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Plasma surface modification of advanced organic fibres

Part III *Effects on the mechanical properties of aramid/vinylester and extended-chain polyethylene/vinylester composites*

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Aramid and extended-chain polyethylene fibres have been treated in ammonia and oxygen plasmas in order to enhance adhesion to vinylester resins and thereby improve fibre/resin interfacial properties in composites made from these materials. For both aramid/vinylester and extended-chain polyethylene/vinylester composites, the plasma treatments result in significant improvements in interlaminar shear strength and flexural strength. Extended-chain polyethylene/vinylester composites also exhibit increased flexural modulus. Scanning electron and optical microscopic observations have been used to examine the microscopic basis for these results, which are compared with results previously obtained for aramid/epoxy and extended-chain polyethylene/epoxy composites. It is concluded that the increased interlaminar shear and flexural properties of vinylester matrix composites are due to improved wetting of the surface-treated fibres by the vinylester resin, rather than covalent chemical bonding.

1. Introduction

In the quest for stronger, more durable fibre-reinforced polymer composites, much attention has been focused on developing new matrix resin systems, improving existing matrix resins and increasing fibre/matrix interfacial adhesion through fibre-surface modification. Improvements in interlaminar properties of glass and carbon fibre-reinforced composites have been achieved with silane or titanate coupling agents [1, 2] and oxidative treatments [3], respectively. However, composites containing aramid or extended-chain polyethylene fibres do not achieve the levels of fibre/matrix adhesion reached by those containing carbon or glass fibres.

Attempts to improve fibre/matrix interfacial adhesion in aramid/epoxy composites have been centred on the modification of the aramid fibre surface by wet chemical or gas plasma techniques. Although earlier work resulted in mixed success [4–8], the picture emerging after recent innovative work using wet chemical techniques is one of substantial improvements in fibre/matrix interfacial adhesion following incorporation of pendent amine-terminated or epoxide-terminated groups on to the fibre surface [9–11]. These pendent groups are attached either to the aromatic rings [9, 10] or to the amide nitrogen [11] of the aramid chains. We have also achieved substantial improvements in interlaminar shear strength, as well as flexural strength, of woven aramid/epoxy composites by grafting amine groups on to the fibre surface using plasma treatment [12], thereby confirming the results of earlier studies by Stoller and Allred [7]. Despite the apparent chemical specificity of the improvements in fibre/matrix adhesion, however, it is still not clear whether the improvements result from covalent chemical bonding between the modified aramid fibres and the epoxy matrix [9, 10], or from increases in fibre wettability following fibre surface treatment or other mechanisms such as hydrogen bonding [11].

Extended-chain polyethylene (ECPE) fibre-reinforced composites are characterized by very poor fibre/matrix interfacial adhesion [13], due to the very low surface energy of ECPE fibres (dispersive component 36–46 $mN\,m^{-1}$ depending on draw ratio [14], compared to 65 $mN\,m^{-1}$ for aramid fibres cleaned by Soxhlet extraction in acetone [15]), and the consequent poor wetting of the fibres by organic resins. Significant improvements in interlaminar properties of ECPE/epoxy composites have been reported following oxidative treatments (chemical oxidants, corona discharge or oxygen plasma treatment) of the fibre, which increase the polarity of the fibre surface [13, 15–19]. The improvements in these cases are assumed to result mainly from the increased wettability of the fibres by the resin. We have shown that the interlaminar shear strength, flexural strength and flexural modulus of woven ECPE/epoxy composites

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are substantially increased following ammonia plasma treatment of the fibres [13], and have attributed these increases to covalent chemical bonding between the amine groups on the fibre surface and the epoxy matrix.

There has been relatively little work undertaken on interfacial adhesion between aramid or ECPE fibres and other resin systems, such as polyesters and vinylesters, which are cured by free radical addition polymerization. As for ECPE/epoxy composites, the simplest approach to improving fibre/matrix adhesion in these systems is to introduce polar groups on to the fibre surface to enhance fibre wettability by the resin. Another approach is to try to induce covalent chemical bonding between the fibre and the addition polymerizable matrix by the introduction of specific chemical groups. Thus, for example, a free radical initiator such as a peroxide radical, may be introduced on to the fibre surface [20], or alternatively, vinyl functionalities grafted on to the fibre surface; each may become involved in the addition polymerization, thereby forming a direct chemical bond between the fibre and the matrix.

