Adhesion and toughness in carbon-fibre reinforced plastics

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FOR REFERENCE ONLY
ADHESION AND TOUGHNESS

IN

CARBON-FIBRE REINFORCED PLASTICS

by

J. A. ENEVER, B.Sc. M.Sc.,

A Doctoral Thesis submitted in partial fulfilment
of the requirements for the award of Ph.D. of the Loughborough
University of Technology - September 1973

Supervisors: Dr. R. R. Smith
            B. J. Hawthorne, Esq.

C by J. A. Enever, 1973
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SUMMARY

A literature survey of adhesion was undertaken with special emphasis on plastics, glass fibres and existing methods of measuring adhesion and comparing physical properties. The effectiveness of adhesion in carbon-fibre reinforced plastics has hitherto been determined by inter-laminar shear strength testing, although the true meaning of this test may still be obscure. The present work set out to measure adhesion between single carbon fibres and polymers, (a) by pulling single carbon fibres from solidified drops of plastic (a technique not previously reported in the literature) and (b) by stressing clear thermoset resins in which single fibres were embedded. By these means the constituent aspects of adhesion between plastics and carbon fibres were identified and evaluated, and their relative importance determined. Relevant features were the surface nature and area of the carbon fibres, contact angles between liquid polymer systems and carbon fibres, and surface tension and viscosity of the liquid polymers. The surface area was measured by using a modification of the iodine adsorption test not previously found successful with carbon fibres. The contact angles were measured with an apparatus by which liquid drops could be placed on carbon fibres, held at temperatures up to 300°C in an inert atmosphere and then photomicrographed to give the contact angles.

While much of the reported work with carbon fibres has dealt with surface treatments and measurement of inter-laminar shear strengths based on glass-fibre technology there have been moves to measure adhesion more accurately between single fibres and resin, and to assess surface treatments introduced to improve adhesion and toughness of the composites. However, work with carbon fibres has largely ignored toughness measurement, even though this is one of the major problems with the derived composites. The literature indicated possibilities of improving the toughness of carbon fibre composites as well as adhesion, and some of the treatments arising from this literature study were investigated, introducing modifications
Diethylene Triamine (DETA) which can be used to cure epoxies and polyurethanes adheres well to carbon fibres. Polyurethane prepolymer sized onto carbon fibres and cured with DETA can provide a flexible interface to blunt cracks and improve toughness. Epoxy resin composites have been prepared with these sized fibres. Compared with previous systems there was a change in the flexural behaviour, the composite failing in a more ductile manner; and more energy was absorbed in breaking. However high speed 'Charpy type' impact showed few differences.

Measurements made on composites indicated that toughening was likely to result if a softer matrix was used, this allowing the fibres to pull out, not by debonding, but by plastic deformation of the matrix. Blends of polyurethane prepolymer and epoxy resin were therefore investigated to extend the information. These composites gave up to a 300% improvement in 'Charpy type' impact and up to 600% improvement in energy to break. However besides significant decreases of 20% in flexural modulus and 40% in shear strength the composite was particularly difficult to mould and had a very short 'pot-life'. Other possible methods of improving toughness were also considered: model systems, different matrices including elastomers and epoxy curing agents.

Existing methods of measuring toughness are not completely reliable and may be confusing when considering whether a material is ductile or brittle. Recent fracture-toughness studies on metals have given valuable information on the brittle nature of these materials and work was undertaken to obtain a more accurate picture of toughness in the carbon fibre composites produced.
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Main Letters

<table>
<thead>
<tr>
<th>Letter</th>
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<tr>
<td>a</td>
<td>crack length</td>
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<tr>
<td>A</td>
<td>area</td>
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<tr>
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<td>weight of polyurethane in blend</td>
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<td>B</td>
<td>spreading coefficients</td>
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<tr>
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<td>tensile or Young's modulus</td>
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<td>Load on a specimen</td>
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<td>shear modulus</td>
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<tr>
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<td>work done at crack tip on crack initiation or crack arrest (A)</td>
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<td>surface entropy</td>
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<tr>
<td>k</td>
<td>volume fraction of unbonded fibres</td>
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<tr>
<td>K_I</td>
<td>stress intensity factor of on crack initiation (I) or crack arrest (A)</td>
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<td>ra</td>
<td>polar co-ordinate</td>
</tr>
<tr>
<td>S</td>
<td>width of crack</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
</tr>
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<td>Temperature</td>
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<tr>
<td>V</td>
<td>volume fraction</td>
</tr>
<tr>
<td>w</td>
<td>weight of epoxy resin in the blend</td>
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W - Work of adhesion

$W_D$ - Work to debond fibres from matrix

$W_P$ - Work to pull fibres from and shear matrix

**Greek Symbols**

- $\Theta$ - angular direction
- $\phi$ - compliance
- $\sigma$ - tensile stress
- $\gamma$ - shear stress
- $\varepsilon$ - tensile strain
- $\gamma'$ - surface energy
- $\eta$ - viscosity
- $\nu$ - Poisson’s ratio

**Suffixes**

all the digits, $x$, $y$ and $z$ are used as constant digits

- $b$ - bonded fibres
- $c$ - critical
- $e$ - composite
- $f$ - fibres
- $i$ - interface
- $L$ - liquid
- $m$ - matrix
- $R$ - resin
- $S$ - solid
- $u$ - unbonded fibres
- $V$ - vapour
Abbreviated Capitals

CFRP - carbon fibre reinforced plastic
CTBN - carboxyl terminated, liquid butadiene-acrylonitrile rubber
DIM - 4,4' diaminodiphenyl methane
DETA - diethylene triamine
ILSS - inter-laminar shear strength
MOCA - 4,4' methylene bis 2-chloroaniline
PAN - polyacrylonitrile

Other symbols and abbreviations are for registered trade products. These products will be found in Appendix 1. Additional symbols correspond to those used in S.I. units.
EQUATIONS USED

1. \( \sigma_e = \sigma_m V_m + \sigma_f V_f \)
2. \( \varepsilon_e = \varepsilon_x = \varepsilon_m \)
3. \( \varepsilon_e = \frac{E_m \varepsilon_e (1-V_f) + E_f \varepsilon_e V_f}{1} \)
4. \( I_c = \sigma_{f_{\text{max}}} \frac{d_f}{4 \varepsilon_m} \)
5. \( \frac{d_b}{d_u} = \frac{4}{3} \cdot N^2 \)
6. \( \frac{E_u}{E_b} = 1 - \frac{E_p}{E_b} \)
7. \( \cos \Theta = \gamma_{sv} - \gamma_{sl} \frac{dL}{dV} \)
8. \( \cos \Theta = (C_1 - C_2 C_3) + C_2 C_4 T \)
9. \( \frac{d}{dT} = \frac{C_5}{\sin \Theta} \left[ \frac{M_2 - M_1}{E_f} \left( \frac{\gamma}{\gamma_c} \right) \right] \)
10. \( \frac{d (\cos \Theta)}{dV} = f \left( \frac{\gamma_{LV}}{\gamma_c} \right) \)
11. \( W_p = \frac{1}{2} \cdot \tau_m \cdot \tau_c \cdot d_l^2 \)
12. \( W_p = \frac{d_f^2}{24} \times \left( \frac{\sigma_{f_{\text{max}}}}{E_f} \right) \cdot \sigma_{f_{\text{max}}} \)
13. \( \sigma_f = \sigma_{f_{\text{max}}} \left( 1 - \frac{1}{c_{12}} \right) \)
14. \( C = \frac{E}{2(1 + \nu)} \)
15. \( K_I = \sigma \sqrt{\pi a} \)
16. \( r = \frac{1}{\pi} \cdot \frac{K_I}{\sigma_{f_{\text{max}}}^2} \)
17. \( K_{IC} = \sqrt{EG_{IC}} \)
1. INTRODUCTION

A M.Sc Course project carried out by the author at the Railway Technical Centre, Derby, provided the starting point for this research. In connection with the evaluation of reinforced plastic gearwheels, the poor wear characteristics of carbon fibre reinforced plastic gearwheels were noted and microscopy revealed poor wetting of the carbon fibres by the matrix. The project then centred on an investigation of the wetting of carbon fibres by liquid polymer systems, and has now been taken further in work described in the present thesis.

The results of the M.Sc project explained why the carbon fibres did not appear to adhere effectively to the plastic in the gearwheels. However there were problems still to be solved arising from the need to explain the discrepancies in the M.Sc results. This M.Sc project was necessarily a restricted investigation. The following research first of all sought to explain these discrepancies and at the same time to review the field of adhesion. This was intended to give a better understanding of the mechanism by which carbon fibres adhere to plastics in composites. Adhesion is a large field but adhesion in CFRP has been little studied and in the first section of the thesis the actual work carried out was considered and selected by a novel extension of the apparatus and expertise available, the time and resources endowed to the project, and the discussions which looked at the feasibility of different parts of the project.

In the second part of the thesis toughness of carbon-fibre composites was investigated. While studying adhesion between carbon fibres and liquid polymers, several ideas arose which it was hoped would improve the toughness of carbon-fibre composite. The carbon fibre composites being produced were brittle and failed catastrophically under a low energy level of impact. The existing procedure to toughen a carbon-fibre
composite, had been to use a fibre with poor adhesion to the matrix. This in addition had the effect of reducing the composites flexural properties.

The problem was to investigate ways of improving toughness of carbon-fibre composites, and at the same time carefully monitor the physical properties of the composite. In the second part of the thesis this was achieved by considering the composite matrix, fibre and interface in turn with the aim of improving toughness.

Lastly while studying and measuring the toughness of composites it was apparent that the existing standard test methods were inadequate in assessing real-life behaviour. Techniques were employed in order to test the composites, which more accurately indicated their toughness. Fracture toughness parameters as specified for metals have also been considered for composites. Some of the problems apparent with measuring these parameters in composites are discussed and solved and the direction indicated in which further useful research could be carried out.
2. **CARBON FIBRES**

In engineering construction there is a continuing need for materials with a higher specific stiffness and strength. This demand usually starts in the aerospace industry, but as it develops, these materials are often adopted by designers in other fields.

In the last decade metals and alloys have been rapidly reaching their ultimate in performance, at a reasonable cost. Much research has been carried out in the area of fibres and whiskers with a view to improving on the properties of metals as engineering materials. This use of fibres and whiskers, embedded in suitable matrices, held the key to the continued and future development of superior materials. The matrices chosen for such fibres can be metals, ceramics or plastics and must fulfil various functions according to what is required of the composite. However plastics are generally chosen for their ease of fabrication.

Glass fibres have paved the way for reinforcement of composites and have achieved a high degree of acceptance by engineers. Their chief advantages are high strength, low density, established properties and, most important of all, low cost. Their chief disadvantage is their low stiffness. There has been much research directed at producing a similar fibre of higher modulus.

Much of this research has been directed towards producing carbon fibres, from cellulose and polyacrylonitrile. This research had progressed slowly. It has been reported by Gill (1) that Shindo (2) carried out the first work which gave significant improvements in mechanical properties of carbon fibres from synthetic polymer fibres. He introduced an oxidation stage in the production of carbon fibres from
polyacrylonitrile (PAN) before carbonising the fibre. Further important work by Watt, Phillips and Johnson (3) introduced the concept of holding the fibre under tension whilst oxidation took place and this first achieved a truly high-strength and high-modulus carbon fibre.

The first stage of production of carbon fibres is an oxidation stage in air at between 200-250°C under tension (1). If PAN is heated the ordered molecular chains in the polymer twist and intertwine. If the polymer is held under tension while it is heated this does not happen. As indicated in figure 1 there is an uptake of oxygen associated with the formation of good chemical cross-links between the chains so orientating the chains straight, parallel and in a good position for subsequent heat treatments.

Further heat treatments strip from the chains all the elements except carbon to produce a ring structure as indicated in Figure 2. These carbon rings will have an orientation dependent upon that of the original PAN and its oxidised form. This final carbonisation or graphitisation stage takes place in an inert atmosphere at temperatures ranging from 1000°C to 2800°C. The temperature used depends upon whether high strength or high modulus fibres are required. Figure 3 (1) demonstrates how according to the temperature of the final heat treatment stage the properties of the fibre can vary from high strength to high modulus.
HEATING P.A.N.  
(schematic only)

Figure 1

Figure 2
Figure 3

Final Heat Treatment

Tensile Modulus

Tensile Strength

Temperature degC

Tensile Strength G/Nm²

Tensile Modulus G/Nm²
3. COMPOSITES

An ideal composite contains fibres which are well dispersed, uniform, continuous, unidirectional and which are firmly gripped by the matrix so that no slippage can occur at the interface. Figure 4 shows a cross section of such an ideal composite.

In deriving the total load $P_e$ supported by this composite let $P_f$ be the load supported by the fibres and $P_m$ the load supported by the matrix (4).

Then $P_e = P_f + P_m$

or in terms of stress

$$\sigma_e A_e = \sigma_m A_m + \sigma_f A_f$$

$$\sigma_e = \sigma_m V_m + \sigma_f V_f$$

\[ \text{.................. (1)} \]

where $A$ is the corresponding area

and $V$ is the corresponding volume fraction

Since there is no slippage at the interface between the fibre and matrix in this composite, they must elongate by the same amount, i.e. their strain is equal.

$$\varepsilon_e = \varepsilon_f = \varepsilon_m$$

\[ \text{.................. (2)} \]

modulus

$$E = \frac{\text{stress}}{\text{strain}} = \frac{\sigma}{\varepsilon}$$

Combining eqns. 1 and 2

$$\sigma_e = E_m V_m \varepsilon_e + E_f \varepsilon_e V_f$$

also since $V_f + V_m = 1$

$$\sigma_e = E_m \varepsilon_e (1 - V_f) + E_f \varepsilon_e V_f$$

\[ \text{.................. (3)} \]
AN IDEAL COMPOSITE

Figure 4

$P_f$ - Load Supported by Fibres
$P_m$ - Load Supported by Matrix
$P_e$ - Total Load Supported
The ratio of the load carried by the reinforcement, to the load carried by the matrix is:

\[ \frac{E_f E_c (1 - V_m)}{E_m E_c V_m} = \frac{E_f}{E_m} \cdot \frac{(1 - V_m)}{(V_m)} \]

This equation shows how very strong fibres or whiskers, when incorporated in a matrix and the whole composite strained, carry the majority of the load, according to their high modulus. It is for this reason that composites are being developed, to improve on existing materials. Figure 5 exemplifies these points. If carbon fibres are in a matrix such as epoxy, whose modulus is 100 times smaller than carbon and the fibres occupy 60% of the composite volume, then the carbon fibres carry the majority of the load imposed on the composite. Even if glass fibres are incorporated in a matrix such as nylon with a modulus only ten times less than the glass, and occupy only 10% by volume, the glass still carries approx 50% of the load.

This explains why composites have been developed in recent years to utilise high strength, high modulus fibres and whiskers. By incorporating fibres and whiskers in plastics, the physical properties of the plastics can be greatly improved. The high performance fibres and whiskers can also, when in a composite, give materials with superior properties by carrying the majority of the load.
LOAD CARRIED BY FIBRES IN A COMPOSITE

Figure 5

Fibre Modulus / Matrix Modulus

Load Carried by Fibres / Load Carried by Matrix

$V_f = 0.1$

$V_f = 0.6$

$V_f = 0.9$
4. ADHESION TO CARBON FIBRES

4.1 The Role of Adhesion in Composites

An analysis of short and long fibre reinforced composites will elucidate the role of adhesion in bonding the fibres to the matrix in a composite. Long fibres are those in general over about 10 mm in length. Short fibres are those whose length is near the critical length $l_c$ whose meaning is explained below. Composites are only prepared with short fibres, if the processing conditions do not allow long fibres to be used, e.g. Injection moulding.

4.2 Short Fibre Composites

Short fibre reinforced composites will not support their theoretical maximum load as derived in the equations mentioned in the last section. This is because the average load supported by each fibre is less than the ultimate fibre strength. Figure 6 illustrates this point, the graph representing the stress $\sigma_f$ along a fibre, falling to zero at the ends. Let the length over which the stress falls to zero be $l_c/2$. In short fibres $l_c$, the two ends can be a significant proportion of the fibre length and in extreme cases can be greater than the fibre length. In these cases the average stress supported by the fibre is less than the amount it could support if it were stressed to its maximum $\sigma_{f\text{max}}$ along its total length. Consequently the load supported by a composite reinforced by short fibres does not reach the theoretical level if $l_c$ is a significant proportion of the fibre length.

Consider Figure 7 in which a small section $\delta_\alpha$ of a short fibre is represented. The shear stress $\tau_m$ arises from the difference between the moduli of the matrix and fibre when stressed and enables the stress applied to a composite to be carried by the fibres.
Stress in Fibre

Figure 6

\[ \sigma_{f\text{max}} \]

Figure 7

\[ \sigma_f \leftarrow \sigma_f + d\sigma_f \]

\[ \tau_m \]
Since the axial forces on the fibre element are in equilibrium we can derive an expression relating the fibre and matrix properties to the length $l_c$ known as the critical length. (d is diameter).

$$
\delta \sigma_f \cdot \pi \cdot \frac{d_f^2}{4} = \gamma_m \cdot \pi \cdot d_f \cdot \delta x
$$

i.e. $\gamma_m = \frac{d_f \cdot \delta \sigma_f}{4 \cdot \delta x}$

Considering the fibre portion where the stress is not at a maximum and integrating from the fibre end to $l_c$ and $\sigma_f$ increased linearly to $\sigma_f_{\text{max}}$.

Then $\delta x = \frac{d_f \cdot \delta \sigma_f}{4 \cdot \gamma_m}$

Integrating

$$
\int_0^{l_c} \delta x = \frac{d_f}{4 \gamma_m} \int_0^{\sigma_f_{\text{max}}} \delta \sigma_f
$$

and $l_c = \frac{\sigma_f_{\text{max}} \cdot d_f}{4 \gamma_m}$ 4

Here we have a relationship between $\gamma_m$ the shear strength of the matrix to the fibre, and $l_c$ the critical fibre length. If there is poor adhesion and hence low shear strength between the fibre and matrix then the fibre critical length can be long. In any short fibre re-inforced plastic composite there is a limit to the length of the fibre and where the fibre diameter $d_f$ and strength $\sigma_f_{\text{max}}$ are known, then it is obviously important to monitor the adhesion in order to control the composite strength according to eqn. 4 above, which shows the effective fibre strength.
4.3 Long - Fibre Reinforced Composites

A long fibre is generally where its length is much greater than $l_c$. The role of adhesion in long fibres is complicated but important. In general the effect of poor adhesion is easily explained. As the composite is stressed towards its breaking point, certain fibres in the composite will fail before the composite fails. This arises because of the variable strength of the fibres. The composite does not immediately fail because the surrounding fibres are stronger and the stress is thrown on these fibres. The extent to which the stress is transferred to other surrounding fibres depends on the interface between the fibre and matrix. Better adhesion at the interface enables the stress from broken fibres to be more efficiently transferred to unbroken fibres.

A treatment by Gresczuk (5) investigated this problem of stress transfer from broken fibres in composites. Figures 8 and 9 show his main results. These were the variation of shear stress as a function of the x co-ordinate and how the maximum shear stress around a broken fibre encapsulated by unbroken fibres, increased with higher fibre volume fractions, as well as with increased interface shear modulus to fibre Young's Modulus ratio.

A higher shear stress around a broken fibre could exceed the shear strength of the interface and hasten the ultimate failure of the composite. The adhesion between fibre and matrix can determine then the point of ultimate failure after the first fibre failures.

In addition composites with poor adhesion between the fibres and matrix have reduced modulus in flexure (5).
SHEAR STRESS VARIATION AROUND BROKEN FIBRES

Figure 8

![Graph showing variation of shear stress (γ) with angle (θ) and position (x)]

- γ - Shear Stress
- σ - Direct Stress
- r - Fibre Radius

Figure 9

![Graph showing variation of maximum shear stress (γmax) with fibre volume fraction]
Comparison of the two systems in figure 10 of bonded and unbonded fibres gives the respective bonding stiffness where, 

The moment of area $I$ of a single fibre is 

$$I = \frac{\pi d^4}{64}$$

For unbonded fibres the bending stiffness $D_u$ is 

$$D_u = \frac{M.N.E_f.\pi d^4}{64}$$

in which the effect of the resin is ignored.

For the case with the bonded fibres the bending stiffness is $D_b$

$$D_b = \frac{M.N.3.3.\pi d^4}{12}$$

where $D_u = \left[ \frac{E_f}{4} + E_m \left( 1 - \frac{\pi}{4} \right) \right] \frac{Nd_f}{2} - \frac{Nd_f}{2}$$

Simplifying by ignoring the term $E_m (1 = \frac{\pi}{4})$

$$\frac{D_b}{D_u} = \frac{4}{3} N^2$$

However for most composites, the flexural modulus lies between $D_b$ and $D_u$.

For Young's Modulus $E$ the following equation relates the effect of unbonded fibres (5).

$$\frac{E_u}{E_b} = 1 - \frac{E_f}{E_b} \cdot k$$

$k$ - volume fraction of unbonded fibres

$E_f$ - Young's Modulus of fibres
Figure 10

No Resin

Fibres Bonded with Resin

\(d\) - Diameter of Fibres

\(M, N\) - No. of Fibres along Respective Axis

Figure 11

\(\frac{E_u}{E_b}\) vs Fibre Volume Fraction

0.05

0.2

0.5

Fraction of Unbonded Fibres
Figure 11 shows the effect of unbonded fibres on the Young's Modulus. It is only really apparent with low fibre volume fraction composites such as with reinforced thermoplastics. For example a ten per cent volume fraction composite, with only five per cent of its fibres unbonded, would have only fifty per cent of its modulus if there were no unbonded fibres.

Finally for composites that have good adhesion, the fracture behaviour is a well defined break. In contrast composites with poor adhesion progressively fracture, giving bond failure, matrix failure, fibre failure and ultimately composite failure.

Having explained the role of adhesion it is apparent that an investigation into the adhesion between those materials used in composites will lead to a better understanding of composite technology.
5. **THEORY OF ADHESION**

The bond formed in adhesion can be a chemical reaction or a physical attraction, the energy of a chemical bond being an order of magnitude greater and hence more favoured than that of a physical bond. In both cases however the bond can only be formed if a liquid which is adhering to a solid wets the solid well and the molecules consequently come into close contact. Fowkes (6) has looked more deeply into this problem from the physicist's point of view.

The extent to which a solid is wetted by a liquid is dependent upon the relative surface energies. Thermo-dynamics tells us that systems always tend to reduce their free energies and a system can reduce its free energy by an amount dependent upon the surface energies of the solid and the liquid. The interfacial surface energies form the liquid into an equilibrium contact angle \( \theta \) according to equation.

\[
\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \tag{7}
\]

- \( \gamma \): surface energy
- \( sv \): solid vapour
- \( sl \): solid liquid
- \( vl \): vapour liquid

![Diagram of contact angle between vapour, liquid, and solid](image)

**VAPOUR**

\[ \gamma_{vl} \]

**LIQUID**

\[ \gamma_{sl} \]

**SOLID**

\[ \gamma_{sv} \]
High melting point materials and hard materials tend to have high surface energies, whereas liquids and polymers have low surface energies. These hard materials are wet completely by polymers and liquids and show zero contact angles.

