JOURNAL OF MATERIALS SCIENCE 27 (1992) 3167–3172

Plasma surface modification of advanced organic fibres

Part II *Effects on the mechanical, fracture and ballistic properties of extended-chain polyethylene/epoxy composites*

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The interlaminar shear strength, interlaminar fracture energy, flexural strength and modulus of extended-chain polyethylene/epoxy composites are improved substantially when the fibres are pretreated in an ammonia plasma to introduce amine groups on to the fibre surface. These property changes are examined in terms of the microscopic properties of the fibre/matrix interface. Fracture surface micrographs show clean interfacial tensile and shear fracture in composites made from untreated fibres, indicative of a weak interfacial bond. In contrast, fracture surfaces of composites made from ammonia plasma-treated fibres exhibit fibre fibrillation and internal shear failure as well as matrix cracking, suggesting stronger fibre/matrix bonding, in accord with the observed increase in interlaminar fracture energy and shear strength. Failure of flexural test specimens occurs exclusively in compression, and the enhanced flexural strength and modulus of composites containing plasma-treated fibres result mainly from reduced compressive fibre buckling and debonding due to stronger interfacial bonding. Fibre treatment by ammonia plasma also causes an appreciable loss in the transverse ballistic impact properties of the composite, in accord with a higher fibre/matrix interfacial bond strength.

1. Introduction

Extended-chain polyethylene (ECPE) has been developed recently in the form of strong, high-modulus fibres which have found important uses in their own right and as reinforcement in organic matrix composites. ECPE fibres offer the benefits of light weight combined with high specific modulus and strength, as well as good chemical resistance and low water absorption. However, the chemical inertness and very low surface energy of ECPE fibres result in composites with a low fibre/matrix interfacial strength which are, therefore, less than ideal for structural applications. In order to overcome this problem, it is necessary to modify the fibre surface to induce chemical (i.e. covalent chemical bonds) or physical (i.e. dispersive, dipole–dipole or acid–base) interactions with the resin matrix. A broad range of surface treatments, generally oxidative in nature, have been used to increase wettability of the fibres and adhesion to the resin matrix. These include chemical oxidation [1, 2], corona treatment [3] and oxygen plasma treatment [2–6]. The latter has also been shown to cause roughening or micropitting of the fibre surface, and it has been suggested that mechanical interlocking to the matrix resin is also influential in promoting fibre/matrix adhesion [2, 3].

In a previous study [7], we investigated the effect of surface modification of aramid fibres in ammonia plasma on the mechanical, fracture and ballistic properties of aramid/epoxy composites. The incorporation of surface amine groups led to marked improvement in the flexural strength and interlaminar shear strength and a significant loss in ballistic impact properties of these composites. In this paper we compare the effects of ammonia plasma treatment and commercial corona treatment of ECPE fibres on the mechanical, interlaminar and ballistic impact properties of ECPE/epoxy composites, and examine the microscopic basis for failure of these composites.

2. Experimental procedure

2.1. ECPE fabrics

Untreated and corona-treated ECPE fabrics (Spectra® 1000, 650 denier) were used. Preliminary investigations using X-ray photoelectron spectroscopy (XPS) revealed no significant surface contamination of the untreated material; both materials were, therefore, used without cleaning.

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2.2. Plasma treatment of ECPE fabrics

Ammonia plasma treatments were carried out for selected times in a Plasmaprep 500XP plasma reactor. The plasma was generated by a 13.56 MHz capacitively coupled discharge in a cylindrical chamber 23 cm long by 21 cm wide. The samples were mounted on a Perspex® rack in the chamber, which was evacuated to a pressure of 10^{-4} torr (1torr = 1.333×10^2 Pa) prior to the admission of the gas. A reactor power of 100 W, a pressure of 0.25 torr and a gas flow rate of 20 standard $cm^3 min^{-1}$ were used for the plasma treatment. Following plasma treatment, the samples were left in flowing gas for 15 min before the chamber was evacuated and air admitted, in order to allow for the decay of residual surface radicals.

2.3. Surface characterization of plasma-treated fabrics

Plasma treatment in ammonia results in the incorporation of amine groups on to the ECPE fibre surfaces. The surface concentration was measured by dye assay, using the azo-sulphonate dye Crocein Orange G (CI 15970, Sigma Chemicals C-3268) and the technique described by Allred [8]. Full details are given in Reference 7.

