

# Plasma surface modification of advanced organic fibres

## Part V *Effects on the mechanical properties of aramid/phenolic composites*

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Aramid fibres have been treated in ammonia and oxygen plasma to enhance adhesion to resole phenolic resins. The plasma treatments resulted in significant improvements in interlaminar shear strength (ILSS) and flexural strength of composites made from these materials. Composites containing aramid fibres with epoxide groups reacted on to the ammonia plasma-treated fibre surface also showed further improvements in ILSS and flexural strength. Scanning electron and optical microscopic observations were used to examine the microscopic basis for these results, which have been compared with those obtained previously for aramid/epoxy and aramid/vinyl ester composites. For composites containing oxygen and ammonia plasma-treated fibres, the enhanced ILSS and flexural strength are attributed to improved wetting of the surface-treated aramid fibres by the phenolic resin. However, for those containing fibres with reacted epoxide groups on the ammonia plasma-treated fibre surfaces, the enhanced composite properties may be due to covalent chemical interfacial bonding between the epoxide groups and the phenolic resin. Effects of catalyst levels and cure cycle on the ILSS of composites laminated with untreated fabric has also been examined and optimum values have been determined. The catalyst concentration has an influence on the phase-separated water domain density in the matrix which in turn, affects the available fibre/matrix bonding area and hence the composite ILSS and flexural strength.

### 1. Introduction

The development of stronger, more durable and damage-tolerant fibre-reinforced composites has focused on new matrix systems, improved existing matrices and increased fibre/matrix interfacial adhesion through fibre surface modification and more matrix-compatible fibre surface finishes. Most attention has been paid to thermosetting polyester, vinyl ester and epoxy resins due to the good structural properties of composites fabricated from these resins. However, an increasing number of applications require composite materials to have fire-retardant properties. Recently, new resole phenolic resins have emerged [1, 2] that are curable by condensation reactions at low or ambient temperature and pressure by addition of acid catalysts, and are suitable for fabrication of glass and other advanced fibre composites by various techniques. Phenolic resin-based composites yield low levels of smoke and combustion products under both flaming and smouldering fire conditions and are superior in terms of other flammability properties to polyester, vinyl ester and epoxy-based composites [2–5]. Al-

though they have an inherent advantage of superior fire properties, resole phenolic resins also have some disadvantages, such as mechanical properties that are inferior to those of polyester, vinyl ester and epoxy materials, and incompatibility with reinforcing fibre surface finishes or sizes which, in the case of glass, have been developed for use with polyester and epoxy resins [6, 7]. The structural properties of phenolic resin-based composites are thus lower than those of composites based on polyester, vinyl ester and epoxy resins.

Improvements in composite structural properties may be achieved by modifying existing matrix resins, increasing fibre/matrix interfacial adhesion through fibre surface modifications and/or improving the matrix compatibility of the fibre surface finishes. Improvements in interlaminar properties of glass and carbon fibre-reinforced composites have been achieved with silane or titanate coupling agents [8, 9] and oxidative treatments [10], respectively. However, composites containing aramid or extended chain polyethylene (ECPE) fibres do not achieve the levels of

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fibre/matrix adhesion reached by those containing carbon or glass fibres. Improvements in fibre/matrix interfacial adhesion in aramid/epoxy composites have been achieved by modification of the aramid fibre surface by wet chemistry or gas plasma techniques. Although earlier work resulted in mixed success [11–15], more recent work has shown that substantial improvements in fibre/matrix interfacial adhesion can be achieved by incorporation of pendant amine-terminated or epoxide-terminated groups on to the fibre surface [16–18]. We have also achieved substantial improvements in interlaminar shear strength (ILSS) and flexural strength of woven aramid/epoxy and aramid/vinyl ester composites by grafting amine- and oxygen-containing groups on to the fibre surface using ammonia and oxygen plasma treatments [19, 20]. For aramid/epoxy composites, there is strong evidence that the increases in ILSS after ammonia plasma treatment of the fibres is a direct result of covalent chemical bonding between the fibre surface amine groups and the epoxy groups in the resin [21]. However, the improvements are limited by the morphology of the aramid fibres, and cohesive fibre failure seems to be the ultimate determinant of fibre/matrix adhesion. For aramid/vinyl ester composites, the introduction of polar surface groups on to the fibres by ammonia and oxygen plasma treatments improves their ILSS and flexural strength by comparable amounts to those for aramid/epoxy composites using similar treatments. In this case, however, the improvements are attributed to non-specific interactions between the surface-modified fibres and the vinyl ester resin, resulting in increased fibre wettability. The results are consistent with changes in composite failure mechanisms as shown by fracture surface micrographs [19, 20].