Carbon fibres are reported (7) to have low surface energies (\( \gamma_c \) of 44-48 MN/m). This compares with all commonly used polymers which have \( \gamma_c \) values from 20-100 MN/m, \( \gamma_c \) is a parameter derived by Zisman which essentially is the surface tension of a hypothetical liquid which just gives a zero contact angle on the solid (8,9). According to Zisman a liquid or melt which will completely wet another solid, as long as the solid has a high \( \gamma_c \). Carbon fibres then will not necessarily be perfectly wetted out by all polymers.

The contact angle expressed in equation 7 above gives a useful inverse measure of the wettability of the solid by the liquid (8). Poor wetting will reduce the adhesion between a solid and liquid whether the adhesive forces are physical or chemical in nature because it results in a high contact angle \( \theta \).

There are several conflicting opinions on the roles of wetting, surface energies and energy equilibriums, and of their effects on adhesion.

Harford and White (10) and Wu (11) among others, look at the equations below and concluded that in order:

Work of adhesion \( W = \gamma_1 + \gamma_2 - \gamma_{12} \)

Contact angle of 1 on 2 \( \theta \)

\[
\cos \theta = \frac{\gamma_2 - \gamma_{12}}{\gamma_1}
\]

Spreading co-efficient for 1 on 2 = \( b_{12} \)

\[
b_{12} = \gamma_2 - \gamma_1 - \gamma_{12}
\]
to study adhesion it was necessary to know accurate values for surface tension of polymers. Wu (11) applied the values he had measured to known adhesive strengths to give theoretical values for contact angles, work of adhesion and the spreading co-efficients.

Brewis (12) and Huntsberger (13) looked at Zisman's $\gamma_c$ and at contact angle measurements. Huntsberger particularly criticised most published work on wetting, and showed theoretically that even high contact angles could give complete wetting. He quoted the following thermodynamically derived equation.

$$\Delta F = \gamma_{sv} A_{sv} - \left[ \gamma_{sv} A_{sv} + \gamma_{lv} A_{lv} \right]$$

$A_{sv}$ - actual area of solid - vapour interface

$A_{lv}$ - actual area of liquid vapour interface

recalling equation 7 mentioned above.

$$\Delta F = -\gamma_{lv} \left[ 1 + \left( \frac{A_{sv}}{A_{lv}} \right) \cos \theta \right]$$

i.e. unless $\left( \frac{A_{sv}}{A_{lv}} \right) \cos \theta$ is -ve then thermodynamic equilibrium corresponds to a wetted state and this is possible even if $\theta > 90^\circ$ (so discounting surface energy and contact angle measurements as a guide to adhesion).

However although this discounts surface energy, in assessing wetting Huntsberger changed his mind and stated that contact angles would show positions of metastable equilibrium and were an important factor in assessing adhesion. Brewis took up Huntsberger's point about contact angles greater than $90^\circ$ not necessarily leading to poor wetting, but noted that other kinetic factors and surface geometry factors were involved. Brewis also introduced the effect of the different components in adhesion, that is chemical bonds and physical bonds, and stated that in measuring surface tension it was necessary to separate these. Wu also mentioned these components in surface tension which further complicated their measurement and assessment.
The temperature dependence of adhesion has been approached in different ways. Zisman (8) has derived the following equation showing a relation between contact angle and temperature $T$.

$$\cos \theta = C_1 - C_2 C_3 + C_2 C_4 T \quad \text{...... (8)}$$

$C_1$, $C_2$, $C_3$ and $C_4$ are positive constants.

Wu (14) has also expressed a relation between temperature and contact angle.

$$\frac{d\theta}{dT} = C_5 \cdot \left[ \frac{1}{\sin \theta} \right] \cdot \left[ H_2 - H_1 \left( \frac{\sqrt{2}}{\theta} \right) \right] \quad \text{...... (9)}$$

where $H_2$ and $H_1$ are surface entropies given by $\left( \frac{d\theta}{dT} \right)$ and $C_5$ is a constant.

Here Wu's equation 9 shows a different temp. dependence than Zisman's 8.

His eqn. 8 shows a variation only positively proportional to temperature, Wu shows $\theta$ can be proportional negatively or positively to temperature.

However Brewis produced results showing no variation in contact angle with temperature. Harford and White in measuring the temperature variation of surface tension show like Zisman a linear variation with temperature.

Huntsberger (15) looked into the temperature variation most precisely, using two different techniques for measurement and presented data for several polymers. He hypothesized that the extent of wetting controls the adhesion, and that temperature affects this inasmuch as it affects the time to reach equilibrium, viscosity variation, visco-elastic response and interfacial stress concentrations, which all affect the extent of wetting.

The way in which surface roughness affects adhesion was discussed by Haier et alia (16) and Brewis (12). They mentioned that rougher surfaces give better keying and mechanical adhesion. Broughton and Krok (4) looking at adhesion via contact angles showed how a roughened surface will reduce
the contact angle and promote more intimate contact, and hence better adhesion. They give the following equation relating an increase of $C_s$ in surface area, to the contact angle \( \theta \) \( (20,21) \).

\[
\text{Then increased surface area } \quad \cos \theta \quad \text{(increased area)} = C_s \cos \theta \quad \text{(original)}
\]

Little mention in the above discussion has been made of the kinetic effects on adhesion, although several of the authors cited \( (4, 6, 9, 10, 11, 12, 13, 15, 16) \), have used the time dependence of adhesion to explain spurious effects, or have mentioned only in passing how it can affect adhesion. Cherry et alia \( (17) \) rightly investigated the kinetics of adhesion as if its importance were equal to contact angle or surface tension measurements. For obviously in any real situation, as a liquid is wetting a solid it is solidifying, and any voids left at the interface, because the liquid sets in a finite time, will affect the adhesive strength.

Schonhorn and Sharpe \( (18) \) as well as Cherry and Holmes \( (19) \) have derived equations to deal with the kinetics of adhesion. They involved both surface tension $\gamma$ and viscosity $\eta$ of the spreading liquid, which both affect the rate of change of $\theta \times \frac{d(\cos \theta)}{dt}$ at which the equilibrium contact angle $\theta$ is reached.

\[
\frac{d(\cos \theta)}{dt} = \gamma_{LV} \left( \frac{\eta_{LV}}{\eta_L} \right)
\]

\[ \gamma_{LV} \quad \text{surface tension between liquid and vapour} \]

\[ \eta_L \quad \text{Viscosity of liquid} \]

Cherry et alia \( (17) \) have used these equations and shown how they can contribute logically to estimated adhesive strength and add to the information given by contact angle measurements.
6. DISCUSSION FOR EXPERIMENTAL PROCEDURE

In section 5 it was shown that to assess adhesion between a solid and a liquid, either contact angles or surface tension can be measured. These measurements although only strictly a step towards assessing adhesion, have in the past been selected as the most important parameters in this assessment.

Those workers (10, 11, 12) who have assessed adhesion from a theoretical point of view and derived and discussed equations for the adhesive parameters have rather naturally decided that surface tension measurements being exact parameters of materials are the correct approach.

However from a technological point of view surface tension measurements can only be a guide in giving theoretical contact angles, work of adhesion and spreading parameters. None of these parameters can be said to be an exact guide to adhesion. This is borne out by the lack of comparative figures between these parameters and adhesion for those authors (8, 9, 10, 11) using surface tension measurements as a guide. Another disadvantage in using surface tension to assess adhesion between carbon fibres and liquid polymers, is that the surface tension of carbon fibres can only be measured by a contact angle method. Obviously in this example contact angle measurements could well be used to assess adhesion directly. However, surface tension measurements could be valuable when looking at the possible adhesion between two materials as opposed to the actual adhesion.

It was decided in the following work to measure the contact angles of the liquid polymers.
7. EXPERIMENTAL PROCEDURE AND RESULTS

7.1 Contact Angle Measurement

7.1.1 Apparatus

Techniques for measuring contact angles of liquids on surfaces are well established including quite sophisticated null methods (22, 23, 24). However few methods have been developed for measuring the contact angles of liquids on fibres and some of these require elaborate equipment and techniques (25, 26). Grindstaff (27) developed a simple apparatus for measuring the contact angles of liquids on synthetic fibres which was constructed fairly easily. His technique was extensively developed in order that the contact angles of liquid polymers on carbon fibres could be measured. Liquid polymers require to be heated to an accurately known temperature and care taken to stop their degradation. The carbon fibres used were very brittle and only just visible with the naked eye.

The apparatus developed was basically a stage which could be clipped onto a microscope, as shown in figure 12. A rotating turn-table was mounted on the stage with an aperture in the middle. A carbon fibre was then mounted using acrylic dope across the aperture with a loop of wire round it. The loop mounted, over the aperture, held a liquid polymer reservoir so that the fibre polymer interface, could be viewed in a microscope and photographed. Plate 1 shows what could be seen in the microscope and how by rotating the turntable, a null point was achieved giving easier measurement of the contact angle.

Carbon fibres were difficult to handle, being brittle and only about 7 μm thick. However with care the fibres were mounted and the liquid polymers suspended in the wire loop.
MODIFIED MICROSCOPE TO MEASURE CONTACT ANGLES AT ELEVATED TEMPERATURES

Figure 12

- liquid reservoir/heater
- mounted C-fibre
- scale graduated in degrees
- rotating turntable
- mounting blocks
- moving clips
- microscope
- stage as above
- and camera
Contact angle less than 90°.

Contact angle greater than 90°.
Under its first stage of development the apparatus was used to measure the contact angles of epoxy and polyester resins at room temperature (23 ± 2°C). The next stage in its development was to replace the wire loop by a thermocouple wire loop. An electronic circuit was constructed using the technique of Glasser and Miller (28) which enabled the thermocouple to become an alternating heater and thermocouple or 'thermocouple micro-furnace'. The microscope stage was also enclosed in a stream of nitrogen. By this technique a small drop of molten thermoplastic could be held round a carbon fibre at any accurately known temperature up to 300°C in a stream of nitrogen to retard the polymer degradation. This technique to measure contact angles was developed in the M.Sc. course project carried out at the Railway Technical Centre in 1970.

Plate 2 shows a typical contact angle of a thermoplastic on a carbon fibre as photographed through the microscope. From this photograph the contact angle (θ) could be measured or the turntable on the stage rotated to give a null-point and hence θ.

The carbon fibres used for the investigation were all those grades which were then available from Courtaulds. The thermoset resins used in the investigation were both polyester and epoxy resins. Grades in common usage (BXL SR 17449 and Shell Epikote 816/Epikure TET), grades specially recommended as being suitable for carbon fibres (Scott Bader's Crystic 272 and Ciba's Araldite MY 778/HY 956) and an experimental high performance grade (BXL ERLA 4617). The selection of thermoplastics covered most of the common types which could have been reinforced by short carbon fibres. Although the angles were measured in the M.Sc. course the results were not then appreciated and analysed.

7.1.2 Results of Contact Angle given as cosθ

The grades of thermoplastic used were:

High Density Polyethylene - BRP Ltd Rigidex R101
Polypropylene Co-polymer - Shell Cariona P GMT
Acetal Homopolymer - Du Pont Delrin 100
Acetal Co-polymer - Hoechst Hostaform
Nylon 66 - I.C.I. Maranyl A 100

Carbon Fibres were Courtaulds Grafil A, HT, HT-S, HM, HM-S.
See Appendix 1 for quoted Properties.

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>Polymers</th>
<th>Test Temp deg C</th>
<th>Grades of Carbon Fibre Grafil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Polyester</td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Resins</td>
<td>EKX SR 17449</td>
<td>23</td>
<td>0.914</td>
</tr>
<tr>
<td></td>
<td>Scott Bader</td>
<td>23</td>
<td>0.921</td>
</tr>
<tr>
<td></td>
<td>Crystic 272</td>
<td>23</td>
<td>0.914</td>
</tr>
<tr>
<td></td>
<td>Shell Epikote 816/TET</td>
<td>23</td>
<td>0.921</td>
</tr>
<tr>
<td>Epoxy Resins</td>
<td>GIPA</td>
<td>23</td>
<td>0.946</td>
</tr>
<tr>
<td></td>
<td>Araldite</td>
<td>23</td>
<td>0.921</td>
</tr>
<tr>
<td></td>
<td>My 778/HY 956</td>
<td>23</td>
<td>0.743</td>
</tr>
<tr>
<td></td>
<td>EKX ERKA 4617</td>
<td>23</td>
<td>0.743</td>
</tr>
<tr>
<td></td>
<td>HDPE</td>
<td>200-230</td>
<td>0.616</td>
</tr>
<tr>
<td></td>
<td>PP</td>
<td>230-300</td>
<td>0.743</td>
</tr>
<tr>
<td>Thermo-plastics</td>
<td>Acetal Homopolymer</td>
<td>190-230</td>
<td>0.743</td>
</tr>
<tr>
<td></td>
<td>Acetal Co-Polymer</td>
<td>180-220</td>
<td>0.839</td>
</tr>
<tr>
<td></td>
<td>Nylon 66</td>
<td>260-280</td>
<td>0.731</td>
</tr>
</tbody>
</table>

7.2 Surface Roughness

Qualitative results on the roughness of carbon fibres were first obtained by using the scanning electron microscope.
The photomicrographs show

<table>
<thead>
<tr>
<th>Plate</th>
<th>Fibre Type</th>
<th>Diameter μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Grafil A</td>
<td>9.3</td>
</tr>
<tr>
<td>4</td>
<td>Grafil HT</td>
<td>8.45</td>
</tr>
<tr>
<td>5</td>
<td>Grafil HT-S</td>
<td>7.65</td>
</tr>
<tr>
<td>6</td>
<td>Grafil HM</td>
<td>6.95</td>
</tr>
<tr>
<td>7</td>
<td>Grafil HM-S</td>
<td>6.15</td>
</tr>
</tbody>
</table>

To measure the specific surface roughness of carbon fibres vapour adsorption methods have been used (29, 30, 31, 32). Herrick (31, 32) employed the Perkin-Elmer Model 212C Sorptometer to measure the surface area of carbon fibres. Donnet unsuccessfully attempted the ASTM (33) method of iodine adsorption onto carbon black. The same authors (29, 30, 31, 32) also measured surface activity of carbon fibres, presumably to obtain some measure of the chemical activity in bonding carbon fibres. However these results were inconclusive and bewildering. The activity of a large number of chemical groups was measured. Herrick in particular compared the chemical activity, as measured by chemical functionality, to surface area, and found they do increase by a similar amount. He concluded that chemical activity can be used as a measure of surface area.

A similar approach to comparing surface areas is used in the ASTM (33) iodine adsorption test where it has been found that the weight of iodine absorbed compares with their surface area. The work in this thesis looks at surface area by measuring the amount of iodine absorbed on the surface. The problem with this method was that carbon fibres had a much lower specific area than carbon black for which the test was designed. In order to detect the amount of iodine absorbed from an iodine solution by carbon fibres, extremely weak solutions were used and their relative strengths were determined by using an ultra-violet spectrophotometer.
This new technique which was extremely simple and quick to carry out, gave reproducible results but had not previously been reported in the literature.

The ASTM test is D 1510

ASTM D 1510-65 for Iodine Adsorption of Carbon Black

In this test specification carbon fibre was substituted for the carbon black of the original test.

This stated that:

A dried sample, approx half a gram accurately weighed of carbon fibre is placed in a glass vial and 250 ml of standard iodine solution is added. The mixture is shaken vigorously for a minute. The iodine solution is then decanted from the carbon and titrated against a standard sodium thiosulphate solution, using starch as an indicator. From this the amount of iodine absorbed can be calculated.

For carbon fibres solutions were used, an order of magnitude more dilute than for the original carbon black specification (0.005 N iodine and 0.004 N sodium thiosulphate). At this concentration titrations are virtually impossible and so the concentration of the iodine solution before and after shaking with carbon fibres was determined by using spectrophotometry (as mentioned above) to determine the solution concentrations and hence the iodine absorbed from the carbon fibres.

Results

The amount of iodine absorbed on each grade of carbon was:— mg/gm

<table>
<thead>
<tr>
<th>Grafil</th>
<th>A</th>
<th>HT</th>
<th>HT-S</th>
<th>HM</th>
<th>HM-S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.9</td>
<td>1.8</td>
<td>1.94</td>
<td>1.63</td>
<td>1.15</td>
</tr>
</tbody>
</table>
From the photomicrographs (Plates 3-7) the diameters were taken and the surface areas of the different grades of carbon fibre were calculated, assuming they were smooth cylinders.

These areas were:

\[ \text{m}^2/\text{gm} \]

\[
\begin{array}{cccc}
A & HT & HT-S & HM & HM-S \\
0.25 & 0.27 & 0.30 & 0.30 & 0.34 \\
\end{array}
\]

From these two sets of figures the relative roughness of the fibres was estimated assuming, according to the ASTM (33) standards, that the iodine absorbed depended on the surface area.

**TABLE 2**

Relative Surface Roughness mg/m\(^2\) iodine absorbed

\[
\begin{array}{cccc}
A & HT & HT-S & HM & HM-S \\
7.6 & 6.8 & 6.5 & 5.4 & 3.4 \\
\end{array}
\]

7.3 Kinetics of Wetting

Almost no work has been reported on estimating the kinetics of wetting of fibres by liquid polymers. Yamanoto (34) reported a novel method whereby the weight of resin absorbed up a bundle of fibres, the tips of which were immersed in the resin, was monitored with time. However there was little data accompanying the description of this technique.

A more conventional technique was adopted in this thesis of measuring viscosity \(\eta\) and surface tension \(\gamma\) where the wetting rate \(R\) was a function of these two (17).

7.3.1 Viscosity

Two techniques can be used for measuring the viscosity of liquid polymers to give accurate results. These are:

1) Extruders such as in a "Davenport" melt flow index grader
2) Cone and plate methods such as the "Weissenburg Rheogoniometer" or "Shirley-Ferranti" cone and plate viscometers.
Figure 13 (35) shows the limitations for liquid polymers of the two types of viscometer on viscosity measurements. In any real situation where fibres are being wetted by liquid polymers, the polymers would be under low shear and hence the cone and plate type viscometers would be more useful in measuring viscosity in this area.

The Weissenburg Rheogoniometer is more accurate over the range of interest than the Shirley-Ferranti instrument, and since it was available for the author's use, all the viscosity measurements for liquid thermoset polymers were taken on this instrument. Appendix 2 describes this instrument and the way in which viscosities can be measured over a range of shear stresses.

The temperature of thermoset resins affects their viscosity, which therefore was measured from 23°C to 60°C. This was the temperature range of the instrument used. Figure 14 shows this variation. A comparison between polymers was made at room temperature. A shear rate of 45 sec⁻¹ was selected, corresponding to the lowest shear rate consistent with reproducible results for all the thermoset polymers, for the comparison. A standard shear rate was necessary because the polymers' viscosities varied with shear rate by differing amounts.

<table>
<thead>
<tr>
<th>Results</th>
<th>Viscosity $\text{Ns/m}^2$ at Room Temp (23°C) (at a shear rate of 45 sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin</td>
<td></td>
</tr>
<tr>
<td>Araldite MY 778/HY 956 Epoxy</td>
<td>1.00</td>
</tr>
<tr>
<td>Shell 816/TET Epoxy</td>
<td>0.85</td>
</tr>
<tr>
<td>HXL ERLA 4617 Epoxy</td>
<td>0.075</td>
</tr>
<tr>
<td>HXL SR 17449 Polyester</td>
<td>0.65</td>
</tr>
<tr>
<td>Scott Bader Crystic 272 Polyester</td>
<td>0.55</td>
</tr>
</tbody>
</table>
LIMITATIONS ON VISCOSITY MEASUREMENTS

Weissenburg Extends this Region

Minimum Stress on Cone & Plate

Useable Region of Cone & Plate

Cone Slipping

Maximum Stress on Cone & Plate

Minimum Shear Rate on Extruder

Useable Region of Extruder

Maximum Shear Rate Measurable

Viscosity

\( \eta \)

\( \text{NSm}^{-2} \)

Shear Stress \( \text{Nm}^{-2} \)

Figure 13
VISCOSITY VARIATION WITH TEMPERATURE

Figure 14

All Taken at Shear Rate of 45 Sec$^{-1}$
Unfortunately the available Weissenburg did not possess the facility to heat polymers beyond about 80°C, consequently the viscosities of thermoplastics could not be measured on the instrument. However most of the companies supplying polymers, were extremely helpful and supplied the relevant information on viscosities.

### Results Viscosities of Thermoplastics

<table>
<thead>
<tr>
<th>Plastic</th>
<th>Viscosity $\text{Ns/m}^2$</th>
<th>Processing Temp ($^\circ\text{C}$)</th>
<th>Conditions $\text{N/m}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.C.I. Nylon 66 A100</td>
<td>$1.7 \times 10^2$</td>
<td>285</td>
<td>$1 \times 10^3$</td>
</tr>
<tr>
<td>Shell Polypropylene Shell</td>
<td>$1.8 \times 10^4$</td>
<td>232</td>
<td>$1.95 \times 10^4$</td>
</tr>
<tr>
<td>Carlona P GMT</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hoechst Acetal Hostaform</td>
<td>$1.8 \times 10^3$</td>
<td>200</td>
<td>50 sec$^{-1}$</td>
</tr>
<tr>
<td>Du Pont Acetal Delrin 100</td>
<td>$2.5 \times 10^4$</td>
<td></td>
<td>100 sec$^{-1}$</td>
</tr>
</tbody>
</table>

Thanks are due to the relevant companies for the information they supplied on their materials. The viscosities again varied with temperature, shear stress and rate. The conditions chosen were the likely processing temperatures together with the corresponding shear stress and shear rate. Also account was taken of the temperature at which the contact angles were measured.

Appendix I more fully describes the polymer properties.

### 7.3.2 Surface Tension

The surface tension of the liquid thermoset polymers was measured using a torsion balance. The surface tensions of the liquid polymer systems were measured using a platinum ring at 23°C. In this test a gradually increasing force was applied to pull the platinum ring from the liquids until it is just pulled free. This force divided by the length of the platinum ring (conveniently directly calibrated on the instrument used) gave the surface tension.
For the thermoplastics, again no suitable equipment was available for measuring their surface tension at elevated temperatures. However from manufacturers' manuals a certain amount of information was gained.