The number of surface amine groups per nm^2, N, is given by

$$N = \frac{6.023C}{MWA} \quad (1)$$

where M is the molecular weight of the dye, W is the weight of the fabric sample (g), C is the dye concentration (p.p.m.) in a 10 cm^3 sample, and A is the specific surface area of the fibre ($m^2 g^{-1}$). The specific surface area was calculated to be 0.137 $m^2 g^{-1}$ for the 30 μm fibres (density 0.97 $g cm^{-3}$).

2.4. ECPE/epoxy composite fabrication

ECPE/epoxy composites were fabricated using untreated, corona-treated and ammonia plasma-treated fabrics with the diglycidyl ether of bisphenol A (DGEBA) (Epon 828) and diaminodiphenyl methane (DDM) [9]. The fabric was impregnated by passing 250 mm × 100 mm samples through a solution containing 120 g DGEBA, 32.4 g DDM and 234 g methyl ethyl ketone. The solvent was removed by initial evaporation at room temperature for 30 min and then at 80 °C for a further 15 min. The composites were cured for 2 h at 80 °C and 2 h at 120 °C at a pressure of 350 kPa. The matrix content was nominally 34% by weight. Individual values are listed in Tables I–III.

TABLE I Matrix content and interlaminar properties of ECPE/epoxy composites

Surface treatment	Matrix content (wt %)	Interlaminar shear strength (MPa)	Interlaminar fracture energy ($J m^{-2}$)
None	34.6	5.7 ± 0.3 (9 samples)	241 ± 33 (6 samples)
Ammonia plasma (1 min)	37.9	11.1 ± 0.3 (6 samples)	313 ± 27 (5 samples)
Ammonia plasma (2 min)	37.6	11.8 ± 0.6 (5 samples)	415 ± 57 (4 samples)
Ammonia plasma (10 min)	35.4	11.8 ± 1.9 (5 samples)	379 ± 64 (4 samples)
Corona discharge	35.2	7.0 ± 0.8 (5 samples)	272 ± 47 (4 samples)

2.5. Interlaminar shear strength

The interlaminar shear strength was measured using the short-beam shear method [10]. Specimen dimensions were nominally 60 mm × 10 mm × 10 mm (30 plies), with a span to depth ratio, L/d, of 4/1. The interlaminar shear strength, T, by the short-beam shear method is given by the expression

$$T = \frac{3P}{4bd} \quad (2)$$

where P is the breaking load, b is the beam width and d is the beam depth. Specimens were conditioned at 23 °C and 50% relative humidity for 24 h prior to testing using an Instron testing machine at a crosshead speed of 1 mm min^{-1}.

2.6. Interlaminar fracture energy

The opening mode (mode I) interlaminar fracture energy, G_{Ic}, was determined by the compliance

TABLE II Matrix content and flexural properties of ECPE/epoxy composites

Surface treatment	Matrix content (wt %)	Flexural modulus (GPa)	Flexural strength (MPa)
None	35.0	1.34 ± 0.14	33.4 ± 0.6
Ammonia plasma (1 min)	35.0	5.06 ± 0.17	62.9 ± 2.7
Ammonia plasma (2 min)	34.4	4.81 ± 0.44	67.4 ± 2.5
Ammonia plasma (10 min)	35.5	5.04 ± 0.22	67.7 ± 3.4
Corona discharge	32.4	4.60 ± 0.31	51.7 ± 1.5

TABLE III Ballistic impact properties of ECPE/epoxy composites

Surface treatment	Matrix content (wt %)	Areal density ($kg m^{-2}$)	V_{50} ballistic limit ($m s^{-1}$)	V_{50}/areal density ($ms^{-1} kg^{-1} m^2$)
None	33.7	6.24	428 ± 12	68.6
Ammonia plasma (1 min)	30.8	5.98	368 ± 13	61.5
Ammonia plasma (2 min)	32.8	6.15	366 ± 10	59.5
Ammonia plasma (10 min)	32.8	6.16	331 ± 8	53.7
Corona discharge	31.4	5.94	371 ± 7	62.5

method using double cantilever beam (DCB) test specimen geometry [11, 12]. Beam specimens of dimensions 57 mm × 14.5 mm × 10 mm containing mid-ply starter cracks at one end were cut from composite panels. The starter cracks were produced by partially inserting a 0.075 mm thick layer of Teflon film between the mid-plies during composite lay-up. A transverse tensile load was applied at the beam end containing the starter crack through *P*-shaped aluminium plates bonded adhesively to the upper and lower composite surfaces. The load-point crack opening displacement (COD) was recorded using an extensometer with a gauge length of 5 mm.

