JOURNAL OF MATERIALS SCIENCE **36** (2001) 2323–2327

A small area XPS study of the fracture surface of a thermoplastic-modified CFRP

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Small area XPS at a spatial resolution of 30 μm has been used to study the heterogeneity of the fracture surface of a carbon fibre/epoxy composite with thermoplastic PEEK particles incorporated at the interlaminar boundary. Strong evidence was found for a chemical interaction between the PEEK particles and the matrix, in particular the curing agent. Careful charge compensation was required, particularly for the non-conducting PEEK particles alone which had been mounted on insulating adhesive tape, in order to produce a high quality spectrum. It was also observed that, for the fracture surfaces, the application of low energy electrons was successful in eliminating the differential charging observed during the simultaneous analysis of matrix and particle (insulating), or matrix and fibre (conducting). © *2001 Kluwer Academic Publishers*

1. Introduction

CFRP composites are commonly used as high performance materials owing to their impressive strength-to-weight ratio. However, these materials delaminate rather easily, particularly after impact with other objects. Therefore, in order to improve the toughness of these materials, thermoplastic layers [1–3] or particles [4] have previously been introduced at the interply region, and also particles have been interspersed within the resin phase of such composites [5]. Although it is still unclear exactly how the stress is transferred from the resin to the modifying polymer, it has been suggested that the greater ability of thermoplastic particles such as poly(ether ether ketone) or nylon to deform in comparison with the brittle epoxy matrix accounts for a measured improvement in the fracture energy, G_{IC} and/or G_{IIC}, and stress intensity factor, K_{IC} and/or K_{IIC}, required to propagate a crack through the composite.

XPS has been previously been applied to the chemical characterisation of fibre-matrix interfaces within carbon fibre polymer composites (CFRP) [6, 7], and also to the study of resin molecules on carbon fibre surfaces [8]. However, this previous literature tended to focus on how the oxygen content of the fibre surface influences the interlaminar shear strength of the fabricated composite, and does not explore the elemental composition of the fracture surface of the failed composite itself. Undoubtedly, this has been because one of the major limitations of the analysis of heterogeneous surfaces by XPS is the spot size of the impinging X-ray beam, generally of the order of 5–10 mm^2, that meant analysis of individual surface features was not possible. Small area XPS, either achieved by the use microfocused X-ray monochromator or electron-optical selection of the analysis area, has been possible for over a decade but generally restricted to spot sizes of the order of 100 μm. Recently, however, improvements in instrument design has led to the availability of small spot XPS machines which also possess good counting statistices, allowing the possibility of small spot polymer analysis. In this paper, we demonstrate the ability of one such instrument to provide good quality spectra, including chemical state information, using a 30 μm spot size on a heterogeneous carbon fibre/epoxy composite surface featuring conducting and insulating regions. These spectra provide an important insight into the chemistry of the interface between thermoplastic toughening particles and the base epoxy matrix, an issue which is of great technological concern with regard to improving mechanical properties of such composites and widening their applications as engineering materials.

2. Experimental

2.1. Materials and composite fabrication

The carbon fibre reinforced polymer (CFRP) composite was fabricated using Ciba-Geigy Fiberdux 924 prepreg, a standard system widely used in aerospace applications. Twenty-four plies of CFRP prepreg were laid up in a wholly unidirectional orientation (i.e $[0]_{24}$) and cured for 2 hours at a temperature of 177°C and an external pressure of 4.5×10^5 Pa in a pressclave, resulting in a composite laminate approximately 3 mm in thickness. The interface between the two central plies (i.e. between layers 12 and 13) was modified by the application of poly(ether ether ketone) (PEEK, commercially known as Vitrex) powder, supplied by ICI plc. The particles were approximately 50–100 μm in diameter, and were sprinkled over the central ply of the composite prior to consolidation. The particles were dispersed as uniformly as possible and excess powder was removed by brushing the surface of the modified ply manually. The resultant particle loading was assessed by the use of a 5 cm by 5 cm witness panel of pre-preg adjacent to the pre-preg used for composite fabrication. The witness panel was weighed before and after the application of the particulate material to assess the loading as a function of mass per unit area. A value of 2 g m^{-2} of PEEK powder per unit area of pre-preg was determined in this manner. A Melinex release film of thickness 36 μm was inserted between the central plies prior to the curing regime, to form a pre-crack from which fracture of the composite in the opening mode (Mode I) at the modified layer interface could be propagated. A double cantilever beam geometry was used and mechanical testing carried out in the established manner [9] in order to determine the interlaminar toughness of the composite (i.e. its resistance to crack propagation). Small specimenns (approximately 1 cm^2) were cut from the fracture surfaces of the failed test-pieces and clipped to the sample platen of the spectrometer.