In this work, we investigate the effect of ammonia plasma and oxygen plasma treatment of aramid and ECPE fibres, and the effect of commercial corona treatment of ECPE fibres in air, on the interlaminar shear and flexural properties of aramid/vinylester and ECPE/vinylester composites. We also explore the relationship between the chemistry of the treated fibre surfaces and the microscopic aspects of composite failure, and compare the results for vinylester matrix composites with those previously obtained for epoxy matrix composites.

2. Experimental procedure

2.1. Aramid and ECPE fabrics

Aramid fabric (Kevlar® 49, style 352, 1150 denier), was woven and scoured by Clark-Schwebel Fiber Glass Corporation. The fabric was cleaned by Soxhlet extraction in water and then acetone, and dried for 24 h at 105 °C before further use. Untreated ECPE fabric and fabric which had been corona-treated in air (Spectra® 1000, 650 denier) were used without cleaning.

2.2. Plasma surface treatment of fabrics

Plasma treatments were carried out with ammonia or oxygen 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 and 21 cm diameter using a reactor power of 100 W, a pressure of 0.25 torr (1 torr = 1.333×10^2 Pa) and a gas flow rate of 20 standard $\text{cm}^3\,\text{min}^{-1}$. Fabric samples, 20 cm × 40 cm, were mounted on a Perspex® rack in the chamber, which was evacuated to a pressure of 10^{-4} torr prior to the admission of the gas. After plasma treatment, the samples were left in flowing gas for 15 min before the chamber was evacuated and air admitted.

2.3. Characterization of plasma-treated fabrics

Plasma treatment in ammonia results in the incorporation of amine groups on to the fibre surface. The surface concentration was measured by dye assay, using the technique described previously [12]. The effect of oxygen plasma or corona treatment of the fibre surface is less easy to quantify. XPS studies of ECPE fibres [21] before and after surface treatment in oxygen plasma or corona discharge show that various oxygen species, including alcohol/ether, aldehyde/ketone and ester functionalities, are grafted on to the fibre surface, and that oxygen plasma treatment tends to generate a more highly oxidized surface than does corona treatment.

2.4. Composite fabrication

Aramid and ECPE composites were fabricated from both untreated and treated materials using Derakane® 8084 vinylester resin with 0.3% cobalt naphthenate (6% active) as the promoter and 1.5% methyl ethyl ketone peroxide as the initiator. This formulation has a gel time of approximately 40 min at 23 °C. Each fabric ply was impregnated with resin and 20 ply (aramid), 12 and 30 ply (ECPE) composites were then cured in an autoclave for 1 h at 40 °C and 1 h at 80 °C at a pressure of 350 kPa. The matrix content was nominally 32% for the aramid composites and 34% for the ECPE composites. Individual values are given in Tables I and II.

2.5. Interlaminar shear strength

The interlaminar shear strength of the aramid/vinylester composites was determined using the four-point shear test method of Browning *et al.* [22]. Specimens were of nominal dimensions 50 mm × 10 mm × 4 mm (20 plies), with a support span/depth (L/d) ratio of 11.5 and a load span of half the support span. The interlaminar shear strength of the ECPE/vinylester composites was measured using the short-beam shear method [23]. Specimen dimensions were nominally 60 mm × 10 mm × 10 mm (30 plies), with L/d of 4/1. 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 2 $\text{mm}\,\text{min}^{-1}$ (aramid) or 1 $\text{mm}\,\text{min}^{-1}$ (ECPE).

The interlaminar shear strength, T, by both the four-point and the short-beam shear methods is given by the expression

$$T = \frac{3P}{4bd} \qquad (1)$$

where P is the breaking load, b is the beam width and d is the beam depth.

2.6. Flexural properties

The flexural modulus and flexural strength of the composites were determined in accordance with standard flexure test procedures [24] using, for ECPE specimens, a four-point loading system with a load span equal to one-third of the support span, and for aramid specimens a three-point loading system and L/d ratios recommended by Zweben *et al.* [25]. Aramid and ECPE modulus specimens of nominal dimensions 300 mm × 10 mm × 4 mm (20 plies aramid, 12 plies ECPE) with L/d of 60 were tested at 20 mm min^{-1}. Aramid strength specimens of nominal dimensions 150 mm × 10 mm × 4 mm with L/d of 32 were tested to failure at a speed of 5 mm min^{-1}. ECPE strength specimens of nominal dimensions 80 mm × 10 mm × 4 mm with L/d of 16 were tested to failure at a speed of 2 mm min^{-1}.