**Results**

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Surface Tension N/m</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystic 272</td>
<td>0.0370</td>
<td>23</td>
</tr>
<tr>
<td>BML SR 17449</td>
<td>0.0390</td>
<td>23</td>
</tr>
<tr>
<td>Shell 816/TET</td>
<td>0.0400</td>
<td>23</td>
</tr>
<tr>
<td>Ciba MY 778/HY 956</td>
<td>0.0397</td>
<td>23</td>
</tr>
<tr>
<td>BML ERLA 4617</td>
<td>0.0462</td>
<td>23</td>
</tr>
<tr>
<td>I.C.I. Nylon 66</td>
<td>0.0354</td>
<td>285</td>
</tr>
<tr>
<td>Shell Polypropylene</td>
<td>0.0202</td>
<td>222</td>
</tr>
</tbody>
</table>

*White Electrical Instrument Ltd Direct Reading Torsion Balance.*

### 7.3.3 Wetting Rate

The wetting rate $R$ of the polymers was then found from the equation (17).

$$ R = \frac{C_6}{\eta} $$

However four of the thermoset polymers cure at room temperature, and the time during which they could flow after mixing the components together was measured (Pot Life). This was carried out by noting the temperature with time of a fixed amount (1 ml) of the curing polymer insulated from the environment. Generally when the temperature climbed to a maximum, the polymer would no longer flow. Although this is not directly relevant to the wetting rate, a short pot life might hinder the wetting out of the fibres.
TABLE 3

<table>
<thead>
<tr>
<th>Plastics</th>
<th>Pot Life (min)</th>
<th>Wetting Rate m sec(^{-1})</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystic 272) Polyester</td>
<td>19</td>
<td>6.7 x 10(^{-2})</td>
<td>23</td>
</tr>
<tr>
<td>HXL 17449 (1%) accelerator</td>
<td>160</td>
<td>6.0 x 10(^{-2})</td>
<td>n</td>
</tr>
<tr>
<td>Shell 816/TET (12.5 phr)</td>
<td></td>
<td>4.0 x 10(^{-2})</td>
<td>n</td>
</tr>
<tr>
<td>Giba HY 778/114 (25 phr)</td>
<td>114</td>
<td>4.7 x 10(^{-2})</td>
<td>n</td>
</tr>
<tr>
<td>HXL ERLA 4017 4.0</td>
<td></td>
<td>6.6 x 10(^{-2})</td>
<td>n</td>
</tr>
<tr>
<td>I.C.I. Nylon 66 (A100)</td>
<td></td>
<td>2.1 x 10(^{-4})</td>
<td>285</td>
</tr>
<tr>
<td>Shell Polypropylene</td>
<td></td>
<td>1.1 x 10(^{-6})</td>
<td>222</td>
</tr>
<tr>
<td>Hoechst acetal Hostaform</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Du Pont acetal Delrin 100</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The relevant information was not available for these grades.

7.4 Adhesion Measurements

Inter-laminar shear strength tests on composites have been used to assess the adhesion between the fibre and matrix in the composite\(^{(36)}\). However the choice of shear test\(^{(37)}\), size and shape of specimen alters significantly the shear result obtained. In considering the physical parameters of individual carbon fibres and resins, and comparing these with adhesion, it was considered essential to measure the adhesion between single fibres and resin. Broutman\(^{(38)}\) and Trivissanno\(^{(39)}\) examined the relation of single fibre to resin bond strengths and laminate strength in flexure, and concluded that although there was sometimes a simple relationship between flexure tests, this was not always the case.
The measurement of single carbon fibre to plastic adhesion was difficult because of their small fibre diameter, brittle nature and opacity. There has been no published work on measurements of the adhesion between single carbon fibres and plastics, because of which the author applied the established techniques for glass fibres, to carbon fibres. These techniques include pulling single fibres out of resin discs; and embedding single fibres in specially shaped resin blocks which are then compressed.

7.4.1 Shaped Cast Resin Specimens

Figure 15 shows the curved neck and rectangular column resin block specimens in which the single fibres were embedded for compression tests to give adhesion values. For glass fibres a single fibre is embedded in a block of resin, the faces are polished and the block compressed in the manner shown in the diagram. Since glass fibres are transparent nothing can be seen in the resin block. When the interface between fibre and resin fails the fibre can be readily seen. Bond strength tests to fail the interface in shear, adopt the rectangular block specimen with the fibre embedded in the length of the block. A curved neck specimen can fail the interface in a tensile manner. The shear bond strength $\tau$ generally quoted in adhesion work can be estimated, knowing the average axial stress $\sigma$ in the resin block when the fibre interface fails.

$$\tau = 2.5 \sigma$$

Broutman (38) quotes the 2.5 figure and referred to Edelman's work (40) showing the stress concentrations round embedded fibres.

Unfortunately with carbon fibres the technique was found not to work. Carbon fibres are opaque and can be seen even when bonded to the resin. Broutman acknowledges the difficulty with opaque fibres and
CURVED NECK SPECIMEN

Figure 15

RECTANGULAR COLUMN SPECIMEN
suggests illuminating the fibres with a microscope lamp. Broutman's work with boron fibres revealed highly reflective regions when the interface failed. However with carbon fibres these were not apparent in polarised or unpolarised light. Although exhaustively tested, this technique did not seem to be suitable for measuring the adhesion between carbon fibres and plastics.

7.4.2 Fibre Pull-out Specimens

Glass-rod specimens pulled from resin have been used\(^{(38)}\) to measure adhesion simulating a glass reinforced plastic composite, and a typical specimen and test trace are shown in Figure 16. Fibre specimens are suitable for testing in this manner, as long as the cast resin is sufficiently thin.

The adhesive strength $\gamma$ is then (equation 4).

$$\gamma = \frac{\sigma_m d_f}{4 l_R} \quad \text{4}$$

$\sigma_m$ is stress applied to rod

$d_f$ is rod diameter

$l_R$ is embedded rod length

This method has been successfully applied to glass fibres\(^{(38)}\) which are thicker and less brittle than carbon fibres. The problem with carbon fibres was to embed them in less than 1 mm of polymer and then, without breaking the fibres, pull them from a thin strip of polymer.

As shown in Figure 17 the technique employed used a carbon fibre, mounted on a card, with its centre cut out. Two wires were glued either side of the fibre after Andreavska\(^{(41)}\), so that they were close to it. The resin under test was then dropped onto the intersection of the two wires and fibre and lengths of fibre down to 0.2 mm were embedded in this way. The card was mounted in the fibre jaws.
Figure 16

![Diagram showing a glass rod embedded in resin with applied stress and strain graph.](image)

- **Applied Stress**
- **Resin**
- **Embedded Length (l)**
- **Glass Rod**
- **2r - Rod Diameter**

The graph shows the relationship between **Stress** (σ) and **Strain** (γ), indicating the adhesive strength.
CARD MOUNTED CARBON FIBRE FOR ADHESION TEST

Figure 17

[Diagram showing a card mounted with carbon fibre and wires, labeled Glue, Carbon Fibre, Resin Under Test, and Wires.]
of an Instron, the fibre broken at A, the card cut at B and tested in the Instron Tensile Testing Machine, giving a graph as shown in Figure 16. The load at which the fibre pulled out was taken from the graph and knowing the embedded length, the bond strength of the fibres could be calculated in the resin under test.

Results

All five grades of Grafil (A7 HT, HT-S, HM, HM-S) were tested with EKL SR 17449 polyester resin; however only HM type fibre would pull-out from the resin. The other fibres were either not strong enough or were embedded in too thick a strip of resin to give a pull-out test.

The variation in measured values was ± 50%, so about ten samples were tested with each resin to HM fibre, yielding the following results:

<table>
<thead>
<tr>
<th>Resin Type</th>
<th>Bond Strength to HM Fibre</th>
</tr>
</thead>
<tbody>
<tr>
<td>EKL SR 17449</td>
<td>3.69 MN/m²</td>
</tr>
<tr>
<td>Scott Bader</td>
<td>3.46 MN/m²</td>
</tr>
<tr>
<td>Crystic 272</td>
<td>3.90 MN/m²</td>
</tr>
<tr>
<td>Shell Epikote 816/TET M778/HY 956</td>
<td>3.24 MN/m²</td>
</tr>
</tbody>
</table>

7.4.3 Embedded Fibres

A variation of the technique used in section 7.4.1 where fibres were embedded in resin became apparent after noting the work of Wadsworth and Spilling (42). This method involved embedding fibres in resin, as before, but now the resin was stressed in tension rather than in compression. A thin layer of resin was spread on a strip of annealed and etched aluminium whose dimensions are shown in Figure 18. While the resin was still a liquid several carbon fibres were embedded in the resin. The resin was then cured and post cured.
Figure 18

Resin

Carbon Fibre

Stress

Unloaded

Minimal Strain Recovery

Strain
Rolled aluminium sheet approximately 2 mm thick annealed for 2 hours at 500°C, provided a material which would extend plastically with little elastic recovery after straining according to the graph in Figure 18. With such a material a strain was imposed, on the layer of resin and the embedded fibres by an Instron tensile testing machine. The resin fibre composite which adhered to the aluminium strip was strained and inspected under a microscope to observe the failure and debonding behaviour of the composite. The extension of the strip was noted using a travelling microscope on scribed marks.

In practice the composites on the aluminium were extended in 0.1% strain stages and the carbon fibres ends observed in the microscope at each stage to see when they debonded from the resin. When the fibres debonded, knowing the extension of the resin adhesive at failure, Young's Modulus of resin and hence tensile stress in the resin, the stress at which the fibre debonded could be calculated. The failure extension was taken when some part of every fibre embedded in the resin had debonded. Generally this occurred in every fibre at the same incremental extension of the resin. The debonding axial stress in the resin was taken as the adhesive strength, of the resin to the fibre.

The average of three aluminium strips with between 3 and 6 fibres per strip gave reasonably consistent results. It should be noted that the preparation and testing of the strips was a time-consuming process and any further effort to reduce the error would have lengthened unnecessarily the testing time. The results obtained showed significant differences sufficient for the comparison to physical parameters of the resin and fibre.
<table>
<thead>
<tr>
<th>Carbon Fibre</th>
<th>A</th>
<th>HT-S</th>
<th>HT</th>
<th>HM-S</th>
<th>HM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EKL SR 17449</td>
<td>26.9</td>
<td>24.0</td>
<td>16.3</td>
<td>15.2</td>
<td>11.7</td>
</tr>
<tr>
<td>Crystic 272</td>
<td>58.6</td>
<td>31.3</td>
<td>21.0</td>
<td>24.5</td>
<td>12.1</td>
</tr>
<tr>
<td>Shell Epikote</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>816/TET</td>
<td>28.4</td>
<td>25.5</td>
<td>22.0</td>
<td>13.8</td>
<td>10.9</td>
</tr>
<tr>
<td>Ciba Araldite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MY 778/HY 956</td>
<td>32.7</td>
<td>31.5</td>
<td>25.6</td>
<td>18.7</td>
<td>10.1</td>
</tr>
</tbody>
</table>

Adhesion as measured in MN/m$^2$
8. DISCUSSION OF RESULTS

In discussing the work only those polymers whose adhesion, contact angle and wetting rate were measured will be initially introduced. The other polymers, notably the thermoplastics will be introduced towards the end of the section and their possible adhesion discussed.

The property of the carbon fibres measured was surface area/surface activity as in the ASTM test method D1510-65. This was correlated to the scanning electron microscope photographs of the fibres. These photographs showed that A grade fibres were the roughest, HT and HT-S next and HM and HM-S the smoothest. Figure 19 completes the picture in comparing surface roughness with adhesion. Both tests show how the additional heat treatment HM grade fibres receive, compared to HT fibres and HT fibres compared to A fibres smothes their surface. This smoothing phenomena corresponds with a steady decline in the adhesive strength of carbon fibres to polymers, and a steady decline in the variation in adhesive strength between polymers to a specific grade of carbon fibres.

The iodine absorption test revealed some interesting phenomena concerning the effects of surface treatments and the resulting adhesion to the carbon fibres. The surface treatment on HM grade fibres is far more effective than on HT grade fibres as is also indicated in the Courtaulds Grafil Data (Appendix 1). These treatments correspond to a greatly reduced surface area, the greater the reduction the more the improvement in adhesion. These treatments are believed to be a wet oxidation brought about by a sodium hypochlorite solution(43,44). This thesis demonstrates that the surface treatment gives the fibres not only the expected etching(43,44) but also a surface cleaning effect as shown by the reduced surface area. Gill(1) also enquires whether these surfaces treatments, do in fact, clean as well as etch the surface.
Range of Adhesion between Resins and a Grade of Carbon Fibres

- **Surface Roughness**
- **mg Iodine Absorbed**
- **Area in m²**

Adhesive Strength MNm⁻²

- **HM Grade**
- **HT Grade**
- **HT-S Grade**
- **A Grade**

Figure 19
The surface of a solid in an adhesive joint could have two conflicting effects, a rough surface would be expected to key in well to an adhesive, and bond well, but if the rough asperities are too sharp, then they will act as stress concentrators and fail the bond through crack propagation. These effects are apparent in carbon fibres where as the overall surface is smoothed by heat treatment and the fibre surface looses its ability to key with the resin, the adhesion falls off. However a surface treatment on any fibre improves the adhesion by removing the surface debris which can initiate a crack and cause premature failure. This surface debris presumably arises as a result of the heat treatment on the fibres. More debris arises with the heat treatment used on the IM grade, giving an opportunity for greater improvement in adhesion.

The most interesting phenomenon measured was the decreasing contact angles between carbon fibres and liquid polymers resulting in improved adhesion. On Figure 20 contact angles have been plotted as \( \cos \Theta \), where increasing \( \cos \Theta \) corresponds to decreasing contact angles and improved wetting. If accurate and appropriate contact angle values can be obtained then it could be possible to establish a quality control test on carbon fibres to estimate the likely adhesion of a particular grade, as well as the effectiveness of any treatments used to improve adhesion.

In considering Figure 20 there are obvious inconsistent data: note H-M-S fibre with the Araldite resin and HT fibre with the Shell resin. However it can be deduced from the graph that a larger \( \cos \Theta \) (smaller \( \Theta \)) of a resin on a fibre will give better adhesion. The variation in contact angle on a fibre seems more critically to reflect adhesion for carbon fibres which have poor adhesion to polymers. There is a good correlation between adhesion and contact angles for one type of polymer (e.g. polyester resins) and one grade of carbon fibre.
Figure 20

VARIATION OF CONTACT ANGLE WITH ADHESION

- HM Grade Fibre
- HM-S
- HT
- HT-S
- A

A - Ciba Resin
S - Shell
C - Scott Bader Resin
B - BXL Resin

Adhesive Strength MNm$^{-2}$
Measurement of contact angles was difficult and time-consuming and the photographs obtained could be interpreted to give a range of contact angle values. Yamamoto\(^{(34)}\) has measured contact angles of polymers on carbon fibres, but the photographs he produces clearly give contact angles considerably smaller than the values he attributed to the photographs. It is important to realise, as did Yamamoto, the difficulty in measuring and recording sensible and appropriate contact angle values. However despite this critical look at contact angles, it was thought that the results obtained were sensible partly, because of the critical approach. Yamamoto gives results relating contact angles to inter-laminar shear strength which only very roughly correlate. However, as explained previously, there is not a good correlation between adhesion and inter-laminar shear strength and there is no scientific basis to expect contact angles to directly relate to inter-laminar shear strength.

Figure 21 depicts the wetting rate of the polymers, against carbon fibre adhesion to those polymers, these being an average for all the carbon fibre grades. The wetting rate goes some way towards explaining the variation between different grades of the same polymers, (polyester or epoxy resins). A comparison of Figure 20 showing wetting rate variation against adhesion, with Figure 19 showing contact angle variation against adhesion explains the variation of adhesion between similar polymers as detected by the contact angles, according to the wetting rate of the polymer.

For Example

The better adhesion of polyester resin C, over B, correlates well with polyester resin C's faster wetting rate: Similarly for the epoxy resins. However although the polyester resins tested had a faster wetting rate, than the epoxy resins, the adhesion was no better. This reflects the different nature of the two polymers and the way in which they bond to the fibres.
VARIATION OF WETTING RATE WITH ADHESION

Figure 21

Adhesive Strength MNm^{-2}

B - BXL SR 17449
C - Scott Bader Crystic 272
S - Shell Epikote 816
A - Ciba Araldite MY 778
The adhesion values measured by the two different methods showed large differences for HM fibre. The test method with the embedded fibre gave a bond strength about 3.8 times that measured by pulling the HM fibre from the resin. This partly was expected, and found by L.J. Broutman (37). An explanation for this is that the length of fibre which adhesively fails in the fibre pull-out method of adhesion test (7.4.2) was 50 times the length which adhesively fails in the embedded fibres adhesion test (7.4.3).

The failed length here is the short section at the end of the whole embedded fibre which visibly debonds. A smaller area of adhesion under test, will generally give higher bond strengths because in a large area, as one point in the bond fails the stress in the rest of the bond increases, leading to more bond failures and even greater stress on the remaining bonded area. Obviously a larger bonded area is more subject to premature failure because of this effect.

The important point about the two sets of results is that they agree with HM type fibre having a similar bond strength to all the resins. This reinforces the case for stating that the technique of measuring adhesion by stressing aluminium (with carbon fibres bonded to polymers on the aluminium) is a relevant single fibre to polymer adhesion test, for comparative work.

The results indicate that epoxy resin adhered no better to carbon fibres than polyester resin. This was not the case with glass fibres (45) where epoxy bonded better than polyester, tested by fibre pull-out or embedding of fibres in resin. The reason for this is not clear, but probably reflects that neither bond particularly well to carbon fibres. The 'Instron' trace of the fibre pull-out test from epoxy resin as in Figure 16 showed a sharp drop of about 30% of the peak load, and then a residual load due to friction as HM carbon fibre was pulled from epoxy resin. With polyester resin there was no sharp fall in load when the bond failed. Instead, the
load on the trace gradually dropped as the fibre was pulled from the resin. This indicates that a significant contribution to the adhesion between carbon fibres and epoxy resin is due to physical/chemical bonding. With polyester resins the adhesion to carbon fibres is almost entirely due to friction. Polyester resins shrink up to 7% by volume on curing, which gives their frictional adhesion, whereas epoxy resins shrink only 1% on curing.

In a composite where the fibre volume is about 60% the resin is not encapsulating the fibres, but just filling the spaces in between them. As polyester resin cures in a high fibre volume fraction composite, it would shrink away from the fibres giving rise to poor adhesion. Epoxy resin however in a similar high volume fraction composite would not shrink away from the fibres, but give composites with fibres well-bonded to the matrix. This different behaviour explains why, although polyester and epoxy resins have similar bond strengths to carbon fibres, as found in this thesis, do not give composites with similar properties. Work on glass fibres by Vasta and Zronar(46) also discussed this phenomenon and devised some interesting tests to highlight it. In these tests they compared the bond strengths of glass rods pulled from cast resin and glass tubes with resin rods bonded inside them. In the former the resin shrank onto the glass rod, and in the latter the resin would shrink away from the glass tube. They then identified the relative proportion of the adhesive strengths of glass to polyester and epoxy which could be attributed to friction and physical/chemical forces.

Not mentioned in the above discussion was ERLA 4617: This resin was a prepreg resin involving a long cure cycle at elevated temperatures and therefore could not easily be compared with the other room temperature curing thermoset resin polymers. However knowing its wetting rate and contact angles on carbon fibres enables an estimate of likely adhesion to be made.
The wetting rate of ERLA 4617 was an order of magnitude greater than the other epoxy resins (see Figure 21). It is unlikely that the adhesion of this resin to fibres is an order of magnitude greater, but it should be considerably greater. The adhesion to carbon fibres assessed by contact angles is shown in Figure 22. Together the information indicates that adhesion to HT-S, HT and A grade carbon fibres might well be greater than with other thermoset polymers. However the adhesion of this resin to HM and HM-S grade fibres should be of a similar order compared to the other resins.

The contact angle variation of the thermoplastics with the various grades of carbon fibres is shown in Figure 23. The graph indicates that nylon 66 and high density polyethylene do not wet carbon fibres easily. Polyacetals wet carbon fibres much better, and polypropylene is intermediate. HM grade and A show the most variation of contact angles with the thermoplastics. The wetting rates of the thermoplastics indicate that nylon 66 could compensate its high contact angles with faster wetting, especially on the A, HT, HT-S and HM-S fibres where the contact angles are not excessively high. Polypropylene has a slow wetting rate and this would reduce its adhesion below that indicated by contact angles alone. The polyacetals have intermediate viscosities, probably leading to intermediate wetting rates, however this will not alter the likely adhesion performance of polyacetals as assessed by contact angles. In general it might be expected that polyacetals would bond best of the tested thermoplastics to carbon fibres, especially to the HM and HM-S grades of fibre which are generally difficult to adhere to. This is because polyacetals have neither a high contact angle nor poor wetting rate with carbon fibres.
CONTACT ANGLE VARIATION OF EPOXY RESINS ON C-FIBRES

Figure 22

Angle in Degrees

50

40

30

20

A

HT

HT-S

HM

HM-S

Grade of C-Fibre

Shell

Ciba

BXL

Shell – Shell Epikote 816 system
Ciba – Ciba Araldite MY 778 system
BXL – BXL ERLA 4617 system
CONTACT ANGLE VARIATION OF THERMOPLASTICS ON C-FIBRES

Figures 23
The original work on contact angles was in support of an investigation at British Rail's Plastic Development Unit of adhesion to carbon fibres when they reinforce thermoplastics. It was expected that those combinations which appeared to adhere best would perform in a superior manner. This was predicted by the contact angle measurements mentioned above, and later confirmed. It was found that acetal plastics reinforced by carbon fibres demonstrated superior wear properties, as predicted by above.
PART III

9. TOUGHNESS

9.1 Introduction

The effect of adhesion on the toughness of carbon fibre composites has been discussed briefly in Section 4.3. Although little work had at the time been conducted on the effect of adhesion on toughness, Harris et alia (47) had discussed its connection with inter-laminar shear strength (and adhesion).

Many authors who had been investigating adhesion in carbon-fibre composites did not measure the toughness of their modified composites. Their work is reviewed in the next section but it should be realised that toughness was not considered to be a problem when the carbon fibres were first being produced. Consequently for this thesis a study was made of the treatments which had been expected to improve adhesion of resins to carbon fibres with a view to selecting and assessing their suitability for improving toughness. In addition a review was undertaken, of those improvements in toughness which had been achieved in glass-fibre reinforced-plastic technology; again with the purpose of assessing the successful techniques and adapting them to carbon fibre composites. Work on toughness in all materials was considered in order to plan a coherent investigation of toughness in carbon fibre composites.

Toughness testing is currently being developed from simple pendulum tests to fracture toughness techniques which give accurate, and applicable results. A separate section in this thesis is devoted to a review of fracture toughness testing, applied to carbon-fibre composites, as they are relatively new materials for which testing techniques are only just being developed.

9.2 Fibre Surface Treatments

The following survey selected from the literature the relevant information which could be significant in research on the toughness of carbon-fibre composites.
Goan and Prosen (36) theorised that carboxyl and phenolic groups on the surface of oxidised carbon fibres should be able to react with isocyanate groups in a urethane prepolymer coating on a carbon fibre. Other isocyanate groups in the coating should be able to couple with the resin matrix. The polyisocyanates would act as bridging or coupling agents between the polymer and the resin. When composites were made by Goan and Prosen to investigate this theory the composites exhibited no significant improvements over composites made from fibres, which had not been treated with polyurethane prepolymer. The significant improvements expected were in inter-laminar shear strength. They also investigated other fibre coatings in anticipation of improved inter-laminar shear strength (I.L.S.S). These coatings were nylon, which gave no improvement in I.L.S.S., and the glass size A-1100 silane (gamma-aminopropyltriethoxysilane) which gave a slightly improved I.L.S.S.

Herrick (31) however treated oxidised carbon fibres with A1100 silane and found no improvement in I.L.S.S. of the resulting composite. Herrick also tried other fibre treatments both for adhesion and improvement in I.L.S.S. of the resultant composites. Out of a series of amines investigated by him only diethylenetriamine (DETA) gave any evidence of adhesion to carbon fibres.

Broutman (45) listed the roles of coatings which have been applied to glass fibres:

(a) Coupling agents which increase the adhesive strength of the glass-polymer interface.

(b) Coupling agents which provide low modulus, flexible layers at the interface.