2.2. Constituents of the CFRP

The base epoxy resin of Fiberdux 924 is tetraglycidyl diamino diphenylmethane (TGDDM), the chemical structure for which is shown in Fig. 1a. The corresponding structure for the curing agent, diaminodiphenyl sulphone (DDS), is shown in Fig. 1b. It reacts with the resin molecule during the curing regime, to produce a thermosetting matrix, which is reinforced with Toray T300 carbon fibres. The PEEK particles were added to the mid-plane interlaminar region of the composite in order to assess the effect that its presence had upon the interlaminar toughness of the cured composite. The chemical structure of PEEK is shown in Fig. 1c.

2.3. Scanning electron microscopy (SEM)

SEM of the composite fracture surfaces was performed on an Hitachi 3200N variable pressure microscope, with an electron beam energy of 20 keV. The samples were coated with gold using a vacuum sputter coater to avoid sample charging problems.

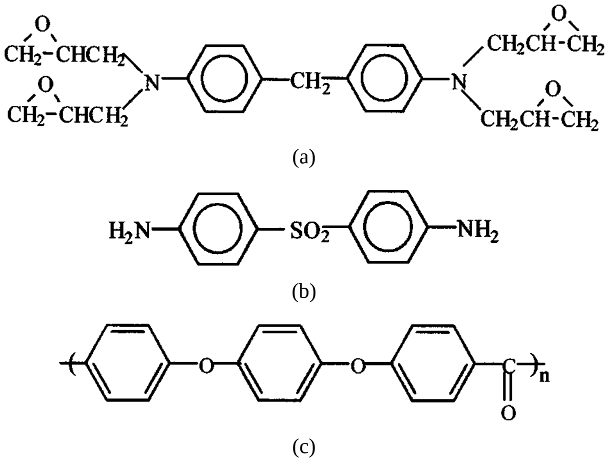

Figure 1 (a) Tetraglycidyl diamino diphenylmethane (TGDDM), (b) diamino diphenyl sulphone (DDS), and (c) poly(ether ether ketone) (PEEK).

2.4. X-ray photoelectron spectroscopy (XPS)

XPS analysis was performed using a Thermo VG Scientific Sigma Probe using a microfocusing monochromatic AlKα X-ray source. The spectrometer is capable of a spatial resolution of less then 15 μm, although in this study, spot sizes of 30 μm were used for the composite fracture surfaces and 50 μm for the as-received PEEK particles. The Sigma Probe utilises a Radian lens which, as a result of a large acceptance angle, allows improved sensitivity and reduces acquisition time, which can be critically important when analysing damage-sensitive polymer specimens such as the as-received PEEK particles investigated in this study. Charge compensation was carried out using a LEG 51 flood gun, using a focused 14 eV electron beam for the larger 50 μm spot size, and a focused electron beam operated at the lowest electron energy mode available for the smaller analysis areas (30 μm). This was to avoid the possibility of electron stimulated ion emission (ESIE), that has been shown to degrade the surface of polymers during analysis [10].

3. Results and discussion

Fig. 2 shows an SEM image of the composite opening mode fracture surface. The PEEK particles can be observed easily, and are approximately 100 μm in diameter. It is also possible to distinguish two regions in the surrounding matrix which have distinct differences in morphology. The controlled crack is propagated parallel to the fibres, and it can be seen that the fracture surface in the crack path of the particles appears smooth and does not show evidence of any fibre morphology. This observation is thought to be related to the magnitude of the particulate material (ca. 100 μm diameter) relative to the thickness of the individual sheet of prepreg which is 125 μm thick. This may prevent efficient consolidation in the immediate area of the particle and lead to the resultant fracture morphology. This is in contrast with other regions in the fracture surface, which appear to be present where there is no particle lying in the crack path, revealing distinct exposed fibre surface features and exhibiting regions where fibres have fractured. At higher magnification (not shown), it appears that a discrete layer of matrix material remains adhered to the fibre surfaces.

