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Surface analysis of carbon fibres modified with PVAL coating and the composite interfaces

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High-resolution X-ray photoelectron spectroscopy (XPS) has been used to analyse the fibre surface and composite interfaces with and without polyvinyl alcohol (PVAL) coating (both fibres being commercially surface-treated and sized). Major functional groups on the fibre surface are also identified by Gaussian curve-fitting of carbon peaks to study the correlations of surface chemistry with the observed failure mechanisms of the uncoated and coated fibre composites. The main difference in the fracture surface of the fibre composites with and without the coating is that the latter has a significant amount of silicon (about 6 at% concentration) associated with the epoxy matrix, but silicon is almost absent in the PVAL-coated fibre composites. This suggests that the debonding mechanism in the uncoated fibre composite, which has a strong interfacial bonding, is controlled by the combination of cohesive failure of the matrix material and adhesive failure at the interface. In contrast, the PVAL coating promotes adhesive failure due to the weak bonding at the fibre–matrix interface. This observation is consistent with SEM observations in that the uncoated fibre composite consists of significant deformation of matrix material which covers the majority of the fracture surface and tiny epoxy resin particles adhering to the debonded fibre surface, whereas the coated fibre composite shows a lesser amount of matrix deformation with relatively clean fibre surface.

1. Introduction

In our previous work [1], a polyvinyl alcohol (PVAL) coating applied to the fibre has been shown to enhance the transverse fracture toughness of carbon fibre and Kevlar fibre–epoxy matrix composites (KFRP and CFRP) by 100% depending on the test temperature, without any loss in flexural strength. Major mechanical properties of the CFRPs with and without the PVAL coating are summarized in Table I. The thermoplastic coating not only forms a compliant ductile layer which satisfactorily functions as a stress relief medium but also reduces the interfacial bond strength which effectively augments the fibre debonding and subsequent frictional pull-out mechanisms with large contributions to the total composite fracture toughness. The beneficial effect of the fibre coating with PVAL on the transverse fracture toughness is shown to sacrifice little damage tolerance of the composite against interlaminar fracture. In the present study, as a continuation of our previous work, high-resolution X-ray photoelectron spectroscopy (XPS) has been used to analyse the surfaces of carbon fibres with and without the PVAL coating and the composite fracture surfaces to study the correlation between the surface chemistry and the failure mechanisms of the composites.

2. Experimental procedure

The fibre used was Torayca T300 (Toray, Japan) in the form of unidirectional continuous roving. The as-received fibres were commercially surface-treated (probably electrolytically) and sized, allowing compatibility with epoxy resins. Fibres were coated with PVAL by immersing in a coating solution and subsequently dried for over 4 h. The amount of coating was controlled by the concentration of the coating solution and 4% solution was used in this study. The matrix material was an epoxy resin Araldite GY 260 (Ciba Geigy, Australia), a diglycidyl ether of bisphenol A (DGEBA), and piperidine as a curing agent in the ratio of 100:5 by weight. The details of fabrication procedures for the composites are given elsewhere [1]. The fibre volume fraction was approximately 50%. The composite fracture surfaces were obtained after mixed-mode I/II delamination. X-ray photoelectron spectra were obtained on a Kratos XSAM 800 spectrometer using MgK_α radiation operating in a vacuum of pressure less than 10^{-9} torr. An analyser pass energy of 80 eV and a spot size 600 μm in diameter were employed for all analyses. All binding energies are quoted against the principal C1s at binding energy 284.6 eV. The spectrometer was interfaced to a computer which permits acquisition, storage and

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TABLE I Impact fracture toughness and flexural properties of CFRP tested at ambient temperature (mean values ± one standard deviation)

Fibres	Impact fracture toughness ($kJ\,m^{-2}$)	Flexural strength (MPa)	Interlaminar shear strength (MPa)	Debond length (mm)	Fibre pull-out length (mm)
Uncoated	50.3 ± 13.0	683 ± 38	58.9 ± 2.3	1.36 ± 0.22	0.22 ± 0.04
PVAL-coated	98.7 ± 20.3	758 ± 47	50.0 ± 3.3	1.65 ± 0.35	0.65 ± 0.08

processing of spectra using the software provided by the manufacturer. High-resolution SEM photographs were taken of the carbon fibres and composite fracture surfaces using a Jeol JSM 6300F scanning microscope.