The general expression for G_{Ic} is

$$G_{Ic} = \frac{P_c^2}{2b}\frac{dC}{da} \quad (3)$$

where P_c is the load required to extend a crack of length a (from the load line) in a specimen of thickness b, and C is the specimen compliance. Specimens with various length starter cracks were loaded elastically and C was obtained from the load, P, versus COD curves. Crack length measurements were made from the line of load application which, with P-shaped end-tabs, coincides with the specimen end for small displacements. The relationship between C and a was found to be most accurately represented by an nth order power curve, with powers in the range 2.0–2.5.

The crack was extended by a few millimetres in each of a series of loading/unloading cycles, and measured using a travelling microscope. The load at which crack advancement was observed was taken as P_c, which was determined for each new value of a. Values of G_{Ic} were then calculated from Equation 3 and averaged over all except the initial crack growth cycles.

2.7. Flexural properties

The flexural modulus and flexural strength of the composites were determined in accordance with standard flexure test procedures [13] using a four-point loading system with a load span equal to one-third of the support span. Modulus specimens with nominal dimensions 300 mm × 10 mm × 4 mm (12 plies) were tested using a support span of 240 mm at a speed of 5 mm min^{-1}.

The tangent modulus of elasticity, E_B, was calculated from the relationship

$$E_B = 0.21\frac{L^3 m}{bd^3} \quad (4)$$

where L is the length of the support span, m is the slope of the initial linear portion of the load–deflection curve, b is the specimen width and d is the specimen thickness.

Flexural strength specimens of nominal dimensions 80 mm × 10 mm × 4 mm were tested using a support span of 64 mm and a load span of 21.3 mm at a speed of 5 mm min^{-1}. Under these conditions the flexural strength is given by

$$S = \frac{PL}{bd^2} \quad (5)$$

where P is the load at failure, and L, b and d are defined as for Equation 4. Equation 5 is valid for fibre strains up to 5%. The deflection (at midpoint) D, at which the fibre strain is 5% is given by setting r equal to 0.05 in the equation

$$D = 0.21\frac{rL^2}{d} \quad (6)$$

2.8. Ballistic properties

The transverse ballistic impact properties were determined using the Materials Research Laboratory gas-gun facility [14] and 17 grain fragment-simulating projectiles [15]. The V_{50} data (projectile velocity at which the probability of target penetration is 50%) were determined according to the procedures of MIL-STD-662 E [16].

2.9. Fracture surface examination

The fracture surfaces were coated with gold, and were examined in a Cambridge S250 Stereo-scan Mark 2 scanning electron microscope (SEM) using secondary electrons.

3. Results and discussion

3.1. Plasma surface amination of ECPE fabrics

Untreated ECPE fabric was plasma-treated in ammonia for times ranging from 0.25–20 min. The number of amine groups incorporated on to the fibre surface was determined as a function of time using the dye assay technique described above. The results are plotted in Fig. 1. Whereas for aramid fabrics the number of amine groups reaches a limiting value of about 0.4 groups/nm^2 after a treatment time of 30 s [6], the degree of surface amination of ECPE continues to increase, although the rate of increase appears to decrease with time. The difference between aramids and ECPE is probably due to the greater number of sites on ECPE to which an amine can be grafted. Fibres treated for 1 min (0.49 amine groups/nm^2), 2 min (0.83 amine groups/nm^2) and 10 min (1.75 amine groups/nm^2), were chosen for composite fabrication.

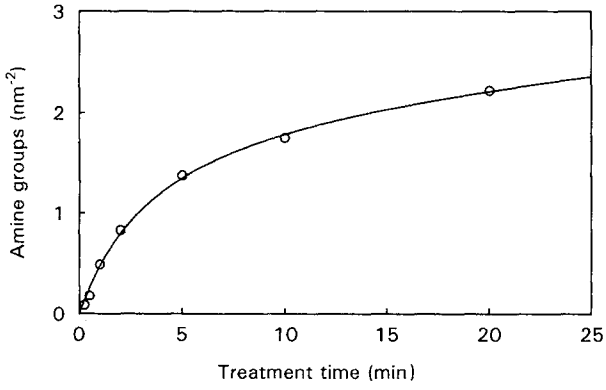

Figure 1 Degree of fibre surface amination as a function of treatment time in ammonia plasma for ECPE fibres (13.56 MHz, 100 W, 0.25 torr, 20 standard cm^3 min^{-1} gas flow).