The flexural modulus (tangent modulus of elasticity), E_B, and the flexural strength, S, were calculated from the relationships

$$E_B = k_1 \frac{L^3 m}{bd^3} \quad (2)$$

$$S = k_2 \frac{PL}{bd^2} \quad (3)$$

where L is the length of the support span, m is the slope of the initial linear portion of the load–deflection curve, $k_1 = 0.25$ and $k_2 = 1.5$ for the three-point method and $k_1 = 0.21$ and $k_2 = 1$ for the four-point method and P, b and d are defined as above.

2.7. 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. Aramid/vinylester composites

The interlaminar shear strength of the aramid/vinylester composites was calculated using Equation 1. The results presented in Table I show that both oxygen and ammonia plasma treatment of the aramid fibres give rise to increases of about 50% in composite interlaminar shear strength. The plasma treatments also result in a change in shear failure mechanism, as shown by the fracture surfaces in Fig. 1. With untreated fibres, the composite has failed at the fibre/matrix interface, with virtually no fibre fibrillation or matrix cracking (Fig. 1a). However, with ammonia or oxygen plasma-treated fibres, there is considerable evidence of fibre fibrillation (Fig. 1b) and matrix cracking (Fig. 1c), indicating that fibre/matrix interfacial failure is no longer the dominant failure mode.

The flexural properties of the aramid/vinylester composites, calculated using Equations 2 and 3, are also reported in Table I. The flexural modulus is unchanged by the plasma treatment, as was observed for aramid/epoxy composites [12] (Table I), confirming that the interfacial properties are not a major factor in determining flexural modulus in these composites. The flexural strength, however, is increased by more than 50%. Within the error bounds, there is no significant difference in flexural strength between composites made from ammonia and oxygen plasma-treated fibres. This result is consistent with the interlaminar shear results.

The increases in interlaminar shear and flexural strength following plasma treatment of the fibres are consistent with an increase in fibre/matrix interfacial adhesion. Optical microscopic examination of failure modes in flexural test specimens from untreated and plasma-treated fibres shows that the increase in flexural strength results from a reduction in compressive fibre buckling as the composite is flexed, which is due to increased fibre/matrix interfacial bonding. Because the two plasma treatments result in the incorporation of different chemical species on to the fibre surface, the similarity of the increase in interlaminar shear strength indicates that the improved fibre/matrix adhesion is probably not due to specific chemical bonding; the plasma treatments increase the wettability of the aramid fibres by the vinylester resin, and covalent chemical bonding does not appear to be important. This situation can be compared with that for aramid/epoxy composites [12]. Table I shows that the increases in interlaminar shear and flexural strength of aramid/vinylester composites after fibre treatment in an ammonia plasma are comparable to those in aramid/epoxy composites after similar fibre treatment. These results suggest that the strengths of the aramid/epoxy composites are enhanced more by increased fibre wettability than by covalent chemical bonding. However, the growing body of evidence that fibre surface amine groups do react with epoxide groups in epoxy resins [9–11] cannot be discounted. Kalantar and Drzal [26] have postulated the existence of a cohesive weak boundary layer on aramid fibres. If this postulate is correct, then any covalent chemical

TABLE I Matrix content of aramid/vinylester composites and comparison of the mechanical properties of aramid/vinylester and aramid/epoxy composites[a]

Surface treatment	Matrix content (wt %)	Interlaminar shear strength (MPa)	Flexural modulus (GPa)	Flexural strength (MPa)
None	32.4	20.7 ± 0.2 (24.2 ± 0.4)	32.5 ± 0.8 (31.0 ± 0.7)	253 ± 9 (305 ± 16)
Oxygen plasma (2 min)	32.1	31.3 ± 1.5	32.2 ± 0.6	419 ± 33
Ammonia plasma (5 min)	33.0	31.2 ± 0.9 (33.2 ± 1.2)	32.2 ± 0.6 (32.5 ± 0.8)	382 ± 19 (442 ± 18)

[a] Values in parentheses are taken from [12].

