THE STRENGTH AND FAILURE BEHAVIOUR OF
SHORT GLASS FIBRE REINFORCED POLYAMIDE 6

by

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of Philosophy in the University of Surrey

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The strength and failure behaviour of nylon 6 reinforced with short E-glass fibres has been studied. The fibres were treated with different sizing compounds in order to modify the interface between the glass and polymer. The principal objective of the work was to assess, by means of mechanical testing and microscopy, the role of the interfacial bond in controlling the properties of these materials.

It has been shown that the mechanical behaviour of glass reinforced nylon 6 is controlled mainly by the fibre concentration, length, and orientation and that stiffness enhancement can be adequately predicted by a modified rule of mixtures expression. The behaviour is also strongly influenced by the type of sizing compound employed on the fibres. The results clearly demonstrate the beneficial effects of silane coupling agents. In the 'dry' condition some composites exhibited a 30% strength reduction on omission of the silane, but in others this caused little variation. In the wet state however, silane treatments produced far superior properties in all cases. In addition, the size apparently exerts considerable control over the properties, indirectly, by effecting the fibre dispersion and breakage during compounding and moulding.

The failure mechanism as assessed by optical and scanning electron microscopy and by acoustic emission analysis, was shown to be of a dual nature. Failure was initiated by fibre-matrix debonding in the core region of the mouldings, the debonded areas interlinked and became visible on a macroscopic scale as strain bands across the samples. The strain banding phenomenon in turn initiated a catastrophic brittle failure sequence, the resulting fracture surfaces exhibiting the characteristics of both weak and strongly bonded systems.
Acknowledgements

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K. Hartley, for the loan of so many useful textbooks and the telephone answering service.

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A
Peak area (DSC)

\(a_L\)
Thermal expansion coefficient, longitudinal direction

\(a_T\)
Thermal expansion coefficient, transverse direction

B
Chart setting divided by heating rate (DSC)

\(b_s\)
Impact sample breadth

C
Orientation parameter

\(D_p\)
Plunger diameter

\(d\)
Nominal fibre diameter

\(\bar{d}\)
Average fibre diameter

\(d_f\)
Fibre diameter

\(d_s\)
Impact sample depth

\(\gamma_{nc}\)
Charpy fracture energy

\(\gamma_{ss}\)
Energy input to fracture tensile samples

\(\gamma_x\)
Fibre pullout fracture energy term

\(\Delta H_x\)
Enthalpy of crystallisation

\(\Delta q_s\)
Y-axis range (DSC)

\(\Delta T\)
Temperature change

E
Cell calibration coefficient

\(E_c\)
0.5% secant modulus

\(E_f\)
Fibre modulus

\(E_L\)
Longitudinal modulus

\(E_m\)
Matrix modulus

\(E_T\)
Transverse modulus

\(e, e'\)
Electron energy

\(\varepsilon_{AE}\)
Acoustic emission onset strain

\(\varepsilon_c\)
Composite strain

\(\varepsilon_i\)
Specific strain, (Bader-Bower equation)

\(\varepsilon_{LL}\)
Longitudinal strain in longitudinal ply

\(\varepsilon_m\)
Matrix strain
<table>
<thead>
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<th>Symbol</th>
<th>Description</th>
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<tr>
<td>$\varepsilon_{TL}$</td>
<td>Longitudinal strain in transverse ply</td>
</tr>
<tr>
<td>$\varepsilon_{uc}$</td>
<td>Composite failure strain</td>
</tr>
<tr>
<td>F</td>
<td>Force</td>
</tr>
<tr>
<td>$F_{po}$</td>
<td>Pullout force</td>
</tr>
<tr>
<td>HC</td>
<td>Heat cleaned</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Coefficient of restitution</td>
</tr>
<tr>
<td>L</td>
<td>Fibre length</td>
</tr>
<tr>
<td>$\bar{L}$</td>
<td>Volume average fibre length</td>
</tr>
<tr>
<td>$L_c$</td>
<td>Critical fibre length</td>
</tr>
<tr>
<td>$L_{po}$</td>
<td>Pullout length</td>
</tr>
<tr>
<td>$L_s$</td>
<td>Impact sample length</td>
</tr>
<tr>
<td>M</td>
<td>Mass of impact sample</td>
</tr>
<tr>
<td>$M_f$</td>
<td>Fibre mass</td>
</tr>
<tr>
<td>$M_{fs}$</td>
<td>Fibre plus size mass</td>
</tr>
<tr>
<td>$M_P$</td>
<td>Polymer mass</td>
</tr>
<tr>
<td>$M_s$</td>
<td>Size mass</td>
</tr>
<tr>
<td>N</td>
<td>Number of fibres per unit area</td>
</tr>
<tr>
<td>$\bar{R}$</td>
<td>Average aspect ratio</td>
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<tr>
<td>$R_c$</td>
<td>Critical aspect ratio</td>
</tr>
<tr>
<td>$R_i$</td>
<td>Aspect ratio, subcritical fibres</td>
</tr>
<tr>
<td>$R_j$</td>
<td>Aspect ratio, supercritical fibres</td>
</tr>
<tr>
<td>$r_f$</td>
<td>Fibre radius</td>
</tr>
<tr>
<td>$r_{fs}$</td>
<td>Fibre/size combination radius</td>
</tr>
<tr>
<td>$\rho_f$</td>
<td>Fibre density</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>Size density</td>
</tr>
<tr>
<td>SC</td>
<td>Solvent cleaned</td>
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<tr>
<td>SFRTP</td>
<td>Short fibre reinforced thermoplastics</td>
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<tr>
<td>$\sigma_c$</td>
<td>Composite stress</td>
</tr>
<tr>
<td>$\sigma_{ci}$</td>
<td>Composite stress at strain $\varepsilon_i$</td>
</tr>
<tr>
<td>$\sigma_f$</td>
<td>Fibre strength</td>
</tr>
<tr>
<td>$\sigma_{LL}$</td>
<td>Longitudinal stress in longitudinal ply</td>
</tr>
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</table>
\( \sigma_{MY} \) Yield stress of polymer melt
\( \sigma_n \) Maximum surface stress
\( \sigma_{TL} \) Longitudinal stress in transverse ply
\( \sigma_{uc} \) Ultimate composite strength
\( T_m \) Melting point
\( T_s \) Punch shear test sample thickness
\( t_L \) Thickness of longitudinal ply
\( t_T \) Thickness of transverse ply
\( \tau \) Interface shear strength
\( \tau_{po} \) Frictional bond strength
\( \tau_m \) Matrix shear strength
\( U_c \) Impact energy
\( U_s \) Stored elastic strain energy
\( U_x \) \( U_c - U_s \)
\( V_f \) Fibre volume fraction
\( V_i \) Volume fraction of subcritical fibres
\( V_j \) Volume fraction of supercritical fibres
\( V_m \) Matrix volume fraction
\( v \) Impact sample velocity
\( W_{po} \) Pullout work
1. INTRODUCTION AND OBJECTIVES

The principle of composites is well established and the consumer is aware of such materials in the form of pleasure boats, car bodies, sports equipment etc. In addition to these more obvious applications, components fabricated from composites are widely used in virtually all industries including automotive, transportation, marine, appliance and electrical. However, as often happens with successful new technical developments, what might be termed the 'technological art' of these materials is still ahead of their science, a balance which is unlikely to be redressed for some time.

Improvements in the properties of most thermoplastic materials can be gained by the incorporation of suitable filler materials such as glass ballotini, talc and fibres and whilst the particulate fillers may offer some mechanical property enhancement and cost reduction, the fibrous fillers are capable of greatly enhancing both stiffness and strength.

Fibre reinforced thermoplastics (FRTP) comprise one group of composite materials in which short, stiff, and thermally stable fibres are incorporated in a suitable thermoplastic polymer matrix thereby improving its properties and range of application considerably. Improvements in strength, stiffness, dimensional stability, heat distortion temperature and creep resistance are obtained but these are generally at the expense of some of the important properties of the unreinforced materials e.g. impact resistance, isotropic shrinkage and excellent flowability.

One of the principal attractions of thermoplastics as engineering materials is their ability to be easily moulded into complex shapes using rapid inexpensive techniques such as injection moulding. It is important therefore to retain these desirable
characteristics when reinforcing the polymer with fibres and, to achieve this, the fibres must necessarily be incorporated in short discrete lengths and to limited volume fractions.

In examining the properties of composite materials there are three basic considerations of importance, the matrix material, the dispersed phase and the interface between them, and a sound understanding of the contributions and interactions of each is necessary in predicting the properties and behaviour of a given composite.

When considering the mechanical properties of fibre reinforced materials, the simplest case is of a uniaxially aligned continuous fibre composite, even so, a number of basic assumptions must be made. Obviously, as the fibres become misaligned and/or discontinuous the complexity of the situation increases. Short fibre reinforced thermoplastics are amongst the most complex of composite materials since they consist of a viscoelastic matrix containing short fibres of variable length, orientation and concentration, and, as such are distinctly anisotropic in their behaviour. There is as yet no complete mathematical analysis but a combination of empiricism with adaptions of models appropriate to the simpler composites has improved our understanding of these materials.

Previous work at the University of Surrey (1) has shown that the observed premature failure of glass reinforced nylon 6.6 is due to an embrittlement effect caused by the stress concentrating effect of the fibre ends. The stiffness enhancement was adequately predicted by a modified rule of mixtures expression provided that a reasonably strong interfacial bond existed.

In this investigation the matrix material chosen was nylon 6 which, compared to nylon 6.6, is more ductile and easier to process due to its wider softening temperature range. The change was made in
order to determine if the observed embrittlement was a function of the fibre presence or the matrix properties. Other variables to consider when examining the strength of short fibre composites are the efficiency of the fibre-matrix interfacial bond and the degree of fibre attrition during compounding and moulding.

The objectives of this investigation can therefore be summarised:

(i) To study by means of mechanical testing the role of the interfacial bond on reinforcement efficiency; strength, stiffness, ductility and toughness and the relationship between these parameters.

(ii) To examine in detail the failure behaviour of these materials using optical and scanning electron microscopy in order to determine the sequence of events leading up to, and the cause of, final failure.

(iii) To study the effect of fibre related parameters such as aspect ratio and orientation distribution on the mechanical properties and failure behaviour.

(iv) To study the effect of the compounding and moulding operations on fibre length degradation.

(v) To investigate the role of fibre sizing agents, other than coupling agents (i.e. film formers and lubricants), on the control of fibre distribution.
2. LITERATURE REVIEW

2.1 The properties of fibre polymer and interface

2.1.1 Fibre Fillers

By definition, the principal function of a reinforcing filler is to confer enhanced mechanical properties to the base polymer. Almost any form of fibrous reinforcement may be used with thermoplastic matrices from ceramic whiskers and short asbestos fibres to continuous tows of glass and carbon fibres. The choice of fibre must depend upon a number of considerations such as properties, economics, compounding techniques and the end use of the composite. The different types of reinforcing fibre available are adequately reviewed by Hollingsworth, Parrat and Kelly in references (2-5).

At a reasonable level of loading, and given good interfacial adhesion between the filler and matrix, improvements in stiffness and strength will be functions of the properties of the filler. In addition, with fibrous fillers, the improvements can be further magnified by the influence of the fibre aspect ratio and the anisotropic effect of fibre orientation. The most effective reinforcing fibres are therefore those possessing high modulus and strength.

The reinforcement in most commercial fibre reinforced thermoplastics is provided by glass fibres and the most commonly used form is E-glass, an alumina borosilicate low alkali glass which draws well into strong fibres. Other glasses, such as A and S glass are available but are not normally used due to their poorer properties and high cost respectively. Glass fibres are produced in continuous filament form by a drawing process, molten glass is passed from a furnace to a series of bushings (generally of platinum) each containing approximately 200 accurately dimensioned jets or tips. Fine filaments are drawn downwards from the tips at high speeds to
a collecting point where a size is applied and are then brought
together to form a strand, the strands then being wound singly
or as multiple strands (rovings). For a given type and melt viscosity
of glass, the filament diameter is controlled by the drawing speed,
typical commercial filaments lying within the range 9-18 μm.

Carbon fibres are available in a number of forms, type I a
high modulus fibre, type II a high strength fibre and type III a fibre
with intermediate properties (actually lower in strength and modulus
than type II but a higher failure strain). The property variation is
a result of their respective fabrication techniques, different carbo­
nisation temperatures being required for each. All types of carbon
fibre may be used to reinforce thermoplastics although the high modulus
material can be difficult to handle due to its low failure strain.
Typical properties of some commercially available fibre types are given
in Table 2.1.1.

An inherent drawback in most high strength fibres is their
brittleness and consequent sensitivity to defects such as surface
flaws. Thus, as their length increases so does the probability of
including a serious flaw in that length and the average fibre strength
falls. Strengths of virgin defect free glass fibres can be in excess
of 3.5 GNm⁻² (4) and this has been shown to be independent of length
and diameter (6,7). However, since glass is very sensitive to surface
damáge, even normal careful handling will readily reduce the strength to
the order of 2 GNm⁻² (the typical commercial figure) by introducing
flaws in the surface. The actual form of the flaws and their operative
conditions, i.e. stress level and gauge length, is well reviewed by
McCrum (8). Since a range of fibre strengths exists, fibre bundles are
inevitably weaker than monofilaments, the weakest fibres fail at low
stresses thus imposing additional loads on the other fibres causing
them in turn to fail (9).
Table 2.1.1

Properties of some commercially available forms of fibrous reinforcement (Data from ref. 5).

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Strength (G.Pa)</th>
<th>Modulus (G.Pa)</th>
<th>Density ($10^3$Kgm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-glass</td>
<td>3.5</td>
<td>72</td>
<td>2.55</td>
</tr>
<tr>
<td>S-glass</td>
<td>4.6</td>
<td>84</td>
<td>2.50</td>
</tr>
<tr>
<td>Silica</td>
<td>6.0</td>
<td>72</td>
<td>2.19</td>
</tr>
<tr>
<td>Carbon type I</td>
<td>2.0</td>
<td>390</td>
<td>1.90</td>
</tr>
<tr>
<td>Carbon type II</td>
<td>2.6</td>
<td>240</td>
<td>1.90</td>
</tr>
<tr>
<td>Boron Nitride</td>
<td>1.4</td>
<td>90</td>
<td>1.90</td>
</tr>
<tr>
<td>Boron/Tungsten</td>
<td>2.8</td>
<td>380</td>
<td>2.63</td>
</tr>
<tr>
<td>Chryostile asbestos</td>
<td>4.5</td>
<td>164</td>
<td>2.55</td>
</tr>
<tr>
<td>Crocidolite asbestos</td>
<td>2.8</td>
<td>180</td>
<td>3.37</td>
</tr>
<tr>
<td>Alumina whiskers</td>
<td>2-20</td>
<td>470</td>
<td>3.96</td>
</tr>
<tr>
<td>Silicon carbide whiskers</td>
<td>2-20</td>
<td>470</td>
<td>3.17</td>
</tr>
<tr>
<td>Silicon nitride whiskers</td>
<td>2-10</td>
<td>380</td>
<td>3.18</td>
</tr>
</tbody>
</table>
2.1.2 Polymer Matrices

The utilisation of the matrix material differs with the type of composite under consideration, its contribution in continuous fibre composites is minimal, the strength and stiffness being derived from the fibres, the matrix serving only to provide shear strength and to locate the fibres. In SFRTP however, its role is considerable since it is the only medium by which stress is transferred to the fibres. The choice of matrix material is virtually unlimited, depending on the properties required from and the end use of the composite. The more general properties of polymers are adequately reviewed by Billmeyer, Ogorkiewicz, and Andrews in references (10-12) respectively.

Two main classes of thermoplastic polymer exist, namely amorphous and semi-crystalline. The latter are already a form of composite since their stiffness is imparted by the crystalline regions and their ductility by the rubbery or glassy amorphous region. The crystalline regions are formed by a molecular chain folding process to give lamellae which may be stacked to form spherulites (polymeric 'grains') or extended when mechanically oriented by drawing. Since the spherulites contain, and are surrounded by, amorphous regions, no polymer can attain one hundred per cent crystallinity. Amorphous polymers possess no intrinsic microstructure above the molecular level but may be artificially oriented.