3. Results

3.1. X-ray photoelectron spectra and elemental compositions

The spectra obtained for the uncoated and PVAL-coated carbon fibres and the composite fracture surfaces are shown in Figs 1 and 2, respectively, and the elemental compositions are summarized in Table II. The survey spectra of both the uncoated and coated fibres and the composites display the expected strong signals due to the carbon and oxygen. High-resolution spectra showed that the shapes of the C1s peak are different between the two fibres, reflecting the chemistry of the PVAL coating. The intensity of the C1s signal is much higher than that of the O1s for the uncoated fibres, whereas the converse is true for the PVAL-coated counterparts (Fig. 1). However, quantification identifies the actual surface compositions of the two fibres with and without the coating to be essentially the same (Table II). Apart from carbon and oxygen, there were no other strong signals observed.

TABLE II Elemental compositions of carbon fibres with and without PVAL coating and composite fracture surfaces

Material	C (%)	O (%)	N (%)	Si (%)
Carbon fibre				
Uncoated	81.9	18.1	–	–
PVAL-coated	79.3	20.7	–	–
Composite				
Uncoated	71.6	22.3	–	6.1
PVAL-coated	74.3	25.7	–	–

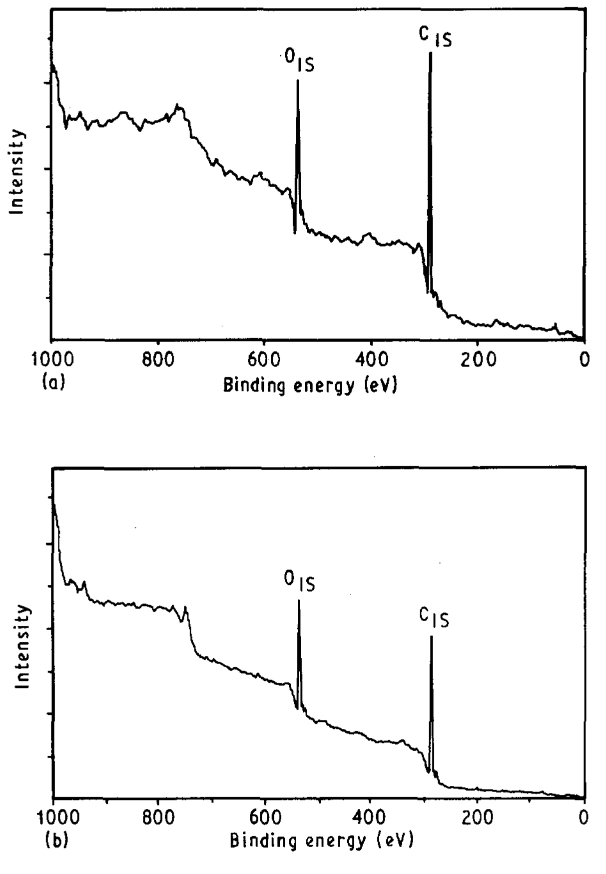

Figure 1 X-ray photoelectron survey spectra of (a) uncoated and (b) PVAL-coated carbon fibres.

