The bonding of carbon fibres to epoxy resins as affected by the manufacturing and surface treatment processes

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The differences in the bonding to epoxy resins, as measured by the interlaminar shear strength (ILSS), of three nominally similar carbon fibres were related to differences in the manufacturing and surface treatment operations. Two of the fibres (denoted A and C) were determined to have emerged from the manufacturing process essentially identical, with the same crystal length, electrical resistivity and diameter. However, the subsequent surface treatments were very different, which resulted in different surface compositions (as measured by Auger electron spectroscopy), and a higher ILSS value for the composite made from fibre A as compared with one made from fibre C. By contrast, fibre B emerged from the manufacturing process differing slightly from fibres A and C, as determined by different graphite crystal lengths, electrical resistivities and diameters. Fibre B was found to be more ordered, and thus less susceptible to surface treatment, than for example fibre A. The ILSS value of the composite made from fibre B was lower than the value for the composite made from fibre A.

Key words: carbon fibres; bonding; epoxy resins; composites; manufacturing; surface treatment; interlaminar shear strength; Auger electron spectroscopy

In recent years, carbon fibres have received considerable attention as a reinforcement for high performance composites. A critical factor in determining the performance of the carbon fibre-reinforced material is the nature of the fibre-matrix interface, which in turn is influenced by the surface of the carbon fibre. To increase the strength of the fibre-matrix bond, carbon fibres are generally surface treated prior to their incorporation into the matrix. Several surface treatments are commonly in use including gas or liquid oxidation, electrochemical oxidation and electrochemical deposition[1].

Surface treatments are known to have a two-fold effect on the fibre surface: 1) the treatments remove a weak outer fibre layer present initially on the fibre; and 2) chemical groups are added to the fibre surface, which increase the attraction between the fibre and the matrix. Surface treatments can also increase the fibre surface area, but this is not an important factor in promoting fibre-matrix adhesion[2].

The purpose of the present work was to investigate the factors that affect fibre-matrix bonding. The two main factors studied were 1) the fibre manufacturing process (eg, the carbonization process); and 2) the fibre surface treatment. The manufacturing process influences the structure, or order, of the fibres, which in turn affects the susceptibility of the fibres to the surface treatment. Here, fibres undergoing the same manufacturing process, but different surface treatments, and fibres with different structures (hence different manufacturing treatments) but the same surface treatment, were studied in relation to one measure of adhesion between the fibres and an epoxy matrix (interlaminar short beam shear test). Other chemical and physical tests were used to corroborate the results of the short beam test by relating to the manufacturing process or the surface treatment.

Experimental

Materials

The epoxy resin used in this study comprised 100 parts tetraglycidyl 4,4'-diaminodiphenyl methane (Araldite MY-720, Ciba-Geigy Co) cured with 115 parts methyl

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nadic anhydride (Hardener HY906, Ciba-Geigy Co) and a small percentage 4 weight % of accelerator (Epikure K61B, Shell Chemical Co). The composites, made by a hand impregnation and lay-up procedure, were cured at 120°C for 45 min followed by post-cure at 180° for 2 h. The nominal fibre volume fraction was 0.6.

The type II carbon fibre was obtained from Afikim Carbon Fibers (ACIF-XHT 12 S/E) and was made from a polyacrylonitrile precursor. Three batches of fibres were studied. The batches were reported by the manufacturer to yield different values of the interlaminar shear strength (ILSS) for a carbon fibre-reinforced epoxy composite, even though the batches had nominally undergone the same manufacturing, surface treatment and finishing processes. The fibre batches were designated as follows: A) good ILSS values; B) moderate ILSS value; and C) poor ILSS value.

ILSS test

The ILSS values of the composites were measured by the short beam test. Specimens measuring 2 mm thick × 10 mm wide × 12 mm long were used in the test, under a span-to-depth ratio of 5:1. The ILSS values were computed using

$$\text{ILSS} = (3P)/(4WT) \tag{1}$$

where P is the load at failure, W the specimen width and T the specimen thickness. At least nine specimens were tested at a crosshead speed of 1 mm min^{-1} for each fibre.

Mechanical properties

The nominal elastic moduli and tensile strengths of the fibrew were tested in single-fibre tension tests. A gauge length of 22 mm was used. Single fibres were glued to paper frames and mounted in an Instron tensile testing machine. The edges of the frame were cut and the test was initiated. The fibre diameters were measured microscopically, and the average diameter for each type of fibre was used in the modulus and tensile strength calculations. Twenty to thirty fibres were tested at a crosshead speed of 2 mm min^{-1} for each fibre type.