There has been relatively little work undertaken on interfacial adhesion between aramid fibres and resole phenolic resins. Using pull-out tests, Subramaniam *et al.* [22] showed that a zirconate coupling agent improves the ILSS of aramid/modified phenolic composites. In the current work, we have investigated the effect of ammonia and oxygen plasma treatments of aramid fibres, as well as the effect of incorporating an epoxide group on the aramid surface after ammonia plasma treatment, on the ILSS and flexural properties of aramid/phenolic composites. We have also explored the relationship between the chemistry of the treated fibre surfaces and the microscopic aspects of composite failure, and compared the results with those previously obtained for epoxy and vinyl ester matrix composites. In addition, the effects of variations in the aramid/phenolic composite cure cycle and catalyst levels on the ILSS and flexural properties have been determined.

## 2. Experimental procedure

### 2.1. Aramid fabric

The aramid fabric (Kevlar® 49, style 352, 1150 denier), woven and scoured by Clark–Schwebel Fiber Glass Corporation, was cleaned by Soxhlet extraction in

water and then acetone, and dried for 24 h at 105 °C before further use.

### 2.2. Plasma surface treatment of fabric

Plasma treatments were performed with ammonia or oxygen using an ENI HPG-2 plasma reactor. The plasma was generated by a 150 kHz 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 =  $1.333 \times 10^2$  Pa) and a gas flow rate of 20 standard  $\text{cm}^3 \text{min}^{-1}$ . Fabric samples, 20 cm  $\times$  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. Chemical treatment of ammonia plasma-treated fabric

After ammonia plasma treatment, the fabric containing surface amine groups was immersed in a solution of 15 g Epon® 828 in 150 ml cyclohexane at 95 °C for 30 min. The fabric was then washed with tetrahydrofuran in an ultrasonic bath for 30 min and cleaned in a Soxhlet extraction unit for 8 h to remove any traces of epoxide groups not chemically bonded to the fibre. The fabric was then dried in an oven for 24 h at 105 °C.

### 2.4. Characterization of plasma-treated fabric

Plasma treatment of ammonia results in the incorporation of amine groups on to the fibre surface. The surface concentration was previously measured by a dye assay technique [19]. The effect of oxygen plasma treatment of the fibre surface is less easy to quantify. XPS studies of ECPE fibres [23] before and after surface treatment in oxygen plasma show that various oxygen species, including alcohol/ether, aldehyde/ketone and ester functionalities, are grafted on to the fibre surface.

### 2.5. Composite fabrication

Aramid composites were fabricated from both untreated and treated fabric using closely related Resinox® CL1579 or Resinox® CL1723 resole phenolic resins (Huntsman Chemical Company) with 4%–8% Resinox® H1196 (phenol sulphonic acid) as the catalyst. Each fabric ply was impregnated with resin and 20 ply composites were then cured in an autoclave at a pressure of 350 kPa. Composites were also cured using a vacuum bag pressure of 100 kPa. The cure cycles were varied to obtain the optimum cure conditions. The matrix content was nominally 38% by weight. Individual values are given in Table I.

TABLE I Matrix content and mechanical properties of plasma-treated aramid/phenolic composites and comparisons with previous work on aramid/epoxy and aramid/vinyl ester composites.

