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# The structure of the interface in carbon fibre composites by scanning Auger microscopy

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Scanning Auger microscopy (SAM) has been used to study the fibre/matrix interface of composite materials. This novel application of Auger spectroscopy enables further understanding of the mechanism of failure in composites when applied to carbon fibre-reinforced epoxy material. Initial work was carried out on carbon fibres prior to their incorporation into the resin matrix. Auger spectroscopy can be used to detect the presence of thin polymeric layers on the carbon fibres if a suitable, matrix-specific element is chosen to form the scanning Auger image. Two composite materials have been investigated. They differ from each other by the fracture mechanisms. In the case of unidirectional continuous fibre composites, a high volume fraction of conducting carbon fibres makes Auger analysis possible although the failure surface is predominantly polymer residues. For short-fibre composites the technique is more difficult considering the low volume fraction of fibres, but Auger spectroscopy enables the identification of microfailure mechanism and of the effect of fibre surface treatment on the failure mode.

## 1. Introduction

The knowledge of the failure mechanism helps to improve the quality of composite materials. Understanding of the macroscopic failure can be obtained from microscopic information and scanning electron microscopy (SEM) has been widely used in the fractography of composites. But this technique has limitations; it is difficult to detect a very thin polymeric layer over the surface of carbon fibres in composites. More recently, scanning secondary ion mass spectroscopy (SIMS) has been used to characterize the failure surfaces [1] but at high spatial resolution this is still an essentially destructive technique.

Scanning Auger microscopy (SAM) is suitable for studying the fracture surface of composite materials as it provides an image at high spatial resolution ($\simeq 0.5\,\mu$m) together with information concerning the spatial distribution of the elements by way of chemical maps. SAM is generally not suitable for analysing non-conducting materials such as polymers, but if the layer of polymer is thin enough, the carbon fibres of composites materials provide a conducting environment. Recent work from this laboratory has also indicated that Auger spectra can be obtained from the interfacial region of polymer-coated metals if suitable preparation methods are employed [2]. To obtain such data, experimental conditions within the microscope must be carefully optimized. In addition, this surface analysis technique is not destructive.

In this paper, we present the results obtained from carbon fibres and carbon fibre composites by SAM.

## 2. Materials

### 2.1. Carbon fibres

The carbon fibres (Torayca T300) are manufactured by Toray. A size is present over the surface of fibres. The fibre diameter is about 8 $\mu$m and the thickness of the size is between 0.1 and 0.2 $\mu$m. The fibre size consists of an epoxy polymer.

### 2.2. Epoxy matrix 828

The polymer is composed of an epoxy-base resin DGEBA (Shell Epon 828), cured with 80 parts per hundred of resin (p.h.r.) of nadic methyl anhydride (NMA) and 0.5 p.h.r. of benzyl dimethylamine (BDMA) accelerator.

### 2.3. Composite materials

Two types of composite material have been studied: short-fibre composites (SFC) and continuous fibre composites (CFC). The short-fibre composites are manufactured from T300 carbon fibres; the length of the fibres is 5 mm. The matrix is the epoxy matrix 828.

The curing cycle used for the SFC is 80° C for 2 h followed by 16 h at 125° C and a post-cure at 150° C for 2 h.

The continuous fibre composites consist of undirectional continuous T300 carbon fibres and an epoxy matrix (CIBA BSL914). The matrix is a mixture of an

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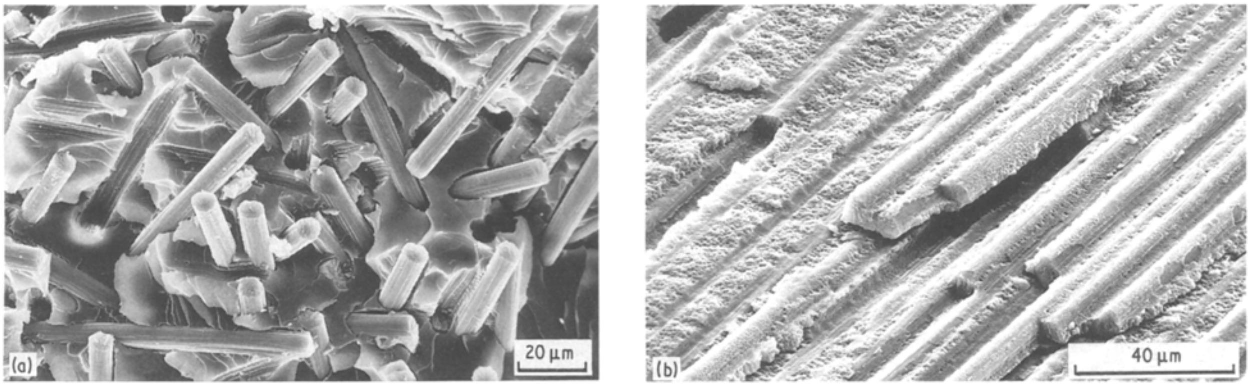