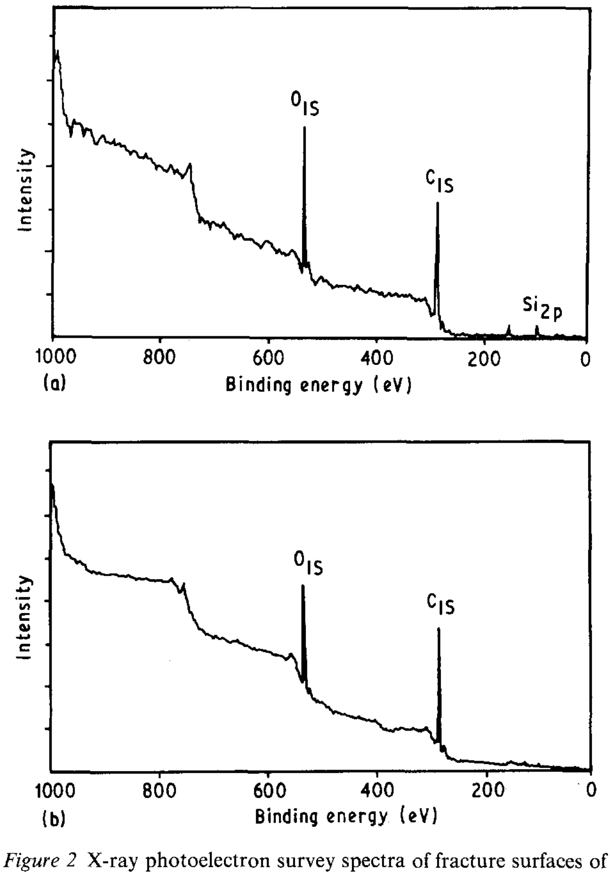

Figure 2 X-ray photoelectron survey spectra of fracture surfaces of composites containing (a) uncoated and (b) PVAL-coated carbon fibres.

In particular, neither nitrogen nor sodium were detected on the two fibre surfaces.

This observation seems to be in agreement with the recent results on similar T300 carbon fibres by Cazeneuve *et al.* [2, 3] who observed a small amount (normally less than 4%) of nitrogen and sodium in the unsized fibres at binding energies approximately 400 and 1070 eV, respectively. These elements were completely absent in the sized fibre surface as confirmed by Auger analysis. Sodium was also observed on the surface of untreated Fortafil-3 fibres (Great Lakes Carbon Corp., USA), which completely vanished upon treatment with a plasma of acrylonitrile [4]. The source of sodium is thought to be the residual sodium compounds used in the processing of carbon fibres (e.g. the polyacrylonitrile spinning process [5]). Therefore, it can be rationalized that sizing or plasma polymerization almost completely covers the fibre surface so that the small amount of impurities existing underneath the size or plasma coating cannot be detected by XPS or Auger analysis. It should be reiterated here that the carbon fibres used in the present study are already surface-treated and sized by the manufacturer. There is little difference in the elemental composition of the fibre surfaces between the two (Table II): the concentration of oxygen is approximately 20% and the balance is carbon. The high oxygen contents for both fibres is a direct result of previous surface (oxidative) treatments and partly due to adsorption of some water and/or oxygen from the atmosphere. The oxygen of the PVAL molecules (C_2H_3OH) also contributes, to a lesser extent, to the high oxygen content in the coated fibre surface.

The spectra of the composite fracture surfaces (Fig. 2) are basically similar to those of carbon fibre surfaces, except that for the composites with uncoated fibres, additional peaks are observed near binding energies 100 and 150 eV. The binding energies of these peaks are indicative of silicon, and in particular the Si2p at 104 eV reveals that silicon is present as silicon oxide (i.e. Si(IV)). Silicon contributes approximately 6 at % of the uncoated fibre composite surface. In contrast, there is little evidence for silicon in composites containing PVAL-coated fibres. These observations, along with the SEM observations on composite fracture surfaces, strongly suggest that the silicon originates from the epoxy matrix and is not an intrinsic impurity of carbon fibres, in support of the suggestion of Cazeneuve *et al.* [2].

3.2. Functional groups

There are obvious differences in the appearance of the C1s and O1s lines of the fibres and composite fracture surfaces with and without PVAL coating. The shape of the C1s peak reflects varying amounts of oxidized surface functional groups: the more highly oxidized species are characterized by higher C1s binding energies. Using a Gaussian curve fitting procedure [6] as shown in Fig. 3 for the uncoated carbon fibres, it is possible to identify four major sites which are ascribed as pure carbon (C–C), hydroxyl group (C–O), carbonyl group (C=O) and carboxyl group (O–C=O) at bonding energies 284.6, 286.1, 287.3 and 288.5 eV, respectively. The relative amounts of the four species of carbon are summarized in Table III. The O1s signals were typically broad without any clear features and thus did not provide any information as to the exact nature of the surface oxides. The main difference between uncoated and PVAL-coated fibres is the amount of C–O group which is significantly larger for the PVAL-coated fibres. A slightly smaller amount of O–C=O group is also noted for the coated fibres.

