Carbon fibre/epoxy composites: Effect of epoxy network and surface treatment of fibres on interfacial shear strength

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The paper deals with studies on interfacial shear strength (τ) of carbon fibre composite using single fibre fracture test. Surface modification of desized carbon fibres has been done by argon or oxygen plasma. The effect of network structure on τ has been studied by using difunctional or multifunctional epoxy resins. Interfacial shear strength depends on (i) chemical structure of the epoxy resin (ii) nature of gas used in plasma generation and (iii) duration of plasma treatment. An increase in cross-link density resulted in a decrease in τ, thereby indicating that a more flexible interface is superior for better adhesion with fibres. Oxygen plasma treated carbon fibres gave highest values of τ.

Carbon fibre reinforced epoxy resins are being extensively used for aerospace and defence applications primarily because of their high strength-to-weight ratio, superior performance and excellent mechanical properties. The major requirement in ensuring durability and stability of such composites is the ability to bond together the two constituent materials. The transmission of stress between fibre and matrix depends on a strong interfacial bond which resists failure. For this reason the degree of contact and the cohesive forces at the interface are of considerable importance.

In fibrous composites the interface or interfacial zone comprising of near surface layers of fibres and matrix and any other layers of material existing between these surfaces is a controlling factor in obtaining optimum mechanical properties. The properties that are influenced by the interface include composite strength, Young's modulus, interlaminar shear strength, bending stiffness and compressive strength. The mode of composite failure also depends upon interfacial bonding. A good interfacial bond leads to sharp well defined break while poor interfacial bonding leads to matrix failure followed by fibre failure. The failure mechanism is an important problem in applications as diverse as aerospace and defence vehicles, dental devices and microelectronic circuits.

Good adhesion between fibre and matrix can be achieved by (i) surface treatment of fibres and (ii) manipulation of adhesive composition. Surface treatment of carbon fibres for improving interlaminar shear strength of composites have been extensively reported in literature1-3. Controlled surface modification of the fibre surface by plasma treatment has also been examined4. Generally, adhesion and weatherability is improved by plasma treatment5-6. The effectiveness of a given plasma treatment depends on a large number of process parameters such as power, pressure, gas flow rate and treatment gas/substrate material combination. Plasma of acrylonitrile, styrene, ethylene and styrene/air mixed gases has been recently used for modification of graphite fibre surfaces7. Oxygen plasma can cause extensive surface oxidation leading to the formation of carboxyl, carbonyl and hydroxyl groups on the surface. In the inert atmosphere (Ar, He) the plasma treatment may affect the fibre surface by ablation of the low molecular weight compounds8. Oxidation may also take place subsequently when these fibres are exposed to oxygen.

In the present studies the surface modification of carbon fibre was done by plasma treatment in argon and oxygen atmosphere. The effect of structure of epoxy network on interfacial shear...
stress was evaluated using a difunctional and a tetrafunctional epoxy resin.

In order to characterise the stress transfer at matrix-fibre interface, single fibre was embedded in the matrix and the specimen was stretched along the fibre axis until fibre breakage reaches a saturation level. The average fibre length \( L_f \) is then related to interfacial shear strength \( \tau \) according to relationship

\[
\tau = \frac{\sigma_t d}{2L_f}
\]

where \( d \) is the fibre diameter and \( \sigma_t \) is the fibre tensile strength. Since the fibre-matrix interface is placed under shear, therefore, the calculated value of \( \tau \) is expected to be an excellent estimate of the shear strength between fibre and matrix.8

**Experimental Procedure**

Tenax J carbon fibres (grade HM-35A-6000) having a tensile strength of 3000 MN/m² and diameter 6.5 \( \mu \)m were obtained from Toho Rayon Co. Ltd., Japan. Sizing of the fibres was removed by overnight soxhlet extraction with acetone. The tensile strength of single fibres (desized and plasma treated) (gauge length = 1 cm) was evaluated by Instron tensile testing machine model No. 1112. A cross-head speed of 1 cm/min and a chart speed of 10 cm/min was used. More than twenty fibres were tested and average tensile strength was determined.

In order to study the effect of epoxy resin on the interfacial shear strength, two epoxy resins were used, i.e., diglycidylether of bisphenol-A (Araldite-Cibatul Ltd.) and a tetrafunctional epoxy, MY 720 (Ciba Geigy). Cured resins have been designated as A and MY respectively in the subsequent discussion. Curing of epoxy resins was done by using a stoichiometric amount of 4,4'-diaminodiphenyl methane. The amine was purified by crystallisation from water.

**Equipment for plasma treatment**—Plasma treatment of carbon fibres was carried out in a 25 cm² diameter plasma chamber. A glow discharge plasma was generated by applying potential between the two disc shaped aluminium electrodes facing each other. Argon or oxygen plasma was obtained by continuously supplying either of these gases. Working pressure of \( 10^{-4} \) torr was maintained throughout the experiment. A bundle of unsized carbon fibres were placed axially between the electrodes by means of glass support suspended from the chamber side wall. In order to ensure clean working environment, the chamber was flushed with the corresponding gases for 30 min prior to starting the fibre treatment. Typically 40-50 mA current was recorded in argon/oxygen plasma for a discharge voltage of 540 V. Carbon fibres were treated with argon plasma for 10 min and 30 min and with oxygen plasma for 30 min.