Although excellent spatial resolution from the small spot size is available, it is not possible to obtain a unique signal from a single fibre region. This is because the fibre diameter is only 6–7 μm and each fibre is surrounded by resin, or there may be a thin layer of resin on the fibre/particle which is not apparent by optical or electron microscopy. Therefore, the three distinct regions identified by SEM in Fig. 2 are termed fibre-rich, matrix-rich, and particle-rich. The chemical nature of these different regions identified in Fig. 2, was analysed by selecting a 30 μm diameter beam and positioning the sample accordingly. As with any small-area analysis technique, alignment of the beam is vital. Correct beam alignment was achieved by using a phosphor sample to check that the beam position lay in the centre of

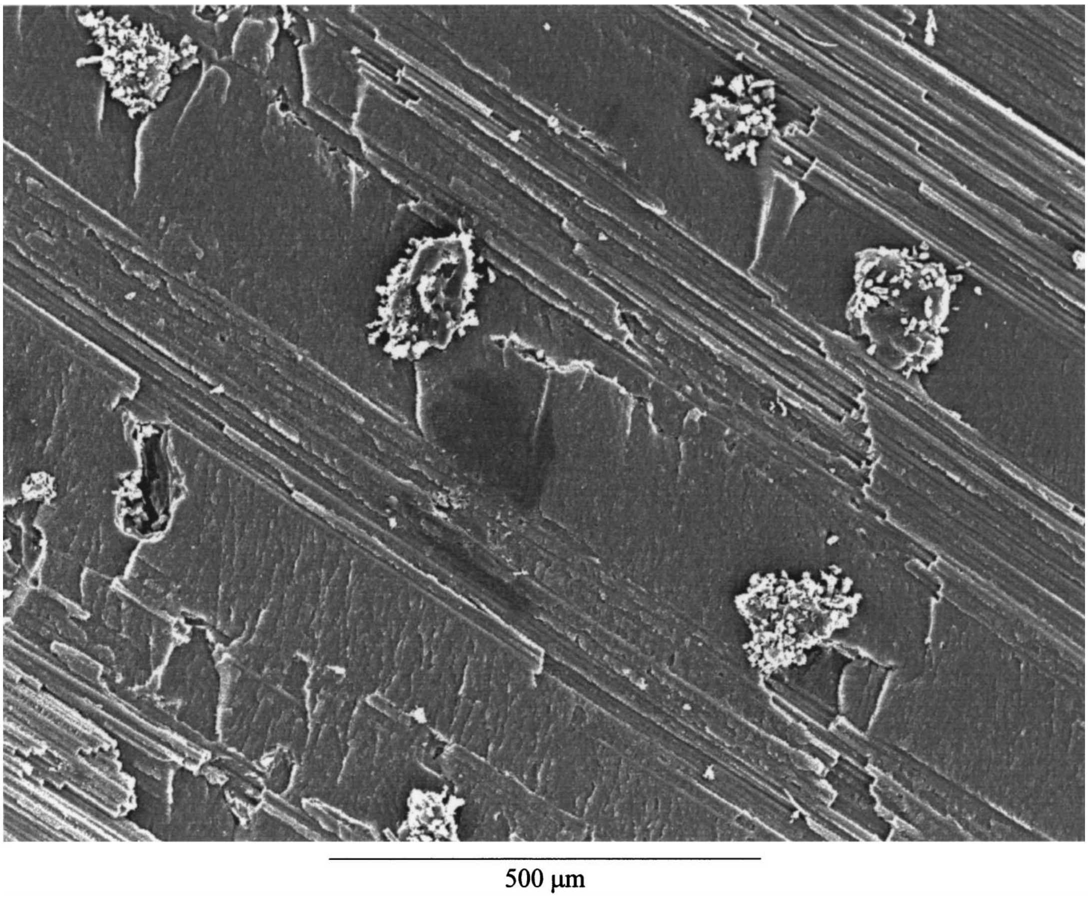

Figure 2 Secondary electron image of the fracture surface of PEEK modified CFRP. The PEEK particles are cleary visible in the micrograph.

the on-screen circular graticule and was also coincident with the probe (a probe light is reflected from the monochromator crystal, highlighting the analysed area, therefore following the X-ray path). 30 μm spot sizes were chosen to ensure that analysis of the composite fracture surface was carried out from each of the distinct regions without contribution from any surrounding phase.