(c) Coupling agents which promote better wetting between the polymer matrix and the reinforcement surface.
W.J. Eakins (48) indicated the concepts to be understood when developing an effective treatment with which to toughen carbon fibre composites. He visualised a small crack forming in a composite under stress, at a void or inclusion. The crack advances towards and perpendicular to a fibre surface. If it is assumed that there is no energy spreading mechanism and that the resin is bonded to the fibre surface, then the full force of the spreading of the crack surfaces as it advances is concentrated at the crack tip. Any work mechanism distorting or aligning the resin that may have been possible in the region between the fibres cannot take place at the interface because of the restraining influence of the bond to the fibres. The crack impacts the fibre and penetrates it. A brittle fracture is the result. Consider tough laminates of glass-reinforced plastics, they are assumed to have failed when the fibres are visible, or the cracks round them are visible. Since all cracks and delaminations greater than 0.5 μm would be visible, the energy absorption mechanism in these laminates must be efficient and it is this sort of efficiency that must be developed in carbon composites.

If the resin is bonded to the fibres not securely; but in a random fashion, then the interface would either not yield or would completely fail, depending on the area of the interface. This behaviour is the energy absorption mechanism found in high quality glass laminates. However, if the bonds to the fibre are concentrated in groups, then the interface could fail in jerks, rather like tearing a textile weave. Both these bonding arrangements will absorb energy. However the second one would be more effective at restraining further debonding. What we want in an ideal surface treatment is a bond which will break progressively, when it is needed.
to stop cracks propagating, but will absorb a considerable amount of energy in doing so, and stop the crack propagating without any tendency for them to start again.

Consideration of the brittle failure mechanism outlined by Eakins leads to an investigation of ways in which a crack can be blunted at the fibre-polymer interface, and the interface made to absorb energy as it is pulled away from the fibre. According to Broutman (45) "Coupling agents can provide flexible, low modulus layers at the interface" and a coupling agent with sufficient strength could fail in the manner described by Eakins. Such material properties are supplied by polyurethane rubbers, which were investigated by Goan and Prosen (36) as a surface treatment for carbon fibres. The polyurethane tried by Goan and Prosen neither increased nor decreased the adhesion to carbon fibres. However using DETA to cure the polyurethane (recall work by Herrick (31)) could possibly improve the adhesion to carbon fibres. The polyurethane bonds to the epoxy resin, according to Goan; in addition it is compatible with epoxy resin and the two should, under the right conditions, form a graded and intermixed interface.

Herrick et alia (31) discussed a flexible coating on carbon fibres to overcome brittle fracture of composites. Herrick coated carbon fibres in his work with nylon 8, but after discussing possible toughness improvements, quoted only I.L.S.S. results, which were unchanged. Other coatings on carbon fibre were investigated by Herrick, but none of the resulting composites were tested for impact strength.

Trivisanno (39) while investigating the effect of flexible coatings on glass fibres in glass-reinforced plastics found "significant increases in fibre-resin bond strength and flexural strength ... but they did not achieve a complete improvement in properties".
His coatings were compatible "synthetic rubbers .. or polyvinyl-butyrat e" unlike those tried by Herrick. In this work it had already been decided that compatible fibre coatings would show most promise in improving toughness.

These are the reasons why the surface treatments were developed in the present research work, and just what its expectations were. The blocked polyurethane rubber Adiprene ML-16 should bond well to the carbon fibre extended by the DETA, and to the epoxy resin by a compatible graded matrix. Using this system, a flexible low modulus coating was placed at the interface to blunt cracks. It should debond from the carbon fibres only with difficulty due to the good adhesion, but absorb energy under deformation.

It has been mentioned how the energy absorbed at fracture is greater when the fibres debond and pull out, rather than break. It is useful at this stage to relate the work of Kelly\(^{49}\) who shows, by comparing possible fracture models, just where the energy is absorbed. Kelly compares the fracture modes discussed by Cooper and Kelly\(^{50}\) and Outwater and Murphy\(^{51}\). This thesis compares in addition the relevant work of Harris\(^{47}\) and Piggott\(^{52}\) who have more recently investigated this problem.

Cooper and Kelly\(^{50}\) state that the major amount of work of fracture is absorbed during fibre pull-out and matrix shear. The remainder being derived from the elastic energy stored in the fibres, together with the fracture energies of the fibre and matrix.

The work to pull the fibres out of the matrix \(W_p\) is

\[
W_p = \frac{1}{2} \tau_m \cdot \pi d_f \cdot l_f^2
\]

where \(\tau_m\) is the stress resisting fibre pull out

\(l_f\) is the embedded fibre length

\(d_f\) is the fibre diameter.
Outwater and Murphy suggested that the major portion of the work involved in fracture is due to debonding of the fibre. If one can imagine the stress-strain curve of a fibre being pulled from a matrix, then the area under this curve is equal to the energy absorbed by the fibre and stored as elastic energy after bond failure. When a fibre debonds from the matrix the strain energy contributing to the fracture toughness over a length $L_f$ is $W_D$

$$\sigma_f \text{ max} \sim \text{ultimate tensile strength}$$

$$W_D = \frac{\pi d_f^2}{24} \cdot \frac{\sigma_f \text{ max}}{E_f} \cdot \sigma_f \text{ max} - 12 E_f - \text{fibre modulus.}$$

Cooper and Kelly then compared $W_P$ and $W_D$ and assumed

$$\gamma_m = \frac{\sigma_f \text{ max} \cdot d_f}{4 \cdot L_f} \ ... 4$$

Then

$$\frac{W_P}{W_D} = \frac{\frac{1}{2} \cdot \gamma_m \cdot \pi \cdot d_f \cdot L_f^2}{\frac{\pi d_f^2}{24} \cdot \frac{\sigma_f^2 \text{ max}}{E_f}}$$

$$= \frac{E_f}{\sigma_f \text{ max}}$$

Where $E_f/\sigma_f \text{ max}$ is at least of the order of 100 : 1, as is usual with carbon fibres in composites, then at least 300 times as much energy can be absorbed by pulling the fibres out of the composite and shearing the matrix than debonding the fibres from the matrix.
Piggott (52) in discussing possible methods of toughening composites suggests rather arbitrarily that a low shear stress material at the interface between the fibre and matrix would seem worth investigating. He came to this conclusion by theoretically analysing composites in an attempt to correlate the fracture toughness parameter \( K_c \) with other physical properties of the composite. Although the model is not practical, nor is it usually possible to equate \( K_c \) with other physical parameters (53), his work defines most of the important parameters upon which toughness is considered to depend. These are high fibre strength, large fibre diameter and a high volume fraction of fibres in the composite.

Harris (47) concluded that fracture energy in composites was greatest for those with a weak interface, where a large area of fibres were pulling from the matrix.

The analysis of Cooper and Kelly, Outwater and Murphy, Piggott and Harris give additional support to the decided course of the present research programme undertaken. A weak, flexible, low modulus surface coating well bonded to the carbon fibre and compatible with the epoxy matrix, fulfills most of criteria and suggestions of the many authors reviewed. This system should blunt cracks at the interface, allow fibres to pull-out from the matrix without initially debonding, and being well bonded to matrix and fibre should not seriously degrade the other composite properties.

9.3 Toughened Matrices

The development of the 'Ideal' matrix for carbon fibres has been discussed (54). The ideal matrix, however, does not necessarily give the best toughness, if toughness is required, but rather the best average values for all the various properties.
The use of thermosetting resins as structural materials or as matrices for fibre reinforced composites is often limited by brittleness and a tendency to catastrophic failure. McGarry and his co-workers\(^{(55)}\) have investigated ways in which elastomeric inclusions could be used to increase the resistance of thermoset resins to fracture and cracking. The successful work to date has centred largely on the use of Hycar CTBN, a carboxyl-terminated, liquid butadiene-acrylonitrile copolymer. Hycar CTBN has been used to toughen epoxy resin by an in-situ formation of small rubber particles in a glassy resin. The liquid rubber was added at low levels (as low as 2.5 phr) and small particles of rubber were precipitated during gelation of the resin. The elastomer polymer chain has reactive sites which form bonds in the resin between areas of high rubber concentration and the cross-linked cured epoxy resin.

McGarry\(^{(56)}\) and Sultan have shown that Hycar CTBN blended with epoxy resins gave a ten-fold improvement in fracture energy of the epoxy resin. Burhans and Soldatas\(^{(57)}\) have shown that a Hycar CTBN modified cycloaliphatic epoxy resin (ERL-4221) improved its tensile strength and elongation from 7,500 psi \((51.6\ \text{MN}\!\text{m}^{-2})\) and 1.9\% to 12,000 psi \((82.6\ \text{MN}\!\text{m}^{-2})\) and 5\% together with a drop of only 7\% in modulus.

However there are problems with using Hycar CTBN. A paper by Drake et alia\(^{(58)}\), investigating the use of liquid rubbers to toughen thermoset resins, indicated the elaborate mixing procedure necessary and the problems which arise in casting the resin. Phillips and Rogers\(^{(59)}\) in discussing the use of Hycar CTBN state that, although the matrix material is toughened, the behaviour of the composite is complex and the modified composite gives disappointing results. In these materials they recall the strain to failure is limited by the reinforcement, and it is the way in which the fracture energy is absorbed at the crack tip which is important. The disappointing results are not surprising since it seems that the toughening is not being placed where it is required, on the fibres.
The cycloaliphatic epoxy resin EXL ERLA 4617 already mentioned in the work on adhesion, gives properties which are unusual. It has a high modulus and high elongation. Work by Rogers et alia\(^{(60)}\) on the ballistic impact resistance of treated carbon fibre composites, where the matrix was ERLA 4617, yielded some interesting results. An eight-fold improvement over a conventional epoxy novolac resin with untreated fibres was quoted. What is important here is that by increasing the elongation of the resin, treated fibres can have good impact resistance with good bonding to the resin. However ERLA 4617 is a difficult resin to handle, the cure cycle is very complicated and has poor resistance to water immersion.

Conventional epoxy resins have been toughened or made less brittle by using low modulus curing agents, such as in polyamide extended epoxy resins. In this research work more flexible epoxy resins were formulated and used as matrices in composites; for it was considered that conventional flexibilisers for epoxy resins had not increased the impact strength sufficiently. Owen and Rose\(^{(61)}\) in their work also concluded that the fracture toughness of epoxy was not significantly improved, using conventional flexibilisers.

Polyurethane rubbers can be used to improve the impact and flexibility of epoxy resins to a greater extent than with conventional flexibilisers. Du Pont issue a bulletin\(^{(62)}\) on this subject and reveal that a range of properties in between those of epoxy resin and polyurethane rubber can be achieved, since they are completely compatible.

Kelly\(^{(49)}\) suggested a mechanism to improve toughness, by allowing fibres to pull out from the matrix and deform... the matrix as discussed in section 9.2 'Toughening by Fibre Surface Treatments.' He showed that the work absorbed in fracture was maximised(Figure 24), when the actual fibre length pulled out from the matrix equalled the fibre critical length.
VARIATION OF FIBRE STRENGTH WITH FIBRE LENGTH

Figure 24

MAXIMUM WORK OF FRACTURE
The work of fracture absorbed by the composite if it fails according to the mechanism described by Kelly is \( W_p \) where

\[
W_p = \frac{1}{2} \pi r_f \gamma_m l_f^2
\]

\( r_f \) = fibre radius
\( \gamma_m \) = matrix shear strength
\( l_f \) = fibre pull-out length

For maximum work of fracture the fibre pull-out length should equal the fibre critical length \( l_c \) where

\[
l_c = \frac{\sigma_{f\,\text{max}} d_f}{4 \gamma_m}
\]

\( \sigma_{f\,\text{max}} \) = ultimate fibre strength
\( d_f \) = fibre diameter
\( \gamma_m \) = matrix shear strength

The problem then with this mechanism is whether the length of fibre pulled from the matrix is the fibre critical length.

The work in this section of the thesis involved finding the composite requirements for maximum work of fracture assuming a mechanism as discussed above. Wadsworth and Spilling\(^{42}\) noted in a composite that the fibres break down into smaller lengths as the stress on the composite is increased. This is obviously necessary, if to absorb energy at fracture fibres are to pull out from the matrix. The lengths into which they break should equal the critical lengths of the fibre for maximum work of fracture. The lengths into which the fibres break depend on their strength, see Figure 24 according to Wadsworth and Spilling\(^{42}\). They give the change in fibre strength with fibre length, for RAE HM fibre and assuming a similar behaviour for Courtaulds HT-S fibre the change in fibre strength for length is shown for this fibre.
A standard epoxy resin has a shear strength of 50 MN/m² and carbon fibres a diameter of 10 μm. This gives a ratio of (eqn. 4)

\[
\frac{\sigma_{f_{\text{max}}}}{l_c} = \frac{200}{10} \frac{\text{MN/m}^2}{\text{m}} = 20\frac{1}{1}
\]

For maximum work of fracture the fibre pull-out length equals the fibre critical length where the length of fibres pulled from a matrix depends on the length which they have broken down to on straining the composite. From Figure 24 this occurs when the fibre length is 250 μm and fibre strength is 5 GNm⁻² (matrix shear strength 50 MNm⁻²).

This gives a Work of Fracture \( W_p \)

\[
W_p = \frac{1}{2} \pi l_c r_f r_m \frac{l_c^2}{l_f^2} 11
\]

\[
= \frac{1}{2} \times 3.142 \times 5 (\text{μm}) \times 50 (\text{GNNm}^{-2}) \times \frac{250^2}{4} (\text{μm})
\]

\[
= 2.5 \times 10^{-5} \text{Nm} (\text{Joules}) \text{ per fibre}
\]

In a composite with a 60% fibre volume fraction, there are \( 7 \times 10^9 \) fibres/m².

\[
W_p = 1.75 \times 10^2 \text{ K Joules/m}^2
\]

Then for a 60% volume fraction composite of Courtaulds HT-S fibres in epoxy resin, the work of fracture should be \( 1.75 \times 10^2 \text{ K Joules/m}^2 \).

A matrix such as polyurethane rubber has a shear strength of 10 MNm⁻². This leads to a fibre critical length as before

of \( l_c (\text{mm}) = \frac{\sigma_{f_{\text{max}}}}{4} (\text{GNNm}^{-2}) \)
From Figure 24 this gives a fibre critical length of 1 mm and a fibre strength of 4 GNM⁻². A composite of Courtaulds HT-S fibre in polyurethane could have a work of fracture of \( W_p \).

\[
W_p = \frac{r_f \cdot \tau_m \cdot l_c^2}{2 \cdot l_f^2} \text{ per fibre}
\]

\[\times 7 \times 10^9 \text{ (fibres/m}^2 \text{ in a 60\% vol. fraction composite)}\]

\[= 7 \times 10^2 \text{ KJ/m}^2\]

By selecting a softer matrix for a composite the work of fracture of that composite could be quadrupled. The selection of a softer matrix is investigated in this thesis as a means of improving toughness. However, such a composite would have a reduced average tensile strength \( \sigma_f \) according to equation (13):

\[
\sigma_f = \sigma_{f,\text{max}} \cdot \left(1 - \frac{l_c}{2l_f}\right)\cdot \frac{1}{l_f} \quad \text{fibres/m}^2 \text{ in a 60\% vol. fraction composite}
\]

For the 50 MNm⁻² shear strength matrix the average tensile strength \( \sigma_f \) of the fibre would be almost 5 GNM⁻². For the composite with the softer matrix the fibre average tensile strength could be reduced up to 20\% below 4 GNM⁻² i.e. an overall strength reduction of at least 25\%.

9.4 The Role of the Fibre

Kelly (49), Piggott (52) and others have discussed the desirable fibre properties for high fracture toughness. These are high strength, large diameter and a high volume fraction of fibres in the composites. These can be simply checked by noting the parameters in the equation derived by Kelly and mentioned earlier \( W_D \) and \( W_p \) (work of fracture by two methods) (9.2).

Selection of Courtaulds HT or HT-S carbon fibres gave high strength fibres for the work in this thesis. These fibres together with other manufacturers' type 2 fibres give the maximum attainable, as was apparent from the introduction relating to the manufacture of carbon fibres (section 2). Fibre diameters have been increased slightly by the
fibre manufacturers, up to 25% since the introduction of carbon fibres. However significant increases in toughness would only come from far larger increases in diameter. Since the manufacturing process is essentially pyrolysis, the time taken to pyrolyse thicker polyacrylonitrile fibres is so much longer as to be uneconomic. The longer time to pyrolyse is necessary because the gases evolved in the pyrolysis of thick fibres would not easily escape through the already pyrolysed fibre outside layers. Lastly carbon-fibre composites are anyway fabricated with a high volume fraction of fibres, generally between 60% and 70%, and it is difficult to significantly increase the fibre volume fraction. Different manufacturers have produced their own fibres with slightly different strengths and diameters, and it has been shown(63) that those with the greatest area under the stress-strain curve give the greatest toughness. Kelly(49) suggested that to improve toughness, cracks, which are propagating through a failing composite should be obliged to take a longer path. This mechanism can be compared to the path a crack takes when a 'green-stick' is broken. The crack goes backwards and forwards along the stick and absorbs considerable energy in doing so. A similar mechanism has been reported (64, 65) to improve the fracture toughness of particulate-filled composites. The improvement was achieved by a selection of particles whose size distribution was such that the spaces in between the particles were filled by smaller particles. This packing of the composite resulted in fracture cracks taking a longer path through the composite and adsorbing more energy. Applying this technique to carbon-fibre composites could give a fibre distribution in the composite as shown in Figure 25. If the small fibre was carbon with a diameter of 10 μm then the other fibres surrounding it should have a diameter of 64 μm. As already mentioned,
Figure 25

10:64 Ratio of Small to Large Fibre
carbon fibres are only manufactured with a diameter of 10 μm and there is considerable difficulty involved in manufacturing larger carbon fibres. The small fibre occupies only 3% of the total volume occupied by all the fibres and this technique could be used as a way of reinforcing glass fibres to give a stiffer stronger composite. However glass fibres are not normally produced as thick as 64 μm and a special batch of glass fibres would be required in order to investigate this system.

Lastly Morley's (66) concept of a duplex fibre offered another possible solution to the toughness problems of composites. He described the duplex fibre as a hollow outer element strongly bonded to the matrix and an inner element relatively weakly bonded to the outer element. The outer element and its interface with the matrix were discussed as being able to withstand the longitudinal shear stresses and transverse tensile stresses. However a crack propagating through the matrix would crack the outer element, but not the weakly bonded inner element which would pull out from the outer element. Work would be absorbed in pulling the inner from the outer. No experimental work has as yet been published using 'Morley type fibres'. Any possible process for making them would almost certainly be very expensive.
10. TOUCHENED COMPOSITES BY FIBRE SURFACE TREATMENT

10.1 Materials Selection

Courtaulds Grafil HT-S grade carbon fibre was selected here as a high strength fibre, which as previously discussed in section 9.4, should give composites with a high fracture toughness. The fibre used was supplied in 48 inch (1.3 m) long tows of 10,000 filaments, each weighing approximately 1 gram. The physical properties of HT-S fibres were as in Appendix 1. The S in HT-S indicates an additional oxidising surface treatment for improved adhesion. All the composites were fabricated from one batch of fibres PPM 42/336 Z.

Most carbon fibre articles are produced from prepregs, and for convenience in this work the fibres were made into prepregs. Prepregs are produced by impregnating carbon fibres with a solution of epoxy resin, the solvent evaporated and the resin partly cured. This gives a material which can be handled easily and readily prepared for moulding. Shell produces a series of epoxy resins for making prepregs, the most useful of which for this thesis were Epikote DX210 cured with Epikure BF3 400 and Epikote DX 231 cured with Epikure DX 125. The former mixture requires 4 hours at 170°C to cure, the latter either 4 hours at 140°C or 1.1/2 hours at 150°C to cure. Both systems require a precure at around 100°C for a few minutes and could be stored at room temperature, after this precure stage, for several months before final curing.

The surface treatment to be used on the carbon fibres was a polyurethane rubber. Since polyurethane degrades above 150°C the epoxy system Epikote 231/Epikure 125 was chosen as its lower curing temperature was more suitable. Conventional polyurethane prepolymer, as supplied by Du Pont in its Adiprene series, can be cured with DETA as discussed in the introduction. However an isocyanate terminated polyurethane would...
cure prematurely when mixed with DETA before the coated fibres could be encapsulated in the epoxy matrix. A precured polyurethane would stop the hoped for intermingling of the epoxy and polyurethane to give a graded interface. Du Pont supplied Adiprene BL-16, a blocked polyurethane prepolymer which cures when heated to 130°C with DETA. Fibres coated with this polyurethane prepolymer would allow intermingling with the epoxy matrix and give the graded interface to stop cracks propagating and in addition would not prematurely cure.

10.2 Prepreg Preparation and Moulding

Carbon fibre tows dipped in a solution of the polyurethane prepolymer were aligned on Melinex (67) sheet. This solution contained between 1% and 10% by weight of a mixture containing Adiprene BL-16 and the stoichiometric amount of DETA (100 parts BL-16 12 parts DETA), in acetone. The acetone evaporated quickly to leave a light coating of the polyurethane prepolymer on the fibre. The epoxy resin Epikote DX 231/Epikure DX 125 was then spread over the carbon fibres in solution form. The solvent was allowed to evaporate and was followed by a 40 minute precure at 90°C. After removing the last solvent traces in a vacuum, the now formed prepreg was stored in a freezer until required.