**Fabrication of steel and rubber mould**—Mild steel mould having eight dogbone shaped specimen was machined according to the ASTM standards. RTV silicone rubber (MetroArch) was used for transfer moulding and to obtain 7 cm long dogbone specimen cavities having a width, depth and gauge length of 0.3, 0.15 and 2.6 cm.

**Fabrication of composite specimens**—Single filaments were picked from the fibre bundle and were mounted with the help of a sticking tape on a paper cut tensile chamber and then placed onto the silicone rubber mould. The mixture containing the epoxy and the amine was thoroughly compounded at 80°C and degased prior to pouring in the mould. The assembly was then transferred to an oven and maintained at 50°C overnight and 80°C for 1 h. After cool down in the oven, the mould was then curled away from the specimen parallel to the fibre to prevent fibre damage.

**Tensile and photo-elastic measurements**—The epoxy tensile coupons having a single carbon fibre at the centre were tested on tensile testing machine (Polymer Laboratories-Minimat) which was mounted on a Leitz polarizing microscope having a Wild MPS45 camera facility at the top. The carbon fibre encapsulated coupons were loaded in tensile mode. The changes were monitored by polarised microscope.

**Results and Discussion**

**Effect of plasma treatment on fibres**—The SEM photographs of unsized carbon fibres and plasma treated fibres are shown in Fig. 1. No significant difference in the structure is observed on treatment with argon plasma. In oxygen plasma, on the other hand, certain amount of longitudinal ridges and valleys were present on the surface.

**Critical length and interfacial shear strength studies**—The stresses generated within the fibre-
Fig. 1—SEM photographs of (a) desized carbon fibre (b) Argon-plasma treated fibre (10 min) (c) Argon-plasma treated fibre (30 min) (d) Oxygen-plasma treated fibre (30 min)

Fig. 2—Polarized transmitted light micrographs of carbon fibre in MY resin (x100)

Fig. 3—Polarized transmitted light micrographs of carbon fibre treated in argon plasma for 30 min in A resin (x100)

Matrix interface observed in each specimen were recorded photographically with increasing strain. After a break an intense photo-elastic region appears around the end of the fibre (Fig 2). With increasing strain, this region rapidly expands down the fragment away from the break. This results in a stress pattern that has alternating light and dark areas in the micrograph, thereby leading to an increase in the gap between fragments with increasing strain. Coupons with plasma treated fibres showed that fragment separation was reduced by the presence of well bonded fibre. Lower values of critical lengths were observed with treated fibres thereby showing an increase in adhesion of carbon fibre with epoxy matrix.

Carbon fibres treated with argon and oxygen plasma for 30 min were also used for fabrication of single fibre composites. Such a treatment of carbon fibre resulted in a decrease in critical length and increase in interlaminar shear strength (Figs 3 and 4).

In Table 1, the results of interfacial shear
Table 1—Results of interfacial shear strength of carbon fibre epoxy composites

<table>
<thead>
<tr>
<th>Resin</th>
<th>Plasma treatment of C fibre</th>
<th>$l/d$</th>
<th>$\sigma_f$ (MPa)</th>
<th>$\tau$ (MPa)</th>
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<tr>
<td></td>
<td>Atmosphere</td>
<td>Time (min)</td>
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<td></td>
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<tr>
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<tr>
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<td></td>
<td>O$_2$</td>
<td>30</td>
<td>29.9</td>
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<tr>
<td>A</td>
<td>–</td>
<td>–</td>
<td>79.7</td>
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<tr>
<td>MY</td>
<td>Ar</td>
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<td></td>
<td>O$_2$</td>
<td>30</td>
<td>32.1</td>
<td>1697</td>
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Strength in these single fibre epoxy composites are given. The critical length decreased with the argon or oxygen plasma treatment of the fibres. This is expected because the surface impurities removed by plasma treatment and functional groups are generated in oxygen plasma.

It is also obvious from these results that the chemical structure of the matrix resin (A or MY) influences the shear strength. The 'A' based epoxy resin composites had almost twice the shear strength than the MY composites when unsized or argon plasma treated (10 min) carbon fibres were used. The multifunctional epoxies yield a highly cross-linked matrix resin which may not be deformable to that extent at interface as the less cross-linked A resin is expected to be. In other words, a deformable interface may be a better approach in getting higher interfacial shear strength.

Another explanation which can account for these results is the shrinkage of matrix resins. A highly cross-linked resin is expected to undergo more shrinkage on cooling. Residual stress is thus developed at the interface due to differential shrinkage of fibres and matrix.

Increase in duration of argon plasma treatment of carbon fibres only marginally affects the fibre/resin A composites by increasing the duration of plasma treatment from 10 to 30 min, in case of MY resin composites, a 30% improvement in $\tau$ values was observed. In argon plasma only surface cleaning (ablation of adsorbed species) is possible. The polar groups present on the surface of the fibres thus become more accessible to the polar groups of the matrix and thus improvement in interfacial shear strength was observed. The concentration of polar hydroxy groups which are generated in the matrix resin due to opening of oxirane rings of the epoxy resins is more in tetrafunctional MY resin as compared to difunctional A resin and this may be responsible for the observed increase in $\tau$ values. Oxygen plasma on the other hand generates polar groups on the surface of carbon fibres. A better interaction of epoxy and polar groups of fibre surface is responsible for the observed high strength values.

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References