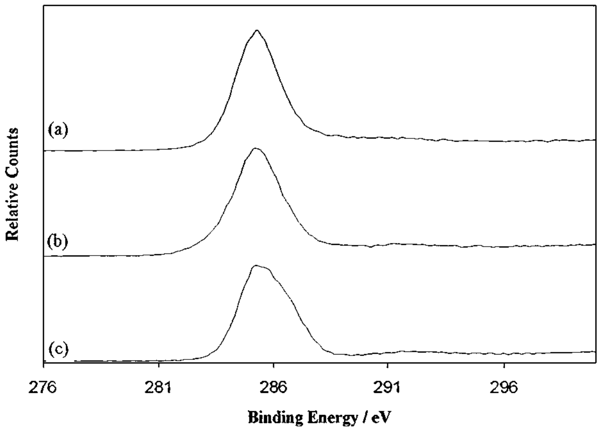

Figure 3 Small area XPS (30 μm) high resolution spectra of the C 1s region from: (a) fibre-rich area, (b) matrix-rich area, and (c) particle-rich area of a composite fracture surface.

Differential charging is a problem that is often encountered in XPS with samples which contain components possessing different electrical properties, as is the case with the fracture surface shown in Fig. 2. Such differential charging may give rise to broadening of the XPS spectrum [11] or the generation of a second spectrum removed from the other by several electron volts. The resultant separation has been used to some effect in electron spectroscopy [12] and imaging XPS [13] studies of carbon fibre composite fracture surfaces, in order to separate the signals from the matrix and the fibres. It does, however, effectively preclude the extraction of chemical information from the photoelectron spectrum as it is not easy to assign components to one phase or the other unambiguously. The solution available with monochromated XPS is the use of effective charge compensation across the field of analysis. The test of such effectiveness is to ensure that the C1s spectrum is observed as a single envelope, a feature observed throughout the present work. The quality of the carbon 1s spectrum obtained from the fracture surfaces is shown in Fig. 3, the consistency of the leading edges confirming effective management of surface charge. The PEEK spectrum of Fig. 3c shows the $\pi \rightarrow \pi^*$ shake-up satellite some 6 eV removed from the main peak to a higher binding energy. This feature is diagnostic of aromaticity within the analysis and is quite consistent with the structure of PEEK as shown in Fig. 1c. The similarity, both in peak shape and position, of Fig. 3a which is predominantly conducting carbon fibres and Fig. 3b which is predominantly insulating matrix material, indicates that the contribution from the component susceptible to electrostatic charging in the analysis area, the matrix, has been dealt with effectively.

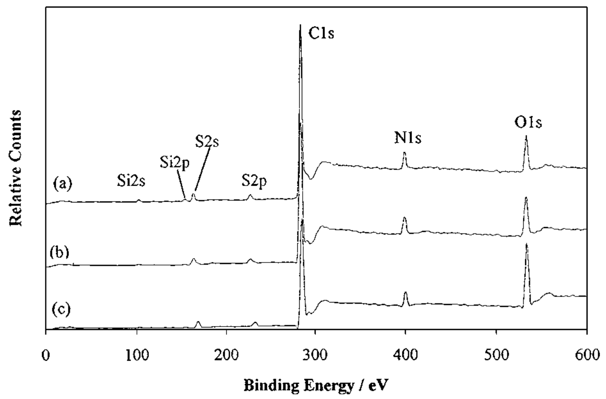

Figure 4 Small area XPS (30 μm) survey spectra taken from the three different regions of the composite fracture surface: (a) fibre-rich area, (b) matrix-rich area, and (c) particle-rich area

TABLE I Experimentally determined concentrations in atomic percent

	PEEK	Matrix-rich	Fibre-rich	Particle-rich
C 1s	86.0	81.1	83.5	75.8
O 1s	12.9	9.2	7.2	15.4
N 1s	—	5.9	5.4	5.5
S 2p	—	3.0	2.3	2.6
Si 2p	1.1	0.7	1.6	0.7