Plasma treatment	Matrix content (wt %)	Interlaminar shear strength (MPa)	Flexural modulus (GPa)	Flexural strength (MPa)
Resinex® CL1579				
None	34.7	8.6 ± 0.2	26.8 ± 1.9	122.8 ± 2.4
2 min oxygen	40.1	13.4 ± 0.5	23.4 ± 0.2	155.2 ± 3.3
5 min ammonia	38.6	13.9 ± 0.3	28.6 ± 0.7	185.0 ± 5.1
5 min ammonia/Epon® 828	41.3	15.0 ± 0.3	26.6 ± 0.4	219.0 ± 6.3
Epoxy [19]				
None	33.6	24.2 ± 0.4	31.0 ± 0.7	305 ± 16
5 min ammonia	32.6	33.2 ± 1.2	32.5 ± 0.8	442 ± 18
Vinyl Ester [20]				
None	32.4	20.7 ± 0.2	32.5 ± 0.8	253 ± 9
2 min oxygen	32.1	31.3 ± 1.5	32.2 ± 0.6	417 ± 33
5 min ammonia	33.0	31.2 ± 0.9	32.2 ± 0.6	382 ± 19

## 2.6. Interlaminar shear strength (ILSS)

The ILSS of the aramid/phenolic composites was determined using the four-point shear test method of Browning *et al.* [24]. 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. 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 mm min<sup>-1</sup>.

The interlaminar shear strength,  $T$ , is given by the expression

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

where  $P$  is the breaking load,  $b$  is the beam width and  $d$  is the beam depth [25].

## 2.7. Flexural properties

The flexural modulus and flexural strength of the composites were determined in accordance with standard flexure test procedures [26] using a four-point loading system with a load span equal to one-third of the support span and  $L/d$  ratios recommended by Zweben *et al.* [27]. Aramid modulus specimens of nominal dimensions 300 mm × 10 mm × 4 mm with  $L/d$  of 60 were tested at 20 mm min<sup>-1</sup>. 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<sup>-1</sup>.

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,  $k_1$  is 0.25 and  $k_2$  is 1 for the four-point method and  $P$ ,  $b$  and  $d$  are defined as above.

## 2.8. 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

The ILSS results, calculated using Equation 1, are shown in Table II for autoclaved and vacuum-bagged aramid/Resinex® CL1579 composites and autoclaved aramid/Resinex® CL1723 composites. These results indicate that both the cure cycle and the catalyst level influence the ILSS. The best ILSS results are obtained with 4% catalyst and a cure cycle of 1 h at 60 °C, 2 h at 80 °C and 1 h at 120 °C. This cure cycle and catalyst level were therefore used for composites laminated with the plasma-treated fabric.

SEMs of cured composites show that the material is characterized by phase-separated water domains in the matrix, as shown in Fig. 1. Examination of SEM fracture surfaces shows that the domain density and diameter vary with the catalyst level. For the same cure cycle, the matrix in autoclaved Resinex® CL1579 and Resinex® CL1723 composites as well as vacuum-bagged Resinex® CL1579 composites contains a greater density of water domains when cured at a 6% or 8% catalyst level than with 4% catalyst. Vacuum bagged Resinex® CL1579 (Fig. 2) also has a significantly greater water domain density than the corresponding autoclaved composite. The above phenomena are attributed to the more rapid curing reaction at higher catalyst levels, as well as the formation and trapping of more water as phase-separated domains from the condensation reaction.