*Figure 1* Scanning electron micrographs of fracture surfaces of (a) short-fibre composite, (b) continuous fibre composite.

epoxy resin (TGMDA and TGPAP) with diacyanodiamide (DDA) as hardener and polyether sulphone (PES) as flexibilizer.

The cure cycle of the laminates is $1\frac{1}{2}$ h at 155° C then 1 h at 175° C and 4 h at 190° C for the post cure.

These two types of composite were chosen for their different fibre volume fraction (SFC: 30%, CFC: 60%). Their failure mechanism is also different. The fracture surface for SFC (T300/828) consists of fibre pull-out and matrix (Fig. 1a), the fracture surface of CFC (T300/914) is of aligned fibres with matrix resin overlayer if the crack occurs within the matrix (Fig. 1b), or apparently devoid of matrix is the crack occurs at the fibre/matrix interface.

## 3. Experimental data

Two surface analysis techniques were used: Auger spectroscopy and X-ray photoelectron spectroscopy (XPS).

The Auger analyses were obtained with VG Scientific MA500 scanning Auger microscope, interfaced to a link AN10000 data system which permits acquisition, storage and processing of spectra and images. Imaging of secondary electrons enables microscopic selection to suitable analysis area. Several such areas were studied as a test of reproducibility. A primary electron beam at 10 keV and 15 nA specimen current was used for carbon fibres, but, in order to limit charging effects, lower energy and current were used for composites (3 keV, 2 to 4 nA).

Spectra were obtained by point analysis prior to obtaining complete chemical maps of the area of interest. We used high magnifications, so the scanned area is about 0.04 $\text{mm}^2$ for fibres and SFC and 0.25 $\text{mm}^2$ for CFC. Extended acquisition times were employed to collect a series of maps. The spectra recorded were 1700 eV survey spectra (Fig. 3a) and regions defined according to the elements detected in the XPS analysis (Figs 3b and c).

The spectra in XPS were obtained using a VG Scientific ESCALAB MkII system with Al$K\alpha$ radiation. The analyser pass energy was set at 50 eV. The spectrometer was interfaced to a VGS-500S data system based on a DEC PDP 11/73 computer. Each specimen was analysed by a combination of 1100 eV survey spectrum and 20 eV high-resolution scans for all the elements detected. Quantification was achieved using the manufacturer's standard software.

### 3.1. Sample preparation in Auger spectroscopy

In order to reduce the charging effect and to achieve a good contact with the holder, the composite specimens were covered with conducting silver paint except in the exposed zone. The fracture surfaces were obtained after a tensile loading for SFC and after bending loading for CFC. The carbon fibre analyses were acquired by clamping sized and unsized fibres in a standard specimen holder.

## 4. Results

### 4.1. Carbon fibres

In order to assess the utility of Auger spectroscopy in detecting thin polymeric layers on carbon fibres, both sized and unsized fibres were analysed. To obtain