3.2. Interlaminar shear strength

The interlaminar shear strengths of the composites made with untreated, plasma-treated, and corona-treated ECPE fabrics are presented in Table I. These results indicate that there is a substantial improvement in interlaminar shear strength when the fabric is treated in an ammonia plasma prior to composite fabrication (95% after 1 min). The most interesting feature of these results is that the improvement is not significantly increased by longer treatment times, although the degree of surface amination continues to increase up to at least 20 min plasma treatment (Fig. 1). This improvement in interlaminar shear strength is greater than that obtained by corona treatment (23%), and is consistent with increased fibre/matrix adhesion due to chemical bonding between the amine groups on the ECPE fibre surface and the epoxy resin, although direct evidence for chemical bonding is difficult to obtain. The increase in composite interlaminar shear strength after fibre treatment in a corona discharge probably arises from the increased wettability associated with oxygen-containing functional groups on the fibre surface. Similar results have been obtained by Kaplan *et al.* [3] for woven ECPE/epoxy composites containing untreated, corona-treated and oxygen-containing gas plasma-treated fibres, although for melt-spun polyethylene/epoxy composites, Ladizesky and Ward [2] have reported significantly larger interlaminar shear strengths for both untreated and oxygen plasma-treated material.

The fracture surfaces (Fig. 2) show that the limit to any improvement in composite shear strength appears to be related to the inherent shear strength of the fibres. Failure in the specimen containing 10 min plasma-treated ECPE has clearly occurred within the fibres, whereas failure has occurred at the interface of the untreated specimen and mainly at the interface in the 1 min plasma-treated specimen. Thus, increasing the treatment time increases the surface amine concentration and the interlaminar shear strength until the latter is greater than the inherent shear strength of the fibres, after which the fibres commence to fail internally.

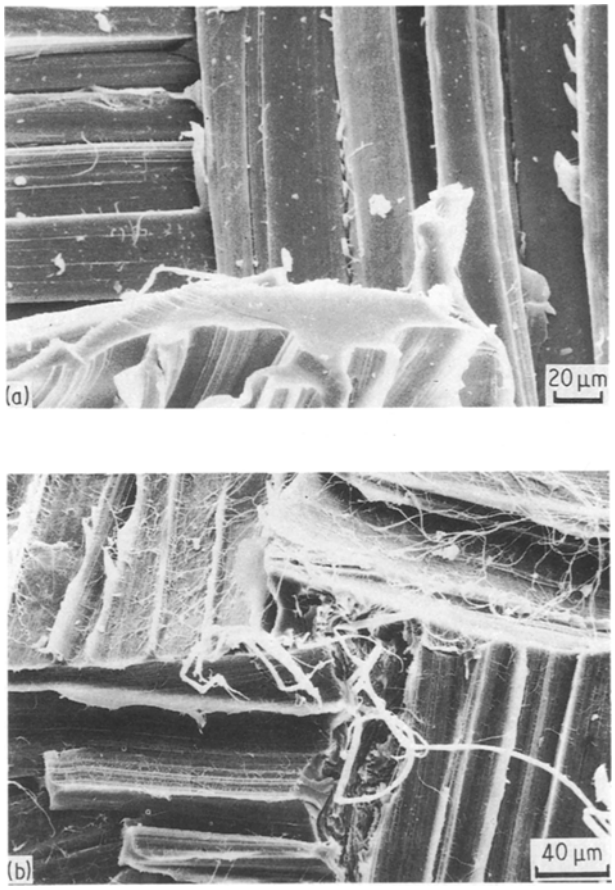

Figure 2 Interlaminar shear fracture surfaces of ECPE/epoxy composites made from (a) 1 min ammonia plasma-treated fibres, showing failure at the fibre/matrix interface, and (b) 10 min ammonia plasma-treated fibres, showing internal shearing of the fibres.