X-ray diffraction

Wide-angle X-ray diffraction provides a measure of the size of the graphite crystals and the spacing between graphite layers. The crystal length, L_c, was calculated from[1]:

$$L_c = K\lambda/(B\cos\theta) \tag{2}$$

where $K = 1$ (a constant), $\lambda = 0.1542$ nm, 2θ = angle of peak position, and B is the line breadth at the half-height of the diffraction peak (in radians). The interlayer spacing, d, was calculated from Bragg's equation:

$$n\lambda = 2d\sin\theta \tag{3}$$

where n is the order of the diffraction (here equal to 1).

Electrical resistivity

The electrical resistivity is known to be extremely sensitive to the graphitic order of carbon fibres[3]. The specific resistivity, ρ, was measured in a four electrode system, and calculated from $\rho = RS/L$, where R is the resistivity in ohms, S, the fibre cross-sectional area, and L = fibre length.

BET surface area

The change in surface area is often the largest topographical change which occurs with fibre surface treatments. Nitrogen desorption at 77 K was used to determine the carbon fibre surface area. The measurements were made on a Quantasorb apparatus (Quantachrome Corporation, Syosset, NY).

Auger electron spectroscopy (AES)

The outer surface of the carbon fibres was investigated by AES using a Scanning Auger Spectrometer THI, model 590-A, operating at 3 kV and 1 μA in order to correlate the ILSS results with the surface atomic composition[4, 5].

Oxidative thermal stability

The thermal stabilities of the different fibres were measured in air at 325°C for 740 h. The fibres were periodically removed from the oven, weighed, and then returned to the oven.

Results

ILSS test

The results of the ILSS test are shown in Table 1. It can be seen that fibre A yielded composites with the highest ILSS value, fibre B slightly lower, and fibre C yielded a composite with a very poor ILSS value. The ILSS values reported here, for fibres A and B, are comparable with the commonly accepted ILSS values for carbon fibre-reinforced epoxy composites.

Mechanical properties

The results for the strength, modulus, density and diameter are presented in Table 1. Except for the modulus, the values are, in general, comparable with those commonly reported for type II carbon fibres. The low modulus values result from the measurement technique, in which a nominal value was calculated from the load/displacement data of the tensile testing machine, instead of measuring the strain of the fibre. It should also be noted that fibre B exhibits somewhat lower values of modulus and diameter compared with fibres A and C. This point is further discussed below.

Table 1. Properties of the fibres and composites

	Property values		
Property	Fibre A	Fibre B	Fibre C
ILSS* (MPa)	99	93	60
L_c (nm)	2.18	2.49	2.24
d (nm)	0.34	0.34	0.34
ρ (mohm cm)	1.61	1.32	1.51
E (nominal, GPa)	198	188	191
Tensile strength** (nominal, MPa)	2650	2440	2730
Diameter (μm)	7.5	7.0	7.5
Density (g cm^{-3})	1.72	1.72	1.73
BET[†] surface area (m^2 g^{-1})	0.43	0.60	0.64

*Typical coefficient of variation, 7.2%
**Typical coefficient of variation, 25%
[†] Brunauer, Emmet and Teller

X-ray diffraction

The graphitic structure of carbon fibre is known to be related to the concentration of faults and also peripheral atoms of the graphite layer at the surface which are able to be attached to functional groups during surface treatment. The higher the order of the fibre, the less reactive the fibre is to the surface treatment[6]. The graphitic order improves during thermal treatments and can be modified by changing the time-temperature profile and the degree of stretching of the fibres during the stabilization and carbonization stages. The precursor material also has an influence on the degree of graphitization. Graphite crystal length, as determined by wide-angle X-ray diffraction, is known to be related to the graphitic order. Higher degrees of graphitization result in larger graphite crystals.

The X-ray charts obtained for fibres A, B and C are presented in Fig. 1; the crystal lengths of fibres A, B and C, and the interlayer spacings, are listed in Table 1. Reported values of the crystal length for polyacrylonitrile-precursor material range from 1.5 to 2.5 nm for heat-treatments at 1000°C to about 6 nm for a 2600°C heat-treatment[7]. The interlayer spacing varies between 0.37 and 0.34 nm, depending upon heat treatment temperature[1]. Thus, the values of L_c and d reported here are consistent with literature values for carbon fibres. The difference between the crystal length results for fibres A and C are not significant, but the results for fibre B indicate that it is more ordered than the other two fibres. The interlayer spacings are essentially equivalent for the three fibres.

Electrical resistivity

The results of this test are shown in Table 1. They are in good agreement with values of the electrical resistivity, ρ, as a function of the modulus of carbon fibres reported elsewhere[3]. The values in Table 1 confirm the X-ray diffraction results. Fibre B has the lowest resistivity, and thus the highest order, whereas there is no significant difference between fibres A and C. It is known[3] that resistivity is inversely related to modulus. For the materials discussed here, fibre B has the lowest ρ value, but also the lowest modulus (see Table 1). However, analysis of the statistical variance indicated that the modulus values of fibres A, B and C are homogeneous, ie, are not statistically different.