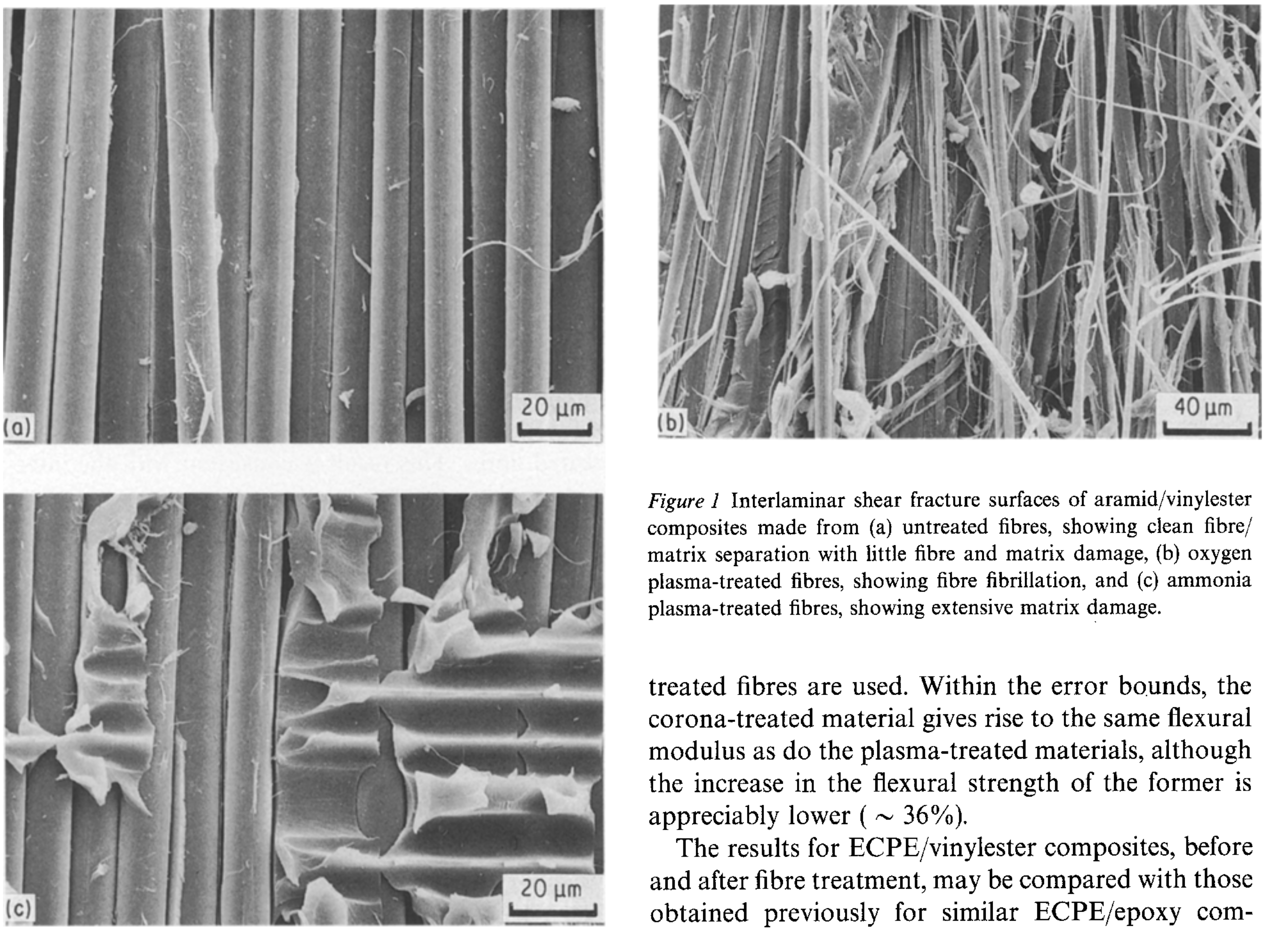


Figure 1 Interlaminar shear fracture surfaces of aramid/vinylester composites made from (a) untreated fibres, showing clean fibre/matrix separation with little fibre and matrix damage, (b) oxygen plasma-treated fibres, showing fibre fibrillation, and (c) ammonia plasma-treated fibres, showing extensive matrix damage.

bonding between fibre and epoxy matrix might be masked by cohesive fibre failure, which may be the limiting factor in improving interfacial properties. Therefore, although it may be concluded from the similar increases in mechanical properties of aramid/vinylester and aramid/epoxy composites that property enhancements are due mainly to non-specific interactions, covalent chemical bonding between surface amine groups and the epoxy matrix remain a possibility.