The properties of both classes of polymer are very temperature dependent especially about the brittle-ductile or glass transition temperature (Tg). Thus amorphous polymers such as P.M.M.A, P.V.C. and polystyrene are glassy and brittle at room temperature and polymers such as plasticised P.V.C. and ethylene vinyl acetate (EVA) are rubbery and ductile. Similarly, semicrystalline polymers; polyethylene, polyamides and polypropylenes behave in a brittle manner at low temperatures but are generally ductile at room temperatures above their glass transition ranges.
Some polymers, polyamides in particular are ideal mediums for reinforcement, they are easily processed and excellent property enhancement is achieved. Details of moulding techniques and properties of commercially available filled and unfilled nylos are reviewed in references 11 and 13. Polyamides are amongst the most useful engineering thermoplastics being tough, strong, abrasion resistant and resistant to chemical attack. The major disadvantage is their hygroscopic nature, water or water vapour can be absorbed from the surroundings in a diffusion controlled process to proportions approaching ten per cent by weight depending on the polymer type. The effect of moisture is similar to that of a plasticiser, its presence facilitating molecular chain movement thus decreasing the stiffness and strength and correspondingly increasing ductility (14).

Considering Nylon 6 in particular, since it is the matrix material used in this investigation. This is manufactured by the polymerisation of \( \epsilon \)-caprolactam, the repeat unit being \[ \text{H}_2\text{N} \left( \text{CH}_2 \right)_5 \text{CO}_2 \]. The actual process is known as ring scission polymerisation and the principal commercial techniques are either hydrolytic or anionic polymerisation (14).

Bessell et al (15) have investigated the effect of polymerisation conditions on the properties and fracture behaviour of spherulitic nylon 6 (anionically polymerised). Increasing the polymerisation temperature resulted in an increase in spherulite size and molecular weight, causing a change in the fracture behaviour from a brittle to a ductile tough polymer. In addition, specimens having constant molecular weight and spherulite size exhibited three distinct fracture modes dependent upon the degree of crystallinity; the fracture surfaces having a brittle appearance at high crystallinities (~44%), brittle and ductile combined at intermediate crystallinities and a completely
ductile fibrillar topography at crystallinities of \( \approx 32\% \) and less. The toughness and fracture stress decreased with increasing crystallinity and the yield stress and modulus increased with crystallinity. There appeared to be a critical crystallinity of \( \approx 39\% \) above which toughness decreased rapidly.

Russell and Beaumont (16-18) have conducted a fairly comprehensive study of the structure and properties of injection moulded Nylon 6 and observed a significant variation in structure and morphology through the thickness of the mouldings. No molecular orientation was found and density measurements showed a low crystallinity at the moulding surface (\( \approx 27\% \)) and a higher crystallinity in the core (\( \approx 35\% \)), this is related to the cooling rate and is dependent on the mould temperature. The surface layers were devoid of spherulites while the core material contained spherulites of \( \approx 6 \mu \text{m} \) diameter. Exposure to boiling water was seen to increase the crystallinity, effectively reversing the density-distance relationship of the dry mouldings but not effecting the morphology. Parabolic residual stress distributions were observed in the mouldings, being compressive at the surface and tensile in the core, this being attributed to non-uniform volume changes due to differential cooling rates. Boiling water treatments reversed the residual stress distributions due to inhomogeneous volume changes as a result of water induced crystallisation. The yield stress-crystallinity relationship was similar to that observed by Bessell (15) as was the toughness-crystallinity relationship, a critical value at \( \approx 40\% \) being observed but not explained. Water increased the toughness, decreased the yield stress and changed the failure mode from brittle to ductile rupture. The yield stress was only slightly strain rate sensitive but toughness decreased significantly with increasing strain rate. Three modes of failure were observed, brittle, semi brittle and ductile, these were a function of strain
rate and testing temperature and were stated to be independent of
crystallinity, in contrast to Bessell.

It is therefore apparent that the morphology and properties of
nylon 6 are considerably influenced by the fabrication techniques and
the presence of water and that these have a pronounced effect on the
failure behaviour.

2.1.3 The fibre-matrix interface

The fibre-matrix interfacial bond is perhaps the most important,
but least well understood factor affecting the properties of composite
materials. This is especially true for short fibre reinforced thermo­
plastics since the ability of the matrix to transfer stress to and
from the fibres is dependent on the strength and efficiency of the
bond.

The type of bonding can theoretically be utilised in the design
of composite materials since a weak bond should give a tough composite
through crack blunting by interfacial debonding, conversely a
strong bond should enhance stiffness but at the expense of toughness.
Various surface treatments are available to improve bond strength but
their actual mechanism of operation is not well understood. The
importance of the interface is emphasised when the surface areas
involved are considered e.g. 1mm$^3$ of a 50% (by volume) fibre composite
with a fibre diameter of 7.5 μm contains approximately 6500mm$^2$ of
interface area (19).

Two principal types of glass fibre surface treatment are used
(20); a size, containing a coupling agent to improve the bond strength,
a lubricant to facilitate handling and minimise abrasive surface
damage and a binder to preserve strand integrity by overcoming static
charges. The second, a finish containing only a coupling agent which
is applied to heat cleaned fibres generally in fabric form.

Commercially used sizes are generally applied from aqueous emulsions or solutions to the freshly drawn glass fibres, the concentrations employed being dependent upon the coupling agent present (41). In glass reinforced thermoplastics the size serves a number of functions. It must be able to protect the glass during the high shear environments encountered in extrusion compounding and injection moulding and also provide an effective degree of adhesion between the fibre and polymer (42). If the glass fibres are being used in chopped strand form, the size must facilitate easy chopping and ensure that the chopped strand can be easily handled, i.e. is free flowing. Additionally, the size must maintain bundle integrity until dispersion is required in the compounding and moulding operations.

Bonding between fibre and matrix arises from one, or a combination of, three possible mechanisms; physical bonding such as wetting, chemical bonding or mechanical bonding. The latter mechanism is mainly due to matrix shrinkage onto the fibres or Poisson's ratio effects on loading. Many theories have been proposed to account for the exact adhesion mechanism at the interface but none have completely succeeded (20). Originally the bond was considered due to simple wetting and surface tension effects, this theory was generally rejected when it was shown that fibres treated with a coupling agent were less easily wetted by water and resins than untreated fibres but still imparted improved properties (20,21). The deformable layer theory implied that the finish was plastic at the interface and thus able to accommodate differential shrinkage, this is clearly impractical since the interfacial coupling agent layer would be too thin. The theory was modified (22) on the assumption that the size in some way modified the resin structure surrounding the fibres giving a thicker inter-phase layer which could accommodate relaxation stresses, its effect is
however open to conjecture. The restrained layer theory stems from the assumption that stress transfer between high modulus fibre and low modulus plastic matrix can most uniformly occur if there is an interphase region of intermediate modulus. Thus, the theory suggests that silane coupling agents function by 'tightening up' the polymer structure at the interface, while simultaneously providing groups for bonding on the glass surface. It is however difficult to reconcile this concept with the need for stress relaxation at the interface to compensate for differential thermal shrinkage. Most of the theories have been discarded in favour of a chemical bonding mechanism which utilises a bifunctional coupling agent capable of forming covalent and/or hydrogen bonds with both fibre and matrix.

The most common commercially used coupling agents are silanes having the general formula, $X_3\text{Si}(\text{CH}_3)_n\text{Y}$, where $X$ is a hydrolyzable group on the silicon which generates covalent bonds with the fibres by formation of intermediate silanols which then condense with silanols on the glass surface. The $Y$ group is an organofunctional group selected for polymer compatability (23). Typical commercial silanes are listed in Table 2.1.2 with their respectively compatible polymers.

Thermoplastic polymers are generally considered to be comparatively inert materials due to the almost complete removal of functionality during polymerisation (25). Several workers (21,23,24) have however proposed that thermoplastics may be divided into two categories when considering their reactivity with the organofunctional $Y$ group:

(i) "Non-reactive" polymers, principally polyolefines that do not contain any reactive groups and thus require a coupling agent capable of generating active sites on the polymer backbones. Polystyrene, polyethylene and polypropylene are representative of this category.
(ii) "Reactive" polymers, such as polyamides in which the Y
group is capable of reacting directly with the polymer back-
bone or P.M.M.A and P.V.C. where the reaction is with a side
group.

In order to exploit fully the capabilities of the coupling agents
therefore, the chemistry of the silane must be carefully matched to that
of the reinforced polymer (25). In addition, for the silanes to function
properly in thermoplastics, they must be thermally stable at the maximum
temperatures encountered during moulding and must be capable of reaction
under the sometimes severe moulding conditions (26).

Plueddemann (23,26) has proposed a dynamic equilibrium mechanism
which is essentially a combination of the other theories and accounts
for stress relaxation at the interface without permanent bond disruption.
The mechanism relies on the ability of a silanol to compete with water
molecules at the glass surface and form hydrogen bonds and/or -oxane
bonds, both of which are reversible. e.g.

\[
R - \text{Si} - \text{O} + \text{MOH} \rightleftharpoons R - \text{Si} - \text{OM} + \text{H}_2\text{O}
\]

\[
R - \text{Si} - \text{O} + \text{MOH} \rightleftharpoons R - \text{Si} - \text{OM} + 2\text{H}_2\text{O}
\]

Where M is a metal oxide (Si, Al, Fe etc)

The reversible nature of the bond relies on the presence of free silanols,
resulting from hydrolysis of a bond, remaining at the interface which
can then reform the bond or make a new bond with an adjacent group
(Fig. 2.1.1). This is claimed to account for all the observed phenomena
of adhesion to hydrophillic surfaces through silane coupling agents.
The mechanism is supported by both laser Raman studies and mechanical
property measurements, the bond strength being reversible after boiling in water or methanol. (27).

Many techniques have been used to investigate the nature of the interface including; electron microscopy, radioisotope studies, spectroscopy, ellipsometry, thin layer chromatography and simple mechanical testing, these are adequately reviewed by Ishida and Koenig (27). Despite the intense study, controversy still reigns over the exact adhesion mechanism. The majority of workers assume the existence of some form of covalent bonding but its elucidation is complicated by the extremely small relative amounts of material present at the interface. Rosen and Goddard (28) have described a new technique known as a filler desorption test (FDT) which involves observations of surface tension changes occurring when a silane treated filler is floated on a water surface, the rate of surface tension change giving a measure of the adhering tendency of the polymerised silane film.

It is well known that silane treatment of glass surfaces improves initial composite strength and strength retention under adverse environmental conditions, however the number of chemical bonds required for optimum properties is not known. The average optimum layer thickness certainly exceeds the theoretically desirable monomolecular layer, the thickness appearing to depend on the nature and concentration of the coupling agent (21,29). Efforts to remove the coupling agent in boiling water resulted in a decreasing desorption rate, the thickness approaching a monomolecular layer only after extended periods and it was concluded that the coupling agent consisted of easily removed outer layers and a tightly bonded polymer film at the surface. Shrader (30) has shown a similar decreasing desorption rate behaviour when the coupling agent was extracted by boiling water and proposed that the silane layer be subdivided into three fractions based on their tenacity to extraction. These consist
of an easily removed physisorbed layer which may be as much as 98% of the total, a thinner chemisorbed layer and a highly tenacious chemically reacted layer at the glass surface, of monolayer dimensions. Ishida and Koenig (137) have extended this theory showing that the uniformity and extent of crosslinking of the layers increases as the glass surface is approached, the type of structural gradient depends on the coupling agent and controls its hydrolytic stability. Electron microscopy studies have shown that there is a preferential buildup of silane in the capilliaries between individual filaments and some agglomeration on the filament surfaces, thus explaining why silane loadings required for optimum strength are greater than calculated amounts for monolayers (21).

Many authors have demonstrated the improved properties that are obtained with silane treatments prior to composite lay up. Broutman (31) has obtained up to forty percent increases in the tensile strength of glass fibre/polyester systems and over one hundred and fifty percent in the wet boiled composite. Sterman and Marsden (21,24) and Plueddemann (23) have found improvements in the mechanical properties of silane treated glass fibre filled thermoplastics, compared to the untreated materials. Table 2.1.3.

Modification of the matrix microstructure adjacent to the fibre surface can occur, resulting in localised matrix property variations from the bulk material. This effect has been observed by Bessell et al (32,33) in the in-situ polymerisation of caprolactam (to produce nylon 6) on carbon and glass fibres. The fibres are shown to nucleate a columnar spherulitic structure at the interface, the effect was most pronounced with the carbon fibres which is attributed to physical matching of the structure with the graphite crystallites. The presence of a surface treatment appeared to have little effect on the phenomena. With glass
fibres however, a different behaviour was observed, the columnar structure was non-uniform and was influenced by the presence of the size. Electron microscopy studies showed that the size distribution was non-uniform on the glass surfaces and it was postulated that nucleation of the nylon was caused by the size dissolving at the polymerisation temperatures. This was supported, since removal of the size resulted in a reduction in columnar growth, and it was shown that the glass fibres themselves did not nucleate spherulites.

The interface between the modified structure and the bulk polymer was found to be a source of weakness, acting as a preferential crack path during fracture which was possibly due to an accumulation of foreign material rejected from the fibre surface by the growing spherulites. It has also been shown that polymer properties vary drastically with spherulite size (15,16-18), thus regions of modified polymer may be of considerable importance in fibre filled thermosto- plastics. In addition degradation of polyamides by oxidation is known to occur more rapidly at glass fibre surfaces in the presence of oxygen. Free oxygen is unlikely to be present during injection moulding, but water present in the nylon and at the hydrophilic glass surface will cause polymer hydrolysis resulting in a lower molecular weight and greater degree of crystallisation, and hence, a more brittle polymer in the interface regions (34).

Various test methods have been proposed to determine the interfacial bond strength (19,31), some are concerned with adhesion between plane surfaces and others measure the load required to extract glass rods embedded in polymer. The relevance of such macroscopic studies is questionable and correlation of end results with real composite systems difficult. Tests employing single glass fibres are preferable, Andreevskaya (35) has measured the load required to
extract fibres embedded in resin seams supported by two glass rods, relating this to the bond shear strength. Favre and Perrin (36) cast small resin discs around fibres, again measuring the load to extract the fibre. Broutman (31) investigated tensile debonding failure and interfacial shear strength using trapezoidal specimens designed to fall at the interface in tension, or shear under compressive loading. A Split-Dee test, which is recognised as a standard test for filament wound composites, gives limited information on the effect of surface treatments by evaluating the shear strength (37). Fraser et al (38) have embedded single filaments in tensile samples; on testing the filaments fracture into numerous fragments giving an experimental fibre length distribution. A computer optimization technique then gives values of interfacial shear strength which compare well with values from other methods. Indirect techniques of measuring the interface bond strength such as the interlaminar shear stress (ILSS) have been used by many authors including Harris (39), this is considered unsatisfactory however since failure at the interface cannot be assured. Shortall and Yip (138) have studied the feasibility of various methods of evaluating bond strength and concluded that the most useful method was Broutman's shear debonding specimen which involves the uniaxial compression testing of a block of resin containing a single discontinuous fibre.