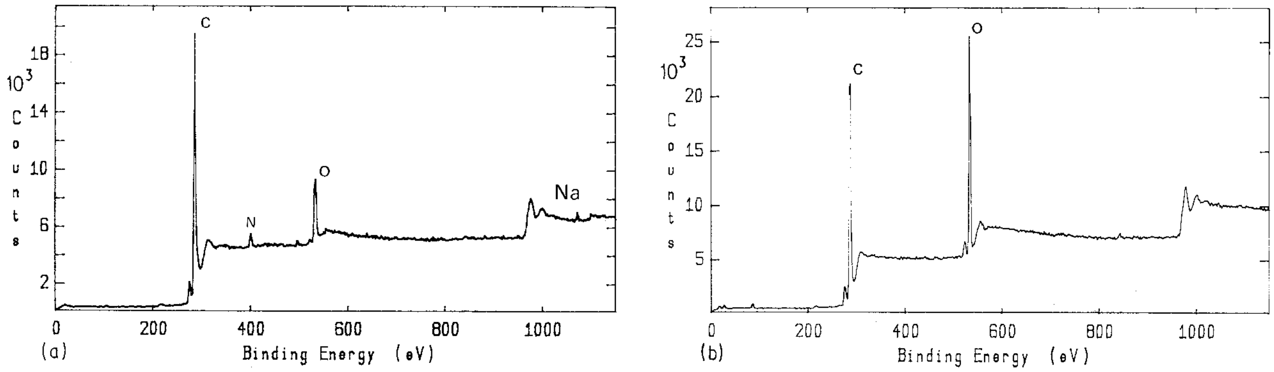


*Figure 2* (a) Unsized and (b) sized T300 carbon fibres.

TABLE I XPS analysis, elemental composition of carbon fibres

| Carbon fibres T300 | C (%) | O (%) | N (%) | Si (%) | S (%) | Na (%) |
|---|---|---|---|---|---|---|
| Unsized | 81.5 | 12.7 | 5.3 | – | – | 0.8 |
| Sized | 79.2 | 20.0 | 0.8 | – | – | – |

unsized fibres, the size was removed by chemical dissolution.

The elemental compositions of carbon fibres were obtained by XPS: the results are presented in Table I. The main difference between sized and unsized fibres is the quantity of nitrogen (5% in unsized fibres, 0.8% in sized fibres). The XPS spectra are shown in Fig. 2. Nitrogen could be a residue of the PAN precursor (carbonization phase), or from the surface treatment at the end of the manufacturing process. Sodium is thought to be a residue of sodium thiosulphate solution used to dissolve the precursor prior to spinning.

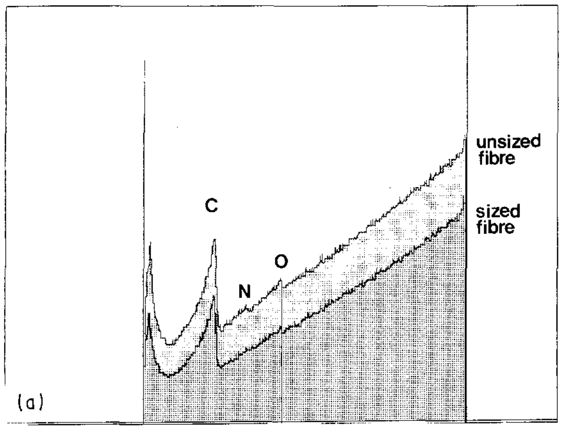
The Auger spectra are shown in Fig. 3a. The peaks are clearly identifiable. There are slight kinetic energy shifts identical for both fibres which are probably caused by charging effects.

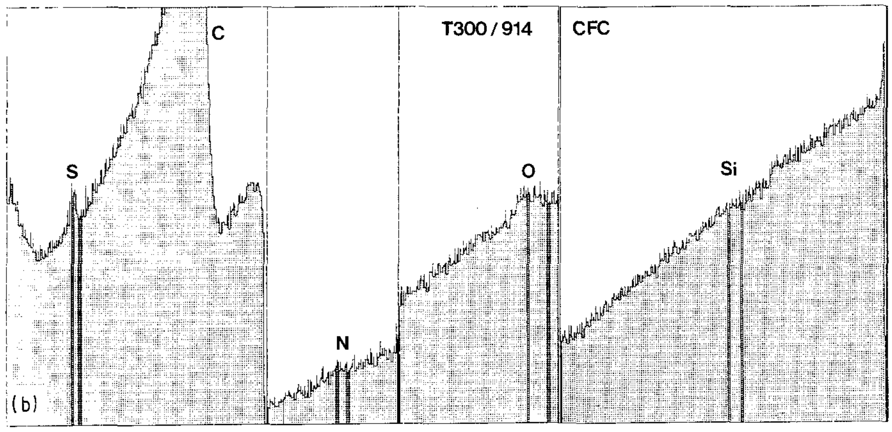
The carbon peak intensity (peak area) is more important for the unsized carbon fibre – the oxygen peak is nearly the same for both fibres. Therefore, quantification from Auger spectra does not give the same results as XPS. According to a recent work, these experimental conditions used in Auger spectroscopy are suitable for qualitative analysis, but they are not optimized to quantify the data.