Two sizes of specimen were moulded. One size was 2\(\text{m} \times 2\text{m} \times 0.2\text{m} \) (51 mm x 51 mm x 2.5 mm) for falling weight impact tests. The other size was 12\(\text{m} \times 1/2\text{m} \times 0.2\text{m} \) (300 mm x 13 mm x 5 mm) for flexural modulus, short span three point bending tests and charpy type impact tests. The specimens were prepared by cutting the prepreg to size and moulding at 140°C for about 4 hours under a mould pressure of 0.7 MN/m\(^2\). The specimens were moulded to about 60% by volume of fibre in the composite.
10.3 Results

A series of specimens were prepared, varying the amount of polyurethane in the sizing solution from 1% to 10%. The 12inch (300 mm) long specimens were first tested for flexural modulus at a 40:1 span to depth ratio. Four samples were cut from this specimen and tested to failure in three point bending at a 5:1 span to depth ratio to give I.L.S.S. and area under the I.L.S.S. curve. Next the remainder of the specimen was cut into 8 samples and tested on the Hounsfield Plastics Impact Tester (Section 14.1), in a charpy type test. Part of the specimen was used to find the fibre volume fraction. For this, the resin was dissolved; using a hot concentrated mixture of sulphuric acid and hydrogen peroxide. The flexural modulus and I.L.S.S. tests monitored the change in properties of the material. The charpy type test, and area under the I.L.S.S. measured the change in toughness of the material. Once the optimum coating level (10 gm P.U./100 gm C.F. from a 4-5% P.U. sol.) had been established a series of specimens were prepared for falling weight impact tests. These specimens were 2" (51 mm) x 2" (51 mm) x 0.1" (9.25 mm) and were moulded with biaxially orientated fibres and uniaxially orientated fibres.
### Table 6

<table>
<thead>
<tr>
<th>Sample Treatment</th>
<th>Fibre Content % by vol</th>
<th>Flex Mod G(\text{Nm}^{-2})</th>
<th>ILSS M(\text{Nm}^{-2})</th>
<th>Area Under ILSS N(\text{m})</th>
<th>Charpy Type Impact Test Joules</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>52.0</td>
<td>129</td>
<td>61.1</td>
<td>1.53</td>
<td>0.89</td>
</tr>
<tr>
<td>None</td>
<td>59.1</td>
<td>138</td>
<td>62.6</td>
<td>2.16</td>
<td>1.20</td>
</tr>
<tr>
<td>None</td>
<td>57.6</td>
<td>125</td>
<td>37.8</td>
<td>5.49</td>
<td>1.05</td>
</tr>
<tr>
<td>None</td>
<td>54.6</td>
<td>150</td>
<td>53.7</td>
<td>3.26</td>
<td>1.24</td>
</tr>
<tr>
<td>1%</td>
<td>62.9</td>
<td>119</td>
<td>45.4</td>
<td>2.04</td>
<td>1.37</td>
</tr>
<tr>
<td>2%</td>
<td>66.3</td>
<td>144</td>
<td>53.3</td>
<td>2.89</td>
<td>1.32</td>
</tr>
<tr>
<td>2%</td>
<td>60.3</td>
<td>143</td>
<td>48.1</td>
<td>3.16</td>
<td>1.35</td>
</tr>
<tr>
<td>2%</td>
<td>61.0</td>
<td>142</td>
<td>34.8</td>
<td>3.53</td>
<td>1.56</td>
</tr>
<tr>
<td>3%</td>
<td>69.5</td>
<td>149</td>
<td>49.9</td>
<td>4.50</td>
<td>1.32</td>
</tr>
<tr>
<td>4%</td>
<td>66.9</td>
<td>142</td>
<td>36.6</td>
<td>7.06</td>
<td>1.44</td>
</tr>
<tr>
<td>4%</td>
<td>62.6</td>
<td>148</td>
<td>43.8</td>
<td>3.67</td>
<td>1.47</td>
</tr>
<tr>
<td>5%</td>
<td>60.2</td>
<td>106</td>
<td>34.8</td>
<td>9.08</td>
<td>1.49</td>
</tr>
<tr>
<td>5%</td>
<td>58.0</td>
<td>129</td>
<td>55.0</td>
<td>4.67</td>
<td>1.31</td>
</tr>
<tr>
<td>6%</td>
<td>66.3</td>
<td>100</td>
<td>32.6</td>
<td>6.53</td>
<td>1.38</td>
</tr>
<tr>
<td>7%</td>
<td>56.1</td>
<td>83.2</td>
<td>30.2</td>
<td>7.85</td>
<td>1.10</td>
</tr>
<tr>
<td>10%</td>
<td>44.7</td>
<td>29.4</td>
<td>14.4</td>
<td>3.66</td>
<td>1.53</td>
</tr>
</tbody>
</table>

#### 10.4 Falling Weight Impact Tests Results

Falling weight impact tests are more representative of the type of impact actually encountered by real specimens in service (See Section 14.1). With carbon-fibre composites, there is no clear distinction between a failed composite and an undamaged composite, after being impacted. The specimens were progressively damaged by repeated low level impact tests. The damage was monitored by measuring the flexural modulus at 45° to the fibre orientation of the biaxially orientated composites between the impacts. The impact loads were such that more than one test was required to fail the specimens. The flexural moduli quoted below are the gradient of the load deformation curves divided by the specimen thickness cubed.
### 10.4.1 Uniaxial Orientated HT-S Fibres in DX 231/DX 125

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (mm)</th>
<th>Fibre Content (% by Vol)</th>
<th>Init Mod</th>
<th>1st Impact</th>
<th>Flex Mod</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.62</td>
<td>63.6</td>
<td>20.3</td>
<td>0.27</td>
<td>Failed</td>
</tr>
<tr>
<td>2</td>
<td>2.68</td>
<td>62.0</td>
<td>20.4</td>
<td>0.14</td>
<td>23.3</td>
</tr>
<tr>
<td>3</td>
<td>2.50</td>
<td>53.8</td>
<td>19.6</td>
<td>0.19</td>
<td>23.6</td>
</tr>
</tbody>
</table>

**Impact Load - Joules**  
**Flex Mod = M*Nm^-2 x constant**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flex Mod Failed under impact</th>
<th>Flex Mod Failed under impact</th>
<th>Flex Mod Failed under impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23.3</td>
<td>23.3</td>
<td>23.3</td>
</tr>
<tr>
<td>2</td>
<td>17.1</td>
<td>10.7</td>
<td>10.7</td>
</tr>
<tr>
<td>3</td>
<td>0.27</td>
<td>0.13</td>
<td>0.16</td>
</tr>
</tbody>
</table>

**Room temperature ≈ 21°C.**

### 10.4.2 4% P.U. Coated HT-S Fibres Uniaxial Orientated in DX 231/DX 125

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (mm)</th>
<th>Fibre Content (% by Vol)</th>
<th>Init Mod</th>
<th>1st Impact</th>
<th>Flex Mod</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.55</td>
<td>50.3</td>
<td>17.7</td>
<td>0.164</td>
<td>Failed</td>
</tr>
<tr>
<td>2</td>
<td>2.60</td>
<td>57.9</td>
<td>9.2</td>
<td>0.136</td>
<td>Failed</td>
</tr>
<tr>
<td>3</td>
<td>2.54</td>
<td>56.7</td>
<td>13.6</td>
<td>0.164</td>
<td>Failed</td>
</tr>
</tbody>
</table>

**Conditions as with 10.4.1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flex Mod Failed in test</th>
<th>Flex Mod Failed in test</th>
<th>Flex Mod Failed in test</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.6</td>
<td>10.7</td>
<td>14.4</td>
</tr>
<tr>
<td>2</td>
<td>7.4</td>
<td>11.8</td>
<td>13.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>2nd Impact</th>
<th>Flex Mod</th>
<th>3rd Impact</th>
<th>Flex Mod</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.217</td>
<td>7.9</td>
<td>0.271</td>
<td>4.7</td>
</tr>
<tr>
<td>2</td>
<td>0.190</td>
<td>7.2</td>
<td>0.271</td>
<td>6.0</td>
</tr>
</tbody>
</table>
These uniaxial specimens had virtually no impact strength, the composites cracking along the fibre direction, through the resin. For these samples there was a fairly clear division between failed and unfailed specimens, again reflecting the significant role of the brittle resin matrix.

The average fibre volume fraction was 50%-60%.

Impact strength of Untreated uniaxially orientated composite = 0.2 Joules
" " " treated " " " = 0.2 Joules

10.4.3 Biaxially Orientated HT-S Fibres in DX231/DX 125

TABLE 9
Conditions as with uniaxial specimens

<table>
<thead>
<tr>
<th>untreated HT-S fibres in DX 231/DX 125</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>Thickness mm</td>
</tr>
<tr>
<td>Fibre Content</td>
</tr>
<tr>
<td>Initial Mod</td>
</tr>
<tr>
<td>1st Impact</td>
</tr>
<tr>
<td>Flex Mod</td>
</tr>
<tr>
<td>2nd Impact</td>
</tr>
<tr>
<td>Flex Mod</td>
</tr>
<tr>
<td>3rd Impact</td>
</tr>
<tr>
<td>Flex Mod</td>
</tr>
<tr>
<td>4th Impact</td>
</tr>
<tr>
<td>Flex Mod</td>
</tr>
<tr>
<td>5th Impact</td>
</tr>
<tr>
<td>Flex Mod</td>
</tr>
<tr>
<td>6th Impact</td>
</tr>
<tr>
<td>Flex Mod</td>
</tr>
</tbody>
</table>

+6 more Impacts of 2.71 Joules
failure on 12th Impact
<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness mm</th>
<th>Fibre Content % by Vol</th>
<th>Initial Mod</th>
<th>1st Impact</th>
<th>Flex Mod</th>
<th>2nd Impact</th>
<th>Flex Mod</th>
<th>3rd Impact</th>
<th>Flex Mod</th>
<th>4th Impact</th>
<th>Flex Mod</th>
<th>8th Impact</th>
<th>Flex Mod</th>
<th>12th Impact</th>
<th>Flex Mod</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.79</td>
<td>47.3</td>
<td>23.8</td>
<td>2.17</td>
<td>19.6</td>
<td>3.25</td>
<td>15.6</td>
<td>4.89</td>
<td>13.7</td>
<td>5.70</td>
<td>11.3</td>
<td>2.71</td>
<td>20.1</td>
<td>2.71</td>
<td>17.0</td>
</tr>
<tr>
<td>2</td>
<td>2.48</td>
<td>54.2</td>
<td>28.0</td>
<td>2.71</td>
<td>26.8</td>
<td>5.70</td>
<td>(all 15.7</td>
<td>5.70</td>
<td>5.70</td>
<td>2.71</td>
<td>15.3</td>
<td>2.71</td>
<td>15.3</td>
<td>2.71</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.59</td>
<td>39.2</td>
<td>25.7</td>
<td>5.70</td>
<td>19.4</td>
<td>8.67</td>
<td>2.71</td>
<td></td>
<td>8.67</td>
<td></td>
<td>21.0</td>
<td>2.71</td>
<td>15.1</td>
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<tr>
<td>4</td>
<td>2.47</td>
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<td>28.4</td>
<td>8.67</td>
<td>21.0</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td>15.1</td>
<td></td>
<td></td>
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<td>5</td>
<td>2.65</td>
<td>42.9</td>
<td>25.4</td>
<td>12.2</td>
<td>15.1</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

There was a different fracture behaviour between the treated and untreated biaxially orientated fibres composites.

In general:

1. The treated fibre specimens localised the impact damage (the untreated fibre specimens were extensively delaminated).

2. The treated fibre specimens had a hole punched in them and the overall stiffness dropped to only about 60% of its original value).

3. The treated fibre specimens required more energy to break them, about 50% more. This was despite the fact that the fibre content was (on average) just over 3% less. See Figure 26 for sketches of failure modes.
PUNCHED HOLE

EXTENSIVE DELAMINATION
The polyurethane Adiprene BL-16 used to coat the fibres was not cured exactly in accordance with the technical bulletin issued by Du Pont. (rather the epoxy cure schedule was followed). Because of this samples of the polyurethane were cured, according to the Du-Pont bulletin and following the three recommended cure schedules for the epoxy resin Shell Epikote DX231/Epikure DX 125. In addition a cure cycle for the polyurethane was followed according to the cure cycle for Shell Epikote DX 210 Epikure BF400.

These cure cycles were

| PU/1 | 3 hrs at 130°C in a vacuum |
| PU/2 | 45 mins at 90°C + 4 hours at 135°C in vacuum (DX231/DX125) |
| PU/3 | 45 mins at 90°C + 1.1/2 hours at 145°C in vacuum (DX231/DX125) |
| PU/4 | 45 mins at 90°C + 1.1/2 hours at 145°C + 2 hours at 170°C (DX231/DX125) |
| PU/5 | 10 mins at 100°C + 4 hours at 165°C. |

The second stage of PU/2 to PU/5 was taken 5°C lower than the recommended temperature, because the mould used in the press was 5°C lower than the platen temperature.

PU/4 and PU/5 completely degraded and could not be tested.

<table>
<thead>
<tr>
<th>TABLE 11</th>
<th>Tensile properties</th>
<th>PU/1</th>
<th>PU/2</th>
<th>PU/3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elongation at Break %</td>
<td>467</td>
<td>314</td>
<td>453</td>
<td></td>
</tr>
<tr>
<td>Tensile Stress at 100% Ext MN m⁻²</td>
<td>1.08</td>
<td>1.23</td>
<td>0.69</td>
<td></td>
</tr>
<tr>
<td>&quot; &quot; &quot; 200%</td>
<td>2.14</td>
<td>2.57</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td>&quot; &quot; &quot; 300%</td>
<td>3.12</td>
<td>3.77</td>
<td>2.61</td>
<td></td>
</tr>
<tr>
<td>Tensile Strength MN m⁻²</td>
<td>6.50</td>
<td>3.83</td>
<td>4.15</td>
<td></td>
</tr>
</tbody>
</table>

The recommended cure cycle (PU/1) was most closely followed by an average of PU/2 and PU/3. A platen temperature of 145°C for 2.1/2 hours giving a mould temperature of 140°C would give the best urethane properties.
In discussing the ideas which led to the introduction of the particular fibre coating used, intermingling of the polyurethane coating and epoxy matrix was expected to give a graded interface. By precuring the coated fibres, before preparing the prepreg with the epoxy resin solution, this intermingling could be progressively precluded. The variation in properties with the amount of intermingling at the graded interface could also give some insight into the behaviour of the fibre coating, in the composite. The coating would be completely cured after 3 hours at 130°C. Consequently precures of 10 mins, 30 mins and 90 mins were investigated.

Figure 27 shows the variation of physical properties with increasing precure of the polyurethane coating.

The only property to improve with the precure was the interlaminar shear strength, the flexural modulus remaining essentially unchanged and the toughness falling significantly.

A certain amount of microscopy was undertaken in order to investigate the nature of the coating.

Scanning electron micrographs of Charpy type fracture surfaces (plate 8 and 9) revealed little difference between the coated and uncoated fibre specimens.

Attempts were made at sectioning the composite with a view to staining, and or etching of the resin. However this procedure failed, for the carbon being very hard dropped out or was not included in the resin sections cut. Only resin sections with holes where the fibres had been could be cut for electron microscopy.

Lastly treated fibre composites were sectioned flat and the flat surfaces hydrolysed for several hours, and several days. It was hoped that the
Figure 27

Time in Minutes of Coating Precure Before Resin Impregnation
COMPOSITE FRACTURE SURFACES

Coated Fibres  Plate 8

Uncoated Fibres  Plate 9
polyurethane would hydrolyse more than the epoxy resin and show its relative position to the fibres in a composite. After hydrolysing the specimens were lightly metal-coated and photographed in the scanning electron microscope. As photographs 10 and 11 show it was difficult to interpret what changes, if any, there were to the composites. However whether the technique failed to highlight the polyurethane layer at the interface or whether the graded interface effect hindered the selective hydrolysis, it was considered impossible to separate the polyurethane and epoxy layers. 

Figure 28 gives some idea of the chemical nature of the interface. The polyurethane chains can bond into the bulk of the epoxy, as well as being linked by the amine DETA. The DICY curing agent links together the rigid epoxy chains to give a stiff matrix round the soft polyurethane layer. The DETA probably bonds with the carbon fibre by being physically absorbed onto the surface.

10.6 Discussion

There was a significant improvement in fracture behaviour of the carbon fibre composites when the fibres were coated with the polyurethane solution, the most significant improvement occurring with a coating of 10 gm of the urethane mix per 100 gms of 'Grafil' HT-S carbon fibre. This urethane mix (100 pph Du Pont's Adiprene HL-16 12 pph DETA) was deposited from a 4% to 5% (by weight) solution. Figures 29, 30, 31, 32, 33 and 34 indicate the changes that occurred with changing solution coating strength.

The coated fibre composites showed a small and significant improvement in Charpy-type impact strength Figure 29 when comparing the optimum coated composites with the uncoated composites. It should be noted however that there was a large experimental variation in the results for any type of composite.
Figure 29

Impact Strength versus % Polyurethane Solution Size

- Impact
- Strength
- Joules

% P.U. Solution Size
The I.L.S.S. (short span three point bend test) showed a significant improvement for the optimum coated fibre composite compared to the uncoated, see figure 30. The uncoated fibre composites failed abruptly, whereas the coated fibre composites failed gradually and absorbed more energy in failing. In some cases the coated fibre composites after failing could still be highly stressed. This increased energy absorbed to final failure is illustrated in figure 31 by the total area under the I.L.S.S curve. The area after the first failure, indicating the suddenness of failure, was three times for the coated fibre composites; the area up to first failure, and was only 1/20 to 1/5 the area up to failure for the uncoated fibre composites. This area after first failure, under the I.L.S.S. curve, had increased to a maximum for the composites coated with 4-5% solution of P.U.

The last of the tests which indicated the improved impact strength of the coated fibre composites was the falling weight impact test. The behaviour of the composites in these tests is illustrated in figure 32 where the cumulative impact energy is plotted against the falling flexural modulus of the composite. The modulus was taken as the gradient from the load-deformation (measured at 45° to the fibre angle) divided by the thickness cubed. The coated fibre composites, localised the damage arising from the impacts. The specimens were impacted until they were either destroyed, or had a hole punched through them. For the 2 ft-lb (2.7 Joule) and 4.2 ft-lb (5.7 Joule) impacts, the coated fibre specimens localised the damage and had a hole punched in them. In general when the uncoated fibre composites were completely destroyed, the coated fibre composites having absorbed a similar amount of energy still retained 60% of their original stiffness. Note also in this graph that the coated fibre composites at their optimum level had a higher initial modulus than the uncoated fibre composites. This is confirmed by figure 33. The uniaxial orientated fibre composites
Stress

Uncoated Fibre Composite

Coated Fibre Composite

Strain
Figure 32

REPEATED FALLING WEIGHT IMPACTS

DROP IN FLEXURAL MODULUS WITH

Polyurethane Sized Fibre Composite

Hole Punched

Standard Composite

Cumulative Absorbed Energy

0.2 ft.lbs. (2.7 Joules)

6.4 ft.lbs. (8.7 Joules)

0.4 ft.lbs. (5.7 Joules)
Figure 33

VERSUS % POLYURETHANE SOLUTION SIZE

FLEXURAL MODULUS

GNm^-2

Flex. Mod.

% :P.U. Solution :Size
prepared for falling-weight impact tests had such a low impact strength that they are not worth discussing. Their impact strength reflects their matrix strength, as under impact the matrix split along the fibre axis.

Figure 33 shows the slight rise in (5-10%) flexural modulus with a thin (3% solution) coating of polyurethane on the fibres. This coating at the 3% solution level amounts to 10% of the resin in the matrix. The flexural moduli were high (145 GNm⁻²), compared to the Courtaulds Grafil Data sheet (Appendix 1). It was expected as shown that the composite would become more flexible with thicker coatings on the fibre, especially as the polyurethane was compatible with the epoxy. The improved modulus with thin polyurethane coatings could be explained by an analogy to the 'tie-coat' or undercoat adhesive treatments sometimes require. The polyurethane could act as a 'key' coating to which the epoxy resin matrix could more easily adhere. Another explanation of the improved modulus with a thin flexible polyurethane coating on the fibres could be that fibre re-alignment occurs under stress. The fibres could more correctly take up positions in the composite so as to transfer stress between the fibres and carry equal loads.

Figure 34 shows how the interlaminar shear strength of the composite was reduced with an increasing amount of polyurethane coating. The 4% solution coated fibre specimens showed a 25% drop in inter-laminar shear strength. This simply reflected the reduced strength of the matrix with coated fibres. The reduced I.L.S.S. could be improved by precuring the coating a little if necessary as shown in Section 10.5. The balance of properties selected would depend on the composites' requirements.

The most important variable in composites is the fibre volume fraction although to a much lesser extent, the following can all affect composite properties:
1) Prepreg properties including fibre/resin ratio, volatile content, fibre alignment and degree of cure advancement.

2) Matrix properties including surface tension, viscosity, volatile content of liquid resin, and strength, modulus and elongation of solid resin.

3) Fibre properties including property variations and effectiveness of surface treatment.

4) Laminating process including removal of excess resin, maintenance of pressure, fibre damage and alignment and extent of voids.

However fibre volume fraction was shown earlier in Section 3 to directly affect composite modulus. The effect fibre volume fraction has on Izod impact strength is shown in Figure 35 (68). This graph is assumed, to apply in general to the variation in Charpy type impact tests measured in this thesis: Since the volume fraction in the preceding sections on Charpy type impacts was 52% ± 13% this graph was used to correct these Charpy type tests to the traditional 60% volume fraction for one example in Figure 29. The dotted line and arrow shows how much the variation in volume fraction could reduce the result of a particular example which had a volume of over 60%. Other examples could have had increased corrected impact strengths if their volume fractions were less than 60%.

Because of this large variation, in all further work, fibre volume fraction in the composites was more carefully controlled. Of all the properties monitored with increasing coating weight, flexural modulus showed the least scatter from a smooth curve. Since there was a considerable scatter in fibre volume fraction we can deduce that flexural modulus is not so dependent on fibre volume fraction as the other properties. This is in disagreement with the composite theory discussed in Section 3.
VARIATION OF IZOD IMPACT ENERGY
WITH FIBRE VOLUME FRACTION

Figure 35
Fairbairn et alia\cite{69} have shown that composite properties and I.L.S.S. in particular always show some random variation because of the listed reasons above. The variation they found for I.L.S.S. tests was $\pm 20\%$ even in composites made under carefully controlled identical conditions. From all the available evidence it seems that flexural modulus was the least affected by fibre volume fraction and impact strength the most affected. This initial work was by way of introduction to composites and in the next stage of the work in this thesis processing requirements were much better understood and monitored.

There was a slight variation in the weight of coating on a fibre as a result of impregnating the carbon fibres with a specific solution concentration. However this variation could have had only a very small influence on the impact strength for example, as indicated by the solid arrows on figure 29. The impact strength of the composites was their most variable property. After precuring the polyurethane coating, before preparing the prepreg, the physical properties of the ensuing composite deteriorated. This deterioration supported the hypothesised graded interface for the precuring reduced the graded interface which it was anticipated would lead to improved impact strength. The presence of a graded interface was also supported by the lack of success in the photomicroscopy of the etched surfaces.
11. TOUGHENED MATRICES FOR TOUGHENED COMPOSITES

11.1 Materials Selection

Courtaulds HT-S Grafil carbon fibre was again used. Blending polyurethane rubbers and epoxy resins gives matrices whose toughness varies from that of epoxy to polyurethane. Du Pont issue a Bulletin \(^{(62)}\) on mixtures of epoxies and polyurethanes, using a polyurethane rubber such as Du Pont's Adiprene L-167 and an epoxy such as Shell's 828. The mixtures can be cured with MOCA \((4,4'\text{methylen}-\text{bis 2-chloroaniline})\) to give a resin with a reasonable pot life. Other curing agents are available, but with a high percentage of polyurethane often give a short pot life. Such curing agents are methylene dianiline and \(m\)-phenylene diamine. Methylene dianiline is particularly interesting however because it gives a 50% stiffer and 25% tougher matrix than MOCA.

The % by weight of curing agent \(X\) required is given by the following equation.

\[
X = \frac{M}{4} \left[ \frac{w}{e} + \frac{b \times \% \text{ NCO}}{2500} \right]
\]

\(M\) = molecular weight of curing agent \((\text{e.g. MOCA 267})\)

\(w\) = weight of epoxy resin in the blend

\(e\) = epoxide equivalent of the epoxy resin \((\text{e.g. Epikote 828-190})\)

\(b\) = weight of polyurethane in the blend

\(\% \text{ NCO}\) = isocyanate content of polyurethane prepolymer \((\text{e.g. Adiprene L-167 6.30})\)

The range of properties available from blends of the epoxies, polyurethane rubber and curing agents was investigated in order to ascertain which materials might give improvements in the toughness of a composite. The properties obtained from the matrix blends were compared to those properties published by Du Pont in their bulletin, and experience gained on the handling requirements of the blends.
Four materials were prepared for testing:

B 1 - 100 parts Adiprene L-167 19.5 parts MOCA cured for 1 hr at 100°C

B 2 - 70 parts L-167 30 parts Epikote 828 28 parts MOCA cured for 4 hrs at 140°C

B 3 - 50 parts L-167 50 parts Epikote 828 33.5 parts MOCA cured for 4 hrs at 140°C

B 4 - 100 parts Epikote 828 35.5 parts MOCA cured for 5 hrs at 140°C

Du Pont recommended that a little more than the stoichiometric amounts of MOCA should be used, whether this was because of handling losses or chemical losses was not made clear.