Agarwal and Bansal (40) have recently conducted a theoretical analysis of the effect of interfacial conditions on the properties of discontinuous fibre composites using a finite element technique. Various interfacial conditions are simulated by assigning different property values to an interfacial layer (e.g. layer with low modulus represents a weak bond). The measures of bond efficiency are the load transfer length and the critical interaction length, these both decrease as the bond becomes stronger (higher allocated modulus) and level off
when the interfacial modulus exceeds the matrix modulus. Since the interaction length is related to volume fraction of fibres, this indicates fibres are effective in small amounts providing the bond is strong enough. They show that the composite modulus is not significantly affected by interfacial conditions whereas strength is very significantly affected, which agrees with experimental observations.
### Table 2.1.2

**Typical Commercial Silane Coupling Agents (23-41)**

<table>
<thead>
<tr>
<th>No.</th>
<th>Silane Name</th>
<th>Formula</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>γ-Aminopropyltriethoxysilane (A-1100)*</td>
<td>( \text{H}_2\text{N}(\text{CH}_2)_3\text{Si(OCH}_3\text{)}_3 )</td>
<td>Epoxies, Phenolic, Nylon</td>
</tr>
<tr>
<td>2</td>
<td>β-(3,4-Epoxycyclohexyl)-Ethyltrimethoxysilane (A186)*</td>
<td>( \text{CH}_2\text{CH}_2\text{O(CH}_2\text{)}_3\text{Si(OCH}_3\text{)}_3 )</td>
<td>Epoxies</td>
</tr>
<tr>
<td>3</td>
<td>γ-Glycidoxypropyltrimethoxysilane (A187)*</td>
<td>( \text{CH}_2\text{=CHSi(OOCCH}_3\text{)}_3 )</td>
<td>Almost all resins</td>
</tr>
<tr>
<td>4</td>
<td>Vinyltriacetoxy silane (A188)*</td>
<td>( \text{CH}_2\text{=C-O(CH}_2\text{)}_3\text{Si(OCH}_3\text{)}_3 )</td>
<td>Unsaturated polyesters</td>
</tr>
<tr>
<td>5</td>
<td>γ-Methacryloxypropyltrimethoxysilane (A174)*</td>
<td></td>
<td>Unsaturated polyesters</td>
</tr>
</tbody>
</table>

*Union carbide designation*
**TABLE 2.1.3**

Physical properties of injection moulded glass reinforced Nylon 6.6, 30% glass. (24)

<table>
<thead>
<tr>
<th>Size</th>
<th>Flexural Strength (GPa)</th>
<th>Flexural Modulus (GPa)</th>
<th>Tensile Strength (GPa)</th>
<th>Tensile Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry</td>
<td>Wet</td>
<td>Dry</td>
<td>Wet</td>
</tr>
<tr>
<td>Commercial No.1</td>
<td>2.69</td>
<td>7.65</td>
<td>1.78</td>
<td>1.49</td>
</tr>
<tr>
<td>Commercial No.2</td>
<td>2.12</td>
<td>6.41</td>
<td>1.47</td>
<td>1.29</td>
</tr>
<tr>
<td>A-1100*</td>
<td>1.72</td>
<td>5.30</td>
<td>1.02</td>
<td>1.01</td>
</tr>
<tr>
<td>A-186*</td>
<td>2.07</td>
<td>6.41</td>
<td>1.54</td>
<td>1.31</td>
</tr>
<tr>
<td>A-187*</td>
<td>2.16</td>
<td>6.89</td>
<td>1.41</td>
<td>1.09</td>
</tr>
<tr>
<td>Virgin roving</td>
<td>1.18</td>
<td>5.58</td>
<td>0.69</td>
<td>0.59</td>
</tr>
<tr>
<td>No glass</td>
<td>0.86</td>
<td>1.65</td>
<td>0.61</td>
<td>0.57</td>
</tr>
</tbody>
</table>

*See Table 2.1.2*
Fig. 2.1.1 Bonding of rigid polymers to mineral surfaces through silanes (23).
2.2 The Mechanical Properties of Composites

2.2.1 Continuous fibre composites

It is possible to derive theoretically the properties of aligned continuous fibre composites using a simple rule of mixtures approach (4,5,43). The fibres are assumed to be continuous, parallel and uniformly distributed and, in addition, perfectly bonded to the matrix such that no slippage can occur at the interface. The elastic energy of the system is then the sum of the volume averages of the two phases.

\[ U_c = U_f V_f + U_m V_m \]  

(2.2.1)

Where \( U \) = elastic energy and \( V \) = volume fraction. The subscripts \( c,f,m \) refer to composite, fibre and matrix respectively. If the elastic energy is expressed in terms of stress, \( \sigma \), and strain, \( \varepsilon \), then:

\[ \frac{1}{2} \sigma_c \varepsilon_c = \frac{1}{2} V_f \sigma_f \varepsilon_f + \frac{1}{2} V_m \sigma_m \varepsilon_m \]  

(2.2.2)

There are two limiting states, the condition of uniform strain which sets an upper bound (Voigt) to the composite properties and results in equations 2.2.3 and 2.2.4.

\[ \sigma_c = \sigma_f V_f + \sigma_m V_m \]  

(2.2.3)

\[ E_c = E_f V_f + E_m V_m \]  

(2.2.4)

Where \( E \) = Youngs modulus.

The lower bound (Reuss) is the condition of uniform stress in the composite and results in the following equations.

\[ \varepsilon_c = \varepsilon_f V_f + \varepsilon_m V_m \]  

(2.2.5)
The Voigt estimate is approximately correct when applied to the tensile modulus parallel to the fibres and the Reuss estimate gives a less accurate approximation to the transverse modulus, neither however provide a satisfactory estimate of shear modulus. For short fibre composites the uniform strain state is no longer strictly true and this combined with the effects of fibre misalignment cause the modulus to deviate from the rule of mixtures expression. More rigorous derivations (5,44) give results which differ only slightly from the rule of mixtures expressions for the aligned modulus, Kelly (5) has estimated the typical deviations to be at most, two percent, thus equation 2.2.4 is a sufficiently accurate approximation for most purposes.

In considering the tensile strength of uniaxially aligned composites, many authors (4,5,39) have used the simple rule of mixtures approach. The idealised model (eqn. 2.2.3) however, suffers from a number of deficiencies; it is only exact in the limiting case of equal fibre and matrix failure strains and should be modified by two constants \( \lambda_f \) and \( \lambda_m \) which are dependent on the component failure strains e.g.

\[
\sigma_{uc} = \sigma_{uf} V_f \lambda_f + \sigma_{um} V_m \lambda_m \tag{2.2.7}
\]

If the fibre failure strain is less than the matrix failure strain \( \varepsilon_{uf} < \varepsilon_{um} \) then one of two situations occur; the composite fractures when the fibres are raised to a unique failure stress \( \sigma_{uf}' \) and the composite strength, \( \sigma_{uc}' \) is given by equation 2.2.8, where \( \sigma_m' \) is the stress in the matrix at composite fracture.
Alternatively, at low fibre loadings, the matrix may be capable of supporting the additional load and multiple fibre fracture results. Fig. 2.2.1. The strength of the remaining weakened material is given by:

\[ \sigma_{uc} = \sigma_{um} (1-V_f) \]  

(2.2.9)

This effect results in a minimum composite strength at some critical \( V_f^c \):

\[ V_{min} = \frac{\sigma_{um} - \sigma'_m}{\sigma_{uf} + (\sigma_{um} - \sigma'_m)} \]  

(2.2.10)

Such behaviour has been observed experimentally and is shown in Fig. 2.2.2.

If the fibre failure strain is greater than the matrix failure strain (\( \varepsilon_{uf} > \varepsilon_{um} \)), matrix failure may initiate composite failure prior to the full load bearing capacity of the fibres being reached, the composite strength is then given by equation 2.2.11 where \( \sigma'_f \) is the fibre stress at matrix fracture.

\[ \sigma_{uc} = \sigma'_f V_f + \sigma_{um} V_m \]  

(2.2.11)

Alternatively at high fibre loadings the fibres may be capable of supporting the extra load and multiple matrix cracking results, the matrix segment length being determined by the interfacial adhesion and final composite failure occurs when the fibre failure stress is reached (Fig. 2.2.1). This behaviour has also been observed experimentally (5).
The major criticism of the simple rule of mixtures approach is its use of a single fibre failure stress and while this may be correct in metal fibre systems, brittle fibres such as carbon and glass exhibit a range of strengths which are dependent on a number of variables, principally gauge length (Section 2.1.1).

Composites containing brittle fibres with a range of failure stresses, thus exhibit complex failure behaviour. The dominating failure mechanism is generally agreed to be that the first fibre fracture at the most severe flaw is accommodated by local matrix flow and debonding, so that the load shed by the broken fibre is redistributed into adjacent fibres, thus allowing further increases in load which leads to ultimate fracture at less severe flaws (37). Theories predicting failure stresses based on this mechanism differ only in the criteria taken for final composite breakdown.

The properties of aligned fibre composites depend to a large extent on the orientation of the fibres relative to the applied stress. If the stress axis is shifted from the fibre direction, the matrix and interfacial shear properties become increasingly important and less tensile stress is applied to the fibres. The variation of modulus with angle, $\theta$, to the fibres has been predicted using the basic properties of the constituent materials and the assumption of elastic behaviour (44, 46). The treatments use the composite axial modulus $E_L$ and Poisson's ratio $\nu_{LT}$ which can be determined from the rule of mixtures. The shear modulus $G_{LT}$ and the transverse modulus $E_T$ which are also required, need a more complex treatment. This has been done by Tsai et al (47) who assume the fibres are in a square array, they used elasticity theory and solved the equations using a finite difference technique. The major elastic constants are then used to
estimate the elastic moduli at any angle $\theta$ to the fibres. Equations of the form below result (43).

$$\frac{1}{E_{\theta}} = \left[ \frac{\cos^4 \theta}{E_L} + \frac{\sin^4 \theta}{E_T} + \sin^2 \theta \cos^2 \theta \left( \frac{1}{G_{LT}} - \frac{2v_{LT}}{E_L} \right) \right]$$  \hspace{1cm} (2.2.12)

Dimmock and Abrahams (46) have investigated experimentally the variation of composite modulus with angle in glass and carbon fibre epoxy systems. Excellent agreement with theory is obtained for the latter case (Fig. 2.2.3) though the agreement is not so good in the former. This was attributed to lack of knowledge of the matrix properties combined with the lower stiffness of the glass. It is apparent that the modulus decreases rapidly with increasing fibre angle which demonstrates the extreme anisotropy of these materials.

A number of theories have been used to predict the variation in composite strength with angle $\theta$ (5,45,48). The maximum stress theory propounds three failure modes; firstly fibre failure in tension at small angles, $0^\circ \leq \theta \leq 5^\circ$, secondly matrix or interface shear failure parallel to the fibres in the range $5^\circ \leq \theta \leq 60^\circ$ and thirdly, transverse failure at higher angles, this may be of the matrix, fibre, or interface which ever is the weakest. The stress, $\sigma_\theta$, to initiate failure in each of these modes is given in equations 2.2.13 - 15.

$$\sigma_\theta = \sigma_{uc} \sec^2 \theta \hspace{1cm} (2.2.13)$$

$$\sigma_\theta = \tau_u \ 2\csc 2\theta \hspace{1cm} (2.2.14)$$

$$\sigma_\theta = \sigma_t \ \csc^2 \theta \hspace{1cm} (2.2.15)$$

Where $\tau_u = \text{composite shear strength and } \sigma_t = \text{transverse strength.}$

The failure mode with the lowest possible operative strength at $\theta$
particular angle is assumed to dominate composite failure. Kelly et al (5) have used the maximum stress theory to predict composite strength and a comparison with experimental values for a metal matrix composite is given in Fig. 2.2.4, showing the good agreement obtained.

The maximum strain theory (48) is similar to the maximum stress theory but based on the ultimate failure strains of the three modes.

The maximum distortional work theory which is based on the Von Mises failure criterion predicts composite strength at any angle to the fibres, the theory assumes that failure will occur when the total distortional work exceeds a certain level. The model uses the axial, transverse and shear strengths of the composite ($\sigma_c$, $\sigma_t$ and $\tau_u$ respectively), the axial strength being computed from the rule of mixtures and the transverse and shear strengths assumed to be equal to the matrix tensile and shear strengths respectively. The composite strength, $\sigma_\theta$, is given by:

$$\frac{1}{\sigma_\theta^2} = \left[ \frac{\cos^4 \theta}{\sigma_c^2} + \frac{\sin^4 \theta}{\sigma_t^2} + \frac{\cos^2 \theta \sin^2 \theta}{\tau_u^2} \left( \frac{1}{\sigma_c^2} - \frac{1}{\sigma_t^2} \right) \right]$$  \quad (2.2.16)

Tsai (48) has shown that in glass/epoxy composites, the work theory fits the experimental data more closely than the maximum stress theory. Dimmock and Abraham (46) have investigated the strength variations with fibre orientation using carbon and glass fibre-epoxy systems and demonstrated good agreement with the maximum work and maximum stress theories at high angles where both predict similar values. At small angles, agreement is more satisfactory with the maximum stress theory for the carbon material, but the glass composites agreed better with the maximum work theory. However, considerable scatter of results was apparent in all cases. (Fig. 2.2.5). The authors comment that the rule of mixtures overestimates composite axial strength since it takes no account of fibre and matrix flaws. Thus differences observed at small
angles may be a result of a change in fracture mechanism not accounted for by any of the theories.

Experimental work has demonstrated that none of the theories accurately predicts strength variations with fibre angle and that each theory is an oversimplification in some respect. The maximum stress and strain theories wrongly assume independent fracture modes and the maximum distortional work theory assumes that the rule of mixtures can predict composite longitudinal strength which is not the case, due to fibre and matrix flaws.
Fig. 2.2.1 Conditions for multiple fracture.

Fig. 2.2.2 Ultimate tensile strength of copper/tungsten wire composites as a function of $V_f$ (5).
Fig. 2.2.3 Variation of composite modulus with fibre direction for carbon fibres in epoxy resin, $V_f = 0.57$, $1 \text{ hPa} = 10^7 \text{Pa}$ (45).

Fig. 2.2.4 Variation of composite strength with fibre direction for silica fibres in aluminium $V_f = 0.5$ (5).
Fig. 2.2.5 Variation of composite strength with fibre direction for carbon fibres in epoxy resin, $V_f=0.57$. (46)
2.2.2 Discontinuous Fibre Composites

In discontinuous fibre composite systems, the fibres cannot be loaded directly at their ends and stress must therefore be transferred into them by shear forces at the fibre-matrix interface. The shear forces, which arise because two materials of very different elastic moduli are constrained to deform together, build up from zero at the fibre ends. Thus, a portion of each fibre near its end will not be fully loaded and will be less effective in reinforcing the composite. The rate of stress buildup will be dependent on the strength of the interfacial bond and this will therefore influence the composite behaviour to a much greater extent than in continuous fibre systems. High bond strength will result in rapid stress buildup and more efficient fibre utilisation than weakly bonded systems.

Numerous theories have been proposed to describe in detail the variation in stress distribution with fibre length, these are adequately reviewed by Holister and Thomas (49). The theories can be categorised into two distinct approaches which are dependent on the behaviour of the fibre and matrix.

The first set of theories, initially proposed by Cox (50) and subsequently modified by Dow (51) and Rosen (52) consider the fibre and matrix in the elastic state. The theories rely on perfect fibre matrix bonding with no stress transfer across the fibre ends. The resulting expressions are all of the form:

\[ \sigma_f = K_1 \left[ 1 - \frac{L}{2} - x \right] \frac{K_2}{\cosh L/2} \]

(2.2.17)

and differ only in the values of the constants \( K_1 \) and \( K_2 \). \( L \) is the fibre length and \( x \) the distance along the fibre (see ref. 49). The
stress distribution is shown graphically in Fig. 2.2.6. Outwater (53) presented a theory specifically for reinforced plastics in which he assumed that the load was completely carried by the fibres and stress at the interface was constant. The actual stress level was dependent on the coefficient of friction between the fibre and matrix, and the frictional forces developing from differential fibre-matrix shrinkage on curing. The resulting equation has the form:--

\[ \sigma_f r_f^2 \pi = 2\pi r_f \mu x \]  
(2.2.18)

Where \( P \) = radial resin pressure acting on fibre
\( \mu \) = coefficient of friction
\( r_f \) = filament radius

Thus stress is built up in a linear fashion from the fibre ends over a characteristic transfer length:

\[ \frac{x}{2} = \frac{\sigma_f r_f}{2 \mu} \]  
(2.2.19)

The second approach is due to Kelly and Tyson (54) who, working with tungsten wires in a copper matrix, presented a theory for elastic fibres in a plastic matrix. This so-called 'shear lag' analysis relies on a constant interfacial shear stress, the fibre stress builds up linearly from the fibre end to a maximum value, where the strain in the fibre and matrix are equal, over a characteristic length known as the semi-critical transfer length \( L_{c/2} \). Initially, on applying a tensile load both fibre and matrix deform elastically, above a certain load (defined by the Tresca yield criterion, 49) plastic flow occurs in the matrix while the fibre continues to deform elastically. Such plastic flow originates at the fibre ends and has the effect of
limiting the interfacial shear stress, \( \tau \), to the shear yield stress of the matrix, \( \tau_y \). Since the fibre still behaves elastically, then at any strain \( \varepsilon \), the maximum fibre stress is \( \sigma_f = \varepsilon E_f \) (since \( \sigma_f/\varepsilon = E_f \)). For fibre failure to occur the stress transferred must be equal to the tensile strength of the fibre, therefore

\[
\pi r_f^2 E_f \varepsilon E_f = 2\pi r_f \tau x \tag{2.2.20}
\]

and since \( x = L_c/2 \) (the semi critical transfer length) the critical length

\[
L_c = \frac{E_f r_f}{\tau} = \frac{\sigma_{uf} r_f}{\tau} \tag{2.2.21}
\]

This is shown schematically in Fig. 2.2.7. Comparison of equations 2.2.18 and 2.2.20 shows that the Outwater and Kelly theories are identical if \( \tau \) is substituted for \( \tau_y \) and \( \varepsilon E_f \) is substituted for \( \sigma_f \) in the former. The concept of critical length has been discussed by Kelly in a review paper (55) and is defined as the minimum length of fibre required to attain the ultimate fibre strength. This is clearly demonstrated in Fig. 2.2.7 from which it is apparent that fibres having a length greater than \( L_c \) can be stressed to failure while those of subcritical length are incapable of being stressed to this limit.