3.2. ECPE/vinylester composites

The interlaminar shear and flexural results for ECPE/vinylester composites are presented in Table II. The interlaminar shear strength more than doubles after a 2 min oxygen or ammonia plasma treatment of the fibres, and increases by ~ 70% for composites containing corona-treated fibre. Interlaminar shear fracture surfaces (Fig. 2) provide clear evidence that the increased shear strength is related to a change in failure mode from interfacial failure to fibre fibrillation. The lower result for corona-treated material is also reflected in the fracture surfaces. At higher magnifications, it is evident that the degree of fibre damage is lower than that for plasma-treated fibres. This may be attributed, in the case of the oxygen treatment, to the higher level of fibre surface oxidation caused by the plasma [21].

The flexural modulus and flexural strength of ECPE/vinylester composites exhibit increases of about 85% and 70%, respectively, when plasma-treated fibres are used. Within the error bounds, the corona-treated material gives rise to the same flexural modulus as do the plasma-treated materials, although the increase in the flexural strength of the former is appreciably lower (~ 36%).

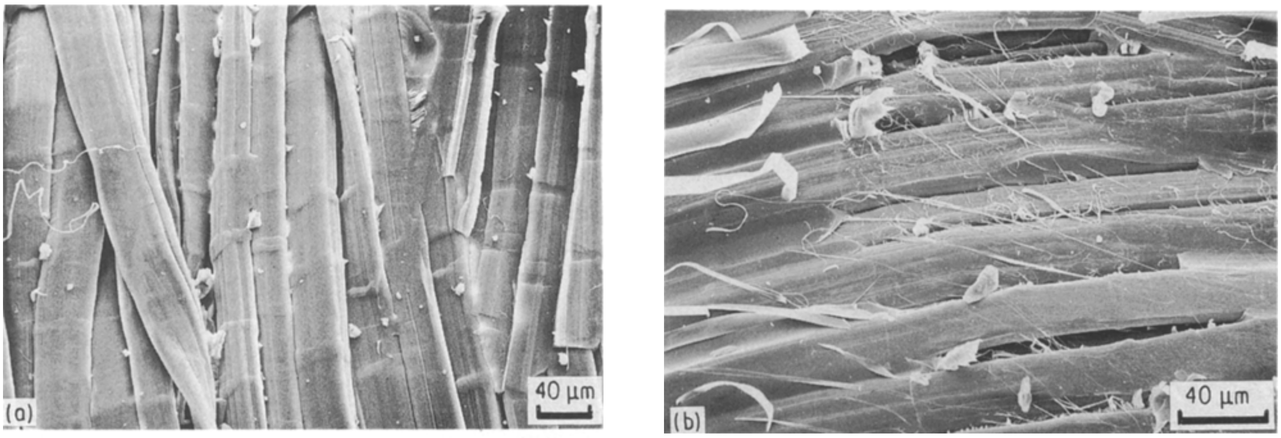
The results for ECPE/vinylester composites, before and after fibre treatment, may be compared with those obtained previously for similar ECPE/epoxy composites under the same test conditions [13] (also given in Table II). The most salient feature of the results is that ECPE/epoxy composites containing ammonia plasma-treated fibres have by far the highest interlaminar shear strength. This result is clearly related to the overall level of fibre/matrix interfacial adhesion in these composites. We believe that the mechanism for improved fibre/matrix adhesion is covalent chemical bonding between the ammonia plasma-treated fibres and the matrix, and that the level of increase in shear strength is limited by the internal strength of the fibres [13, 21]. For ECPE/epoxy composites made from oxygen plasma-treated or corona-treated fibres, the interlaminar shear strength is approximately the same as that for ECPE/vinylester composites made from corona or plasma-treated fibres. These results give credence to our previous contention [13] that there is covalent chemical bonding between surface amine groups on ammonia plasma-treated ECPE and epoxy resin. Chemical bonds are not formed between surface amine groups and vinylester resins, or between surface oxygen species and epoxy or vinylester resins. In these cases, the improvements in interlaminar shear strength are all comparable and are attributed to an increase in fibre/matrix interfacial strength arising from non-covalent chemical interactions. We believe that if covalent chemical bonding could be induced between surface modified ECPE fibres and a vinylester resin, then interlaminar shear values similar to those obtained for ammonia plasma-treated ECPE/epoxy composites could be achieved.