Very few curing agents are suitable for both epoxy resins and polyurethane prepolymer. Besides MOCA as mentioned above methylene dianiline (4,4’ Diaminodiphenylmethane) (DDM) could be used, but for mixtures of the two, the 'pot life' was too short (seconds). To slow down the reaction of DDM with the blend the possible courses are

1. to make a salt of DDM with lactic acid

\[
\text{NH}_2 \text{--CH}_2\text{--NH}_2 + \text{HO}--\text{C}---\text{COOH} \text{ } \text{ } \text{CH}_3
\]

DDM

either 1 mole of DDM to 1 mole of lactic acid or 2 moles of lactic acid

2. to make a salt of DDM with succinic acid

\[
\text{HOOCCH}_2\text{--CH}_2\text{--COOH} \text{ } \text{ } \text{CH}_3
\]

again 1 mole of DDM to 1 mole or 2 moles succinic acid.

3. to make a salt of DDM with glacial acetic acid \(\text{CH}_3\text{--COOH}\)

4. to complex DDM with Sodium or Potassium Lactate using 1/2% to 2%

5. or to use instead p-phenylene diamine.
P-phenylene diamine gives no better physical properties than MOCA according to the Adiprene bulletin. With lactic acid because of the volatiles given off during the reaction, the cast resin produced was unusable. Also, the pot life was only slightly extended for this system. It was considered that because of the volatiles given off, lack of improvement in physical properties or short pot life, only MOCA could be used as a curing agent for blends of the polyurethane prepolymer and epoxy resin.

The impact strength and flexural moduli of the four resins moulded were tested. The results are shown in the table and in figure 36, and were compared to those published in the Du Pont Adiprene bulletin.

**TABLE 12**

*Matrix Properties*

<table>
<thead>
<tr>
<th>Samples</th>
<th>Impact Strength KJm(^{-2})</th>
<th>Flexural Modulus GNm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>None (Bends)</td>
<td>0.0480</td>
</tr>
<tr>
<td>B2</td>
<td>25.1</td>
<td>0.180</td>
</tr>
<tr>
<td>B3</td>
<td>4.4</td>
<td>1.40</td>
</tr>
<tr>
<td>B4</td>
<td>2.9</td>
<td>2.08</td>
</tr>
</tbody>
</table>

The impact strength quoted is the strength of the specimen in Charpy type test, divided by the area under the notch.

The area of interest with this blended matrix, obviously lies with the blend ratios of 50 : 50 to 70 : 30 polyurethane to epoxy blend. Here the flexural modulus is declining and impact strength increasing.

**11.2 Composite Preparation and Moulding**

The curing agent used, MOCA, was not very suitable for preparing a prepreg. MOCA cures at room temperature, and even at 0°C MOCA will cure a polyurethane epoxy blend slowly. Consequently, the carbon fibres were preimpregnated with a solution of the epoxy/polyurethane/curing agent mixture, and the composite pressed and cured within an hour of impregnating. The procedure was to prepare a solution of the
BLENDED MATRIX PROPERTIES

Figures 36

As Tested Impact Strength Du Pont Bulletin

KJm²

20
10

ft.lb/in. notch

1.0

2.0

GNm²

2.0
1.0

0 50 100 0 50 100

P.P.H. Adiprene L-167 in a Blend with Epikote 828
resins and curing agents in ethyl acetate and then extract the solvent from the composite after impregnation, by using a vacuum.

The composites were moulded at 140°C. The viscosity of the blend rose quickly in the press at this temperature, and it was necessary to use a high clamping force on the prepreg 1 ton (15 MN/m²) in order to consolidate it.

Two specimen sizes were moulded: 2" (51 mm) x 2" (51 mm) x 0.1" (2.5 mm) for falling weight impact tests, and a 12" (300 mm) x 0.5" (13 mm) x 0.2" (5 mm) specimen for testing flexural modulus, ILSS, area under ILSS curve and Charpy type impact.

11.3 Results

As mentioned in the discussion on the fibre-coated specimen results, the most important parameter to be monitored, besides the blend ratio, was the fibre volume fraction of a composite. In the following work, these two parameters were continuously monitored. Thirteen composites were moulded, each with a different fibre volume fraction and blend ratio of polyurethane to epoxy. Contour graphs were then drawn, following the technique of Bertsch (70), showing how each of four physical properties varied with the blend ratio and fibre volume fraction.

These four physical properties were ILSS, flexural modulus, area under ILSS curve and Charpy type impact strength. The impact strength results were corrected for area under the notch, and are quoted as KJ/m², although the area did not vary much from one specimen to another.

Since falling weight impact tests require a considerable number of specimens, only one sample type (with a fixed fibre content and blend ratio) was used for this test at the most interesting blend ratio.

An attempt was made to monitor void content, but because the density of the matrix and the fibre volume fraction varied throughout a specimen inconsistent results were obtained. However, it became
apparent from the work that void content depended upon the fibre volume fraction to some extent. Higher fibre volume fractions had lower void contents because they required more pressing in the mould.

The following results were then obtained:

**TABLE 13**

<table>
<thead>
<tr>
<th>Blend Ratio</th>
<th>Fibre volume fraction %</th>
<th>Impact Strength KJm⁻²</th>
<th>Area under ILSS curve Joules</th>
<th>Flexural Modulus GNm⁻²</th>
<th>ILSS MNm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>HB/1</td>
<td>100:0</td>
<td>55.4</td>
<td>55.2</td>
<td>61.6</td>
<td>33.0</td>
</tr>
<tr>
<td>HB/2</td>
<td>70:30</td>
<td>59.4</td>
<td>30.5</td>
<td>16.04</td>
<td>92.9</td>
</tr>
<tr>
<td>HB/4</td>
<td>50:50</td>
<td>62.6</td>
<td>27.2</td>
<td>11.04</td>
<td>104.7</td>
</tr>
<tr>
<td>HC/1</td>
<td>100:0</td>
<td>30.3</td>
<td>32.4</td>
<td>4.08</td>
<td>24.5</td>
</tr>
<tr>
<td>HC/3</td>
<td>70:30</td>
<td>39.0</td>
<td>19.4</td>
<td>8.52</td>
<td>34.4</td>
</tr>
<tr>
<td>HC/4</td>
<td>50:50</td>
<td>40.4</td>
<td>12.8</td>
<td>6.47</td>
<td>73.5</td>
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<tr>
<td>HD/1</td>
<td>100:0</td>
<td>74.1</td>
<td>38.1</td>
<td>6.3</td>
<td>59.5</td>
</tr>
<tr>
<td>HD/3</td>
<td>70:30</td>
<td>65.0</td>
<td>58.3</td>
<td>10.96</td>
<td>111.0</td>
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<tr>
<td>HD/4</td>
<td>50:50</td>
<td>80.0</td>
<td>37.0</td>
<td>6.3</td>
<td>136</td>
</tr>
<tr>
<td>D1</td>
<td>100:0</td>
<td>64.3</td>
<td>48.0</td>
<td>7.95</td>
<td>74.8</td>
</tr>
<tr>
<td>D2</td>
<td>80:20</td>
<td>61.9</td>
<td>50.4</td>
<td>13.1</td>
<td>70.4</td>
</tr>
<tr>
<td>D3</td>
<td>40:60</td>
<td>80.7</td>
<td>40.5</td>
<td>4.86</td>
<td>169.7</td>
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<tr>
<td>D4</td>
<td>20:80</td>
<td>43.0</td>
<td>14.7</td>
<td>3.87</td>
<td>78.3</td>
</tr>
</tbody>
</table>

The test conditions were as follows:

1. **Test temperature = 21°C ±2°C**

2. **Impact Strength - Hounsfield Miniature Charpy Impact tester 2.75 J capacity and strike velocity of 2.54 msec⁻¹** specimen dimensions- 45 mm length, notch 4.45 mm for back face, and 5.0 mm thick.

3. **Flexural modulus - Instron tensile tests - test speed 0.5 mm/min 40:1 span: depth ratio, 3-point testing (6.35 mm support roller diameter). Specimen 5.0 mm thick.**
4. ILSS test: Instron tensile tests - test speed 1 mm/min, 5:1 span: depth ratio, 3-point bend test (6.35 mm support roller diameter) specimen 5.0 mm deep.

11.4 Falling-Weight Impact Tests
Composites with a matrix whose blend ratio was 70 parts Adiprene L-167 to 30 parts Epikote 828 cured with 28 parts of HQeA were prepared for falling weight impact tests. This ratio was judged to give the most interesting combination of properties, together with a high fibre volume fraction (70%).

The damage which occurred with repeated impacts was again monitored by measuring the flexural modulus at 45° to the two fibre directions. 2" (51 mm) x 2" (51 mm) x 0.1" (2.5 mm) specimens were moulded. For this series of tests only biaxially orientated fibre composites were prepared for as discussed, the previously prepared uniaxially orientated composites have only a very low impact strength. Six samples were prepared for testing with the above blend ratio and biaxially orientated fibres. Four samples had a fibre volume fraction of 64% ± 3% and 2 samples of 49% ± 2%.

The tests as before were carried out in accordance with B.S. 3068 with a drop height = 2 ft (610 mm)
impact probe = 0.5" (12.5 mm) diameter,
and test temperature = 21°C ± 2°C.
Biaxially Orientated HT-S in blended matrix of 70:30 L167:828

<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness mm</td>
<td>2.33</td>
<td>2.77</td>
<td>2.55</td>
<td>2.52</td>
<td>2.55</td>
<td>2.24</td>
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<tr>
<td>Fibre content Vol % by</td>
<td>64.5</td>
<td>66.4</td>
<td>61.0</td>
<td>64.0</td>
<td>50.8</td>
<td>47.3</td>
</tr>
<tr>
<td>Initial Modulus</td>
<td>12.3</td>
<td>7.2</td>
<td>5.7</td>
<td>5.6</td>
<td>2.3</td>
<td>7.3</td>
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<tr>
<td>1st Impact</td>
<td>2.71</td>
<td>5.70</td>
<td>8.67</td>
<td>12.3</td>
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<tr>
<td>3rd Impact</td>
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<tr>
<td>Flex Mod</td>
<td>3.3</td>
<td></td>
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<tr>
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<tr>
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<td>13th Impact</td>
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<td>Flex Mod</td>
<td>0</td>
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</table>

The modulus is the gradient of the load-deformation curve divided by the thickness cubed.

Modulus = MN/m^2 x Constant

Impact energy = Joules.
The energy which the blended matrix composite absorbed, as tested by the falling-weight impact, was similar to the coated fibre composites, that is 12.3 Joules. The blended matrix composite had a very low flexural modulus at 45° to the fibre orientation. This low value reflected the lower modulus of the matrix. The flexural modulus did not fall off with increasing impact damage as in previous tests. However because of low initial modulus this was not significant.

The damage arising from the impacts was neither localised as with the coated fibre composites, nor did the composite break up as with the uncoated fibres in the epoxy matrix. The specimens tended to shear, one fibre layer tearing from another.

11.5 Discussion

A series of contour graphs was drawn from the table of data in section 11.3 which show that virtually any composite properties can be obtained. The Charpy type impact strength contour graph (figure 37) indicates that a maximum amount of energy was absorbed, when the fibre content was 67% by volume, in a matrix containing 73 parts of Adiprene L-167 to 27 parts Epikote 828 (plus MOCA). Presumably at lower epoxy ratios the carbon fibres were not fully utilised in absorbing energy. At higher fibre volume fractions the fibres were not wetted by the resin and consequently the energy to break each fibre could not be utilised. At lower fibre volume fractions and higher epoxy resin ratios in the blend a lower impact strength would be expected.

The contour graph showing the area under the inter-laminar shear strength curve (figure 38), illustrates how this toughness parameter was dependant on both the matrix and fibre volume fraction of a composite. In any test looking at energy under a stress-strain curve, a balance between elongation and stiffness produces the highest value. The ILSS test
CONTOUR GRAPH SHOWING IMPACT STRENGTH (CHARPY TYPE)

Varying with Resin Flexibility and Fibre Volume Fraction

Figure 37

P.P.H. L-167 in a blend with 828
Contours are in KJm⁻²
L-167 - Du Pont's Adiprene L-167
828 - Shell's Epikote 828
Plus Moca
CONTOUR GRAPH SHOWING AREA UNDER THE I.L.S.S. CURVE

Varying with Resin Flexibility and Fibre Volume Fraction

Figure 38

P.P.H. L-167 in a blend with 828

Contours are in Joules

L-167 - Du Pont's Adiprene L-167
828 - Shell's Epikote 828
Plus Moca
carried out, showed this balance when the ratio of the blend was 70 parts L-167 to 30 parts 828 and the fibre volume fraction was 55%.

Maximum toughness for both area under ILSS and Charpy type impact could be achieved with a 65% fibre volume fraction and 70:30 L-167 : 828 matrix blend as tested in the falling weight impact test. A reduction in flexural modulus to 100 GNm$^{-2}$ and ILSS to 30 MNm$^{-2}$ coincided with the composite having a maximum toughness.

The falling weight impact tests (12.3 Joules) carried out on these 'maximum toughness' composites demonstrated that, according to this test, the improvement in toughness was equal to the coated fibre composites. This 'maximum toughness' composite had a soft matrix, which allowed the probe of the falling weight to push through the matrix and force the fibres apart. The composite was torn apart under repeated impact. With a lower fibre volume fraction (50%) the composites with a tough blended matrix showed no improvement in toughness compared to a standard composite (5.3 Joules).

The change in ILSS and flexural modulus (figures 39,40) with matrix blend ratio and fibre content were as expected. The fall in modulus occurring with the fall in modulus of the matrix. The fall in ILSS occurring probably as a result of the drop in matrix shear strength level.

Bertsch (70) discussed how errors are reduced in drawing contour graphs. The symmetry achieved in drawing a contour graph tends to even out any errors present in the results from which they are drawn. This presumes that the errors are random and the property variations lead to smooth curves. The errors present from the earlier work due to fibre volume fraction variations, were not present in these contour graphs, because the variation was monitored.
CONTOUR GRAPH SHOWING FLEXURAL MODULUS

Varying with Resin Flexibility and Fibre Volume Fraction

Figure 39

P.P.H. L-167 in a blend with 828
Contours are in Gm⁻²
L-167 - Du Pont's Adiprene L-167
828 - Shell's Epikote 828
Plus Moca
CONTOUR GRAPH SHOWING I.L.S.S.

Varying with Resin Flexibility and Fibre Volume Fraction

Figure 40

P.P.H L-167 in a blend with 828

Contours are MNm$^{-2}$

L-167 - Dupont's Adiprene L-167
828 - Shell's Epikote 828
Plus Moca
Lastly the scanning electron microscope pictures taken of the Charpy type impact failure surfaces revealed some interesting features (Plates 12 and 13). With the low impact strength specimens the failure was mainly tensile. As the impact strength of a type of composite was increased, the fracture surface displayed a larger area of compressive type failure, with a considerable amount of fibre debris on this surface.

A high impact composite deformed more before failure under impact. A composite grossly deformed (under impact), but not yet failed, was mainly under compression. The fibres had not broken on the side remote from the impact under a tensile stress. Instead the side of the impact under compression, locally buckled to absorb energy. For low impact strength composites the fibres broke on the far side from the impact. The crack travelled towards the impact point, and the composite failed. N. Hancox of Harwell found a similar behaviour with Izod tests.
HIGH IMPACT STRENGTH

Plate 12

LOW IMPACT STRENGTH

Plate 13
12. **TOUGHENED COMPOSITES BY A THEORETICAL APPROACH**

12.1 **Introduction**

In section 9.3 it was estimated that the fracture toughness of composites could be quadrupled from 175 KJoules m\(^{-2}\) to 700 KJoules m\(^{-2}\) when the matrix was changed from epoxy resin with a shear strength of 50 MNm\(^{-2}\) to say polyurethane rubber with a shear strength of about 10 MNm\(^{-2}\).

The theme of this section was to approach the ideal system by a theoretical instead of technological approach.

Carbon fibre composites are required to have high tensile moduli, and these can only be achieved as shown in section 11 by high matrix moduli. Low shear strength materials which could improve fracture toughness usually have low tensile moduli. Since elongations in shear and tensile modes are related, a material is required which has a high tensile modulus and strength as well as a low shear modulus and strength.

Generalised elasticity laws relate shear modulus \(G\) and tensile modulus \(E\) by equation 14.

\[
G = \frac{E}{2(1+\nu)} \quad 14 \quad \text{where } \nu = \text{poisson's ratio.}
\]

For the above requirements a high \(\nu\) is required. The maximum for isotropic materials which could be used as a matrix occurs in rubbers. They have a \(\nu\) of a 1/2.

The ideal material would have a high initial modulus, to give the composite a high initial modulus and then plastically deform at a low shear level.

The material would shear at a steadily increasing level so as to absorb a steadily increasing amount of energy. Finally the stress would suddenly rise leading to further fibre breaks which would absorb more energy. Such an ideal material could have a stress-strain relationship as found in Figure 41.
An Ideal Material

Thermoplastic Polyurethanes
Thermoplastic polyurethane have stress-strain relationships as in figure 41 as well as showing a rubbery behaviour which gives a poisson's ratio of 1/2. They were investigated in this section.

12.2 Materials Selection

Thermoplastic polyurethanes were selected for investigation in this thesis because of the reasons given above. In addition those materials whose properties were investigated in section 11 were included showing property variations between low shear strength polyurethane rubber and the higher shear strength epoxy matrix. To be of use as a matrix to reinforce continuous carbon fibres, it was necessary for the thermoplastic polyurethanes to be readily soluble. B.F. Goodrich market 'Estane' thermoplastic polyurethanes of which 5713 and 5707 are soluble and represent extremes of moduli.

12.3 Results

The shear strength of the range of materials under consideration as matrices for carbon-fibre composites was measured using the ASTM (D732) shown in plate 14. A one inch punch was pushed through a restrained plaque of the material, and the shear strength given by the maximum load required to push the punch through the material, divided by the sheared area. All the materials were moulded into plaques 2" (51 mm) x 2" (51 mm) and tested.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shear Strength (MNm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estane 5713</td>
<td>10.1</td>
</tr>
<tr>
<td>&quot; 5707</td>
<td>16.3</td>
</tr>
<tr>
<td>Adiprene L-1467</td>
<td>10.1</td>
</tr>
<tr>
<td>70:30 L-167 : 828) cured with MOCA</td>
<td>30.5</td>
</tr>
<tr>
<td>50 : 50 L-167: 828) MOCA</td>
<td>47.2</td>
</tr>
<tr>
<td>Epikote 828</td>
<td>48.6</td>
</tr>
</tbody>
</table>
A.S.T.M. SHEAR STRENGTH PUNCH

Plate 14
According to section 9.3, composites prepared with carbon fibres in matrices of Adiprene L-167 or Estane 5713 should have a fracture toughness of four times that of composites whose matrix is Epikote 828.

Composites were made with matrices of Estane 5713 and Estane 5707 by solution impregnation of carbon fibres. The thermoplastics were dissolved in a mixture of the solvents methyl ethyl ketone and dimethyl formamide. After extracting the solvent from the thermoplastic composites, they were compression moulded. The resulting composites had very poor physical properties, too poor to test. This was due to the poor adhesion of the carbon fibres to the thermoplastic polyurethanes resulting from their high viscosity.

The impact fracture toughness of composites with a matrix of Adiprene L-167 was about 60 KJ m⁻²; that of composites with a matrix of Epikote 828 (both cured with MOCA) was about 20 KJ m⁻². Adiprene L-167 shows rubbery behaviour and will have a Poisson's ratio approaching one half. This fulfills another criterion of obtaining the best tensile modulus with a low shear modulus. Unfortunately Adiprene L-167 does not have a good yield point as shown on the ideal stress-strain curve figure 41 and with the thermoplastic polyurethanes.

12.4 Discussion

The composites prepared did fail over part of their surface area by pulling the fibres out. The scanning electron microscope pictures of an impact failure surface with Adiprene L-167 matrix shows (plate 15) carbon fibres pulled from the matrix and the sheared matrix. The composite matrix had a shear strength of 50 MNm⁻². Both the calculated energies were about 10 times too high. The epoxy matrix fracture surface showed that only over half the surface did the fibres pull out and in those areas in clumps of fibres. For the composite whose matrix was Adiprene L-167, less than half the fracture surface
FIBRES COVERED WITH THE SHEARED ADIPRENE L-167 MATRIX

Plate 15
showed fibre pull-outs and in even larger clumps of fibres than with the epoxy matrix. This explains the discrepancies between the measured and calculated toughnesses.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Adiprene L-167</th>
<th>Epikote 828</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated fracture energy</td>
<td>700</td>
<td>175</td>
</tr>
</tbody>
</table>
| As tested $^n$ | 60             | 20          | $^2 \text{KJ m}^{-2}$
13. **CONCLUSIONS ON TOUGHNESS**

The work in this thesis aimed at investigating toughness by considering the fibre, matrix and interface in a composite. Having reviewed past research work in this field, certain areas were clarified and developed by the work described in this thesis.

The system investigated where Courtaulds HT-S fibres were coated by a solution of Du Pont's Adiprene ML-16 cured with DETA and made into a prepreg with Shell DX231/DX125 epoxy resin system yielded particularly interesting results. Taking the most significant coating level, using a 4% solution of the polyurethane to coat the fibres, there was a significant improvement in fracture behaviour. Short-span bending tests resulted not in a sudden brittle failure, as with normal carbon fibre composites, but a more gradual failure behaviour, resulting in up to three times as much energy absorbed. Impact energy as measured by the Charpy test only showed a slight improvement. However the more realistic falling-weight impact test demonstrated how the damage due to impact was localised. In addition the energy required to reduce the flexural modulus to 50% of its initial value was twice as much for a composite whose carbon fibres were coated as for a composite whose fibres were uncoated. The flexural modulus was not reduced by the inclusion of up to 15% by weight of polyurethane into the composite, but slightly increased. The ILSS of the composite was slightly reduced with increasing polyurethane content as a coating.

The second system investigated using a composite whose matrix was Du Pont's Adiprene 1-167 blended with Shell's Epikote 828 cured with Du-Pont's MOCA gave comparable toughness property improvements, with particularly significant improvements in Charpy-type impact strength. Figure 7 shows that improvements by up to 300% were achieved with Charpy-type tests, compared to composites with epoxy matrices. The energy absorbed in fracturing short span specimens was increased by up to 800%.
as shown in figure 38. However the ILSS was reduced by 50% and the flexural modulus by 20% at these levels as shown in figures 39 and 40. The falling-weight impact tests again demonstrated the increased toughness, but because the composite was soft its failure mechanism was unsatisfactory, the composite tending to tear apart.

Lastly the theoretical approach to toughness, although successful in predicting the energy required to pull-out fibres from different matrices, did not take account of the balance between pull-out and compressive failure that occurs in the special shapes of any test such as Charpy. Although a composite with a very soft matrix allows more energy to be absorbed in fracture, the overall physical properties of the composites are unacceptable. However this does show the value in preparing a composite with a soft rubber encapsulating the fibres to absorb energy at fracture, and this coated fibre in a rigid epoxy matrix to give acceptable physical properties. Such a system was investigated in section 10.

figure 42 taken from Harris's work (47) shows the relationship he found between composite work of fracture and ILSS. Plotted on this graph are the composites prepared in this thesis. The standard composite system using Shell DX231/DX125 epoxy resin gave a high impact strength as shown on the graph. The coated fibre composites and blended matrix (both taken at their optimum levels) give much higher work of fracture than, according to this graph, could be expected from their ILSS. This shows how the carbon fibre composites prepared in this thesis were significantly toughened to give a better overall balance of properties.