The actual composite behaviour can probably best be described by a combination of the two approaches, the former in the centre of the fibre which behaves in an elastic manner and the latter at the fibre ends where interfacial shear stresses are high and the matrix may flow or the bond fail. Piggot (56) has attempted such a combination, including a complex elastic transfer term into the Kelly-Tyson equations for the fibre centre section, improvements over the simpler theory were minimal and Lees (57) therefore recommends use of the Kelly/Tyson approach although it is only an approximation of the stress transfer
mechanism.

All of the theories rely on assumptions which are oversimplifications, the stress concentrating effects of the fibre ends are ignored and the magnitude of the shear stresses at the fibre ends underestimated. The theories are thus only applicable to low $V_f$ composites where fibre-fibre interactions and stress concentrations can be ignored.

A modified rule of mixtures approach can quite accurately estimate the initial modulus of short fibre composites assuming strain compatibility. Equations 2.2.22 and 23 give this modulus in terms of the Kelly-Tyson and Cox theories respectively.

\[
E_C = E_fV_f\left(1 - \frac{L_C}{2}\right) + E_mV_m \quad (2.2.22)
\]

\[
E_C = E_fV_f\left(1 - \frac{(1-\beta)L_C}{L}\right) + E_mV_m \quad (2.2.23)
\]

Where $\beta$ is related to the rate of stress transfer.

An alternative stress analysis technique has been used by Chen (58) based on a finite element method. This considers the system as an assemblage of idealised elastic elements joined at discrete nodes, the sum of the moduli at each node giving a moduli matrix for the whole material. Chen has obtained better agreement with experimental results for this method compared to the 'shear lag' analysis but the degree of improvement hardly justifies the use of such a complex technique.

In considering the ultimate strength of aligned short fibre composites the rule of mixtures expression can be used but, since its use implies the existence of uniform stress along the fibres it is necessary to consider two cases. Firstly, fibres longer than the
critical length may be stressed to breaking point, after fracture
the average stress in the fibre, \( \bar{\sigma}_f \), will be less than the ultimate
fibre strength \( \sigma_{uf} \). The actual value of \( \bar{\sigma}_f \) depends on the exact
form of the stress distribution, but if a linear form is assumed,
the mean fibre stress at failure will be

\[
\bar{\sigma}_f = \left(1 - \frac{L_c}{2L}\right) \sigma_{uf} \tag{2.2.24}
\]

The composite strength will therefore be, for \( L \gg L_c \):

\[
\sigma_c = \sigma_{uf} V_f \left(1 - \frac{L_c}{2L}\right) + \sigma_m (1-V_f) \tag{2.2.25}
\]

The second case is that for which the fibres are shorter than
\( L_c \), the maximum fibre stress is only \( 2 \tau L/d \) (eqn. 2.2.21) and since
the mean strength is half this, the composite strength will be for,
\( L < L_c \):

\[
\sigma_c = \frac{\tau L}{d} V_f + \sigma_m (1-V_f) \tag{2.2.26}
\]

where \( d = \text{filament diameter} \).

Since \( L_c = \frac{\sigma_{uf} d}{2 \tau} \) then \( \tau = \frac{\sigma_{uf} d}{2 L_c} \)

and

\[
\sigma_c = \sigma_{uf} \left(\frac{L}{2L_c}\right) V_f + \sigma_m (1-V_f) \tag{2.2.27}
\]

For aligned short fibre composites, the fraction of the ideal
strength of a continuous fibre composite that can be achieved is
strongly dependent on the value of \( L/L_c \) which, in turn, is dependent
on fibre strength, diameter and the interfacial bond. This is
illustrated in Fig. 2.2.8 which plots the ratio of theoretical strengths of discontinuous and continuous fibre composites of the same type against values of $L/L_c$ for various values of $L$, for the hypothetical limiting case of $V_f = 1$. It is seen that some 95% of the strength of the continuous composite can be developed provided $L/L_c$ is greater than 10.

Systems using brittle fibres cannot be treated so simply due to fibre strength variations. Lees (57) has attempted to do so using an equation of the form given in (2.2.25) but the predicted values were found to exceed experimental values. Various theories for the prediction of continuous fibre composite strength may be adapted for short fibre composites, most however over-estimate composite strength.
Stress = shear stress

= tensile stress

\[ \text{Length} \]
\[ L=0 \quad L=1 \]

**Fig. 2.2.6** Fibre stress distribution according to Cox (50)

**Fig. 2.2.7** Variation of tensile stress as a function of length. \( \sigma_f \) is the fibre fracture stress (Kelly/Tyson, 54).
Fig. 2.2.8 Ratio of strengths of composites containing equal volumes of discontinuous and continuous fibres, as a function of $L/L_c$. 
2.3 Short Fibre Reinforced Thermoplastics

Short fibre reinforced thermoplastics (SFRTP) are amongst the most complex of materials. In their finally moulded state they consist of misaligned arrays of variable length fibres dispersed in a viscoelastic matrix. Furthermore, in real materials, significant structural variations are often observed even with nominally identical processing conditions. The principal factors controlling the properties of these materials are thus; fibre length, orientation, dispersion, concentration and interfacial properties. Most authors agree that high fibre length, high volume fraction, good dispersion and mouldability are desirable for optimum reinforcement. These requirements are however often contradictory since good dispersion generally leads to considerable fibre attrition and good mouldability often limits the maximum fibre length and volume fraction that may be utilised, since the materials become increasingly difficult to mould at high fibre lengths and loadings. It is therefore apparent that, to achieve optimum performance in processing and properties, a compromise must be made between the many relevant variables.

2.3.1 Compounding and Moulding

Two principal techniques are employed commercially for incorporating fibres into thermoplastic polymers. The first, coaxial extrusion, involves passing continuous rovings of fibre through an extruder cross-head die where the polymer to be reinforced is extruded round the roving. The coated rovings emerge from the die consolidated as a single strand which is then cooled and chopped into moulding granules. The method is described in detail by Bader and Bowyer (59) and moulding compounds with this coaxial configuration are commercially available in the U.S.A. (60). The principal advantage of the technique is the long fibre lengths retained in the moulding granules, the technique
however also has its disadvantages since moulding requires the use of a screw preplasticizing machine to adequately disperse the fibres.

The second, and more widely used method, is melt or extrusion compounding which involves introducing the fibre directly into the extruder thus predispersing the fibres in the moulding granules. The actual technique used depends on the type of extruder and the method of introducing the fibre. The feed stock for single screw extruders (which are still the most widely used) is generally in the form of premixed polymer and chopped strand. The compounded material is then either chopped at the die face or pulled away in strands, cooled and then pelletised. The major improvements in this method are due to the development of twin screw extruders (60, 61, 62) which allow the fibre, in continuous roving form or chopped strand, to be introduced downstream of the hopper directly into the plasticised polymer hence considerably reducing the fibre break up. The most common take off method is strand extrusion with subsequent cooling and pelleting. The different feed arrangements are shown schematically in Fig. 2.3.1. The granulated material from either method may then be moulded by conventional means such as extrusion, compression moulding or injection moulding.

Other minor compounding methods have been proposed but are of little commercial importance. Attempts have been made to align fibres during the melt compounding stage by rapid drawing of the extrudate, subsequently chopping this into long lengths. The use of such material is however limited since only compression moulding may be used (57). Mixtures of two fibrous forms, one at least of which is a thermoplastic polymer have been used, a solid reinforced material being obtained by compression moulding (63). A further method involves passing rovings through a bed of polymer powder, then through a hot zone and forming die, giving a consolidated strand sim-
ilar to coaxial extrusion, the strand then being pelletised (64).

The degree of fibre attrition during the melt compounding stage is considerable, although its extent varies with the compounding method. The actual processes involved in single screw extruders have been the subject of a study by Lunt and Shortall (65-67). These authors find that fibre breakage occurs principally at the solid-melt interfaces due to the high shear stresses encountered. Relatively little fracture occurs prior to melting because the material travels along the extruder screw flights as a plug, additionally little breakage is observed after melting occurs. Thus, it is apparent that, the introduction of fibres into a preplasticised melt (as in twin screw extruders) can result in less fibre attrition. The authors also identify three main mechanisms by which fibre breakage occurs; (i) By monofilaments bending round the surfaces of other filaments, (ii) By the turbulent motion of the polymer melt producing sufficient stress to cause tensile fracture of the filament, (iii) By breakdown of the size film between adjacent filaments under conditions of high shear resulting in contact of the high modulus glass surfaces and crack propagation. The first two will be governed by the rheological properties of the polymer melt, the third however serves to highlight one of the requisite functions of a size: to protect the glass fibres during the high shear environment that is encountered in extrusion compounding and injection moulding equipment (42).

The above observations and mechanisms also hold true for the injection moulding process, particularly for this investigation where moulding granules of the coaxial configuration are used. The reinforcing fibres are not predispersed but merely encased in a sheath of polymer, dispersion being achieved by use of a screw preplasticising moulding machine with its inherent similarities to the extrusion compounding process.
Many authors have conducted length distribution analysis on moulded articles and observed that fibre length was reduced by over an order of magnitude during the moulding operation (57, 68, 69). Filbert (70) has shown that increasing screw back pressure and screw speed significantly reduces fibre length, similar observations being made by a number of other authors (61, 71, 72). Additionally, Filbert showed that reducing the machine rear cylinder temperature reduced fibre lengths.

Richards and Sims (72) in an investigation of the effect of glass variables, processing conditions, and silane coupling agents on the properties of polypropylene, polystyrene and polyamide 6 have obtained some interesting results. The strength of the nylon-6 mouldings show a decrease and then an increase with increasing screw speeds and screw back times, despite observations that the fibre lengths showed a continuous fall with an increase in these parameters. This was attributed to the low viscosity of the nylon affecting the fibre dispersion, a factor also commented on by Lunt (66). The polystyrene and polypropylene materials however, exhibited the normal expected falls in strength as the fibre lengths were reduced by the processing operation.

It is apparent that the amount of shear and the shear rate are the principal causes of fibre degradation, increasing back pressure increases the former by extending plasticization times and increasing screw speed increases the latter. Other influencing factors include injection speed, fibre concentration (1) and die design (60), increasing the former two to contribute to fibre degradation as do small gates, narrow runners and small radii of curvature. It is difficult to envisage significant improvements in the situation, since both the feedstock requirements and the occurrence of high melt shear during injection moulding ensure that only short fibres will be present in
The effect on the rheological properties of polymer melts of introducing fibres has been the subject of a number of studies. Thomas and Hagan (73) investigated the flow properties of glass fibre reinforced polypropylene with varying fibre loadings by measuring the melt viscosity. At low fibre loadings (10-30 wt%) the filled material was found to flow more easily than the original polymer, an anomaly attributed to polymer degradation affecting the viscosity. The relevance of the work is limited since relatively low shear rates, compared to those experienced in injection moulding, were employed. Crowson and Folkes (74) studied polypropylene and nylon 6.6 filled with different volume fractions of glass fibres and observed that the degree of pseudoplasticity increased with addition of the fibres i.e. the apparent viscosity decreased with increasing shear rate. At low shear rates the presence of fibres increased viscosity much more than at high shear rates, where the viscosities were similar for filled and unfilled melts. This is in contrast with the work of Charder and Reiger (75) who observed no variation with the addition of fibres. The authors (74) found that fibre length had little effect at high shear rates but a considerable effect of low shear rates, long fibres causing a large increase in viscosity.

Die swell has also been observed to decrease with increasing fibre content which is attributed to the fibres constraining the molecular chain contraction and reorientation (74,76).

During processing, the fibres can adopt complex orientation patterns which are retained in the final component. This will affect the physical properties of the mouldings which often exhibit very significant anisotropy due to preferred fibre orientation distributions. This effect has been noted by a number of workers (69,77-80) the mouldings having a layered structure with misaligned fibres in the core.
region and aligned fibres surrounding this. Frequently there are additional surface layers observed which contains relatively less fibres than the bulk material and these are also in a misoriented state. Parratt (4) has predicted that regions of convergent flow should result in considerable fibre alignment. Experimental work agrees with this theory, although the amount of alignment is dependent on the melt viscosity. (79,81). Conversely, regions of divergent flow result in fibre orientations transverse to the flow direction, this is attributed to rapid deceleration of the polymer on entering the large cavity causing compressive forces in the flow direction, which cause the fibres to rotate transverse to the injection direction. McNally (79) attributes the often observed longitudinal alignment adjacent to the skin to 'shear and flow effects'. Bright et al (82) have studied the effect of injection speed on fibre orientation in polypropylene, finding that slow speeds give good axial alignment due to shear flow patterns not present at higher speeds. At high injection speeds, the velocity profile is a lot blunter so the material flows rather like a plug without shearing, except at the mould wall where the occurrence of high shear aligns the fibres. The fibre orientation in the core will therefore be similar to the transverse orientation set up by the divergent flow at the gate. The authors also note that it is possible to control the orientation distribution by programming the injection stroke for different speeds at different stages of filling.

Lockett (83), in work aimed at predicting the fibre orientation patterns in mouldings, comments that flow induced fibre orientation is influenced by purely kinematic constraints and by the mechanical properties of the melt. In extensional flow, the kinematic constraints provide stable conditions for the fibres in the extension direction. In shear flow they prevent fibre orientation across the velocity profile.
The use of slow screw speeds, low back pressures and slow injection speeds combined with good die design will therefore reduce fibre attrition and improve orientation in the final moulding. These conditions are however generally not found in practice, particularly with polymers possessing low melt viscosities and sharp melting ranges such as polyamides, since these require high shear rates to adequately disperse the fibres and high flow rates to prevent the polymer freezing in the gate prior to complete mould filling (13).
Fig. 2.3.1 Schematic of the feed arrangements for different types of extruder. (61).
The Properties of SFRTP

Analysis of the behaviour of SFRTP is complicated by the range of fibre lengths and orientation distributions that exist in injection mouldings. The theoretical treatments available for prediction of the properties of these materials are generally based on the well developed methods applicable to continuous aligned fibre composites and can broadly be divided into two approaches. Firstly, those based on the rule of mixtures approach using various correction factors to account for experimentally observed phenomena and secondly, those modelling the materials as equivalent laminates.

Halpin and co-workers (84-87) have shown that short fibre systems can be modelled mathematically as laminated systems. In such models, thin layers or plies of unidirectional composites of either short or continuous fibres are stacked together, the volume fraction and orientation of each layer being governed by the percentage of fibres at each orientation in the actual material. Since the fibre length is greater than the thickness of each ply, the reinforcement may be considered as a two dimensional random array, this geometric arrangement being described as the 'quasi-isotropic laminate analogy'. The concept derives from the fact that a material possessing isotropic properties can be constructed from plies which are themselves highly anisotropic. The actual number of plies required for overall isotropy is dependent on the variable under consideration, e.g. four for stiffness and two for thermal expansion. The model has been proved adequate for predicting stiffness but Halpin and Kardos (86) have proposed that the strength and stress-strain curves for random short fibre materials may be effectively modelled by the quasi-isotropic laminate approach.