The decline in the composite ILSS at catalyst levels above 4% (Table II) is also attributed to an increase in the density of phase-separated water domains in the matrix at higher catalyst levels. This lowers the

TABLE II Interlaminar shear strength (ILSS) of aramid/phenolic composites fabricated with various cure cycles and catalyst levels

Cure cycle	Catalyst level (wt %)	Autoclaved Resinox® CL1579 ILSS (MPa)	Autoclaved Resinox® CL1723 ILSS (MPa)	Vacuum-bagged Resinox® CL1579 ILSS (MPa)
1 h 60 °C, 2 h 80 °C	4	6.0 (0.3)	7.33 (0.4)	
1 h 60 °C, 2 h 80 °C	6	6.0 (0.2)	5.2 (0.1)	
1 h 60 °C, 2 h 80 °C	8		4.7 (0.2)	
1 h 60 °C, 6 h 80 °C	4	7.5 (0.1)		
1 h 60 °C, 6 h 80 °C	6	6.4 (0.2)		
1 h 60 °C, 2 h 80 °C, 1 h 120 °C	4	8.6 (0.2)	7.9 (0.2)	8.1 (0.4)
1 h 60 °C, 2 h 80 °C, 1 h 120 °C	6	7.3 (0.2)	6.6 (0.3)	6.4 (0.4)
1 h 60 °C, 2 h 80 °C, 1 h 120 °C	8		5.7 (0.2)	5.3 (0.4)

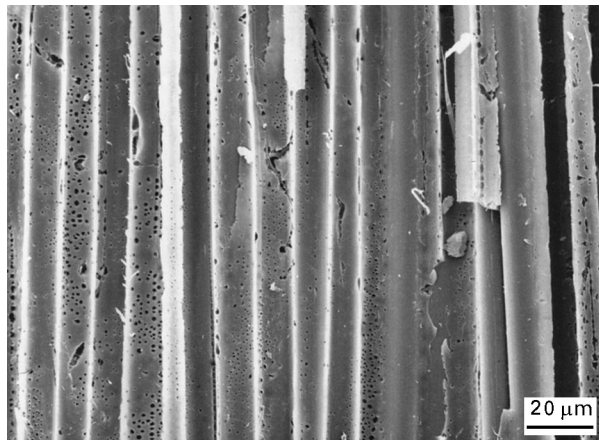


Figure 1 Scanning electron micrograph of the surface of an untreated aramid/Resinox® CL1579 composite sample autoclave cured with 4% acid catalyst for 1 h at 60 °C, 2 h at 80 °C and 1 h at 120 °C, showing phase-separated water domains in the matrix.

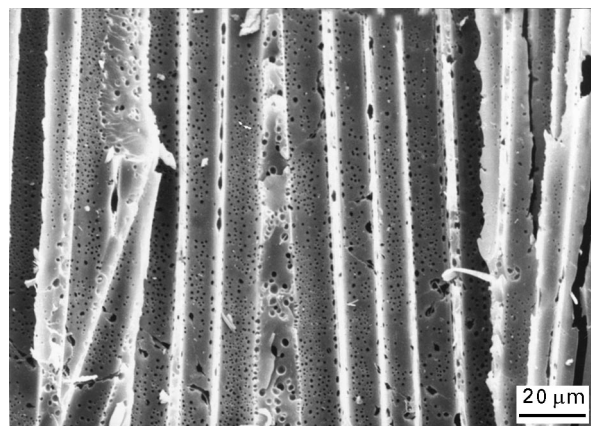


Figure 2 Scanning electron micrograph of the surface of an untreated aramid/Resinox® CL1579 composite sample vacuum-bag cured with 4% acid catalyst for 1 h at 60 °C, 2 h at 80 °C and 1 h at 120 °C, showing a significantly greater water domain density than the corresponding autoclaved composite (Fig. 1).