In conclusion, although the impact strength of carbon fibre composites were dramatically increased by using a blended matrix of polyurethane and epoxy there were practical disadvantages. This system could not
GRAPH COMPARING EARLIER WORK (47) WITH THOSE COMPOSITES PREPARED IN THIS THESIS. THE EXPECTED DROP IN I.L.S.S. WITH IMPROVED WORK OF FRACTURE IS ILLUSTRATED

Figure 42

Blended Matrix Composite
Coated Fibre Composite
Standard Composite

KJ m⁻²

MNm⁻² I.L.S.S.

× Charpy Type Impact
△ Area under Short Span 3-Point Bend Test
Graph from (47)
This Thesis
easily be used to prepare a prepreg because the action of the curing agent could not be delayed. Secondly the impregnation of the fibres and cure procedure required considerable skill and experience to produce acceptable composites. Lastly although the overall balance of properties was acceptable, the composite was very soft, so much so that a piercing impact, forced the fibres apart and tore the matrix. The theoretical approach to improving toughness demonstrated the drawbacks and difficulties, often apparent when theories are put into practice. The conclusion from this work was that an acceptable overall balance of properties including high impact energy could be achieved by fibre pull-out and deformation of the matrix, as long as the fibres encapsulated by soft rubber were in a rigid epoxy matrix.

The coated fibre composites showed the most promise in possible property improvements. In preparing carbon fibres it is quite common to size them (usually with epoxy resin) to reduce the damage to them and to prepare prepregs more easily. As a size a 4% solution of HL-16 cured with DETA was very good, giving fibre tows which could easily be handled, and wetted right through by epoxy resin solution. The prepreg then prepared could be stored as with an ordinary epoxy system for 3 months at room temperature, or for an unlimited time at -20°C. Lastly this prepreg gave improved toughness, very good flexural modulus and only a slightly reduced ILSS. This improvement in toughness was most dramatically demonstrated in falling weight impact tests. Here the damage was localised, the probe simply punching a hole through the composite which retained in a small sample up to 60% of its original stiffness.
14. FRACTURE TOUGHNESS TESTING

14.1 Conventional Test Methods

In order to determine whether a material is brittle or ductile, impact tests are frequently cited. There are three types of impact test used:

1) A pendulum striking a cantilevered specimen (ASTM 256 method A BS 2782 306A)

2) A pendulum striking a specimen in three point bending (ASTM 256 method B, BS 2782 306 B and E)

3) A falling weighted hemisphere striking a disc (BS 2782 306B).

In these tests the relative susceptibility to fracture by shock is quoted as the energy absorbed in breaking a standard specimen, by a standard blow, which has gained energy by falling a standard distance towards the sample. The first test, known as the Izod always uses a notched specimen and the second is known as a Charpy test.

The Izod is widely used although the Charpy simulates better the behaviour of real materials under impact. Unfortunately the Charpy test can give large variations in the results due to the condition of the impact machine and the way in which the specimens are machined and tested. The conditions set out in the ASTM tests gives an impact velocity of 11 ft/sec (3.39 m/sec) which can give results affected by the preparation technique; whereas the B.S. specify 8 ft/sec (2.46 m/sec) which gives results which are more likely affected by imperfections of the notch.
The falling weight test gives more reliable results which better compare with the conditions under which plastics will operate. This is especially true if the material to be tested is used in sheet form. The disadvantage of this test is the number of the test pieces which have to be prepared. When compared to the pendulum tests where the cracks propagate through the specimens at the speed of the pendulum, the cracks propagate through the specimen faster than the falling weight (72).

One of the toughness testers used in this thesis was the Hounsfield miniature Charpy machine with a 2.75 Joules capacity and a striker velocity of 2.54 m/sec. This machine is attractive because it requires less bench space and smaller samples, yet still testing under the Charpy conditions with a notch of 0.010" (0.25 mm). The specimens were cut with a constant depth of material under the notch. The results are quoted in this thesis as the energy in Joules absorbed by the impact divided by the area under the notch.

Another test method used was a variation on that developed by Tattersall and Tappin (73) of measuring the energy required to break in short span three point bending a notched specimen. In this thesis an unnotched specimen was used in conjunction with the ILSS test, by noting the energy under the stress-strain curve. This test gave the total energy to deform and break a specimen slowly, whereas the Charpy impact test gave the energy absorbed in fracturing the specimen at a faster speed.

Impact tests used are often determined on ideally shaped specimens with perfect notches. In reality specimens fail at their weakest point, depending on sharp edges and variable loads. The materials are often fabricated under poor conditions with flaws and inherent design weaknesses. It is often the case that the impact strength of a fabricated article bears no relation to the impact strength of an ideal sample of the material used in that article.
A very important criticism of impact tests is that most objects have to withstand repeated blows. Often several blows at a certain level will fail a sample, where one blow at that level would not. Although important there is no standard test because of the number of variables involved in any repeated impact test. The energy in the blow could affect the number of blows required, as could the velocity of the blows. The frequency of the blows, where they cause a rise in temperature need also to be monitored. It should also be considered, what load a specimen could support as the damage to it increases with the number of blows. Findley and Hintz\(^{(74)}\), Telfair and Nazen\(^{(75)}\), and Heater and Lacey\(^{(76)}\) while looking at the fracture of samples under repeated impact, conclude that there is no direct correlation between repeated impact resistance and the impact strength values obtained from standard tests. Since standard tests do not show how effective a material is under impact in use, it was considered important in the thesis to investigate the effect of repeatedly impacting a specimen and to monitor the damage caused by these repeated impacts. The authors\(^{(74, 75, 76)}\) mentioned above expected that this type of test would more nearly simulate in service conditions.

The apparatus used corresponds to that specified in BS 2782 method 306B. That is where a 0.500" (13.7 mm) hardened hemispherical striker falls vertically 24 ± 0.1" (604 ± 2.5 mm) onto a specimen supported by a hollow steel cylinder of 2.25" (57.2 mm) external diameter, and 2.00" (50.8 mm) internal diameter. The three impact energies for the 3 tests were chosen so that only a few tests would fail the composite at one energy level; only a large number would fail the composite at another energy level; and intermediate energy level was chosen. Then before impacting, the specimens 2" (50.8 mm) x 2" (50.8 mm), were tested for flexural modulus, with a 2" (50.8 mm) span and 0.25" (6.4 mm) support rollers, diagonally across the square sample at 45° to the major fibre axis in 3-point
bending. The specimen was then impacted once, flexural modulus tested again, impacted again and modulus tested again etc. This was continued so that 1, 3, 7, 15, 31 and 63 impacts were made with flexural modulus tests in between each step or until the specimen broke, a hole was punched, or the trend in behaviour was clarified. A graph was then plotted for each sample of accumulated energy against nominal flexural modulus. This graph traced the drop in flexural modulus with each impact. Nominal modulus was taken as the gradient of the stress-strain curve divided by the thickness cubed. The final state of the composite if not delaminated was indicated on the graph.

14.2 Fracture Mechanics

Set out below, are the reasons why the feasibility of using a fracture mechanics approach to assess the toughness of composites was investigated.

The cost of fabricating composites material test specimens is considerably higher than the cost of fabricating other material test specimens. In addition these composites generally require a higher standard of expertise in order to fabricate them. Consequently a given amount of time and money does not produce as many test results that can be correlated and interpreted compared to other materials. Recent research on the fracture of metals, is only now beginning to give an understanding of their fracture behaviour despite the many years metals have been used. Composite technology is new and the use of composites in structural applications, is as yet almost untried, to the extent that the important fracture information which is required for carbon fibre composites will be a long time in coming. The wide variety of fabrication techniques used to make carbon fibre composites, and their attractiveness for 'special' and high performance applications makes the characterisation of these composite more important and more difficult than for conventional materials. The anisotropy inherent in composites makes an exact material specification difficult, especially related to the properties of the constituents of the composites.
Composite fracture information would be expensive and difficult to obtain by methods adopted for conventional materials. Composites also are not exceptional in propagating cracks to complete failure from flaws, at working stress levels which according to elastic considerations are safe. It is the development of the knowledge about these flaws and cracks which lead to Fracture Mechanics. In addition Fracture Mechanics could more cheaply and more exactly describe the behaviour of composites especially in an aggressive environment, at extremes of temperature or under alternating and dynamic load.

It has been known for many years that a sharp crack can prematurely fail, any material at working stresses considerably lower than that which is considered to be safe. Griffith's crack theory\(^{(77)}\) stated that a crack will propagate an elastic material to failure if the available elastic strain energy release rate exceeds the surface energy of the crack. This theory although important was not very helpful since most engineering materials have an elastic-plastic behaviour.

Irwin\(^{(78)}\) equated Griffins energy approach to a stress intensity situation, where fracture occurs when a critical stress distribution (around a crack or inclusion), characteristic of the material is reached, for elastic-plastic materials. This gave the Griffith-Irwin concept of sharp crack fracture mechanics. More recent logical developments had led\(^{(79)}\) to the current concepts of 'Linear Elastic Fracture Mechanics'.

The Linear elastic fracture mechanics theory defines the elastic stress field around a crack tip in a centrally notched plane under tension. Mode I (opening of the crack figure 43) conditions are derived since these are of most practical importance\(^{(80)}\).

The elastic stresses close to the tip of a central crack of length 2a subjected to a uniform stress of \(\sigma\) at infinity can be expressed as\(^{(80)}\).
MODE I CRACK OPENING

Figure 43
(1) \[ \sigma_x = \frac{K_I \cos \frac{\varphi}{2}}{\sqrt{2\pi r_a}} \left( 1 - \sin \frac{\varphi}{2} \sin \frac{3\varphi}{2} \right) \]

(2) \[ \sigma_y = \frac{K_I \cos \frac{\varphi}{2}}{\sqrt{2\pi r_a}} \left( 1 + \sin \frac{\varphi}{2} \sin \frac{3\varphi}{2} \right) \]

(3) \[ \sigma_z = \frac{2 V K_I \cos \frac{\varphi}{2}}{\sqrt{2\pi r_a}} \] (plane strain)

\[ \tau_{xy} = \frac{K_I \cos \frac{\varphi}{2} \cdot \sin \frac{\varphi}{2} \cdot \cos \frac{3\varphi}{2}}{\sqrt{2\pi r_a}} \]

\[ \tau_{yz} = \tau_{zx} \]

where \( \sigma_x, \sigma_y, \sigma_z \) and \( \tau_{xy}, \tau_{yz}, \tau_{zx} \) are the direct and shear stresses respectively in Cartesian co-ordinates, \( r \) and \( \varphi \) are polar co-ordinates starting from the crack tip, \( \nu \) is Poisson's ratio and \( K_I \) is a stress intensity factor.

A crack in figure 43 subject to an applied stress in mode I configuration (2-dimensional) has only \( \sigma \) and \( a \) as dimensions and from the symmetry of the previous equations

\[ K_I = C_I \sigma \sqrt{a} \]

where \( C_I \) has been shown equal to \( \sqrt{\pi} \) \( K_I = \sigma \sqrt{\pi a} \) \( (79) \)

\[ (15) \]
This means that the stress intensity factor at a crack tip depends on the applied stress $\sigma$ and crack length $a$ only. When the crack becomes unstable according to the Griffith-Irwin theory, rapid propagation takes place to failure, then $K_I$ becomes $K_{IC}$ at the critical crack length $a_c$. $K_{IC}$ is a material property which can be found from laboratory experiments.

As mentioned previously, most structural materials behave as elastic-plastic materials and failure occurs when a critical stress distribution is reached with the plastic zone generated at the crack tip behaving as an equivalent extension of the crack. This only breaks down in linear elastic fracture mechanics when the stress approaches the yield stress of the material, but since the concept is only used when considering brittle fracture of engineering materials, this is not usually a problem. The stress intensity factor $K$ in that case includes $r_y$ the radius of the plastic zone.

$$K_I = \sigma_y \sqrt{\pi a (a + r_y)}$$

$\sigma_y$ is stress at yield.

The stress distribution radius covers a notional radius $r$

$$r = a + r_y$$

$$r = \frac{1}{\pi} \cdot \frac{K_I}{\sigma_y^2}$$

(16)

$K_C$ is not now an invariable material property, but depends only on the thickness.

The plastic extension that occurs ahead of the crack tip causes the crack tip to be opened by an amount $S$.

$$S \approx \frac{8}{\pi} \cdot \frac{\sigma_y}{E}$$

$\sigma_y$ - yield stress

$E$ - tensile modulus
Combining (15) and (16)

\[ S \simeq \frac{K_I^2}{E\sigma_y} \simeq \frac{G^2}{E.\sigma_y} \]

since stress at crack tip \( \sim \sigma_y \) and crack is opened by \( S \).

Work done at crack tip \( G \sim \sigma_y (S) \).

There is unstable crack propagation to failure when \( S \) reaches a certain value and \( G \) reaches \( G_C \).

\[ G_C \sim \sigma_y \cdot S_C \]

and hence when \( K_I \) reaches \( K_{IC} \).

\[ K_{IC} = \sqrt{E \cdot G_{IC}} \]

Work done at crack tip \( G \) the crack extension force can be defined as,

\[ G_I = \frac{1}{2} r^2 \cdot \frac{d \phi}{d A} \quad \text{-(18)} \]

- rate of change of compliance with area

\( F \) is load on specimen.

Hence \( K_I \) and \( K_{IC} \) can be found from \( G \) and equation (17).

14.3 Fracture Mechanics versus Conventional Toughness Testing (Charpy Type)

The original argument put forward for the development of fracture toughness \( K_{IC} \) values was a cheaper and more informative method of obtaining toughness data of materials. In addition valuable information on the effect of a corrosive environment and alternating loads has been found. It is these environments which can cause cracks to grow to a critical size whereby unstable crack propagation to failure occurs.

Charpy values are often used, as with other standard test methods, to find the temperature of the brittle-ductile transition. The notch in a Charpy test specimen is blunt compared to fatigue cracks and cracks from inclusions used for \( K_{IC} \) determinations, and these blunt cracks can
have the effect of increasing the apparent toughness of the materials. Ductile-brittle transition temperatures are up to 40°C higher than the same temperatures obtained from fracture toughness work, which explains the differences sometimes found when materials are used as opposed to tested. Consideration of the failure mechanism of materials in use renders Charpy and other tests of limited use whereas $K_{IC}$ values are a more reliable guide to design as opposed to a comparative test.

The toughness of materials predicted by tests such as Charpy cannot always be scaled up to full size, whereas fracture mechanics more easily copes with size effects. Charpy values, although a valuable test for quality control and material improvement work, can only with difficulty be used in design. $K_{IC}$ values can with confidence be used to compare materials for design. Fracture mechanics can also allow for accurate investigations of the strain rate dependence of toughness in a material.

Charpy and falling weight tests have been established as meaningful tests for material improvement comparisons in composites and were used as such in this thesis. However it is apparent that although little work has as yet been carried out on fracture mechanics in composites $K_{IC}$ values could be useful for design work and fatigue considerations of composites.

Summarising the uses of fracture toughness parameters ($K_{IC}$):

1) $K_{IC}$ values can be used to assess the toughness of materials.

2) $K_{IC}$ values can be used to design for materials working at a safe stress level, when the crack or defect size are known.

3) Inspection of materials whose $K_{IC}$ is known can give advance warning of the failure of materials in use, as long as the crack growth is monitored. For when the crack grows to a critical size given by $K_{IC}$ catastrophic failure takes place.
14.4 Estimation of Fracture Toughness in Composites

Waddoups et alia (81) have discussed the use of fracture mechanics in composite design and give some interesting calculations involving stress concentrations around holes in composites. They suggested its use for

1) Prediction of $K_I$ for significant design discontinuities
2) Anticipation of the behaviour of flaws induced in service
3) Prediction of the probability of failure on overloading the design specification. Unfortunately their work did not explain how the $K_I$ values could be obtained.

Sanford and Stonesifer (82) have developed their ideas in a similar way to that followed in the thesis and concluded the fracture mechanics data could give significant improvements to the knowledge of fracture behaviour in composites. They found significant differences in fracture toughness according to fibre strength, type of hardener, state of cure thickness of fibres and type of resin system used. The specimens they used to measure fracture toughness were uniaxial (in order to minimise the reinforcing effect of the fibre) double edge notch and single edge notch specimens as shown in figure 44. These specimens had starter or fatigue cracks initiated at the machined root of the crack. The specimen was stressed and the widening of the notch versus load to widen it was monitored. Knowing the rate of change of stiffness with crack length from a previously obtained calibration curve, the $K_I$ and $G_I$ were obtained.

It was considered that the new composites fabricated in the thesis might have improved crack arrest properties. The thesis has explained how to blunt cracks formed in the matrix at the interface by a graded interface. Crack arrest is the ability of a material to stop cracks
FRACTURE TOUGHNESS TEST SPECIMENS

Figure 44

Double Edge Notch

Single Edge Notch

Double Cantilevered Beam (D.C.B)
running through and failing a material after the cracks have been initiated by an impact. Because of this requirement the D.C.B. (double cantilevered beam) test discussed by Crosley and Ripling (83) was adopted for investigation in this thesis. This test can measure crack initiation and arrest properties. In developing the specimen shape and design in order to measure and calculate $K_I$ and $K_A$ (crack arrest) values the work of Mostovoy (84) and advice of Canon (53) were considered. Mostovoy shows the type of trace to be expected on stressing the D.C.B. and allowing the crack to move along the groove (see figure 45).

A composite containing uniaxially orientated fibres will tend to crack along the axis of the fibres, although in use it is the energy to propagate a crack across the fibres which is of most interest. In order to become familiar with fracture toughness testing techniques, and to use already prepared composites, D.C.B. test specimens were prepared whose cracks would propagate along the fibre axis. The specimens were moulded, 6" (152 mm) x 0.5" (12.6 mm) x 0.2" (5.1 mm) and then machined with 45° notches along their length as shown in figure 46. A starter notch was cut and the specimen stressed as shown. The load and deflection of the test specimen as the arms were separated was recorded. For the determination of $G_I$ and hence $K_I$, the compliance $\phi$ variation with crack length was required. A separate calibration specimen with a sawn crack was loaded, and unloaded before the crack started to extend. The crack was cut deeper and again the arms stressed and unstressed. From a graph of crack length against stiffness of the composite at that crack length, the compliance variation with crack length, and hence $K_{IC}$ can be calculated as below.

Two specimens were prepared.
Figure 45

[Graph showing load vs. deflection with markings for initiation and arrest]

Figure 46

[Diagram showing a starter notch with 6 inches, 0.5 inches, and 0.2 inches measurements]
1) HT-S fibres in DX231/125 (approx 60% fibre volume fraction)

2) HT-S coated in a 4% polyurethane solution embedded in DX231/DX 125 as developed earlier in the thesis.

Both specimens for the D.C.B. tests and calibration tests had the carbon fibres aligned along their length with a starter crack of 0.1" (2.54 mm) and holes to load the specimen drilled 0.175" (4.45 mm) from the end and sides. The crack width was 0.1" (2.54 mm).

The flexural modulus was also required for the calculation of $K_I$. This was measured for the test specimens.

D-1 Untreated fibre composite flexural modulus = 135 GNm$^{-2}$

D-2 Treated " " " " =$ 145$ GNm$^{-2}$

Compliance $\varphi = \frac{1}{stiffness}$

Recall equation 17.

$$K_I = \sqrt{\frac{E G}{C}} \quad E - composite\ modulus$$

and $$18 \ G = \frac{1}{2} F^2 \cdot \frac{\partial \varphi}{\partial a} \quad A - composite\ beam\ area$$

$$= \frac{1}{2H} \cdot F^2 \cdot \frac{\partial \varphi}{\partial a} \quad H - specimen\ width$$

$$a - crack\ length$$

Calibration samples of D-1 and D-2 were used to draw respectively D.C.B. 1A and D.C.B. 2A (figures 47 and 49) showing the compliance $\varphi$ (reciprocal of stiffness) change of the D.C.B. specimens with crack length. From these were drawn the graphs in figures 48 and 50 by taking the gradient of the graphs in figures 47 and 49 and plotting these gradients against the compliances values to which they correspond. This gradient is the rate of change of compliance.
D.C.B. 1A

Figure 47

Compliance

\[ \phi \]

\[ \begin{align*} \text{mm/N} \\ 0.3 \\ 0.2 \\ 0.1 \\ 0 \end{align*} \]

Crack Length

\[ a \text{ mm} \]

\[ \begin{align*} 0 & \quad 50 & \quad 100 & \quad 130 \end{align*} \]

D.C.B. 1B

Figure 48

\[ \frac{\delta \phi}{\delta a} \]

\[ \begin{align*} \text{0.006} \\ 0.004 \\ 0.002 \end{align*} \]

\[ \begin{align*} 0 & \quad 0.1 & \quad 0.2 & \quad 0.24 \end{align*} \]
From tests to failure of the D.C.B. specimens, points of crack initiation (peaks on traces) and crack arrest (troughs on traces) were taken together with their relevant graph gradients to give compliance and from the calibration curves rate of change of compliance. Knowing the specimen width, from the above equations can be found the crack extension force $G_I$ and critical stress intensity factor using equations 17 and 18.

**Critical Stress Intensity Factors $K_I$**

**Untreated Fibre Composites**

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Arrest Load N (A)</th>
<th>Initiate Load N (I)</th>
<th>Compliance $\phi$</th>
<th>$\frac{d\phi}{da}$</th>
<th>$K_{IC}$ MNm$^{-1.5}$</th>
<th>$K_{AC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>123</td>
<td>130</td>
<td>0.02</td>
<td>0.0012</td>
<td>23</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>113</td>
<td>121</td>
<td>0.033</td>
<td>0.0016</td>
<td>25</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>99</td>
<td>100</td>
<td>0.074</td>
<td>0.0023</td>
<td>25</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>41.6</td>
<td>52.9</td>
<td>0.038</td>
<td>0.0017</td>
<td>11</td>
<td>9.0</td>
</tr>
<tr>
<td>5</td>
<td>15.2</td>
<td>23.5</td>
<td>0.192</td>
<td>0.006</td>
<td>9.5</td>
<td>6.2</td>
</tr>
</tbody>
</table>

**P.U. Coated Fibre Composites**

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Arrest Load N (A)</th>
<th>Initiate Load N (I)</th>
<th>Compliance $\phi$</th>
<th>$\frac{d\phi}{da}$</th>
<th>$K_{IC}$ MNm$^{-1.5}$</th>
<th>$K_{AC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70.6</td>
<td>94.2</td>
<td>0.058</td>
<td>0.0024</td>
<td>25</td>
<td>18.5</td>
</tr>
<tr>
<td>2</td>
<td>61.8</td>
<td>84.3</td>
<td>0.096</td>
<td>0.0031</td>
<td>25</td>
<td>18.5</td>
</tr>
<tr>
<td>3</td>
<td>48.0</td>
<td>61.7</td>
<td>0.129</td>
<td>0.0035</td>
<td>19.5</td>
<td>15.5</td>
</tr>
</tbody>
</table>

The above values obtained from the above work are sensible and of a similar order to brittle cast steel (53). Since there had been no published work for the fracture toughness parameters of carbon fibre composites it was reassuring to have data of the right order of magnitude. This work was of only an exploratory nature but clearly shows that further work is possible.
There is little difference between the results of the coated fibre composites and the uncoated fibre composites since the cracks were propagating parallel to the fibres, whereas the coating was positioned to retard cracks propagating perpendicular to the fibres.