The treatment requires a knowledge of the engineering moduli of the individual orthotropic plies, the Halpin-Tsai equations to estimate
these are given below.

\[ E_{11} = E_m V_m + E_f V_f \]  
(2.3.1)

\[ \nu_{12} = \nu_m V_m + \nu_f V_f \]  
(2.3.2)

\[ P_c = P_m \left( \frac{1 + \nu_f}{1 - \nu_f} \right) \]  
(2.3.3)

where \( \eta = \left( \frac{P_f}{P_m} - 1 \right) \left( \frac{P_f}{P_m} + \zeta \right) \)

Here, \( P_c \) is the ply composite modulus \( E_{22} \) or \( G_{66} \), \( P_m \) the corresponding matrix modulus \( E_m \) or \( G_m \), \( P_f \) the corresponding fibre modulus \( E_f \) or \( G_f \), \( \nu_m \) and \( \nu_f \) are the Poisson's ratios of matrix and fibre respectively. \( E_{11}, E_{22}, G_{66} \) and \( \nu_{12} \) are the longitudinal and transverse Young's Modulus, the shear modulus and Poisson's ratio of the ply respectively. \( \zeta \) is a measure of the reinforcement and is equal to \( L/r_f \) for the longitudinal stiffness case, thus showing the sensitivity of short fibre composites to the fibre aspect ratio.

The estimated engineering moduli are used to obtain an overall stiffness matrix:

\[ A_{ij} = \sum_{k=1}^{n} \bar{Q}_{ij}^k a^k \]  
(2.3.4)

Where \( a^k \) is the fraction of the total laminate thickness taken by ply \( k \) and \( \bar{Q}_{ij}^k \) are the plane stress stiffness moduli. The overall engineering moduli of the laminate are then obtained by equations of the form:

\[ E = \frac{A_{11} A_{22} - A_{12}^2}{A_{22}} \]  
(2.3.5)

\[ G = A_{66} \]  
(2.3.6)
Composite strength is predicted by use of the maximum strain theory, the maximum allowable strains for each ply orientation being estimated or determined experimentally. As the laminate is incrementally loaded, each ply fails upon reaching its maximum allowable strain. After all the plies have failed, the incremental stresses and strains are summed to obtain the ultimate stress and strain of the laminate.

In oriented short fibre materials, the stiffness approaches the continuous fibre value at high aspect ratios (85), this is however not the case for strength because of stress concentration effects at the fibre ends. The strength property of a short fibre composite approaches an asymptotic value at high aspect ratios (87), falling considerably below the continuous fibre value. Chen (58) has shown that the strength of short glass fibre-epoxy composites approaches 60% of the strength of the corresponding continuous fibre system. This fact is thus incorporated into the maximum strain theory by reducing the allowable filament longitudinal strain by 60%, agreement between theory and experiment appears to be good (87). Additionally, the authors show that the laminate analogy effectively accounts for volume fraction effects. Halpin and Kardos (86) have estimated strength reduction factors to account for fibre length which are functions of the finite dimensions of the fibre, the fibre and matrix stiffness and the volume fraction of each. These reduction factors are used to reduce the maximum allowable strains for each ply and good agreement with unpublished experimental data is claimed.

Real materials are obviously not isotropic and possess preferred orientations due to moulding conditions, this is accounted for in the theory by weighting groups of angle plies to correspond to actual orientation distributions. Fibre lengths are considered to be constant
Kacir et al (89) have used the laminate analogy to predict the strength and stress-strain characteristics of short glass bundle reinforced epoxy. The engineering moduli of the plies were calculated using the Halpin-Tsai estimates (equations (2.3.1-3)) and also determined experimentally, as were the maximum allowable strains. Good agreement with experiment was obtained and it was found that the experimentally derived ultimate strains were adequate as failure criteria for the strength prediction. Theoretical stress-strain curves coincided with experiment for high fibre alignment but deviated 20-30% at low alignments, despite precise predictions of ultimate strength and modulus. Manera (90) used the laminate analogy in conjunction with Pucks micromechanics formulae to calculate composite moduli, good agreement being obtained with experiment at $V_f$'s between 0.1 and 0.4.

Dimmock and Abrahams (91) have attempted to account for the distribution of fibre lengths and orientations theoretically using modified Halpin-Tsai equations. Experimental moduli from a wide range of fibre filled thermoplastics were found to lie between the predictions for aligned and random fibre composites, this is expected since partial alignment occurs during moulding. The authors attempted to estimate properties by randomly selecting a midway line, the theory however really only provides upper and lower bounds to composite properties.

These approaches cannot be accurately used to predict the properties of SFRTP because of the range of fibre orientations present, the only complete solution is to measure the fibre orientation distribution. This has been attempted, the fraction of fibres at
particular orientations being measured as a function of their position in the mouldings. Two basic techniques have been used. The first, employed by Darlington et al (68,80) is known as Contact Micro-Radiography (C.M.R) and involves placing thin sections of material in contact with an emulsion and exposing to X-rays. The X-ray micrograph obtained enables fibre orientation to be measured with respect to a fixed axis. The second technique involves examination of polished SFRTP sections, the major and minor axis (a & b) of the fibre ellipses being measured and the angle of the fibres calculated using the equation:

\[ \text{Fibre angle} = \sin^{-1} \left( \frac{b}{a} \right) \]  

The results were plotted as histograms or on a stereographic projection. The orientation functions obtained demonstrated substantial positional variations, the authors observing predominant fibre alignment along the injection axis at or near the surface of the mouldings, but misalignment in the central regions (see section 2.3.1).

Thomas and Meyer (92) have used both methods and have discarded the ellipse technique in favour of CMR, this is primarily due to ambiguity in the results since the same ellipse can be formed by two different orientations, but it is also due to the tedious and time consuming nature of the measurement procedure. The authors also used transmission optical microscopy to obtain orientation distributions, this method was again discarded due to the considerable effort involved. Despite the ease of obtaining the CMR micrographs, actual physical measurements of fibre orientations are still time consuming. Polato et al (93) have presented a new technique aimed at solving this problem. The technique uses either a thin transparent sample or a contact microradiograph (if the sample is light opaque) and is based on the diffraction behaviour of the glass fibres (or their images) when exposed to a laser beam. A diffraction pattern is drawn onto a screen placed behind the sample, the screen contains two rectangular
slits, symmetrical about the transmitted light path, which rotate. The angular intensity of the diffraction pattern is measured by a detector placed behind the screen into which the light is focused by a lens. The authors present results from a 30% by weight, glass reinforced injection moulded nylon 6 specimen, and compare the measured angular distribution of the diffraction pattern intensity with a manually counted orientation distribution, the correlation being very good. A statistically based presentation method is also described. The principal advantage of the technique is its speed, since the whole operation can be automated by computer control giving a rapid assessment of orientation distributions in real materials.

Dunn and Turner (94) have measured the positional variation of mechanical properties in injection moulded glass filled PTMT and polypropylene. Fibres were frequently found to be preferentially aligned along the injection axis, leading to considerable anisotropy as indicated by the shear modulus enhancement (by torsion test) being less than half that of the tensile modulus along the injection axis. Modulus and strength in tension were found to vary by a factor of two at angles from zero to ninety degrees to the flow direction.

McCullough et al (95) in an investigation of the flow behaviour of glass filled phenolic resins, found significant variations in fibre orientation even in simple rectangular moulds. The orientation was characterised qualitatively by use of ultrasonic C-scan techniques and quantitative measurements were made from micrographs. The effect on mechanical properties of positional variation (due to orientation variations) was assessed by testing specimens machined from edge and centre sections, the results showing a modulus variation of 17.9 GPa at the edge (aligned fibres) and 9.6 GPa at the centre (misaligned fibres).
Darlington et al (68) have attempted to combine the effects of fibre length and orientation to predict short fibre reinforced thermoplastic properties using both the Halpin-Tsai laminate approach summed over length and orientation, and a rule of mixtures expression weighted to account for orientation. The results were compared with experimental moduli from injection moulded glass filled polypropylene, nylon 6, and PETP and were generally found to underestimate the values. Predictions from both techniques were however very close. No data was presented for the effect of fibre loadings, a fixed $V_f$ being used in all cases.

The rule of mixtures approach modified to account for fibre length and orientation has been used by numerous authors to account for observed properties. The general form of the equation concerning orientation is due to Cox (50) who discussed the variation in properties with fibre angle:

$$E = KE_f V_f + E_m V_m$$

(2.3.9)

The constant $K$ is unity for aligned systems and Cox has deduced that it falls to one third and one sixth for two and three dimensionally random systems respectively. The equation has been frequently used since $K$ can be chosen to fit experiment and is a means of representing fibre orientation by a single parameter. Krenchel (97) has estimated $K$ for the case of planar fibre distributions where $a_k$ is the fibre fraction at an orientation $\theta_k$ to a reference axis.

$$K = \sum_{n=1}^{m} a_k \cos^4 \theta_k$$

(2.3.10)

Fibre length has been accounted for in a similar way, some authors have merely substituted a mean length value, but this is unsatisfactory and really only applicable to lengths greatly exceeding the critical length. The alternative approach is to sum the fibre
contribution over length, the composite modulus applying the Cox theory is then given by equation (2.3.11), where $V_i$ is the volume fraction of fibres of length $l_i$.

\[
E_c = E_f V_f \sum_{i=1}^{n} V_i \left( \frac{1 - \tanh \frac{\beta l_i}{2}}{\beta l_i} \right) + E_m V_m \tag{2.3.11}
\]

(where $\beta$ is related to the rate of stress transfer).

Various methods have been used to determine fibre length distributions, all involve first releasing the fibres by pyrolysing or chemically dissolving away the matrix. The most common method is to photograph the released fibres, subsequently measuring the lengths manually or, alternatively, the distribution may be measured using a Zeiss particle size analyser. A Quantimet image analyser has been used by McNally et al (98), the basic system however has its limitations in that crossed or touching fibres cannot be accommodated and, additionally, the computer cannot distinguish between actual fibres and any miscellaneous particles that may be present in the sample. Sawyer (99) has developed a method for reducing the incidence of crossed fibres and modules are available for the system which allow removal of non-fibrous material from the count. The hardware required is however expensive and difficult to justify for research work. Lunt and Shortall (66) have described a method by which the released fibres are passed through successively finer sieves, the fractions obtained in each sieve are then photographed and analysed in conventional ways to give a full length distribution. The authors comment that where the distribution of lengths is fairly narrow only one or two sieves are required thus reducing the analysis times.

Bader and Bowyer (100-102) have used the rule of mixtures approach combined with the Kelly-Tyson critical fibre length concept.
At a particular composite strain, a critical fibre length exists where strain uniformity is just achieved at the fibre centre.

\[ L_\ell = \frac{E_f \epsilon_f r_f}{\tau} \]  

(2.3.12)

As the strain is increased the critical length also increases so that a greater proportion of the fibres become subcritical in length, thus reinforcing less efficiently. This results in stress-strain curves that are a function of the fibre length distribution. An equation was presented which is capable of predicting the stress at any strain and hence the composite modulus, in terms of contributions due to the matrix and to sub- and super- critical fibres summed over all lengths. Fibre misalignment was accounted for by a constant \( C \) (due to Cox), \( V_i \) and \( V_j \) are the fractions of fibres of subcritical length \( L_i \) and supercritical length \( L_j \) respectively.

\[
\sigma = C \left[ \sum_{L_i=L}^{L_\ell} \frac{E_f \epsilon_f r_f}{2r_f} V_i + \sum_{L_j=L}^{L_\ell} \frac{1}{2L_j} \left( \frac{E_m \epsilon_m r_f}{r_f} \right) V_j \right] + E_m \epsilon_m (1-V_f) \]  

(2.3.13)

Values of \( C \) and \( \tau \) were estimated by fitting the equation to experimental stress-strain curves. Experimental work on glass and carbon fibre filled polypropylene and polyamide 6.6 was presented, the predictions of moduli variation with \( V_f \) showing good correlation, a linear relationship being observed. Composite strength may be estimated if the fibre failure strain is substituted but predictions greatly exceed experimentally observed values. Bader and Bowyer found that strength was enhanced by increasing both fibre length and volume fraction although an embrittlement effect, resulting in a reduction in failure strain at high \( V_f \), was observed to limit the maximum strengths attainable.
Other strength theories using the rule of mixtures approach are similar to that of Bader and Bowyer in that they utilise an orientation correction factor which may be based on theoretical treatments or experimental observations and a fibre length correction, based on the critical length concept, to account for strength reduction. Some authors however have attempted to eliminate, rather than correct for, these variables by considering the fibres to be aligned and of equal length. Actual methods of categorising the length and orientation distributions differ, for example McNally et al (98) uses a reinforcement efficiency factor which is a product of (D), an experimentally determined orientation factor and (A), the efficiency of the 'stress transfer interface'. (A) is determined by summing the average fibre stresses (sub and supercritical) over n fibres and dividing by the total ultimate fibre stress attainable by the n fibres. Thus, strength is given by

\[
\sigma_c = R \sigma_f \frac{V_f}{V_m} + \sigma_m V_m
\]  

(2.3.14)

and \( R = A \times D \) where \( A = \frac{\sum_{i=1}^{n} \frac{T_i n_i}{n \sigma_f}}{n} \)

and \( T_i = \) average stress in the \( i^{th} \) fibre.

(A) can be calculated from the length distribution if \( \tau \), the interface shear strength is known.

Lees (57) has considered the tensile strength of SFRTP, pointing out that this is a complex function of many variables including fibre orientation, loading and length, matrix and fibre strength and thermal stresses induced during cooling. He used the Kelly/Tyson approach for sub and supercritical fibre contributions to composite stress summed over all fibre lengths, deducing an equation which expressed composite strength in terms of the properties of the two phases:-
\[ \sigma_{uc} = \sum_{L_i > L_c} \sigma_{ufi} \left( 1 - \frac{L_i}{L_c} \right) V_i + \sum_{L_j < L_c} \frac{\tau L_j V_j}{L_j^2} + V_m \sigma_m \] (2.3.15)

Where \( V_i \) is the volume fraction of fibres of length \( L_i \), critical length \( L_c \) and strength \( \sigma_{ufi} \). The equation thus includes provision for the strength/length variation of the fibres since the fibre strength \( \sigma_{ufi} \) is included in the summation. This approach however is difficult to apply since the range of fibre failure stresses gives no indication of the actual composite failure stress and Lees does not indicate at which point failure occurs. Comparison with experimental results from specimens manufactured by compression moulding of extruded and drawn fibre filled thermoplastic rods was poor. Lees also attempted to predict strengths of two dimensionally random fibre systems by integrating the maximum stress theory equations (equations 2.2.13-15) over all angles, thus assuming that composite strength is an additive property. A similar approach was also advocated by Chen (58). The maximum stress theory however makes the implicit assumption that the three failure mechanisms are independent, which they may be for continuous aligned composites of the kind for which the theory was first formulated. In random fibre composites however, the individual failure modes will be inhibited by fibres lying at other angles. Lavengood (103) checked the validity of these theories for glass-epoxy composites and concluded that strength is not an additive property, and that the simple integration method is inadequate for predicting the strength of multi-directional composites.

The approaches mentioned for the prediction of short fibre reinforced thermoplastics moduli and stress-strain relationships are generally adequate at low elastic strains but are inadequate at higher strains where fibre-fibre interactions and stress concentrating
effects become more important. Prediction of composite strength is complicated by the anisotropy and inhomogeneous nature of real materials and will thus depend on a number of related variables such as fibre content, fibre orientation, fibre geometry, the properties of the matrix material and the condition of the fibre matrix interface. Most strength theories are based to a greater or lesser extent on fibre fracture being the initiating mechanism of composite failure, the actual fracture mechanisms operating will however depend on the parameters mentioned above and the particular system under consideration.