The quantity of nitrogen (0.8%) on sized fibres is too low to be detected by Auger spectroscopy. The nitrogen is therefore characteristic of the unsized carbon fibres and, more generally, of the carbon fibre surface without polymer. So from the detection of the element nitrogen at the fibre/polymer interface by Auger spectroscopy, the absence of a thin polymeric layer on the fibres can be identified, i.e. failure has occurred in a truly interfacial manner.

Each Auger map (Fig. 4a) was formed from the peak (P) and the background (B) of each element signal. The representation P–B/B was used for eliminating topography effects and is discussed further below.

The scanning electron image of the analysed area (Fig. 4a, SEI, $G = 5000$) corresponds to a part of a single fibre only. The different maps present non-





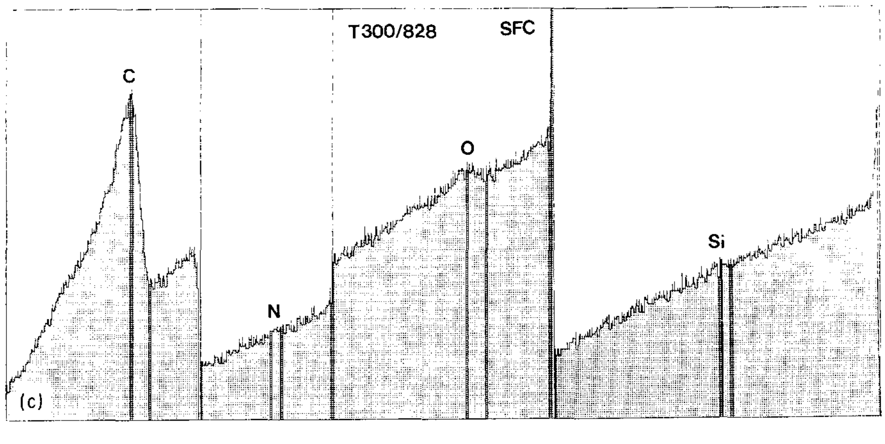


*Figure 3* Auger spectra of (a) T300 carbon fibres, (b) CFC (T300/914), (c) SFC (T300/828).