It is generally accepted that the tensile and compressive properties of the fibre and matrix, rather than the interfacial properties, are the major contributing

TABLE II Matrix content of ECPE/vinylester composites and comparison of the mechanical properties of ECPE/vinylester and ECPE/epoxy composites[a]

Surface treatment	Matrix content (wt %)	Interlaminar shear strength (MPa)	Flexural modulus (GPa)	Flexural strength (MPa)
None	33.2[b], 36.8[c]	3.2 ± 0.1 (5.7 ± 0.3)	3.0 ± 0.5 (1.34 ± 0.14)	31.9 ± 1.9 (33.4 ± 0.6)
Corona	31.6[b], 34.4[c]	5.4 ± 0.4 (7.0 ± 0.8)	6.1 ± 0.4 (4.60 ± 0.31)	43.3 ± 2.6 (51.7 ± 1.5)
Oxygen plasma (2 min)	35.3[b], 35.2[c]	6.9 ± 0.7 (6.6 ± 0.6)[d]	5.5 ± 0.3	58.5 ± 3.4
Ammonia plasma (2 min)	33.6[b], 35.3[c]	6.4 ± 0.8 (11.8 ± 0.6)	5.6 ± 0.3 (4.81 ± 0.44)	53.9 ± 2.3 (67.4 ± 2.5)

[a] Values in parentheses are taken from [13].
[b] Interlaminar shear samples.
[c] Flexural samples.
[d] Taken from [21].



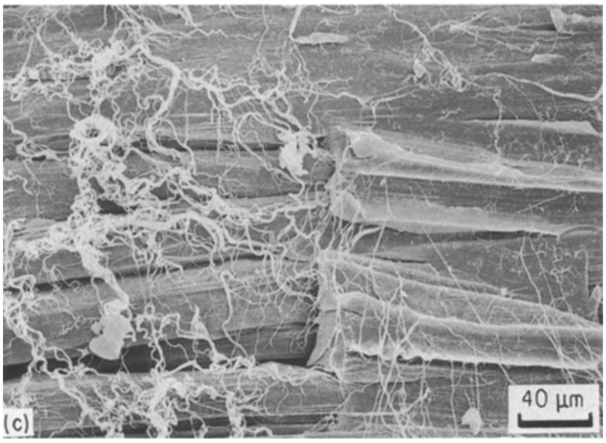


Figure 2 Interlaminar shear fracture surfaces of ECPE/vinylester composites made from (a) untreated fibres, showing clean fibre/matrix separation with very little fibre damage, (b) oxygen plasma-treated fibres and (c) ammonia plasma-treated fibres, both showing fibre fibrillation.

factors to the flexural modulus of composite materials. However, this is not the case for ECPE composites. The low flexural modulus relative to that of aramid composites and the dependence of the flexural modulus of ECPE composites on fibre surface treatment indicate that the interfacial properties and the very low surface energy of ECPE fibres make very significant contributions to the composite flexural modulus. The values for ECPE/vinylester composites are higher than those for the comparable ECPE/epoxy composites (Table II), in accord with the relative magnitudes of the flexural moduli of the matrix resins (Derakane® 8084 vinylester 3.03 GPa; Epon® 828/DDM epoxy 2.69 GPa). However, the very low flexural modulus of the untreated ECPE/epoxy composite relative to the untreated ECPE/vinylester composite cannot be explained. The flexural strengths of the ECPE/vinylester composites are broadly comparable to those found for ECPE/epoxy composites, and the increases after corona or plasma treatment of the ECPE are consistent with a reduction in compressive fibre buckling and debonding resulting from a stronger fibre/matrix interfacial bond.

4. Conclusions

The introduction of polar surface groups onto aramid and ECPE fibres improves the interlaminar shear strength and flexural strength of aramid/vinylester and ECPE/vinylester composites, and the flexural modulus of ECPE/vinylester composites. In the case of aramid/vinylester composites, this is attributed to non-specific interactions between the surface-modified fibres and the vinylester resin. The improvements are comparable to those found for aramid/epoxy composites using similar treatments, although with aramid/epoxy composites it is unclear whether this is due mainly to increased fibre wettability or to additional covalent chemical bonding and the effect of the latter is being negated by a weak cohesive boundary layer on the aramid fibres. For ECPE/vinylester composites, there is clear evidence that the improvements are the result of non-specific interactions between the plasma-treated fibres and the vinylester resin, which contribute to improved wet-out of the fibres by the resin. The numerical results are also consistent with changes in failure mechanisms as shown by fracture surface micrographs. The results of this study are consistent with those found earlier for aramid/epoxy and ECPE/epoxy composites, and in particular offer support for covalent chemical bonding between ammonia plasma-treated ECPE fibres and an epoxy resin.

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