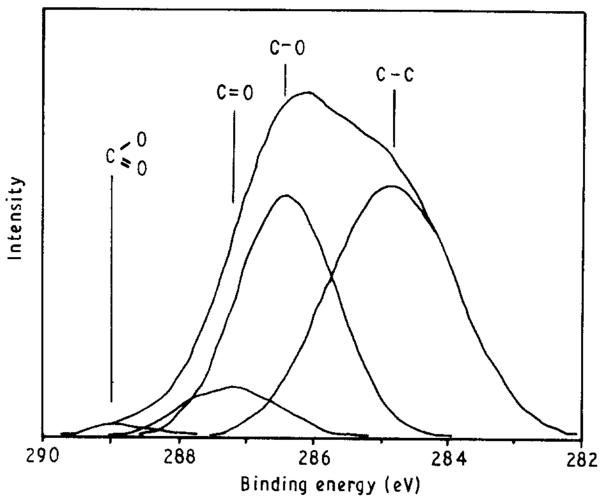

Figure 3 Gaussian peak fitting of the C1s spectrum of uncoated carbon fibres.

TABLE III Concentration of C/O groups as a proportion of C1s peak area for uncoated and PVAL-coated carbon fibres

Carbon fibres	C–C	C–O	C=O	O–C=O
Uncoated	61.6	25.7	7.4	5.3
PVAL-coated	51.3	38.9	8.2	1.6

3.3. High-resolution scanning electron microscopy

Typical high-resolution SEM photographs taken of the carbon fibres and the composite fracture surfaces are shown in Figs 4 and 5, respectively, from which major differences in the surface morphology can be identified. This will help to correlate the surface analysis with the major failure mechanisms of the composites containing uncoated and PVAL-coated fibres. The surface of the uncoated carbon fibre is characterized mainly by the large amount of rugosity produced by the prior oxidative treatments (Fig. 4a), but significantly reduced rugosity is obtained for the PVAL-coated fibre surface (Fig. 4b) suggesting that the coating has partly filled the corrugations. It is shown that the majority of fracture surface for the composite with uncoated fibres is covered by the matrix material as evidenced by the deformed hackle markings and the epoxy layers adhering to the fibre surface (Fig. 5a). A number of tiny particles and broken ligaments of matrix material are attached preferentially (i.e. longitudinally) along the crevices of the debonded fibre

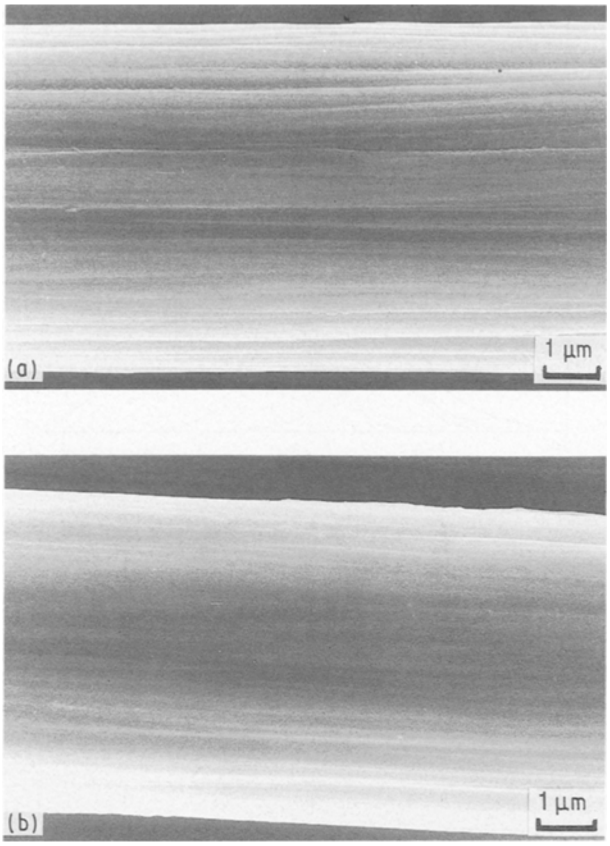

Figure 4 SEM photographs of (a) uncoated and (b) PVAL-coated carbon fibres.

surface (Fig. 5b). In sharp contrast, for the PVAL-coated fibre composites a much lesser amount of shear deformation of the matrix material is observed (Fig. 5c) which covers significantly a smaller portion of the fracture surface. The large fracture surface area of exposure for the coated fibres is promoted by the large number of debonded fibres and multi-plane delamination which bridge the fracture surfaces without being broken during interlaminar fracture [1]. The debonded fibre surface is relatively clean with little evidence of epoxy particles or layers being adhered (Fig. 5d).