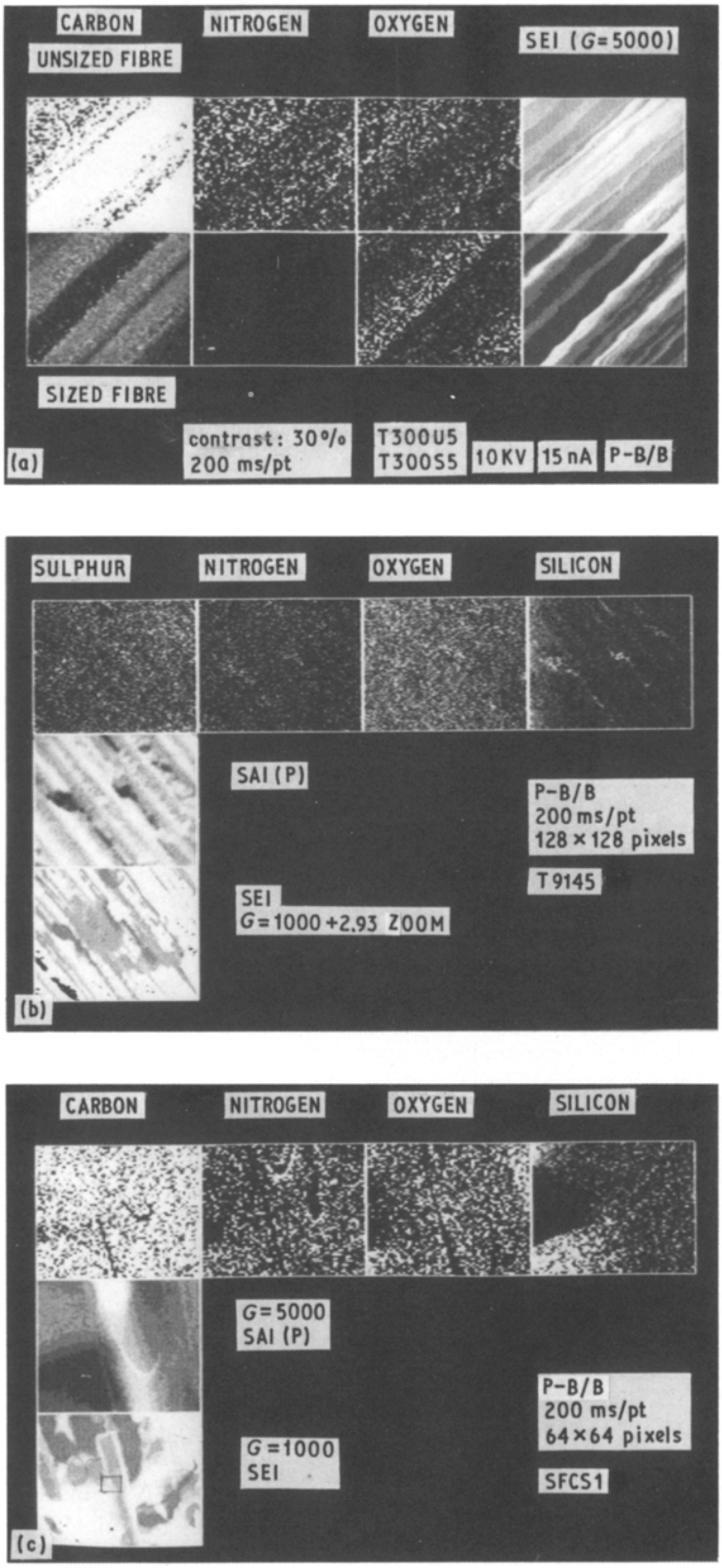


*Figure 4* Auger images of (a) T300 carbon fibres, (b) CFC (T300/914), (c) SFC (T300/828).

uniformity in the signal intensity despite the P–B/B representation. There are zones where carbon is weaker (the darkest zones) which correspond to the areas where oxygen and nitrogen are stronger. Thus, this non-uniformity seems to be caused by a real difference in chemical composition at the fibre surface.

The intensity of the carbon map of the unsized fibre is stronger than that of the sized fibre. This is not the case for the oxygen maps–these results are in relation to the information given by the Auger spectra (Fig. 3a).

The absence of nitrogen on the surface of the sized fibres is confirmed by the nitrogen image.

## 4.2. Continuous fibre composites (T300/914)

Carbon and oxygen are the main elements of the fracture surface (Table II). There are three other elements which are nitrogen, sulphur and silicon but the quantity is less than 5%.

Carbon, oxygen and nitrogen may come from the T300 fibres or the matrix 914, but sulphur is characteristic of the matrix (PES phase). Silicon originates from the matrix but its origin is not well established. It is probably derived from the flow-control agent added to the polymer during the manufacturing process.

Auger spectra (Fig. 3b) clearly exhibit carbon, oxygen and sulphur peaks. The peak position in kinetic energy for carbon and oxygen is the same as that for carbon fibres. Therfore, the shifts seem to be independent of the primary electron beam energy.

The sulphur peak, which appears at 151 eV, has shifted 6 eV lower. The presence of nitrogen is not obvious from the spectrum. However, the concentration of nitrogen and sulphur determined by XPS (Table II) is similar ($\simeq 2\%$). The difference in intensity in these two peaks is perhaps in relation with their cross-section. This cross-section is higher for sulphur than for nitrogen. Silicon is lacking on the spectrum: a result, probably, of its very low cross-section.

Auger maps were formed from a fracture surface which was composed of a part of about ten aligned carbon fibres. These fibres are visible on the scanning Auger image (SAI) in Fig. 4b, formed from the sulphur peak intensity. This image, and indeed images obtained at any energy in the series of peak and background (P and B) channels used, show mainly topographic contrast and are similar to each other and to the true SEM of the surface. In fact they often give better images of the surface topography than the SEI (Fig. 4b) because of the effect of charging on low-energy electrons.

Comparison between the peak image and the image formed by processing the data in the form P–B/B, for sulphur (Fig. 4b), shows that the representation P–B/B eliminates topography effects of the fracture surface. The sulphur Auger image (Fig. 4b) indicates a uniform presence of sulphur on the fracture surface. It means that there is retained matrix on this fracture surface. The SEM image (Fig. 1b) confirms this result. The microfailure occurs within the matrix leaving polymeric residues on the carbon fibre surface indicating that the fibre/matrix interface is strong. This work demonstrates convincingly that Auger maps of a fracture surface can be obtained although the fracture surface consists of polymer residues. The high quantity of conducting carbon fibres beneath the polymer makes the analysis possible.