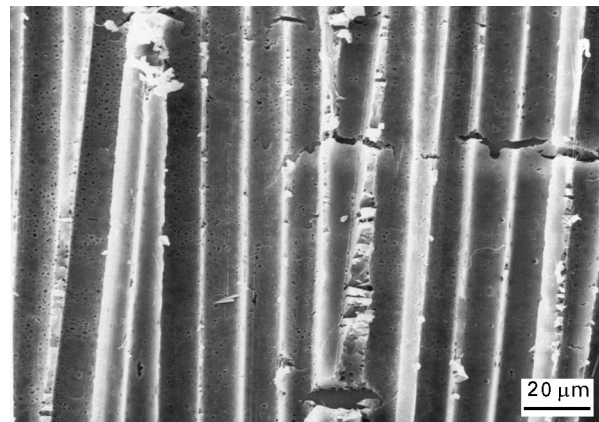
available interfacial bonding area which, in turn, lowers bonding between the matrix and the fibres. Thomason found a similar dependence of ILSS on void content in epoxy/glass composites [28].

We have previously shown that chopped strand mat glass/phenolic composites are characterized by similar phase-separated water domains in the matrix [29]. In this case, depending on the type of binder used with the glass mat, the domain density increases and their diameter decreases in regions adjacent to the fibre surface. For example, a powder binder was found to have little effect on domain density and diameter and an emulsion binder resulted in a ten-fold increase in domain density and a five-fold decrease in domain diameter near the fibre surface. This was attributed to the lowering of surface tension caused by ease of dissolution of the emulsion binder in the phenolic resin. The higher density of water domains again lowers the available interfacial bonding area and increases water retention at the fibre–matrix interface, which will, in turn, result in a significant lowering of the ILSS and the long-term durability of the composite.

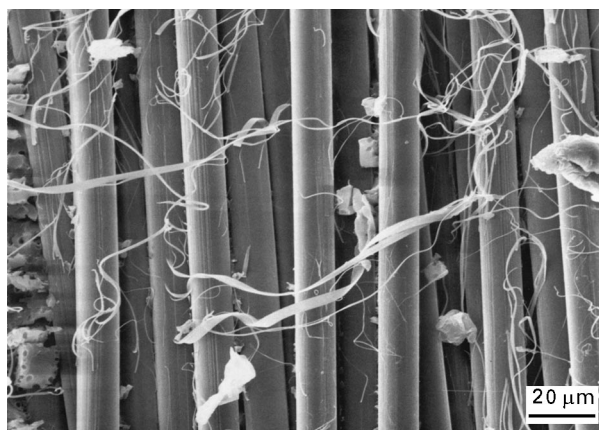
The results presented in Table II show that the ILSS for aramid/Resinox® CL1579 composites are relatively similar after 2 min oxygen and 5 min ammonia plasma treatments with increases of approximately 55% and 60%, respectively, over the value for untreated material. Greater increases (75%) have been achieved with 5 min ammonia plasma-treated fibre which was subsequently reacted with Epon® 828 to form epoxide surface groups. The plasma-treated fibres also resulted in a change in the composite shear failure mechanism. The composites fabricated with untreated fibres failed at the fibre/matrix interface, with virtually no fibre fibrillation (Fig. 3), whereas the treated fibre composites show evidence of fibre fibrillation (Fig. 4). The ammonia and chemically treated



*Figure 3* Scanning electron micrograph of the shear fracture surface of an untreated aramid/Resinox® CL1579 composite sample autoclave cured with 4% acid catalyst for 1 h at 60 °C, 2 h at 80 °C and 1 h at 120 °C, showing clean fibre/matrix separation, indicative of weak interfacial bonding.



*Figure 5* Scanning electron micrograph of the surface of an aramid/Resinox® CL1579 composite sample containing 5 min ammonia plasma-treated fibre autoclave cured with 4% acid catalyst for 1 h at 60 °C, 2 h at 80 °C and 1 h at 120 °C, showing a lower density of phase-separated water domains in the matrix than for untreated fibre composites (Fig. 1).



*Figure 4* Scanning electron micrograph of the shear fracture surface of an aramid/Resinox® CL1579 composite sample containing 5 min ammonia plasma-treated fibre autoclave cured with 4% acid catalyst for 1 h at 60 °C, 2 h at 80 °C and 1 h at 120 °C, showing fibre fibrillation, indicative of enhanced interfacial bonding.

fibre composites show similar fibre fibrillation in fracture surfaces of shear specimens. These observations and the ILSS results are indicative of a strengthening of the interface in composites containing treated fibres. Similar results were found previously with both aramid/epoxy and aramid/vinyl ester composites [19, 20]. However, in these materials, the fibre fibrillation is significantly greater than for the aramid/phenolic composites. This is consistent with the lower ILSS results obtained for the aramid/phenolic composites.