A considerable amount of experimental work has been performed on SFRTP using a wide range of fillers and matrices. Curtis et al (104,105) have investigated nylon 6.6 reinforced with carbon and glass fibres. Some of their results are shown in Fig. 2.3.2 and it is apparent that the fibres impart improved strength and stiffness but reduced ductility over the unfilled matrix. A reduction in fibre length results in significant drops in strength and moduli, an observation made by other authors (3,100-102) thus stressing the need for the retention of long fibres in the mouldings. The carbon fibres are seen to reinforce more efficiently than the glass fibres as would be expected from their improved properties. A linear relationship between $V_f$ and modulus is apparent in all cases which agrees with other workers, for example Lee (106), who investigated twelve thermoplastics reinforced with glass fibres and Ramsteiner (109) who investigated polyamide 6 at different temperatures. The excellent stiffness enhancement obtainable by fibre filling is demonstrated in Table 2.3.1 which gives the moduli of a wide range of commercially available filled and unfilled thermoplastics (60). Strength enhancement generally shows a non-linear relationship with $V_f$, tending to level off at higher $V_f$'s; some authors have observed that strength reaches a
maximum value at a particular $V_f$ and subsequently decreases, (100-103, 107,108). Seiler et al (107) attribute this increasing deviation from the linear behaviour, predicted by a modified rule of mixtures approach, to the increasing importance of fibre-fibre interactions and a change in the fracture mechanism. Heckmann et al (108) attribute the strength reduction to decreasing fibre length and increasing misalignment at high $V_f$'s, a change of fracture mode and premature debonding of the fibres during deformation. The evident reduction in failure strain with increasing fibre loading (Fig. 2.3.2.c) has also been noted by many authors (100-102,110,111). The stress-strain curves of these materials show a pronounced non linear behaviour, the composite modulus decreasing with increasing strain. Dimmock and Abrahams (91) attribute this to fibre debonding and matrix yielding which is in disagreement with Bader and Bowyer (100-103) who consider such behaviour due to the increasing significance of fibre length and fibre effects with strain. The actual cause of the modulus reduction is probably a combination of both assumptions. Blumentritt et al (110,111) have observed that the deviation from linearity is greater in ductile matrix materials and at low volume fractions, thus suggesting that the viscoelastic matrix exerts a significant influence on composite behaviour, a factor which is generally not considered in the commonly used strength theories.

Berry and Stanford (112) have investigated glass reinforced nylon 6.6 and attempted to account for the inherent viscoelastic and hygroscopic nature of the matrix with particular reference to fibre-matrix interactions. The authors used both coupled and uncoupled glass fibres and specimens were tested in the wet and dry conditions. Some typical stress-strain curves are given in Fig. 2.3.3. and it is seen that, while there is little difference in properties in the dry condition, a considerable difference between the coupled and uncoupled materials is apparent in the wet condition. Interfacial shear
strengths calculated by the Bader-Bowyer theory (eqn. 2.3.13) varied from 7.5 MPa for the wet uncoupled materials to 58 MPa for the dry coupled material, indicating that moisture causes a pronounced degradation of the interface. This was further supported by shear modulus measurements, using a torsion pendulum method, which indicated that the moisture presence resulted in both matrix plasticization and interfacial degradation. The authors also note that \( \tau \) increases with volume fraction in the wet condition and that moisture uptake decreases from 7.98% in the unfilled matrix to 5.6% at a \( V_f \) of 0.212.

Ramsteiner and Theysohn (113) have investigated nylon 6, polypropylene and P.M.M.A. reinforced with glass fibres having different surface coatings and tested at various temperatures. The fibres were claimed to be preferentially aligned along the test specimen axis although no structural evidence was presented. Failure stresses were shown to possess a linear relationship with \( V_f \) at intermediate \( V_f \)'s (0.05 < \( V_f \) < 0.15), this being the case at all test temperatures. The deviation at high volume fractions is attributed to shorter fibre lengths, abrasion damage to the fibres and a change of failure mechanism. At low \( V_f \)'s and temperatures, the deviation is attributed to embrittlement resulting from the stress concentrating effects of the fibre ends. In the polypropylene composites, an increase in interfacial shear strength and in fibre length is shown to enhance strength. In addition, matrix shear strength and interfacial shear strength are shown to decrease with increasing temperature.

Impact strength has been investigated by a number of workers, the behaviour is however complex and very dependent on the test method and conditions. Fibres are strong but brittle, thermoplastic matrices tough but weak, so whereas fibre properties are desirable for stiffness and strength, matrix properties are desirable for impact resistance.
Theberge and Hull have presented impact property data for a large number of glass fibre filled thermoplastics, using Izod and tensile tests (114). It was concluded that tests on unnotched specimens provided no basis for toughness comparison since impact strength fell with increasing \( V_f \) and long fibres were found to offer no significant improvement over short fibres. The toughness of notched specimens was generally found to increase with \( V_f \). Davis (115) has performed charpy impact tests on notched glass fibre filled polypropylene observing increased impact strengths for increased \( V_f \) and also fibre length, contrary to the results of Theberge and Hull. The data is given in Fig. 2.3.4 in which charpy impact energy is plotted as a function of \( V_f \). Unnotched samples possessed reduced impact strengths at higher \( V_f \)'s, this is explained in terms of an increasing number of fibre ends acting as potential discontinuities, whereas in notched specimens the biggest discontinuity is already present in the form of the notch and the fibres simply impede the crack propagation. Thomas and Meyer (92) have investigated the effect of fibre orientation on Izod impact properties in glass reinforced PTFE using unnotched specimens, finding that impact strength is superior in samples having fibres aligned perpendicular to the impact direction. In addition they found that for transversely aligned fibre samples, the impact direction (i.e. side or edge of sample) was important.

A number of workers (1,60,113) have observed an initial drop in impact strength at low \( V_f \) and then an increase, which in some systems can exceed the matrix impact strength, such behaviour being more pronounced with long fibre lengths. Thus, in high \( V_f \), long fibre systems, genuine increases in toughness can be achieved over that of the original polymer. Ramsteiner and Theysohn (113) have also observed that impact strength becomes virtually independent of temperature at high \( V_f \)'s.
Seiler et al (107) have investigated the dependence of impact strength on interfacial bond strength. A good bond is shown to significantly improve the impact strength of glass reinforced polyamide 6. Increasing fibre volume fraction increases the impact strength up to a maximum value, after which the strength declines. The actual $V_f$ at which the maxima occur is dependent upon the degree of interfacial adhesion, being higher for a good bond. Such behaviour is contrary to the generally accepted impact behaviour since a weak bond is usually considered to impart better impact strength due to energy absorption by interfacial debonding. This is probably the case for continuous fibre composites but the situation in SFRTP is different, for these materials fibre pullout is the principal energy absorbing mechanism so a higher bond strength will require more energy for fibre pullout and thus result in higher impact strengths. Such behaviour is also supported by the work of Ramsteiner and Theysohn (113).
Table 2.3.1

Moduli of some filled and unfilled thermoplastics (after Titow and Lanham, 58)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Unfilled flexural Modulus (GPa)</th>
<th>30% glass fibre filled flexural modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon 6.6</td>
<td>2.83</td>
<td>8.96</td>
</tr>
<tr>
<td>&quot; 6</td>
<td>2.76</td>
<td>8.27</td>
</tr>
<tr>
<td>&quot; 6.10</td>
<td>1.93</td>
<td>7.58</td>
</tr>
<tr>
<td>&quot; 6.12</td>
<td>1.72</td>
<td>7.24</td>
</tr>
<tr>
<td>&quot; 11</td>
<td>1.07</td>
<td>3.14</td>
</tr>
<tr>
<td>&quot; 12</td>
<td>1.14</td>
<td>6.90</td>
</tr>
<tr>
<td>Polyacetal homopolymer</td>
<td>2.83</td>
<td>8.96</td>
</tr>
<tr>
<td>Polyacetal copolymer</td>
<td>2.59</td>
<td>7.58</td>
</tr>
<tr>
<td>H.D.P.E.</td>
<td>1.03</td>
<td>6.21</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>1.41</td>
<td>5.86</td>
</tr>
<tr>
<td>Polybutene</td>
<td>0.18</td>
<td>3.10</td>
</tr>
<tr>
<td>P.T.M.T.</td>
<td>2.31</td>
<td>8.27</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>2.34</td>
<td>8.27</td>
</tr>
<tr>
<td>Polysulphone</td>
<td>2.69</td>
<td>8.27</td>
</tr>
<tr>
<td>P.P.O</td>
<td>2.48</td>
<td>7.93</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>3.10</td>
<td>8.27</td>
</tr>
<tr>
<td>SAN</td>
<td>3.79</td>
<td>10.34</td>
</tr>
<tr>
<td>ABS</td>
<td>2.41</td>
<td>7.58</td>
</tr>
</tbody>
</table>
**Fig. 2.3.2** Fracture stress, Modulus and Fracture strain as a function of fibre volume fraction for short and long, carbon and glass fibre reinforced Nylon 6.6 (1).
Fig. 2.3.3 Tensile stress-strain curves for coupled and uncoupled glass reinforced Nylon 6, $V_f = 0.17$. (112).

Fig. 2.3.4 Charpy impact strength of glass filled polypropylene as a function of Volume fraction. 0.25 mm notch samples containing different length fibres and unnotched sample containing 0.5mm long fibres (115).
2.3.3. Failure behaviour of SFRTP

Failure of fibre reinforced thermoplastics may be initiated in one of three regions, the matrix, the fibre, or the interface between them. The large differences in the fibre and matrix moduli result in high interfacial stresses; therefore, if the interface (or the matrix surrounding it, the interphase) is weak then debonding will occur and the fibres will pull out of the matrix with little or no fibre fracture. Conversely, if the interface and matrix are strong the predominant failure mode will be fibre fracture. Ductile matrices may be able to accommodate or relieve high stresses by flowing but the presence of the fibres may embrittle the matrix to an extent that this is not possible. Obviously the exact failure behaviour will therefore depend on, and may be unique to, the particular system under consideration.

Although numerous methods have been used to examine failure behaviour, there are four principal techniques; electron microscopy, optical techniques, photoelastic studies and acoustic emission analysis.

Simple optical techniques are capable of providing a great deal of useful information about failure mechanisms and do not appear to have been used as widely as they might. Events leading to failure in these materials, such as fibre debonding, have been observed by many authors, including Koenman and Kicher (116) who have used both single fibres and strands of glass fibre in epoxy resins and tested specimens in tension under an optical microscope. Interfacial failure was observed to occur by the coalescence of small areas of debonding into a crack which propagated along the interface, debonding the whole fibre and initiating failure of the specimen.

Wadsworth and Spilling (117) have used optical techniques to observe the effect of fibre fracture in composite materials using
epoxy resin specimens containing single fibres or bundles of high modulus carbon fibres. Specimens were cast onto aluminium base plates, loaded to predetermined strains then examined for damage, the baseplate preventing catastrophic failure when the specimen cracked. Two fibre surface treatments were used, one resulting in a strong and the other a weak bond. In the latter system the initially continuous fibre fractured into progressively shorter lengths, leaving short cylindrical holes in the matrix with a pattern of light bands observed running across the fibres either side of the fracture. The results were explained in terms of fibre fracture initiating interfacial failure thus causing the fibres to unload and contract, leaving a gap in the resin. The light banded regions were thought to be due to narrow interfacial gaps forming as the fibres contracted on fracture, which thus increased the percentage of light reflected. The well bonded fibre specimens exhibited different behaviour, radial matrix cracks perpendicular to the fibres being observed, fibre fractures were also seen but these tended to be obscured by the matrix cracks. In the fibre bundle samples, the matrix cracks were observed to fracture adjacent fibres.

Mullin et al (118) observed matrix cracking at fibre ends in well bonded boron fibre/epoxy systems, and fibre debonding in weakly bonded systems, similar to Wadsworth and Spilling. In well bonded systems where the matrix was weak in tension, cracks were observed to form in the highly stressed transfer regions near fibre ends, leading the authors to conclude that high bond strength was not necessarily desirable and could lead to matrix cracking and premature composite failure.

Curtis et al (1,119) have attempted to describe the fracture mechanisms in glass and carbon fibre reinforced nylon 6.6 by reference to model systems, namely glass reinforced PMMA and polyester resin. The
models showed all the features normally associated with failure in composite systems; fibre pull out, debonding, matrix cracking etc.
Matrix cracks were commonly observed at stress concentration points such as fibre ends and fibre crossover points, they were also observed at fibre fractures in the model systems but the authors point out that very little if any fibre fracture occurs in real thermoplastic systems and this has been supported by length distribution analysis. Composite fracture is thus assumed to be matrix controlled, and evidence from the model systems suggests that failure is initiated in the matrix adjacent to the fibres by stress concentrations. The observations were supported by scanning electron microscopy of the reinforced thermoplastic fracture surfaces. Despite the apparent agreement between the behaviour of the model and real systems, the direct relevance of observations made on the model systems is questionable.

Photoelastic analysis has been frequently used in the composite materials field to examine the stress build-up at the fibre matrix interface, the effect of fibre ends and fractures, and the importance of fibre geometry and fibre-fibre interactions. Much of the early work has been reviewed by Holister and Thomas (49) and the main conclusions seem to be that the simple Cox and Dow theories considerably underestimate the magnitude of the shear stresses at fibre ends. Schuster and Scala have investigated the effect of fibre end geometry, concluding that square ended fibres produced the maximum stress concentrations and tapered ends the least (49). These authors also investigated interactions between single and arrays of overlapping short boron fibres in epoxy (120). Interaction between parallel single fibres was investigated as a function of fibre overlap and spacing, the results being presented in Fig. 2.3.5. This was found to be a maximum at zero and one hundred per cent overlaps, resulting in maximum shear stress in the matrix, thus implying that bundles should be avoided and maximum dispersion
aimed for in real systems. The matrix shear stress increased with fibre spacing to a maximum and then levelled off at approximately six fibre diameters spacing. Increased applied loads resulted in higher shear stresses with consequent matrix yielding and fibre debonding, although it was noted that matrix cracking could result in brittle systems.

Iremonger and Wood (121-3) have extensively investigated the stress distributions around fibre fractures using photoelastic techniques. Matrix stress concentrations were found to be more severe at fibre breaks than fibre ends, and increased with decreasing end gap, in addition adjacent fibres were also subjected to elevated stresses. It was again noted that stresses were accommodated by matrix cracking in brittle systems. The applicability of results from photoelastic techniques is however limited for real systems since the analysis is elastic and no account can be taken of matrix or fibre plasticity.

Scanning electron microscopy has been used by many authors to examine composite fracture surfaces (1,46,69,92,104,113,119,124-6). The technique is capable of yielding useful qualitative information concerning the fracture behaviour. The strength of the interfacial bond is indicated by the fibre pullout lengths and the condition of the fibre surfaces, i.e. long pullout lengths with little or no matrix adhering are indicative of weak bonds and vice versa. In addition, the pulled out fibres can supply limited information about the fibre orientation distributions. The condition of the matrix fracture surface can show whether the failure was brittle or ductile and also give an indication of the fracture initiation point and crack propagation direction from characteristic surface markings (12). Care should however be exercised in interpreting the results in isolation from other techniques, to avoid misleading conclusions.

Blumentritt et al (124) have investigated the failure behaviour of a range of reinforced thermoplastics and noted, similarly to other
authors, that the failure strains were below that of the fibres. They attempted to identify failure by use of scanning electron microscopy alone, observing that SFTRP fracture primarily by fibres pulling out of the matrix in both ductile and brittle composites. They conclude that matrix cracks were initiated at transverse fibres, fibre ends and fibre crossover points. The authors commented further that, as a result of stress concentrations at the interface, cracks formed at low strains and then coalesced at higher loads with little fibre fracture. The only evidence offered is the lack of fibre fracture from SEM observations and this is not substantiated by any length distribution analysis. Failure by debonding has also been noted by other authors, Ramsteiner and Theysohn (113) noted that the longest pullout lengths were comparable to half the length of the longest fibres present in the mouldings and that the pulled out fibres generally showed matrix adhering to the fibre ends, thus showing that fibre fracture could not have occurred.

Transmission electron microscopy has been used but it is difficult to produce samples thin enough for the technique to be useful due to the presence of brittle fibres. Thomas and Meyer (126) have described a preparation method whereby glass fibres are etched out of polypropylene and PTMT matrices with hydrofluoric acid, thus allowing thin sections of matrix to be examined for morphology changes as a result of fibre presence.

Acoustic emission analysis can provide useful data concerning the events prior to fracture in composite materials, the technique involves the detection of transient elastic stress waves in materials as they undergo deformation or fracture. Primary emission sources are; fibre and matrix fracture, fibre matrix debonding, relaxation of the fibres if they fracture, and fibre pullout against friction during composite rupture (127). Fibre fractures however usually generate
larger amplitude bursts compared with matrix cracking and debonding. Useful 'state of the art' reviews have been presented by Williams and Lee (127) and Guild et al (128).

Composite materials exhibit a complex failure behaviour so, although the total acoustic output may be recorded, no indication of the nature or contribution of each source is obtained. Some success has been achieved with continuous fibre laminates by spectral or amplitude analysis methods (128,129), different sources possessing characteristic output amplitudes. The situation with SFRTP is however more complex since many of the failure mechanisms operate simultaneously and a visual correlation, which is often possible in laminated systems, cannot be conducted so easily. Thus, with the present technology, acoustic emission analysis of SFRTP must remain a qualitative tool serving only to indicate imminent failure, giving little information concerning the actual failure mechanisms.