The diameters of the fibres were measured microscopically, and are reported in Table 1. The smaller diameter of fibre B, which may have resulted from over-stretching during the manufacturing process, is consistent with its higher order. Other tests (see Table 1), such as density, elastic modulus and tensile strength measurements, did not reveal any differences in the properties of the three fibres.

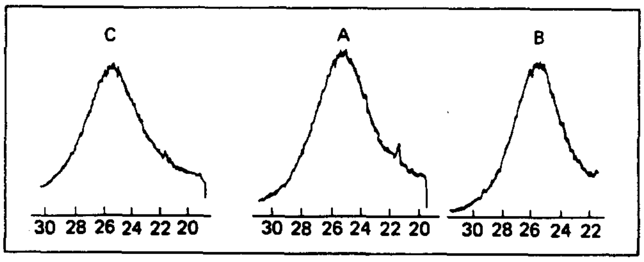

Fig. 1 X-ray diffraction charts for fibres A, B and C

BET surface area

The BET surface area values are shown in Table 1. Fibre A, which has the largest ILSS value, has the smallest BET surface area, whereas fibre C has the smallest ILSS and the largest surface area. This suggests that the surface area is not a major factor in promoting fibre-matrix adhesion, and that the chemical treatment is more important than the surface roughness. It was shown[1] that an effective surface treatment may result in a reduction of the fibre surface area due to etching. Values of 0.3-0.5 $m^2 g^{-1}$ were given for type II carbon fibres[1], which are comparable with the results reported in the present work.

Auger electron spectroscopy

The relationship between the atomic % of the fibre surface and the surface elements for the fibres is shown in Fig. 2. The elements that were detected on the surface of the fibres are:

C — the main element of carbon fibres,
O — oxidized carbon, C=O and C-OH, and oxidized impurities such as SiO,
Ca, Mg — electrolyte impurities deposited on the fibres during the surface treatment,
N — comes from the original nitrile groups and from the nitrogen-containing electrolyte used in the surface treatment; probably present as amine groups[8],
Na, S — results from sodium sulphate contamination, as a consequence of the sodium thiocyanate which is employed in the spinning operation of the PAN precursor[9],
Cl — the electrolyte, the size and the rinsing solution contained chlorides.

Fig. 2 contains a summary of the results obtained from the AES experiments. Fibre A has the highest surface atomic concentrations of O (8.7%), N (4.3%), Ca (1.8%) and Mg (3.0%), whereas fibre C has the lowest surface concentrations of O (3.3%), Na (3.4%), N (1.0%) and S (0.1%), and does not contain Ca and Mg at all.

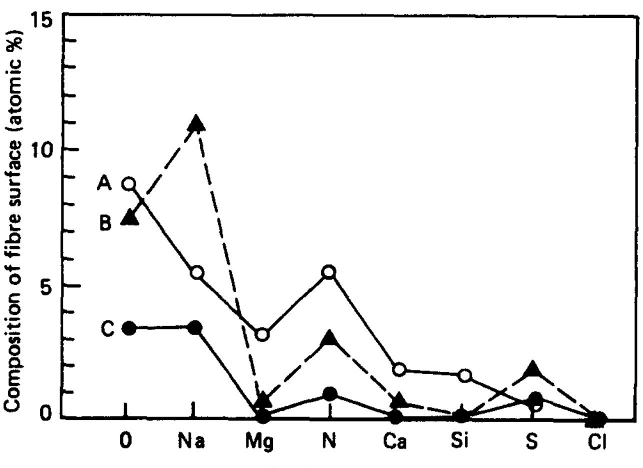

Fig. 2 Auger electron spectroscopy results of the relationship between the atomic % of fibre surface and surface elements, for fibres A, B and C

Fibre B has a high value of Na (10.9%) and S (1.8%) on its surface. The surface atomic concentrations of N found in the present work compare well with surface concentrations of N found in Hercules AU-4 (untreated) and AS-4 (treated) fibres[10].

The surface concentration of N (in atomic % units) in fibre A is higher than the residue of the original N of the PAN precursor. It can be shown that the high value results from the surface treatment operation by performing the AES analysis at different depths below the fibre surface. Fig. 3 shows the N concentration as a function of the depth for fibres A and C. Depth profiling was achieved by spattering the fibre surface with 4K Ar ions prior to performing AES. It can be seen that the N concentration in fibre A reaches, at a depth of 50 nm, a value around 0.7%, which is typical of the residual N content and similar to that of fibre C. This result corresponds to the observation in the literature[10] that the surface concentration of N increases due to the use in anodization of a nitrogen-containing electrolyte. The elemental composition of the surface, as determined by AES, must be differentiated from the overall bulk composition, as determined by elemental analysis. The overall compositions were: C, ≈ 97%; N, ≈ 2-3%; H, ≈ 0.3%; these values are in good agreement with those reported elsewhere[11].