3.3. Interlaminar fracture energy

The G_{Ic} values of the ECPE/epoxy composites are also presented in Table I. The results indicate that ammonia plasma treatment of the ECPE fibres yields substantial increases in G_{Ic} of the composite (30% after 1 min and 72% after 2 min), while corona discharge treatment increases G_{Ic} by 13%. A plasma-treatment time in excess of 2 min does not result in any further increase in G_{Ic}. The effect of plasma treatment on G_{Ic} shows a similar trend to the interlaminar shear results, i.e. any property improvement occurs within a short treatment time (interlaminar shear, 1 min; G_{Ic}, 2 min) even though fibre surface amination continues to increase with longer treatment times. It should be noted that the experimental error in determining G_{Ic} is generally larger than for interlaminar shear measurements (Table I). The interlaminar tensile fracture surfaces (Fig. 3) show evidence of the effect of plasma treatment on the fibre/matrix interface strength. With untreated ECPE the composite has failed at the fibre/matrix interface, while with 2 min ammonia plasma-treated ECPE the composite has failed both at the interface and in the matrix.

These results are in contrast to those obtained previously for aramid/epoxy composites [7], which showed no significant change in G_{Ic} after fibre surface modification in an ammonia plasma. Fracture surfaces of aramid/epoxy DCB test specimens showed that for both untreated and ammonia plasma-treated fibre composites, failure occurred predominantly in the matrix, with only small areas of fibre/matrix separation. However, for ECPE/epoxy composites, plasma treatment did change the fracture mode. For untreated ECPE/epoxy composites, G_{Ic} is not governed by the matrix resin properties but is to a large extent determined by the very weak interfacial properties. The increase in G_{Ic} in plasma-treated fibre composites is attributed to a higher interfacial strength as indicated by the change in failure mode from exclusively interfacial to a mixture of matrix failure and fibre/matrix separation.

3.4. Flexural properties

The flexural modulus and strength of ECPE/epoxy composites are presented in Table II. These results

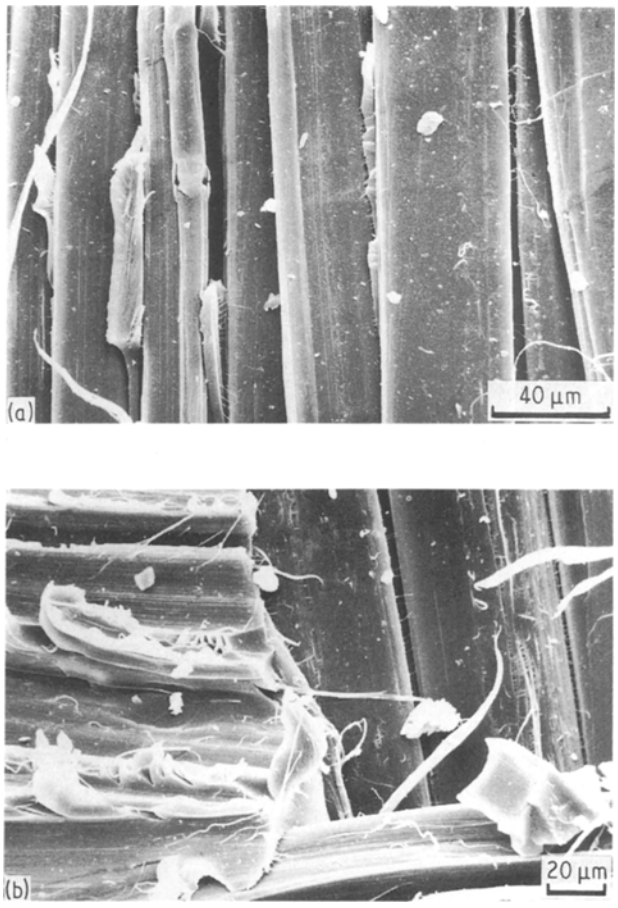

Figure 3 Interlaminar tensile fracture surfaces of ECPE/epoxy composites made from (a) untreated fibres, showing clean fibre/matrix separation, and (b) 2 min ammonia plasma-treated fibres, showing additional matrix fracture.

show that plasma surface treatment increases the flexural modulus by approximately 250% and the flexural strength by approximately 100%. The increase in flexural modulus appears to be slightly larger than that for composites made from corona-treated material, and is also independent of treatment time. It is generally accepted that the tensile and compressive properties of the fibre and matrix, rather than the interfacial properties, are the major contributing factors to the flexural modulus of composite materials. In previous work [7] we found that surface treatment of aramid fibres had no significant effect on the flexural modulus of aramid/epoxy composites. However, increases in the flexural modulus as well as flexural strength of ECPE/epoxy composites with fibre surface treatment have also been reported by other authors [3, 6]. In particular, Kaplan *et al.* [3] found that the increase in flexural modulus with surface treatment was greater with composites made from woven fabrics than with unidirectional composites, and that an unspecified (presumably oxygen or oxygen-containing gas mixture) plasma treatment gave a significantly higher flexural modulus than did corona treatment. One major difference between aramid and ECPE fibres is the very low surface energy of the latter, which makes it very difficult to obtain good wet-out of the untreated fibres by an epoxy resin. This may allow a higher void content in the cured composite, with a consequently adverse effect on the flexural properties.