Heckmann et al (108) have investigated glass reinforced polyamide 6 and observed that the failure behaviour changes with volume fraction. At low $V_f$'s the fracture mode is predominantly by fibre pullout, the fracture surface being perpendicular to the applied stress. At high $V_f$'s however, cracks appear to run locally along fibres inclined to the stress direction, i.e the fracture changes to a shear mode. This is attributed partly to fibre misorientation and partly to undispersed fibres. The authors also examined the extent of debonding by a dilatometry technique, surmising that debonding would cause an increase in volume compared to the unfilled material, this is indeed shown to be the case, especially in the high $V_f$ materials.

Dover et al (125) have investigated the deformation and fracture behaviour of 30% w/w glass filled ABS at different temperatures and strain
rates. They observed that, during testing, localised bands of stress whitening appeared on the specimen surfaces and that these areas increased in number and size perpendicular to the stress direction with increasing deformation. Final failure then occurred at one of the more prominent bands. The fracture surfaces exhibited two distinct regions. A highly stress whitened area - termed the slow growth area - which showed the characteristics of poor interfacial bonding, the pulled out fibres being debonded at their base and free from adhering matrix. Secondly, a catastrophic failure region - termed the fast fracture area - which possessed the characteristics of good interfacial bonding, the fibres being tightly bound and having matrix adhering to them. In addition, the matrix in the slow growth area exhibited extensive drawing around the rubber particles producing a collection of voids while, in the fast growth region, no such behaviour was apparent. It was noted that the extent of the stress whitened areas grew with increasing temperature and decreasing strain rate and that the characteristic crazing behaviour generally associated with ABS was not present. The authors state that since the strength of the interfacial bond obviously can not change within a specimen, the results require the interfacial region to possess viscoelastic properties, i.e. it is strain rate dependent. Calculations of the interfacial shear strength apparently show this to be the case, lower shear strengths being obtained at lower shear rates. The authors note that there is a region of fibre misalignment in the centre of the specimen but they do not indicate if this is a contributory factor in the failure behaviour. The fracture behaviour is thus bimodal, an initial slow crack growth until the crack dimensions are sufficient to satisfy a fast fracture criterion, and then catastrophic failure. The primary failure mechanism is however fibre pullout and not fibre fracture, although the authors do observe a higher incidence of fibre ends in the plane of the fast
crack, indicating some fibre fracture has occurred. The reduced slow crack growth areas observed at higher strain rates are explained; the viscoelastic nature of the matrix and interface require a higher stress and thus higher energy input for slow crack growth at higher strain rates. But, a fast strain rate generates higher stored elastic energy, hence fast fracture requires smaller critical crack dimensions. These factors thus interact, resulting in the observed phenomena.

Curtis et al (1,104,105) have proposed a failure mechanism for glass and carbon fibre reinforced nylon 6.6 that is based on experimental failure observations and analysis of the associated stress strain curves. The model is based on matrix cracking initiated at fibre ends and the authors consider that the cracks develop progressively as the material is strained. The load shed in the region of the crack is accommodated by adjacent fibres which bridge the cracked zone. Composite failure occurs when the extent of cracking in the critical zone causes the bridging fibres to be loaded to their failure stress. The model is based on the observation that the stress-strain curve is in three stages, initially linear, then parabolic, and finally a more complex behaviour. This is supported by optical and scanning microscopy, and acoustic emission analysis during testing. The theory, developed from the observation for aligned fibres of equal length is given below.

\[
\sigma_{uc} = \varepsilon_{uf} E_f V_f' \left( 1 - \frac{\varepsilon_{uf} E_f}{2Lc} \right) + \varepsilon_{uf} E_m V_m' \quad (2.3.1)
\]

Where \( V_f' \) and \( V_m' \) are the effective volume fractions of fibres and matrix in the cracked zone. For real materials the equation is modified by an orientation factor. Comparison between theory and experiment is shown to be quite good for long fibre specimens but poor for short fibres, which is attributed to a significant proportion of the fibres being shorter than the critical length. The equation presented (2.3.1) is a further modification of the rule of mixtures approach and is only applicable
to systems containing aligned fibres of equal length and not to real materials since correction factors rather than full fibre length and orientation distributions are utilised.

It is thus apparent from the preceding discussion that the predominant failure mechanism in SFRTP is by interfacial or interphase debonding and consequent fibre pullout. The actual contributory mechanisms are however complex and difficult to ascertain and will vary depending on the system being studied.
Fig. 2.35a Shear stress concentration versus fiber spacing for the 100%, 50%, and 0% overlap cases. 0.0046 in. diameter, 0.5 in. long boron fibers aligned in the load direction. Specimen thicknesses 0.01 in. (120)

Fig. 2.35b Shear stress concentration versus fiber overlap for ~0.002 and ~0.004 in. spacings. 0.0046 in. diameter, 0.5 in. long boron fibers aligned in the load direction. Specimen thicknesses 0.01 in. (120)
3. EXPERIMENTAL TECHNIQUES

The sequence of events in this investigation can be broadly defined in the following manner. Moulding compounds, manufactured by a coextrusion technique, were injection moulded into test bars. The effects on the mechanical properties of varying the fibre, the interface and the processing conditions were assessed by tensile and impact tests, the former being supported by acoustic emission analysis. Optical and scanning electron microscopy techniques were developed to examine specimens prior to, and after, testing to determine the order of events leading to failure. This is shown schematically in Fig. 3.1.

3.1 Manufacture Of Fibre Filled Moulding Compounds

The materials used comprise a single grade of polyamide 6. (Maranyl F114) supplied by ICI Limited, and a range of E-glass fibre rovings some of which were specially prepared by the manufacturer for this investigation. These are described in Table 3.1.

During the initial stages of this investigation only those fibres designated F and P were available. Fibre F had a polyvinyl-acetate based size incorporating a chromium complex adhesion promoter which was compatible with polyamides. Fibre P however, had a size designed to be compatible with polypropylene and was therefore less likely to be suitable for use within the nylon matrix. Fibres G,H,J and K were coated with a polyurethane based size which, in H and K incorporated a proprietary silane coupling agent. Fibres L, M and N, from a different manufacturer, were sized with a cationic polyelectrolyte film forming compound containing a silane coupling agent in the case of fibres M and N only.
The amount of size applied to the fibres is generally dictated by the compounding method to be employed, for example, it is normal practice to use a relatively heavy application of size to preserve strand integrity and protect the fibres during the potentially damaging processes of chopping and dry blending prior to compounding. However, since an alternative compounding method was to be used in this work the level of size application on fibres L, M and N was reduced. Despite this, it was noted that these rovings were relatively 'hard' or 'stiff' and that the G, H, J and K rovings were significantly softer. Fibre F was the hardest in the range while fibre P was comparable with L, M and N. It was apparent during compounding that fibres possessing a 'soft' size were more easily processed and subsequently dispersed in the polymer matrix. It should also be noted that the overall roving tex did not necessarily reflect the strand tex (table 3.1) in that the strands in fibres F, G and H were significantly heavier than in the other rovings.

Of the available methods for incorporating fibres into a polymer matrix, a coextrusion technique was found the most convenient in that small batches of special compounds could readily be prepared. It is generally accepted that to achieve optimum reinforcement, the fibre length in the moulding should be maintained at the highest level consistent with processability. The technique used has the advantage of retaining long fibres in the moulding pellets (and hopefully in the moulded test pieces) since the fibre does not have to pass through the compounding extruder.

The system used was a modified version of that employed by Bader and Bowyer (59), the basic principles involved however remained the same. Continuous rovings of glass fibre were passed through an extruder crosshead die where the polymer to be reinforced
was extruded around the rovings, which then emerged as a single consolidated strand. This was cooled and finally chopped into cylindrical moulding pellets.

Modifications were made to the original system because of a number of difficulties encountered

(i) The original crosshead die design was based on that of a wire coating die, cylindrical in shape with the fibre passing along the central axis. Any interruption in the process, such as a break or knot in the glass tow resulted in a lengthy dismantling procedure and subsequent cleaning of the die prior to rethreading the rovings, obviously a time consuming operation. In addition, the continuity of the process was interrupted resulting in variable extrudate properties due mainly to the long residence times of the polymer in the extruder barrel.

(ii) Extrudate haul-off and collection was originally achieved by the use of a rotating drum. A constant haul-off speed was found critical in obtaining an even polymer coating and this was difficult to ensure using this method.

(iii) The range of fibre types used required different die feed guide and nozzle diameters due to the variations in tex and size stiffness. Although different nozzle sizes were available, interchanging them required dismantling the die and consequently resulted in the same problems associated with a fibre break.

(iv) It was noted that improved extrudate properties resulted if rapid cooling occurred immediately the strand emerged
from the die, this was not possible with the original system.

As a result of these observations, a new die was constructed, Fig. 3.2, this is rectangular in shape and is split along the fibre path. In the event of a fibre break or snag, the die was split open, the clogged feed guide and nozzle removed and replaced with clean inserts prethreaded onto the tow. Thus, dismantling and reassembly took a matter of minutes and the continuity of the process was preserved. Additionally, more accurate temperature control was achieved by the siting of a cartridge heater along the fibre path.

A 'caterpillar' type haul-off was constructed to ensure constant haul-off speeds and thus give an even polymer coating, an important consideration when determining the volume fraction of fibres in the extrudate.

The cooling medium used was either water or compressed air, the latter method is obviously preferable when the hygroscopic nature of nylon is considered but is only practical with certain fibre types. Fibre tows coated with a stiff size expanded considerably on emerging from the die whilst the polymer coating was still molten resulting in an uneven finish. This was prevented by immediate rapid cooling using a weir type water bath adjacent to the die nozzle. Tows coated with a soft size did not exhibit this expansion to such a great extent and could be cooled rapidly enough with compressed air. The apparatus is shown schematically in Fig. 3.3

Considerable effort was directed towards finding an effective method of chopping the extrudate into good quality moulding granules. Since the fibres are only encased in a sheath of polymer and the roving not fully infiltrated by the polymer, a fast clean cutting
action is required to ensure the fibres do not pull out of the granules. Examples of moulding pellets are shown in Fig. 3.4. The apparatus constructed to chop the extrudate is shown in Fig. 3.5 and consists of a hardened steel blade, spring loaded against a cutting plate, through which an angled hole had been machined for the fibre to pass through. Thus, a double cutting action is achieved simultaneously by the blade and the cutting plate. The spring also allows the blade to lift over the emerging fibre on the return stroke and the rotational freedom allows for minor changes in the blade grinding angle. The length of the moulding pellets could be varied by altering the feed roller speed or the blade speed.

Since the extruder used did not possess any means of venting the barrel to compensate for moisture absorbed by the polymer it was found necessary to thoroughly dry the polymer granules prior to extrusion, failure to do this resulted in extensive bubbling in the extrudate and consequent reduction in quality.

It was considered possible that the mere presence of sizing compounds, principally film formers whose function is to bind the fibres together and thus preserve strand integrity, substantially effected the mouldability and hence composite properties by indirectly controlling the extent of fibre attrition (since a greater degree of plastisization would be required to disperse heavily sized fibres). An attempt was therefore made to remove the size by heat cleaning, the reason for the choice of this method are outlined in section 4.1. The apparatus constructed consisted of two tube furnaces in series through which the rovings were passed, compressed air or oxygen being passed through the tubes simultaneously to aid the oxidation process. This is shown schematically in Fig. 3.6. The treated fibre was then compounded into moulding granules in the same way as fibres in the 'as received' condition.
It should be noted that the maximum attainable fibre volume fraction of the extrusion coated moulding pellets was of the order of 0.4. To achieve this figure the polymer coating was kept as thin as possible by careful manipulation of extrusion and haul off speeds. The $V_f$ of the final mouldings was controlled by blending a proportion of unfilled polymer pellets with the compounds and charging this blend into the injection moulding machine.

3.2 Injection Moulding

A major disadvantage of the coextrusion technique is the lack of fibre dispersion in the moulding granules, the fibres merely being encased in a sheath of polymer. In addition, the fibres themselves are bound together by the film former which preserves strand integrity. To overcome this enforced fibre coalescence and thus ensure good fibre wetting and dispersion a necessary requirement for moulding is a screw preplasticising injection machine. The machine used in this investigation is a BOY 15 automatic single screw preplasticising injection moulder and this is shown in Fig. 3.7.

Two types of mould were used: in the initial stages, tensile, creep, notched and unnotched impact specimens were moulded simultaneously in a four cavity mould (Fig. 3.8), the tensile specimens having a gauge portion 40mm long and 5mm x 2mm cross section. It was possible to blank off the creep and impact cavities when not required and thus mould tensile specimens only, this was generally not done since the resulting reduced shot weight required gave inadequate melt plasticisation and fibre dispersion. In the latter stages a larger tensile specimen was necessary to accommodate the three transducers of a modified acoustic emission system (see section 33). A two cavity mould was constructed which gave end and side gated tensile specimens only, each having a gauge portion 60mm x 12mm x 3mm. (Fig.3.9).
In all cases it was necessary to thoroughly dry the moulding granules in a vacuum oven prior to moulding to prevent the formation of moisture induced voids in the test pieces.

The machine settings used were dependent on the fibre loading in the material, high $V_f$'s requiring higher temperatures and injection pressures to ensure sufficient melt flow to fill the mould cavities. Unfilled specimens, having a crystalline melting point of $\sim 225^\circ C$, required a minimum nozzle temperature of $230^\circ C$ whilst high $V_f$ specimens required temperatures of up to $270^\circ C$. For each batch of material moulded, the injection pressure was adjusted to ensure filling of the cavity without flashing. Whilst every effort was made to maintain the machine parameters at constant values for batches of material with similar fibre loadings, some variation was inevitable due to the interrelated operation of the machine parameters. For example; a slightly longer residence time in the barrel, due possibly to a longer cycle time or an increased back pressure, resulted in a reduced melt viscosity and thus flashing of the moulding which then required an injection pressure adjustment.

It was observed that composite properties varied during a moulding run, particularly if there were any machine holdups. Care was therefore exercised to use only specimens taken from the middle of a long continuous run when equilibrium moulding conditions had been established. It would be normal practice to disregard the first few mouldings in a run, but in this case it was found that the $V_f$ was often reduced in specimens taken from the end of a run. This is attributed to the differential flow properties of the simply mixed filled and unfilled granules causing segregation in the hopper which resulted in preferential feeding of the unfilled material.

The increased melt viscosity of the filled material resulted in shortened screwback times and thus insufficient plasticization to enable
adequate fibre dispersion in the melt, this led to clumps of fibres being retained in the mouldings. It was observed that increasing the screw back pressure extended plasticization times sufficiently to remove all signs of clumping but that considerable fibre attrition resulted. An investigation was therefore conducted in order to determine the effect of the moulding variables on the composite properties, particularly in relation to the degree of fibre attrition and ease of dispersion. This was confined to fibre F since the two fibre types showed only a small difference in properties when tested, thus indicating little difference in the interface, the variation of which was one of the principal points of interest in this project.

During the latter stages of the project, when the remaining fibre types mentioned in table 3.1 became available, it was possible to conduct a more rigorous examination of the effects of fibre variables, particularly the interface, on the properties of the composites. Large tensile specimens containing each fibre type, including fibre F for comparison, were moulded. The back pressures used in each case were the minimum possible consistent with good fibre dispersion.

In addition to the normal pre-test specimen conditioning (see sect 3.3), samples from each batch were boiled in distilled water for periods of 48 hours to artificially raise their water content and thus determine the effect of moisture on the behaviour of the interfacial bond and, in particular, the effectiveness of the coupling agents under such adverse conditions.

3.3 Mechanical testing

All injection moulded test pieces were conditioned prior to testing by storing them at 20°C and approximately 50% relative humidity for a period of 21 days. This is an arbitrary period, insufficient to allow complete equilibrium moisture contents to be achieved, but sufficient to allow enough
moisture absorption to prevent the very brittle behaviour of dry nylon.