Oxidative thermal stability

The thermal stability of carbon fibres is known to be strongly related to the sodium content: higher sodium contents lead to less stable fibres. As indicated in previous X-ray scattering for chemical analysis, ESCA, studies[9], sodium exists in carbon fibres as sodium sulphate. The contamination results from sodium thiocyanate, which is employed in the PAN spinning operation. The weight loss of fibre as a function of time, at 325°C, for the three fibres is shown in Fig. 4. All three fibres lost 90–99% of their original weight after 740 h.

Discussion

The differences in the ILSS values between the three fibres can be understood by drawing a distinction between the fibre manufacturing process and the results of the surface treatment. First, considering fibres A and C, it is apparent that the same base fibre emerged from the manufacturing process, since the X-ray diffraction and resistivity results are virtually identical. However, the surface treatment was effective for fibre A, as evidenced by the high surface oxygen and nitrogen concentrations, the presence of Ca and Mg (electrolyte impurities) and the smooth surface, whereas the surface treatment was totally ineffective for fibre C. The surface oxygen and nitrogen concentrations of fibre C were very low, Ca and Mg were not detected and the surface was relatively rough.

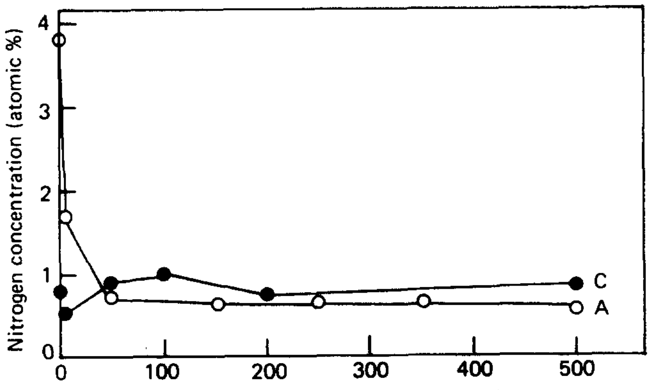

Fig. 3 Auger electron spectroscopy results of the nitrogen concentration (atomic %) versus depth below the fibre surface, for fibres A and C

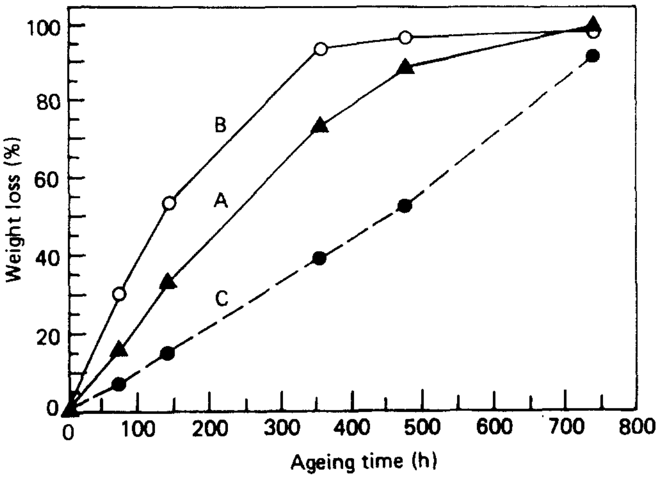

Fig. 4 Weight loss of the fibre versus ageing time at 325°C, for fibres A, B and C

The X-ray diffraction results and resistivity measurements for fibres A and B indicate that slightly different base fibres emerged from the manufacturing process and entered the surface treatment process. The differences in the fibres were probably due to small fluctuations in the manufacturing process, viz, the maximum carbonization temperature. Fibre B had a larger graphitc crystal length and a smaller resistivity, which indicates that fibre B is more ordered than fibre A. Thus, even though fibres A and B encountered the same surface treatment conditions, the higher order of fibre B resulted in a lower sensitivity to treatment. The surface treatment was less effective for fibre B than for fibre A, as evidenced by the lower surface oxygen and nitrogen contents, which contributed to a lower value of the ILSS for composites made from fibre B.

The importance of both the manufacturing and surface treatment steps in producing carbon fibres with acceptable bonding to epoxy resins has been demonstrated. Variations in the surface treatment of idential base fibres can dramatically affect the bonding properties, whereas the degree of order of the base fibre can have an important, although smaller, effect on the bonding.

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