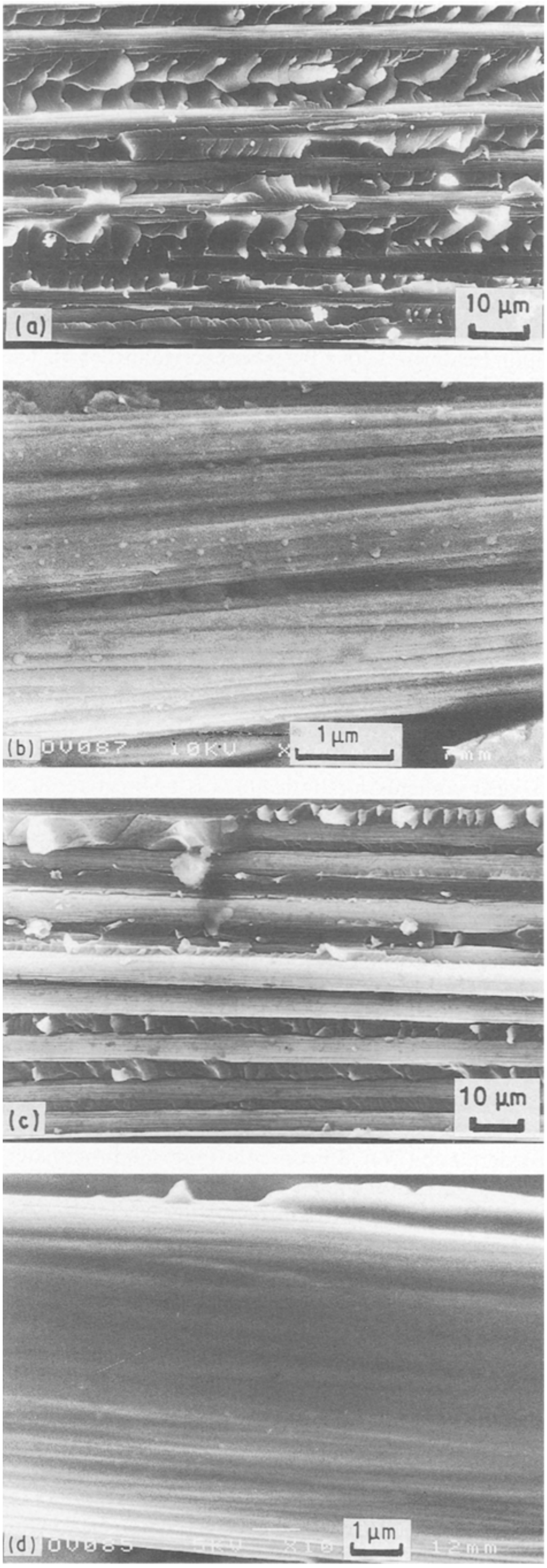

Figure 5 SEM photographs of fracture surfaces of composites: (a, b) uncoated carbon fibres; (c, d) PVAL-coated carbon fibres.

4. Discussion

The results presented in the previous section provide valuable information with regard to the failure mechanisms of the composites with and without PVAL fibre coating. The high concentration of silicon on the composite fracture surface of uncoated fibres (Table II and Fig. 2a) and the marked difference in the composite fractography (Fig. 5) strongly suggest that at least a significant part of the debonded fibre surface is covered non-uniformly with epoxy resin. The dusty and ragged appearance of the debonded fibre (in the composite fracture surface, Fig. 5b), compared to the fibre (Fig. 4a) before being embedded in the matrix material, also supports the foregoing implication. Therefore, it can be tentatively concluded that the debonding mechanism in the uncoated fibre composite during interlaminar fracture is controlled by the combination of cohesive failure of the matrix material near the interface region and adhesive failure at the actual fibre–matrix interface. In contrast, weak bonding at the fibre–matrix interface produced by the PVAL coating promotes adhesive failure at the interface so that the fracture tends to be completely interface-controlled.