The factors contributing to flexural strength are not easy to quantify. In general, flexural failure is a complex process in which tensile, compressive and shear failure modes may be induced to varying degrees in each of the composite phases. In composites made from untreated fibres, no catastrophic flexural failure was observed, and the results presented in Table II were obtained using loads corresponding to a maximum fibre strain of 5% (Equation 6). A typical trace is shown in Fig. 4a. The composites made from surface-treated fibres all exhibited maximum loads at a fibre strain of about 5% (Fig. 4b). All of the specimens showed compressive failure but tensile failure was not observed. The improvement after fibre treatment is attributed to a decrease in compressive fibre buckling and debonding resulting from a stronger fibre/matrix interfacial bond.

The lack of dependence of both flexural modulus and flexural strength on the plasma treatment time mirrors the results found for the interlaminar shear strength and fracture energy, and is probably a result of other mechanisms dominating failure once the fibre/matrix interface has acquired an adequate strength.

3.5. Ballistic properties

Table III gives the V_{50} ballistic impact properties of 12 ply ECPE/epoxy composites (nominal areal density 6.1 $kg\,m^{-2}$ containing untreated, ammonia plasma-treated and corona-treated fibres. For composites containing nominally 32.3% by weight resin, the ballistic performance against 17 grain fragment-simulating projectiles decreases by 10.5%, 13.3% and 21.7% for plasma treatment times of 1, 2 and 10 min, respectively. The commercial corona fibre treatment results in a 9% decrease in ballistic performance.

These results are consistent with previous work which shows that composite ballistic performance is enhanced by a reduction in interfacial properties which allows higher energy absorption via fibre debonding and delamination, and conversely is lowered by an increase in fibre/matrix adhesion and hence

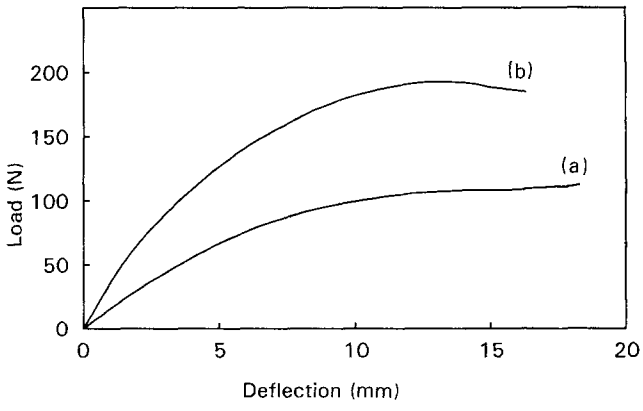

Figure 4 Plot of flexural load as a function of beam deflection for ECPE/epoxy composites made from (a) untreated fibres and (b) ammonia plasma-treated fibres.

composite mechanical properties [17, 18]. These results and previous directly comparable results for aramid/epoxy composites [7] further illustrate that on a weight basis, the ballistic properties of ECPE composites are substantially higher than those of aramid composites for the specified test conditions.

4. Conclusions

Ammonia plasma treatment of ECPE fibre surfaces results in increases in the interlaminar shear strength and fracture energy, as well as flexural properties, and decreases in the ballistic impact properties of ECPE/epoxy composites. These changes are related to the introduction of surface amine groups which enhance the bonding between the fibres and the epoxy matrix, resulting in changes in the interlaminar failure mechanisms. The interlaminar tensile and shear results are in accord with microscopic examinations of fracture surfaces which show clean fibre/matrix separation in the untreated fibre composites and additional evidence of fibre and matrix failure in composites containing treated fibres.

Acknowledgements

The authors thank Dr G.A. George for the X-ray photoelectron spectra of the untreated ECPE fibres, and Dr S. Bandyopadhyay for assistance in obtaining the fracture surface micrographs.

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Received 21 January
and accepted 7 June 1991