution for chemical mapping enables a detailed analysis of the ~ 7 μm fibre surface to be undertaken. In this resin–fibre combination the negative ions of mass 35 and 26, Cl^- and CN^- respectively, have been found to be appropriate markers to identify the individual components in the fracture surface, and in particular, demonstrating the presence of resin overlayers, on some samples. In experiments to be published in future, using a glycidyl amine resin system (MY 720) it was not possible to use a Cl^- ion to locate resinous areas in the fracture. This shows the specificity which

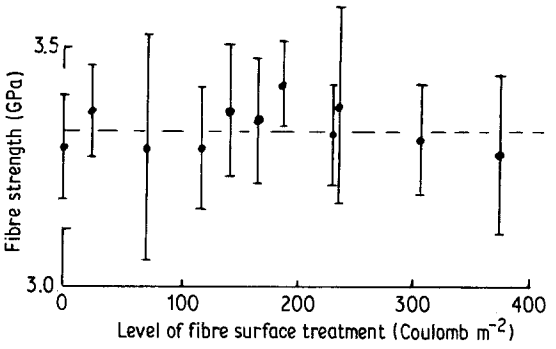

Figure 6 Fibre strength determined from tow tests, against level of fibre surface treatment.

the SIMS technique affords and its potential for furthering understanding in this important area.

The microstructural mechanisms of composite failure are revealed and can be reconciled with the relative interface and matrix strengths. It is confirmed that oxidative treatment of fibres improves adhesion at the interface until at high treatment levels it becomes dominant over the limiting, constant resin strength. This is reflected in a corresponding trend in composite shear strength, which reaches a maximum of 93 MPa.

Definite evidence of relatively thin, retained matrix overlayers on the highly oxidized fibres emerges, whilst in contrast in the absence of surface treatment clean fibres are present. Such a distinct contrast is only unambiguously demonstrated using the Scanning SIMS technique, since conventional electron microscopy cannot resolve layers of features which are $\leqslant$ 10 nm (0.01 μm) in thickness.

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References

1. J. KARGER-KOCSIS and K. FRIEDRICH, *J. Mater. Sci.* **22** (1987) 947.
2. D. BRIGGS, *Surf. Interface Anal.*, **9** (1986) 391.
3. J. T. PAUL, Jr., "Electrolytic Treatment of Graphite Fibres", UK Patent Spec. 1 433 712, London (1976).
4. P. T. CURTISS, "CRAG Test Methods for the Measurement of the Engineering Properties of Fibre Reinforced Plastics" (Royal Aircraft Establishment, Technical Report 85099, London (1985).

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