The higher ILSS for the ammonia and oxygen plasma-treated composites is likely to be due to higher fibre surface energies. It was also noted that the water domain density in the interfacial region appeared to decrease in both the ammonia and oxygen plasma-treated fibre composites (see Fig. 5, ammonia plasma treatment, and Fig. 1, untreated fibre composite). A possible explanation for ammonia plasma-treated material is that the amine surface groups may neutralize the phenol sulphonic acid catalyst. This would reduce the catalyst concentration and hence the water

domain density in the interface region, resulting in slightly higher ILSS (and significantly higher flexural strength) values.

Composite flexural properties, calculated using Equations 2 and 3, are also reported in Table I. The plasma treatment causes no significant difference in the flexural modulus, as was also observed for aramid/epoxy and aramid/vinyl ester composites [19, 20] (see Table I). However, the flexural strengths of the treated fibre composites are significantly greater than that of the untreated fibre composites. Ammonia plasma treatment for 5 min results in an increase of more than 50%, and 2 min oxygen plasma treatment increases the flexural strength by approximately 35%. The increases in ILSS and flexural strength following fibre treatment are consistent with an increase in fibre/matrix interfacial adhesion. Examination of the failure modes in the flexural test specimens from untreated to treated fibres shows that the increase in the flexural strength results from a reduction in compressive fibre buckling as the composite is flexed, which is due to increased fibre/matrix interfacial bonding. However, the similar ILSS after both plasma treatments suggests that there is no specific chemical bonding occurring because these treatments incorporate different chemical species on the fibre surface. This indicates that the interfacial bond improvement is most likely due to increased fibre wettability, as is the case with aramid/vinyl ester composites [20]. Also, covalent bonding is unlikely with amine surface groups as they do not react with formaldehyde or hydroxymethyl phenols in acidic conditions. The reaction is strongly related to pH of the resin [3] and after the addition of the catalyst the pH is approximately 1.0.

The 5 min ammonia/Epon® 828 aramid composites show a significant improvement in flexural strength and ILSS in comparison to the composite laminated with the untreated fibres ( $\approx 80\%$ ). This is also an improvement in the ILSS and flexural strength of the 2 min oxygen and 5 min ammonia plasma-treated fibre composites, which suggests additional covalent

bonding at the interface. Brown *et al.* [21] found that the surface amine groups react with the epoxy resins, and phenols are also capable of reacting with epoxy groups, especially under acid conditions [3]. It is therefore possible that the improvement in the composite properties observed for the 5 min ammonia/Epon® 828 treated fabric may be due to chemical bonding, although this is difficult to prove conclusively in the case of aramid fibres.

#### 4. Conclusion

The cure cycle and the catalyst level have significant effects on the mechanical properties of aramid/phenolic composites. The catalyst concentration has an influence on the phase-separated water domain density in the matrix which, in turn, affects the available fibre/matrix bonding area and hence the composite ILSS and flexural strength. Introduction of polar surface groups on to aramid fibres by ammonia or oxygen plasma treatment improves the ILSS and flexural strength of aramid/phenolic composites. The improved properties are most likely due to increased fibre wettability rather than covalent interfacial bonding. Further improvement in composite ILSS and flexural strength by grafting epoxide groups on to fibre surface amine groups is probably due to additional covalent bonding between the epoxide groups and the phenolic resins.

#### Acknowledgement

The authors acknowledge the contribution of Mr Richard Muscat to this work in providing the scanning electron micrographs of phenolic composite specimens.

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Received 14 June 1996  
and accepted 7 January 1997