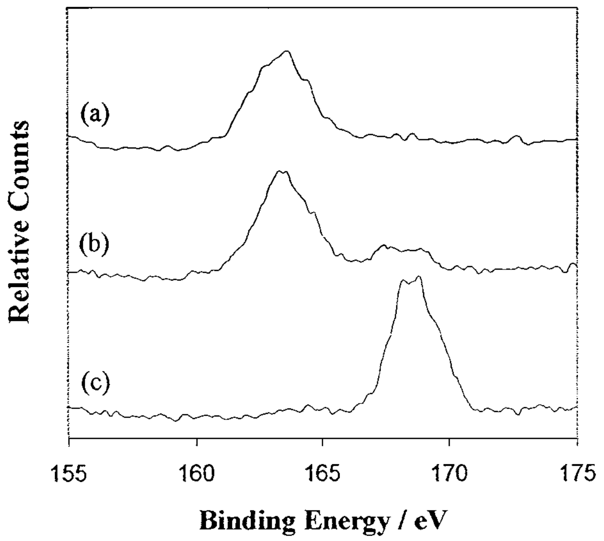

Figure 5 Small area XPS (30 μm) high resolution spectra for the S2p region from: (a) fibre-rich area, (b) matrix-rich area, and (c) particle-rich area of the composite fracture surface.

Survey spectra of the fibre-rich, matrix-rich, and particle-rich regions are shown in Fig. 4a, b, and c, respectively, and the experimentally-determined surface compositions are presented in Table I. The observed concentrations are consistent with the constituents of the system, with two exceptions. First, the carbon concentration is seen to increase in the fibre rich-phase, as expected. However, the increase in the carbon signal should be at the expense of all elements, rather than just oxygen, whose concentration is usually greater than that of nitrogen at the fibre surface after commercial electrochemical treatment [14]. It is also interesting to note that the concentration of sulphur, which is not expected to be present at the fibre surface, is still greater than predicted for the fibre-rich phase. Also somewhat unexpected are the relative atomic concentrations recorded for the particle-rich area. Sulphur and nitrogen are not present in the PEEK structure (Fig. 1c), and the appearance of these elements provides good evidence for a chemical interaction between the epoxy matrix and the PEEK particle. In particular, it indicates that DDS is present on the surface of the PEEK particle, and it appears that a thin layer of resin remains adhered to the particle after fracture.

The high resolution S 2p spectrum of the fibre-rich region is shown in Fig. 5a, and is centred on a binding energy of ca. 164 eV. This binding energy is consistent with the presence of sulphur in its elemental state or as an organic sulphide species (an inorganic sulphide will have a lower binding energy of ca. 161 eV). However, the sulphur atom in the curing agent, illustrated in Fig. 1b, is in a sulphone environment which should have a characteristic binding energy of ca. 168 eV, and there is no peak observed at this binding energy. Fig. 5b shows the high resolution S 2p spectrum for the matrix-rich region of the fracture surface. The peak clearly shows sulphur present in two different oxidation states, with the most intense component appearing as a similar species to that observed in the fibre-rich region, and the minor component present at ca. 168 eV, consistent with the presence of sulphone from the curing agent. Fig. 5c shows the same region of the spectrum obtained from the PEEK particle, and exhibits only one S 2p peak, centred around a binding energy of ca. 168 eV, which is consistent with the structure illustrated in Fig. 1b, i.e. a sulphone component. The presence of this sulphur peak, which is nearly as intense as the sulphide-type peaks observed for the two other regions, suggests that there is a thin overlayer of matrix present on the particle that is not observed by SEM. This indicates that because of the difference in binding energy of the S 2p spectrum of the particle-rich and fibre-rich areas, there is another component in the matrix associated mostly with the fibre-rich region. It is interesting to note here that the polymer containing the sulphide is associated mostly with the fibre-rich region of the composite, and the sulphone (curing agent) with the particle region. A plausible candidate would be a toughening agent (usually a thermoplastic phase) that has been added to the matrix in order to improve the mechanical characteristics of the thermosetting resin, most probably a vulcanised rubber-type polymer [15] or polysulphide [16]. An alternative explanation is that the matrix is toughened with a poly(ether sulphone) which may undergo a cross-linking reaction with other constituents of the pre-preg system, and in the process being chemically reduced. This would lead to a lower binding energy in the XPS spectrum consistent with a sulphide species. Such an option is, however, thought to be unlikely as, from an intuitive point of view, the reduction of an aromatic sulpone to a sulphide in the presence of an epoxy/amine combination would not be a favoured process.