As a result of the work in this thesis and discussions with Meeks\(^{(63)}\), samples were prepared for D.C.B. test specimens which would propagate a crack across the fibres. The first specimen prepared to investigate this effect had a structure similar to that shown in figure 51. The carbon fibres ran across the machined notch, and the glass fibres, at right angles to these ran along the length of the specimen. The original sample was prepared as a 25:50:25 glass:carbon:glass sandwich, with the glass being machined away in the relevant area. Under test this specimen failed by interlaminar shear between the glass and carbon. A simple calculation showed that knowing the onset of shear failure, the notch must be machined to less than 0.010" (0.25 mm). A further specimen was prepared with such a notch and tested. Although the notch did propagate across the carbon fibres, the specimen was too fragile.

A second composite was then prepared which stressed the carbon fibres to a higher level without delaminating them. It was constructed as in figure 52. The carbon fibres were wrapped around steel arms through which holes were drilled to stress the composite. The remainder of the composite was glass, which was machined away in the centre of the composite to leave only carbon fibres running perpendicular to the notch. The notch was a quarter the thickness of the composite (1.25 mm).

When stressed this composite gave a graph as in figure 45 from which fracture toughness parameters could be measured. However the arms of this double cantilevered beam were stiff and the results erratic. A more carefully controlled separation of the arms and a high speed recorder, capable of recording the crack movements was required. Facilities for this more detailed work were available at the Railway Technical Centre, Derby and D. Canon kindly agreed to test a series of samples.
These tests when they were carried out were accidentally destroyed by the British Rail Workshops and could not be tested. Unfortunately there is no further information on this work.

14.5 Conclusions on Fracture Toughness Testing

The standard B.S. and A.S.T.M. impact test methods give the conditions whereby reproducible results can be achieved. However, although useful for comparing improved composites they (especially pendulum tests) do not always compare with actual service conditions of components. The falling weight impact test in the B.S. better simulates actual service conditions. However the two criticisms of a) requiring too many samples and b) failing a sample with one massive blow have been overcome with the procedure described. With only a few samples a method is described whereby meaningful toughness test can be carried out, using repeated falling weight impact.

It is apparent that design fracture toughness parameters developed for steel could be useful\(^{(82)}\), for designing with composite materials. The literature contained a remarkable paucity of experimental details on the design and testing of composites from which to find the fracture toughness parameters. This was despite considerable and varied opinion on the use of such parameters. The work in this thesis demonstrated that sensible fracture toughness parameters can be obtained. A suitable design of a composite was developed which could be used to measure fracture toughness parameters across the fibres. This technique shows considerable scope for further work in order to establish design level fracture toughness parameters. It does however require suitable equipment.
15. **FURTHER WORK**

The work described, where by coating carbon fibres with a low modulus polyurethane elastomer which was compatible with the epoxy resin matrix, gives a pre-preg system with significantly improved handling and processing characteristics. The final cured composites from these pre-pregs additionally have improved physical properties. This work is the subject of British Patent Application No. 12090/71.

The concept of a graded interface with an elastomeric coating, which is compatible and reactive with a rigid matrix could be further investigated. By selecting suitable elastomers and resins and investigating them as in this thesis, could give improved physical properties to a range of fibre reinforced plastic composites.

The latter part of the work discusses the measurement of fracture mechanics parameters for CFRP. It was shown that sensible values could be obtained, and if perfected, fracture mechanics could be a useful tool to more cheaply and accurately assess a variety of composite materials such as CFRP.

These two areas are then worthy of further investigation.
CARBON FIBRE COMPOSITES

The use of carbon fibres is at the present in the classic situation, where the amount of carbon fibres used depends upon their price. Unfortunately their price depends upon their volume usage. The commercial position is in reality a little more complex than this. Carbon fibres are produced from a special grade of polyacrylonitrile, the cost of which is £2 a lb. The treatment with converts this polyacrylonitrile to carbon fibres reduces the weight by a factor of two and increases the price to £4 a lb. Finally the overheads, development costs, profit and sales costs would lead to a figure of about £16 a lb. This at present is the long term low price for carbon fibres produced by conventional techniques. It is conceivable to reduce this price if a general purpose textile grade of polyacrylonitrile was used which could reduce the price to £5 a lb. However many problems will have to be overcome before this is feasible.

Carbon fibres when developed, were an important step forward for plastics. For the first time plastics could be made whose properties exceeded those of steel in the important design areas of strength, modulus and fatigue. Before this only glass fibres had been available in sufficient quantity as a reinforcing material for plastics. Although glass fibres have a high strength, their modulus and fatigue properties were too low to challenge steel in structural designs. Carbon fibres were however much lighter than steel and also, although more expensive, were expected soon to be cheaper.

Perhaps it was unfortunate that their discovery was made in a Government Research Establishment or that much of the initial work with carbon fibres was carried out in Universities. Rolls-Royce in their courageous and
nearly successful attempt to single-handedly launch carbon fibres also
damaged the prospects of carbon fibres, because their fan blade for the
RB211 aeroengine would not meet the specifications.

What was needed many years ago, is now beginning to take place. Carbon
fibre composites are being used where their installation gives real
improvements in simple components.

The industry which produces carbon fibres markets a multitude of grades
and types. Up to four different combinations of strength and modulus
are available. These carbon fibres can be supplied untreated or
oxidatively treated to improve their adhesion to plastics. They are
available in short staple form (less than 10mm), short lengths (up to
1.3m) and long lengths (up to 1000m). The fibres are often coated and
can be supplied as sheet and tapes, in woven and mat form, before
incorporation in plastic matrices.

The most widely used grade of carbon fibre is the cheapest, that with
a modulus in the region of 175 GNm⁻² and a strength of about 2.5 GNm⁻².
The shear strength is good especially when treated, and the toughness
adequate. If the manufacturers priced their fibre to preferentially
promote only a surface treated fibre of the grade indicated above, this
should help both their production economics and simplify the choice for
the user. Other grades could be made available at a premium price.
Essentially only one grade of glass fibre is now sold and there seems to
be no reason why this cannot be the position with carbon fibres.

Carbon fibres can be incorporated in a variety of matrices, although epoxy
resins are most widely used to give outstanding properties with relatively
easy processing. Other matrices, such as a variety of metals, polyimides
and phenolics have been investigated for specialist applications where their particular properties are required. Polyester resin is cheaper than epoxy and in the future it is therefore likely that the technology will be developed to use it more widely.

The development of matrices will improve the properties of carbon fibre composites, and in this thesis blended matrices of polyurethane and epoxy were used to improve the toughness of the composites. In evaluating any matrix improvement the ease of processing was considered. The system which coated the fibres with polyurethane was especially useful for it eased the processing and improved the overall properties of the composite.

In the previous developments of carbon fibre technology the ease of processing had not been considered and much of the research carried out was consequently wasted with the result that production of carbon fibre components has been delayed. Now the demand from industry for carbon fibre composites is dictating the pattern of future supplies of the fibre and matrix type with due consideration to cost, ease of processing and finished quality.

Now that components are made from carbon fibres new fabrication techniques are being developed. Initially carbon fibre composites were made by immersing the fibres in resin squeezing off the excess and curing the composite. This was a development of the most commonly used technique with glass fibres and polyester resin, known as hand lay-up. In order to utilise the full properties of carbon fibre composites it is necessary to use the fibres straight and without a textile handling size. This led to the industrial user demanding carbon fibres in the form of "prepregs" where the fibres, in sheet form, were pre-impregnated with resin and partly cured to give a material which could be cut, formed and cured
relatively easily to give the final product. The majority of industrial users making components reinforced with carbon fibres use them in the form of a "prepreg". It was with this in mind that the work in this thesis prepared specimens for test purposes from prepregs and the systems used to improve toughness were developed so as to be amenable to prepreg production.

Possibly the cheapest method of fabricating articles in reinforced plastics is by filament winding. Filament winding builds up tubes or cylinders by rotating a mould and winding on the fibres in prepreg form or running them through a resin bath, and onto the mould. The fibres can be laid in complex patterns, depending on the stress distribution in the product under load. There is little finishing required to the final product and the labour content is low. However a fairly expensive machine is generally required to obtain consistent results. Another method of fabricating long thin continuous cross-sections is pultrusion. In pultrusion the fibres are coated with a resin which can gel very quickly when heated, then they are pulled through the die which shapes the composite. The die itself is heated and the resin which gels on leaving the die is then cut into lengths and post cured. This technique is important, because it could be used to produce a large volume of carbon fibre composites in their finished form, with low production costs. One of the most promising areas for carbon fibre composites is as long thin sections which can be built into framework structures, which are light, strong and stiff.

Many of the possible uses for carbon fibre composites require intricate placing of fibres, built up layer by layer. Using prepregs and matched die moulding often leads to the fibres moving during resin flow when heat and pressure are applied. If the fibres are built up layer by layer and held in place by a light, soluble size to give a porous composite, then
resin can be injected round the fibres and cured by heat. This allows 
intricate designs to be fabricated, albeit at a high cost, with the 
fibre placings accurately held.

The major problems which have to be solved in order that carbon fibre 
composites can more widely be used will depend upon simple answers. 
These answers will be along similar lines to those developed in this 
thesis; that is by fibre coatings, matrix selection and other simple 
modifications of existing materials and techniques. The key to 
future successful development is therefore simplicity.

Future profitable areas for carbon fibre composites will depend on 
volume usage, not single hovercraft fan blades, but initially with 
sports equipment. In golf clubs where a carbon fibre handle can 
give an extra 20m to a drive, the price will be paid in this already 
costly sport. Other areas include equipment such as skis, tennis 
rackets, squash rackets, sailing boat spars, canoes and racing boats. 
These are the areas which could launch the material and reduce the 
price. As the price is reduced engineering structures using framework 
sections could be developed using components which need to be light. 
The big unknown is the aerospace industry, where the adoption of a 
carbon fibre fan blade could give a tremendous spur to the adoption 
of carbon fibres in general use.

However carbon fibre composites will always be a specialist material 
which will only be used where lightweight, strength and stiffness are 
required.
16. REFERENCES

(1) R.M. Gill - Carbon Fibres in Composite Materials, Iliffe Books
(2) A. Shindo - Rep Osaka Ind Res Inst No 317 (1961)
(3) W. Watt, L.N. Phillips and W. Johnson - Engineer 221, No. 5757, 815 (1966)
(4) J. Broughton and R.H. Kröck - Modern Composite Materials, Adison Wesley
(5) L.B. Greszczyk - Interfaces in Composites ASTM STP 452 (1969)
(6) F.M. Fowkes - Adhesion and Adhesives
(8) W.A. Zisman - Ind Eng Chem, Oct 1963
(9) W.A. Zisman - Adhesion and Cohesion, ed. P. Weiss, Elsevier
(10) J.R.J. Harford and E.F.T. White - Plastics and Polymers, Feb 1969
(11) Souheng Wu - Du Pont House Magazine
(12) D.M. Brewis - Poly Eng and Sci, Jun 1967
(13) J.R. Huntsberger - Chem Eng News, 42 (44), 82-7, (1964)
(16) R.E. Baier, E.G. Safrin, W.A. Zisman - Science, 162, Dec 1968
(20) R.N. Wenzel - Ind Eng and Chem, 28, 988 (1936)
(22) W.K. Adam and R.S. Morell - J. Soc. Chem Ind 53, 255T (1934)
(27) T.H. Grindstaff - Textile Research Journal, Oct 69, 958
J.B. Donnet and M. Dauksch - 1st Int Conf. Carbon Fibre, P.I., Feb 71
J.W. Herrick, P.E. Gruber, F.I. Monsur - AFML - TR-66-178 Part 1
ASTM D1510-65
M.J. Stevens - Private Communications IPT Loughborough University
J.C. Goan and S.P. Prosen - Interfaces in Composites ASTM STP 452
L.J. Broutman - ASTM STP 452
M. Vasta and V. Zvonar - Adhesive Age Oct 1965
B. Harris, Beaumont and Moncinil de Ferran - J. Mat. Sci 6 (1971) 238-251
W.J. Eakins - ASTM STP 452
G.A. Cooper and A. Kelly ASTM STP 452 (1969)
API (1969)
(53) D.F. Canon - Railway Technical Centre, Derby, - Private Communications
(55) F.J. McGarry and A. Willner - R68-6 - March 1969 (MIT)
SPI (1969)
Comp. Div. SPI (1970)
Plast. Conf. BPF (1970)
(59) L.N. Phillips and K.F. Rogers - Polymer Age 3 No. 5 May (1972)
(60) K.F. Rogers, G.R. Sidney and D.M. Kingston-Lee-Composites 2 No. 4
Dec 71
(62) Du Pont Adiprene Urethane Rubber Bulletin No. 2
(63) A.C. Meeks - Shell Research Egham private discussion
(64) F. Lord - ICI Organics Division Blakely private discussion
(67) Melinex - ICI's polyethylene terephthalate biaxially orientated sheet
(68) G.R. Sidey and F.J. Bradshaw - Int Carbon Fibre Conf. P.I. 1971
(69) G. Fairbairn, C.J. Dominic and E.W. Carnish - Int. Carbon Fibre Conf.
P.I. 1971
(70) P.F. Bertsch - Rubber World - June 1961 p75-81
(71) Encyclopedia of Polymer Science and Technology
(72) Dr R.R. Smith - Private Discussions
(73) H.G. Tattersall and G. Tappin - J. Mater. Sci. 1, 296 (1966)
(74) W.N. Findley and O.E. Hintz - ASTM Proc. 43 1 226 (1943)
(75) D. Telfair and H.K. Nazen - ASTM Proc. 43 1·211 (1943)
(76) J.R. Heater and E.M. Lacey - Modern Plastics 41, 9, 123 (1964)
(77) A.A. Griffiths - Phil. Trans. Royal Soc. - Series A; Vol. 221 1920
(78) G.R. Irwin - Proc 7th Sagamore Ord Matts Res Conf 1960 - IV
(79) ASTM - STP N381 (1965)
(80) B.R. Research and Development Internal Publication - Linear Elastic Fracture Mechanics - D. Canon
(82) R.J. Sanford and F.R. Stonesifer - J. Comp Mat Vol. 5 April 1971
(83) P.B. Crosley and E.J. Ripling - J. Basic Eng Sept 1969
(84) S. Mostavoy, P.B. Crosley and E.J. Ripling - J. of Mat Vol. 2 No. 3 Sept 1967
## APPENDIX I

### Courtaulds Grafil

<table>
<thead>
<tr>
<th>Filament Diameter μm</th>
<th>Density Mg/m³</th>
<th>Ultimate Tensile Strength GPa</th>
<th>Tensile Modulus GPa⁻²</th>
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<tbody>
<tr>
<td>Grafil A</td>
<td>7.9</td>
<td>1.9 - 2.25</td>
<td>190 - 240</td>
</tr>
<tr>
<td>Grafil HT</td>
<td>7.8</td>
<td>2.4 - 3.1</td>
<td>240 - 290</td>
</tr>
<tr>
<td>Grafil HM</td>
<td>7.5</td>
<td>1.7 - 2.25</td>
<td>345 - 415</td>
</tr>
</tbody>
</table>

The suffix S (HT-S, HM-S) refers to a surface modification which can improve the adhesion to the fibres.

ILSS is quoted as a measure of the expected improvement.

<table>
<thead>
<tr>
<th>Grafil A</th>
<th>Grafil HT</th>
<th>Grafil HT-S</th>
<th>Grafil HM</th>
<th>Grafil HM-S</th>
</tr>
</thead>
<tbody>
<tr>
<td>ILSS MPa⁻²</td>
<td>55-69</td>
<td>34-48</td>
<td>69-83</td>
<td>21-34</td>
</tr>
</tbody>
</table>

### Bakelite Polyester Resin SR17449

<table>
<thead>
<tr>
<th>As supplied</th>
<th>Viscosity at 25°C m²/s</th>
<th>Density Mg/m³</th>
<th>Acid value mg KOH/gm</th>
<th>Volatiles %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>360</td>
<td>1.112</td>
<td>20</td>
<td>32</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cured unreinforced resin</th>
<th>Hardness</th>
<th>Water absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Brinell 32</td>
<td>24 hrs 10 mg</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7 days 30 mg</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ultimate tensile strength</th>
<th>57.7 MPa⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate flexural strength</td>
<td>82.6 MPa⁻²</td>
</tr>
</tbody>
</table>
Scott Bader Crystic 272

As supplied

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity at 25°C</td>
<td>0.35 Ns/m²</td>
</tr>
<tr>
<td>Density</td>
<td>1.10 x 10³ kgm/m³</td>
</tr>
<tr>
<td>Acid value</td>
<td>18 mg KOH/gm</td>
</tr>
<tr>
<td>Volatile Content</td>
<td>41%</td>
</tr>
</tbody>
</table>

Cured unreinforced resin

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barcol hardness</td>
<td>45</td>
</tr>
<tr>
<td>Water absorption</td>
<td>15 mg 0.17%</td>
</tr>
<tr>
<td>Ultimate tensile strength</td>
<td>62 MN/m²</td>
</tr>
<tr>
<td>tensile Modulus</td>
<td>3.65 GN/m²</td>
</tr>
</tbody>
</table>

Shell Epikote 816/Epikote TET

mixed in ratio 100 : 12.5 by weight

Resin-Hardener mixture

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity at 25°C</td>
<td>1.2 - 1.8 Ns/m²</td>
</tr>
<tr>
<td>Cured Unreinforced Resin</td>
<td></td>
</tr>
<tr>
<td>Ultimate tensile strength</td>
<td>57.2 MNm⁻²</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>2.5%</td>
</tr>
</tbody>
</table>

Ciba Araldite MY778/HY956

mixed in ration 100/25 by weight

Resin-Hardener mixture

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity at 21°C</td>
<td>0.8 - 1.2 Ns/m²</td>
</tr>
<tr>
<td>at 40°C</td>
<td>0.2 - 0.4 &quot;</td>
</tr>
</tbody>
</table>
Cured unreinforced resin

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1.16 Mg/m³</td>
</tr>
<tr>
<td>Water absorption (24h at 23°C)</td>
<td>15–20 mg</td>
</tr>
<tr>
<td>Ultimate tensile strength</td>
<td>55–76 MNm⁻²</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>131–137 MNm⁻²</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>3.4–5.5 GNm⁻²</td>
</tr>
</tbody>
</table>

**HKL ERLA 4617**

Resin Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity at 25°C</td>
<td>0.08 – 0.15 Ns/m²</td>
</tr>
<tr>
<td>Density at 25°C</td>
<td>1.176 Mg/m³</td>
</tr>
</tbody>
</table>

Cast Unreinforced resin

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength</td>
<td>130 MNm⁻²</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>5.40 GNm⁻²</td>
</tr>
<tr>
<td>Flexural Strength</td>
<td>214 MNm⁻²</td>
</tr>
<tr>
<td>Flexural Modulus</td>
<td>5.62 GNm⁻²</td>
</tr>
<tr>
<td>Heat Distortion Temperature</td>
<td>175°C</td>
</tr>
</tbody>
</table>

**Hoechst Hostaform C9020**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
<td>66.7 MNm⁻²</td>
</tr>
<tr>
<td>Elongation at Break</td>
<td>20–30%</td>
</tr>
<tr>
<td>Shore hardness</td>
<td>D 83</td>
</tr>
<tr>
<td>Vicat Softening VSP/B</td>
<td>154°C</td>
</tr>
<tr>
<td>Melt Flow Index</td>
<td>9 gm/10 minutes</td>
</tr>
<tr>
<td>Density</td>
<td>1.41 Mg/m³</td>
</tr>
</tbody>
</table>

**Du Pont Delrin 100**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
<td>68.9 MNm⁻²</td>
</tr>
<tr>
<td>Tensile Secant Modulus (1%)</td>
<td>3.58 GNm⁻²</td>
</tr>
<tr>
<td>Deflection under (0.455 MNm⁻²)</td>
<td>170°C</td>
</tr>
<tr>
<td>Density</td>
<td>1.41 Mg/m³</td>
</tr>
<tr>
<td>Material</td>
<td>Property</td>
</tr>
<tr>
<td>--------------------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>I.C.I. Maranyl A100</td>
<td>Tensile Strength</td>
</tr>
<tr>
<td></td>
<td>Elongation at Break</td>
</tr>
<tr>
<td></td>
<td>Deflection under (0.455 MNm⁻²)</td>
</tr>
<tr>
<td></td>
<td>Density</td>
</tr>
<tr>
<td>Shell Carcona P CMT</td>
<td>Tensile Yields Strength</td>
</tr>
<tr>
<td></td>
<td>Flexural Modulus</td>
</tr>
<tr>
<td></td>
<td>Melt Flow Index</td>
</tr>
<tr>
<td></td>
<td>Density</td>
</tr>
<tr>
<td>B.R.P. Rigidex</td>
<td>Tensile Strength</td>
</tr>
<tr>
<td></td>
<td>Elongation at Break</td>
</tr>
<tr>
<td></td>
<td>Melt Flow Index</td>
</tr>
<tr>
<td></td>
<td>Density</td>
</tr>
<tr>
<td>B.F. Goodrich Estane 5707</td>
<td>Tensile Strength</td>
</tr>
<tr>
<td></td>
<td>Modulus at 300% Elongation</td>
</tr>
<tr>
<td></td>
<td>Shore Hardness</td>
</tr>
<tr>
<td></td>
<td>Processing Temperature</td>
</tr>
<tr>
<td>Estane 5713</td>
<td>Tensile Strength</td>
</tr>
<tr>
<td></td>
<td>Modulus at 300% Elongation</td>
</tr>
<tr>
<td></td>
<td>Shore Hardness</td>
</tr>
</tbody>
</table>
Weissenburg Rheogoniometer

The Weissenburg Rheogoniometer was used in thesis to measure the viscosity of a range of resins over a temperature range from 20-50°C.

The basis of the instrument is a cone and plate, nearly in contact with one another. The liquid fills the space between the two and the plate rotates at a fixed speed. The force transmitted through the liquid exerts a force on the cone. The force exerted is derived from a calibrated torsion beam on which the cone is suspended, and the amount the cone is deflected.

At a particular plate rotational speed there is a constant shear rate.

If the angular velocity is \( w \) rad/sec

Then the circular velocity \( V \) at a radius \( r \) from the centre

\[ V = wr \]

The gap between the cone and plate at a radius \( r \) where the angle between cone and plate is \( \Theta \),

\[ = r \tan \Theta \]

\( r \Theta \) (small angles)

Then the shear rate \( \dot{\gamma} \) in the polymer at this point

\[ \dot{\gamma} = \frac{wr}{r \Theta} = \frac{w}{\Theta} \]

This shows that by using a cone and plate viscometer with a small included angle the shear rate is independent of the radius \( r \)

The viscosity of a liquid = \( \frac{\text{Stress}}{\text{Shear rate}} \)

For a particular instrument with a set angle between cone and plate, the shear rate depends on the angular velocity of the plate. The stress applied to the cone can be deduced from the deflection of the calibrated torsion bar supporting the cone.
The Weissenburg can rotate the plate over several decades of shear rate and detect stresses on the cone to cover this wide range. It can thus be used to show how viscosities of polymers vary with the rate at which they are sheared.