The nitrogen map (Fig. 4b) indicates the uniform presence of nitrogen on the fracture surface. Although the intensity of the nitrogen is still weaker than that of sulphur, we can detect nitrogen with scanned analysis, unlike the point analysis. This aspect is discussed further below.

Silicon (Fig. 4b) seems to be present on the fracture surface but not uniformly: it appears when the sulphur signal is absent. In order to clarify this aspect, the silicon and sulphur images were converted into different colours and superimposed. This confirmed that silicon appears mainly when sulphur is lacking. Perhaps the high cross-section of sulphur presents an overlay image biased in favour of this element.

The brightest map is that of oxygen (Fig. 4b). We expected such an intensity for oxygen maps from the spectrum.

The results demonstrate the possibilities of SAM applied to composite materials. CFC is a reasonably easy case, considering the high volume fraction of conducting carbon fibres.

### 4.3. Short fibre composites (T300/828)

SAM was used for identifying the failure mechanism in SFC and for studying the effect of fibre finish on failure. Two types of SFC composite were therefore analysed: unsized short-fibre composite and sized short-fibre composite.

The fracture surface composition was determined by XPS (Table II). The main components are carbon and oxygen. Silicon is also present (3%). An XPS analysis of the matrix 828 (Table II) shows the matrix contains about 12% silicon. Therefore, silicon in SFC comes from the matrix 828. Nitrogen, which is the marker of carbon fibres, is not present.

Auger analyses were made from the pull-out fibre surfaces. The carbon and oxygen peaks are clearly defined in the Auger spectrum (Fig. 3c). Their energy positions are the same as for the CFC. The presence of nitrogen and silicon is not so evident.

Four Auger maps, one scanning electron image (SEI) and the scanning Auger image (SAI) for the carbon peak are shown in Fig. 4c. The Auger maps were obtained from the surface visible on SEI at high magnification ($G = 5000$). Carbon, oxygen and nitrogen maps are approximately uniform in intensity, but the carbon map is the most intense image. The oxygen image is just slightly more intense than the nitrogen one. The presence of nitrogen is obvious with scanned analysis.

There is a non-uniformity on the silicon map. The bright bottom left-hand side of the image is matrix 828 residue which contains a lot of silicon (Table II). Silicon signals are also obtained on the fibre surface, although they are less strong than in the matrix.

The results obtained for silicon and nitrogen from the spectra differ from those of the mapping for SFC and CFC. We tend to conclude that when an element with a low cross-section is present in low concentrations, it needs to have more carefully optimized conditions for point analysis than for mapping; the longer time on a single spot is certainly more destructive and it is necessary to find a compromise between the three parameters: the current intensity, the analysed area and the acquisition time.

Nitrogen and silicon, which are respectively,

TABLE II XPS analysis, elemental composition of different samples

| | C (%) | O (%) | N (%) | Si (%) | S (%) | Na (%) |
|---|---|---|---|---|---|---|
| Matrix 828 | 70.6 | 17.4 | – | 11.9 | – | – |
| S.F. Composite T300/828 | 83.5 | 13.4 | – | 3.0 | – | – |
| C.F. Composite T300/914 | 76.9 | 15.1 | 2.3 | 3.6 | 2.1 | – |

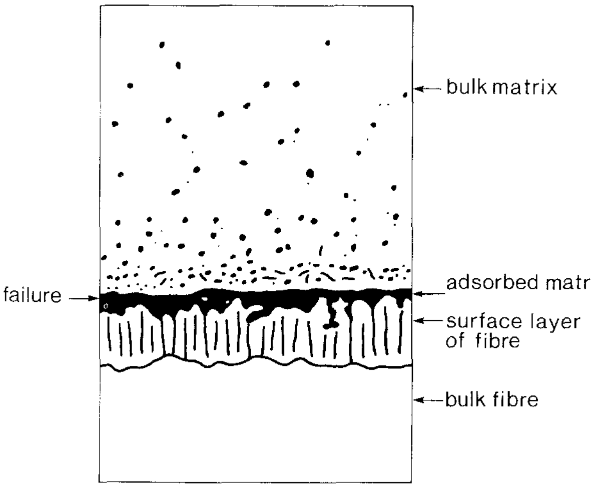


*Figure 5* Schematic illustration of the interface in short fibre composites.

characteristic of the carbon fibres and the matrix, therefore, both appear in maps of pull-out fibre of SFC. Thus there is a layer of matrix on the pull-out region of the fibres, but this layer is thin enough also to allow the recording of a nitrogen signal characteristic of carbon fibres.