In order to eliminate any possibility that the sulphur detected from the particle was present as a result

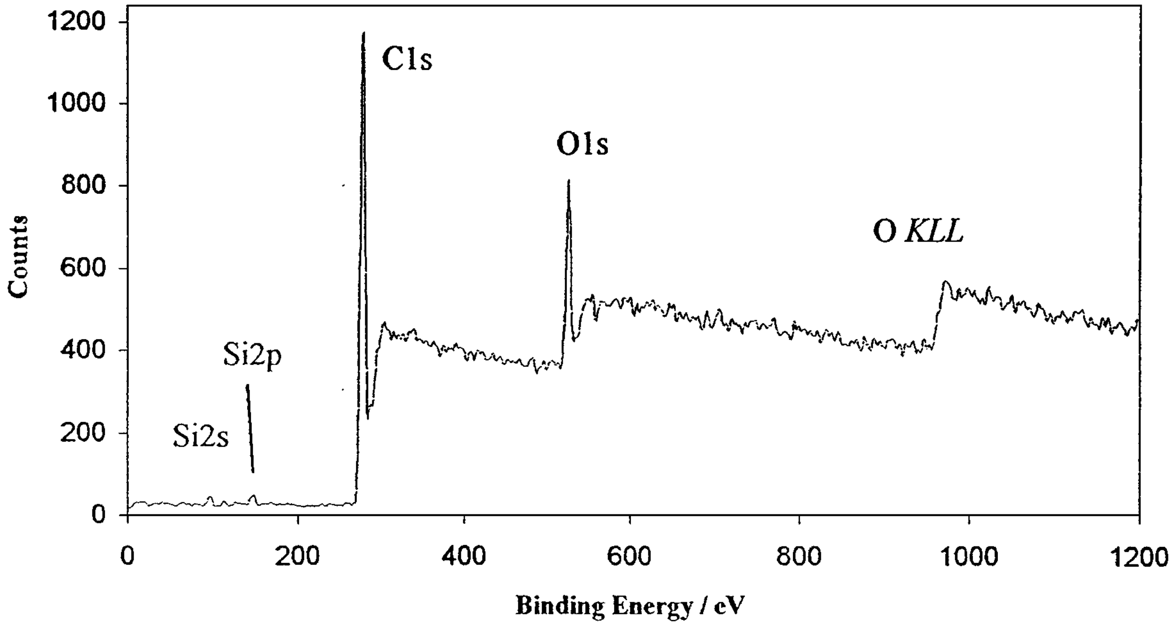

Figure 6 Small area XPS (50 μm) survey spectrum of as-received PEEK particles.

of contamination, PEEK particles were pressed onto double-sided adhesive tape and analysed. Excess PEEK particles were shaken off the adhesive tape (mounted on a 10 mm diameter stainless steel disc) by tapping the edge of the sample with a clean tweezer blade prior to introduction into the spectrometer. The spectrum obtained from the as-received PEEK, shown in Fig. 6, exhibits the expected carbon and oxygen peaks. A very minor contribution from silicon is also observed, originating from the release agent applied during manufacture to the adhesive tape used to mount the particles. The isolated PEEK particle shows no sulphide component, which by contrast to the particle in the environment of the composite would be consistent with a thin layer of matrix material present on the particle surface, indicating effective adhesion between the particle and matrix resulting from a specific interfacial reaction.

4. Conclusions

Small area XPS shows that matrix-particle interactions within complex multi-component composite systems may be evaluated successfully. This has been achieved in this study despite the proprietary nature of the CFRP system studied, and analysis of simpler systems, or of materials with more readily classified components, could prove that this approach to qualifying heterogeneous surfaces can provide comprehensive results.

Evidence for strong interaction between a PEEK thermoplastic particle and the base epoxy matrix in a CFRP, particularly the primary amine curing agent, has been found by the application of small-area XPS.

The effective management of surface charge on insulating polymer samples is readily achieved and leads to the aquisition of good quality XPS spectra at high spatial resolution (~30 μm), and reproducible spectra have also been acquired from particles of such materials mounted on a non-conducting substrate (double-sided adhesive tape) with very good spatial resolution (50 μm).

Differential charging, observed in the matrix material from the non-conducting (matrix) and electrically-conducting (graphite fibre) components was observed at high spatial resolution. This was addressed successfully by the use of charge compensation with a low energy focused electron beam.

Acknowledgements

This work was funded by EPSRC/ROPA GR/L71032. We thank HEFCE for financial support for purchase of the spectrometer by way of the JREI.

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Received 11 January
and accepted 20 July 2000