This observation is rather consistent with the work of Denison *et al.* [7, 8] on two carbon fibre composite fracture surfaces using scanning secondary ion mass spectroscopy (SIMS): the untreated carbon fibre surfaces (which provide a relatively weak fibre–matrix interface bond) are free of any epoxy resin layer, but a thin epoxy layer is present over the treated fibre surfaces (with a strong interface bond) as evidenced by the large degree of overlap between the fibre and resin signals in scanning SIMS images. A similar conclusion has been proposed in the recent work of Cazeneuve *et al.* [2] where scanning Auger microscopy (SAM) reveals a thin layer (0.6–2 nm) of epoxy resin on the pulled-out carbon fibres. They proposed that matrix molecules are absorbed on the fibre through bonding to certain surface functional groups during the cure cycle, and that failure occurs between the first layer of these matrix molecules and the rest of the matrix. Certainly, further research is necessary to provide more convincing evidence of an epoxy layer on the debonded fibre surface (without coating) used in this study. The tiny particles of size smaller than approximately 100 nm observed on the debonded fibre surface (Fig. 5b) seems to be associated with the local concentration of curing agent which can provide strong regions in the matrix.

There is still considerable controversy as to whether chemical bonding, either ionic or covalent, occurs between the carbon fibres and polymer resins, and if it does, to what extent such fibre–matrix bonds contribute to the total bond strength. Over the past two decades numerous studies on the chemical modification of graphite (or carbon) surfaces have provided a clear picture of the oxide groups which can form on either the edge or basal (planar) surfaces within the graphite structure. Assuming the present carbon fibres are graphitic, or at least that the concept of edge and basal sites is valid, then the bonding involving edge sites is expected to provide a greater contribution to the strength at the interface. The functional groups bonded at the edge sites form strong covalent bonds within the planar (sp^2) carbon atoms. Any attachments to the resin and subsequent cross-linkage involving such carbon atoms would serve to strengthen the weak Van der Waals bonds between the planes. Without such attachments, however, cleavage along the graphite basal planes will remain relatively easy. It follows then that the bonding and subsequent cross-linkage of the resin to the basal carbon atoms would not contribute much to strengthening of the interface.

Oxidative treatments of carbon fibres, either dry or wet, certainly increase the number of surface oxide functional groups (see a comprehensive review given recently by the authors [9] on the various treatment methods and their effects on the properties of fibre and composite); the increase is greater at the edge sites than at the basal sites. In a study using laser Raman spectroscopy and a gas-phase chemical modification method coupled with XPS, Nakahara *et al.* [10] have shown that a number of modifiers will covalently bond to such surface sites. Included in the modifiers they studied was α-epichlorohydrin, the epoxy group of which is believed to mimic typically employed resins. The epoxy group is shown to bind more to the edge sites than to the basal sites. In principle, any increase in the amount of observed oxidized carbon (i.e. functional) groups should correspond to an increase in fibre–matrix bonding to a certain extent, since as indicated above oxidation at the edge site is favoured. The use of PVAL coating in the present study, however, limits the validity of this statement since the coating itself contains oxidized carbon groups, in particular the hydroxyl (C–O) groups, which are not active. Rather, the increased oxide formation by the PVAL coating corresponds to weak bonding since it appears that the coating acts as a physical barrier to the chemical bonding between functional groups present in the fibre surface and epoxy matrix. Another important effect of the fibre coating is the partial removal of rugosity and/or pits produced by surface oxidative treatments, thus decreasing the surface roughness and possibly reducing the surface area necessary for bonding. This is thought to be particularly detrimental to mechanical keying of the resin to the fibre which is one of the most important mechanisms contributing to the bonding between carbon fibres and epoxy resins [11].

5. Conclusion

High-resolution XPS and SEM have been used to analyse the carbon fibre surfaces with and without PVAL coating and the composite interfaces. The debonding at the interface region for the uncoated fibre composite (which has a strong fibre–matrix interface bond) is controlled by the combination of cohesive failure of the matrix material and adhesive failure at the interface, while debonding is apparently interface-controlled in the composite containing PVAL coating due to the weak bonding at the fibre–matrix interface.

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