The thickness of this layer was estimated from the depth, $d$, of the emitted electrons which would reduce the nitrogen signal to $\simeq 40\%$ of that on the clean fibre surface

$$d = \lambda_m (E) \cos \theta$$

where $\lambda_m (E)$ is the inelastic mean free path for electrons in an organic matrix [3] and $\theta$ is the angle of emission to the surface normal. $\lambda_m (E)$ is $\simeq 3.0$ nm or 5 atomic layers. So the intensity ratio of nitrogen and silicon indicates that the failure takes place within the matrix, leaving an overlayer of 0.6 to 2 nm adhering to the fibres.

Recently, a similar conclusion was established from scanning SIMS analysis of an epoxy–continuous carbon fibre composites [1]. Our failure mechanism in SFC is represented in Fig. 5: the few monolayers of atmospheric gases adsorbed on the carbon fibre surface are removed by heating during the curing cycle. Then, molecules from the matrix are adsorbed. This process can be physical and/or chemical but presumably bonding to the surface oxygen groups on the fibre will occur. The failure occurs at the surface of carbon fibres but in the adsorbed matrix. The molecule of monomer is approximately 1 nm long and one possibility is that failure occurs between this first layer and the rest of the polymer.

The Auger maps obtained from sized and unsized SFC are similar. The fibre size does not modify the fracture. We explain this result as follows (Fig. 6): the migration of the hardener of the matrix through fibre size can occur before gelation during the curing cycle. This hardener then reacts with the epoxy functionalities of the size. Thus, the composition of the size becomes close to that of the matrix bulk. Previously, in another context, this mechanism of migration of the hardener was given as a hypothesis by other authors [4].

For SFC, Auger spectroscopy is more difficult, considering the lower fibre volume fraction. However, the experience obtained in this study indicates that the success of Auger imaging with SFC is critically dependent on the specimen preparation. If the sample is longer than the specimen holder or poor electrical contact is made between the two, problems may be encountered during analysis.

## 5. Conclusions

This application of SAM to composite materials enables a further understanding of the mechanisms of failure that occur. The difficulty of the analysis is related more to the inadequacies of the sample preparation than those of Auger spectroscopy–SAM is a non-destructive technique to evaluate fracture surface in composites. Extended acquisition times can be employed to collect a series of maps without damage. The high spatial resolution of this technique enables a detailed analysis of the fibre surface.

The components of fracture surfaces have been identified by an appropriate choice of elemental markers for the fibre and the matrix. For continuous fibre composites, chemical Auger maps of fracture surface were obtained although the fracture surface is mainly polymer residues. A high volume fraction of conducting carbon fibres makes Auger analysis possible.

For short-fibre composite the mechanism of failure can be described by the analysis of pull-out fibres. The failure takes place at the carbon fibre surface leaving a very thin layer (0.6 to 2 nm) of absorbed matrix on pull-out fibres. The effect of fibre size on failure was studied; the fracture mechanism is not modified by the presence of the size. We propose that, as the hardener of the matrix migrates to the size, the composition of the size approaches that of the bulk matrix.

In conclusion we have found SAM to be a very useful analytical method for composite materials. In future work we intend to study the nature of bonds between the carbon fibres and the matrix. Therefore,

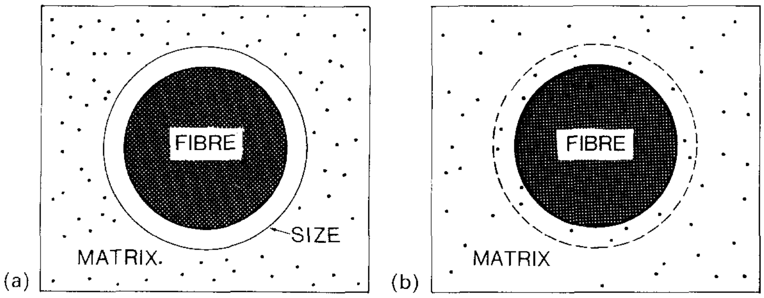


*Figure 6* Schematic illustration of the migration of hardener through the size: (a) initially, and (b) following migration.

a labelling method is now being used to produce chemical reactions with specific groups on carbon fibres in order to block them [5]. This will yield information on the type of bonds across the fibre/matrix interface.

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