**Tensile Testing**

The tensile tests were carried out on model TTD or Model 1195 Instron universal testing machines using crosshead speeds of $3.34 \times 10^{-6} \text{ms}^{-1}$ (strain rate $8.3 \times 10^{-5} \text{s}^{-1}$) for the small specimens and $16.7 \times 10^{-6} \text{ms}^{-1}$ (strain rate $27.8 \times 10^{-5} \text{s}^{-1}$) for the large specimens. Strain was measured with an Instron electrical resistance strain gauge based extensometer and direct plots of force versus strain produced on an X-Y-Y recorder using a chart servo-drive linked to the extensometer. The composite modulus, $E_c$, was taken at an arbitrary strain of 0.005 because of the non-linearity of the plots. This being termed the 0.5% secant modulus. In addition the failure stress, $\sigma_{uc}$, or the maximum stress if drawing occurred, and the failure strain, $\varepsilon_{uc}$, were recorded for each test.

Tests were conducted on unfilled nylon 6 and on the polymer reinforced with all the fibre types listed in table 3.1. In the case of some of the specimens which had been subjected to the boiling water treatment the cross head speed was increased to $83.3 \times 10^{-6} \text{ms}^{-1}$ since the testing times would have been unreasonably extended as a result of the enhanced ductility of the water plasticized material.

**Impact Testing**

Charpy impact tests were conducted on specimens cut from the gauge portions of the large tensile test bars. These were 40 mm long and had a 2 mm deep notch machined into one edge, this was sharpened immediately prior to testing using a scalpel blade. (Fig. 3.10) The tests were performed on a minature charpy type machine using an impact velocity of $3\text{ms}^{-1}$ and a kinetic energy of 5J.
Polymer Shear Strength

An indication of the shear strength of the unfilled polymer was required for comparison with calculated values of the fibre-matrix interfacial shear strength. The data was obtained by use of a punch shear technique, the apparatus for which is shown in Fig. 3.11. A sample cut from a moulded tensile specimen was placed in the jig which was then assembled and compressed in the Instron. The maximum load recorded to punch out a disc of the polymer was used to calculate the shear strength using the equation:

\[ \tau_m = \frac{F}{T_s \pi D_p} \times 10^{-6} \text{ MPa} \]

where

- \( \tau_m \) = Shear strength
- \( F \) = Force in Newtons
- \( D_p \) = Plunger diameter
- \( T_s \) = Sample thickness

It was considered possible from observations of the composite fracture surfaces that the appearance of the matrix was affected by its fracture speed. In order to determine the extent, if any, of such a dependence, the shear tests were performed at crosshead speeds varying from 16.7 \( \times 10^{-6} \) ms\(^{-1} \) to 8.3 \( \times 10^{-3} \) ms\(^{-1} \). The results obtained gave a matrix shear strength in the region of 50 MPa, only a slight reduction being observed at high testing speeds and this can be attributed to a slow recorder pen response.

Acoustic Emission Monitoring

Each tensile test was monitored by an acoustic emission system in an attempt to elucidate the mechanisms involved in failure. Emissions occur due to the release of energy within a material as it is deformed and appear as elastic waves at the surface which can be detected by means of suitably positioned transducers. In the case
of reinforced plastics noise can originate from many sources; fibre fractures and debonding, matrix crack initiation and propagation and also spurious noise from external origins such as the machine grips.

Emissions were monitored by a high frequency piezo-electric transducer held in contact with the specimen and acoustically coupled to it by a thin film of petroleum jelly. The transducer has a resonance frequency in the region of 50KHz and the response of the specimen-transducer combination to a train of impulses is a series of damped oscillations (139). The direct output of the transducer is amplified by a constant factor and fed to a level detector which outputs a pulse each time a preset threshold is exceeded, a mode of operation known as ring down counting (Fig. 3.12). A consequence of this technique is that one or more pulses (or none at all) may be counted from a single "event" depending on the amplitude of the disturbance. The recorded count is also dependendent on the proximity of the acoustic activity to the probe and the attenuation properties of the material.

During the latter stages of the project a modified detection system became available. This had been designed to eliminate all signals arising from outside a given region around the signal transducer by means of a system of guard transducers (Fig. 3.13). Emissions arising from the signal transducer region of the specimen are received by the signal transducer prior to being received by the guard transducers and can be regarded as true specimen emissions. On the other hand, spurious signals from outside sources such as the machine grips are received by the guard transducers first. Both channels are interlocked so that the first to be operated will inhibit the other both during the signal and for a short period afterwards. This time interval is adjustable to allow for various transducer spacings and stress wave velocities.
With both systems the number of counts were displayed electronically on a digital display and recorded directly onto the force-strain plot (using a second pen), either as a cumulative total or as a count rate over a preset time interval (1s). Throughout the testing programme only the most sensitive of the four channels of the equipment was used in order to detect the maximum output. The apparatus used is shown in Fig. 3.14 and a specimen with transducers in position and ready for testing in Fig. 3.15.

It was noted during tensile testing that in most cases the count rate increased significantly prior to failure and this was used as a tool to indicate imminent failure. Correlation of acoustic output with actual events is difficult especially with short fibre reinforced plastics because of the wide range of possible sources. Thus, in this investigation, the use of the acoustic emission detection systems has been in the main qualitative. Some success has however been achieved in correlating acoustic emission and interfacial bond strength with the aid of microscopical observations on failed test pieces and on specimens tested 'in-situ' under the microscope.

3.4 Characterisation of Materials

This section can broadly be divided into two categories, characterisation of the composite and characterisation of its constituent parts.

3.4.1 The Composite

Characterisation of the composite was achieved principally by the determination of the relative volume fractions and length distributions of the fibres present in each batch of material moulded,
and, to a lesser extent by differential scanning calorimetry and
assessment of the fibre orientation distribution.

Fibre Volume Fraction Determination

The fibre volume fraction was determined by heating weighed samples,
cut from mouldings, at ~ 500°C in air for 24 hours to burn the matrix
away. The residual fibres were then weighed. This was done on a
macroscopic scale using samples weighing 1-2 grammes taken at random
from each batch, as a general control check on the \( V_f \). Subsequently
the \( V_f \)'s of the majority of individual samples tensile and impact
tested were determined in an attempt to ascertain whether the scatter
of results was due to fluctuations of the fibre content. The equipment
used was a Stanton Redcroft Thermal Micro balance, sample weights
were approximately 10mg and a graphical plot indicated the proportion
of residual fibres directly as a weight percentage, this was converted
to volume-fractions using the equation:

\[
V_f = \left[ \frac{P_f}{P_m M_f} \left( \frac{M_T - M_f}{M_f} + 1 \right) \right]^{-1}
\]

Where \( P \) = density, \( M \) = weight and subscripts \( f,m \) and \( T \) refer to fibre,
matrix and sample respectively.

Fibre Length Distribution

The distribution of fibre lengths was determined on a small sample
of the fibres released by burn off, these were distributed in a small
petri dish and examined under a photomicroscope. Photomicrographs
were taken of areas chosen at random and 240 x 200mm prints made, a
graticule with 0.01mm divisions was also photographed and printed at
the same magnification for use as a measuring scale. Using suitable
prints, individual fibres were counted and measured, a tedious task
since it was necessary to count up to 1000 fibres to obtain a representative
distribution. Plots of simple and cumulative volume fractions versus fibre length were made, from which the volume average fibre length was determined. This is taken as the length which is exceeded by half the volume fraction of fibres in the sample. Such an analysis was conducted on selected samples from each batch of material moulded, to determine the effect of the moulding operation on fibre attrition. In addition, samples from strained and unstrained regions of failed specimens were analysed to determine the extent of fibre fracture during testing.

**Differential Scanning Calorimetry**

It was noted that a distinct colour difference was apparent between specimens containing different volume fractions of fibre and between specimens filled with fibres obtained from different manufacturers. The former effect can be explained by different refractive indices resulting from the various proportions of matrix and filler present. The latter observation is however not so easily explained. Since the only differences in the composites were the sizing compounds employed by the different manufacturers it was considered possible that these had reacted differently with the matrix during compounding, not only in the interfacial region but also in the bulk polymer. In an attempt to clarify the situation; thermograms of the unfilled moulding granules, unfilled mouldings and filled mouldings were prepared using a DuPont 990 Thermal Analyser with a DSC cell. Samples weighing approximately 20mg were scanned over a temperature range of -50- + 260°C and the results compared. From these traces, the effect of the various fibres on the shape and position of the polymer crystallisation and melting peaks was assessed and the degree of polymer crystallisation estimated.
Fibre Orientation Distribution

The orientation distribution of the fibres in the mouldings was assessed visually using optical microscopy and general comparisons made. Since the majority of techniques available to determine specific orientations are of necessity tedious and time consuming, it was considered impractical to impart on a lengthy programme of quantitative assessment of orientation distributions. This decision was also influenced by large specimen to specimen variations observed on a qualitative assessment. It is therefore doubtful that full orientation distribution analysis measured on a random selection of specimens would have been particularly useful. A partial quantitative assessment was however made on one specimen, principally to check the validity of orientation coefficients calculated using a theoretical treatment.

3.4.2 The Constituents

The characteristics and properties of the matrix, nylon 6, have been adequately covered elsewhere (see literature) and as such only a limited amount of mechanical testing and DSC work was conducted to supplement this. The various fibre types were characterised by measurement of their respective diameter distributions, surface examination by scanning electron microscopy and ESCA, and thermogravimetric measurement of their size loadings.

Diameter Distribution

Assessment of the diameter distributions was considered necessary due to apparently large diameter variations observed during examination of fracture surfaces. Such variations are a result of fluctuations in drawing speeds and viscosity during manufacture. Strands of fibre selected at random from the rovings were mounted in resin, polished and examined under a microscope. Individual fibres were counted,
their diameters measured and the results displayed as plots of cumulative probability versus fibre diameter. The average diameter, $\bar{d}$, was then taken as the arithmetic mean of all measurements in each group and compared with its respective nominal diameter.

Size Loading

It was apparent from examination of the various fibre types that the size loadings on each differed, an attempt was therefore made to measure the size loading using a thermal balance. Bundles of fibres were wrapped in aluminium foil and chopped into short lengths with a scalpel. These short fibres were placed carefully in the platinum crucible of the thermal micro-balance and heated at a preset rate of $30^\circ C \min^{-1}$ to $600^\circ C$ and held at that temperature for 30mins. Sample weights of the order of 10mg were used and a zero offset adjusted to give a sensitive 0.1mg full scale deflection on the chart recorder.

Up to five samples of each fibre were processed and the average weight losses calculated for each, these were less than 1.0% in all cases and no consistent variations with fibre types were detected. A control check was performed by heating larger amounts of fibre ($\sim 300mg$) in a furnace for 24 hours and the results obtained adequately supported the microbalance data.

Fibre Surface Examination

Strands extracted from each batch of fibre were examined in the Scanning Electron Microscope in an effort to determine any differences in the fibre coatings. However, since this technique enables only a visual comparison of major irregularities in the size, a quantitative assessment of the size constituents was felt necessary. This decision was also influenced by anomalies in the observed tensile behaviour of some mouldings which were possibly a direct result of variations in the size components. The method selected to accomplish this was Electron Spectroscopy for Chemical Analysis or ESCA.
Using this technique, the sample to be analysed is bombarded with electromagnetic radiation in the X-ray range, in this case from an MgKα source. Absorption of the electromagnetic radiation causes excitation of electrons from lower to higher energy levels and, if the energy of the radiation is sufficient, ejection of the electrons from the atom or molecule. This phenomena is known as the photoelectric effect. By analysis of the energies of the ejected electrons it is possible to obtain values for the binding energies of all electrons in the atom or molecule. Thus, the atomic constituents of a compound can be determined since the binding energies of core electrons are characteristic of particular types of atom, and, the intensities of the observed peaks are related to the number of atoms present.

This type of analysis is ideal for surface coating studies since the penetration of the electromagnetic radiation is limited by absorption of radiation in the solid. The limiting factor is the escape depth of the photoelectrons; for atoms or molecules at the surface the photoelectrons produced suffer no collision, and enter the spectrometer with energy $e$. Deeper below the surface, collisions with other molecules may occur resulting in a loss of energy, the ejected electron having an energy $e'$, where $e' < e$. All electrons suffering such an energy loss will not give a single peak in the photoelectron spectrum and contribute to the spectrum background. The photoelectron peaks obtained correspond to electrons ejected from the surface up to a maximum depth called the escape depth, below which depth only $e'$ electrons can be ejected. The escape depth is proportional to the excitation energy and inversely proportional to the mass of the atoms present. In this case the escape depth is $\sim 20\,\text{Å}$ which is an order of magnitude less than the estimated thickness of the size coating, thus, the results obtained gave a reasonable indication of the elements present in the coatings.
Fibre Strength

Consideration of the strength of the fibres used was not a major factor in this investigation, however, as a result of inferior properties obtained from composites containing the heat cleaned fibres it was considered probable that these fibres had been degraded by the heat cleaning process. In order to investigate the extent of this strength reduction, laminates of an epoxy resin (MY750) containing uniaxially aligned fibres in the heat cleaned, and, in the 'as received' conditions were fabricated. The laminate plates were cut into tensile test coupons using a diamond saw and aluminium end tags bonded to each coupon to facilitate gripping during testing. Each specimen was extended monotonically in an Instron 1195 machine, the strain being measured by means of electrical resistance strain gauges bonded to the surface and the acoustic emissions monitored for each test.

Microscopy And Fractography

An extensive programme of optical and scanning electron microscopy was conducted in parallel with the mechanical testing in an attempt to elucidate the sequence of events leading to, and the cause of, final fracture.

Sections, cut both longitudinal and transverse to the injection direction, were polished metallographically and examined under a photomicroscope in order to observe fibre distribution and orientation, fibre fracture and matrix damage. Polishing of the samples proved difficult and tedious due to the large difference in hardness and stiffness of the fibres and matrix, the fibres frequently being torn out or damaged in the process. The incidence of polishing damage was, however, useful since it indicated areas of matrix deformation and fibre debonding which were not clearly evident until modes of illumination
other than reflection were used. It also served to give a broad indication of the strength of the interfacial bond, fibres having a weak bond being ripped out more easily.

Reflected illumination was sufficient to examine the fibre orientation distribution and major matrix damage such as cracking but it was more difficult to differentiate between polishing damage and stress damage where smaller scale effects such as fibre debonding and fibre fracture were concerned, since only the surface was visible. Polarised light and dark field illumination proved successful in highlighting subsurface fibre-matrix debonding, but the most useful illumination mode was transmitted light. Nylon 6, filled with low volume fractions of fibre is reasonably translucent; so, with the use of thin specimens and transmitted light, it was possible to examine the composite morphology at depths through the specimen. Test specimens were examined prior to and after testing for signs of damage, the latter generally being confined to a region close to the fracture path.

A number of small test pieces were machined from the gauge portions of moulded specimens and strained in-situ under the microscope using a specially constructed micro-straining rig, Fig. 3.16. These specimens, approximately 0.5mm thick were coated in oil, set between glass microscope cover slips and observed in the transmission mode while being strained. Thus, the sequence of damage events leading to failure were observed on a microscopic scale. The function of the oil was to minimise unwanted reflections and shadows from the surface irregularities of the unpolished specimens.

Fracture surface examination was by means of scanning electron microscopy, the fractured ends of tensile and impact specimens being mounted on small aluminium stubs and sputter coated with a thin layer
of gold to render them conductive. The fracture surfaces of test pieces containing various volume fractions of fibre were examined and compared in an attempt to elucidate any differences that existed in the fracture mechanisms operating. Of particular interest were the fibre surfaces and the fibre pull-out lengths since the condition of these gave an indication of the efficiency of the interfacial bond. Also, the appearance of the fractured matrix was indicative of possible fracture initiation sources. Some sections were cut with an ultramicrotome through visible damage areas, such as strain bands, to observe the extent of internal micro-deformations. Actually obtaining a cleanly cut surface was difficult due to the large difference in hardness of the filler and matrix, some success was however achieved by freezing the sample in liquid nitrogen prior to cutting.
<table>
<thead>
<tr>
<th>Material</th>
<th>Commercial Designation</th>
<th>'In House' Designation</th>
<th>Supplier</th>
<th>Tex</th>
<th>Make Up</th>
<th>Nominal Fibre Dia (μm)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon 6</td>
<td>F 114</td>
<td>-</td>
<td>ICI Ltd.</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>A fast cycling, controlled crystallinity grade giving uniform properties over a range of moulding conditions.</td>
</tr>
<tr>
<td>Glass Fibre</td>
<td>FGRE 1</td>
<td>F</td>
<td>Pilkingtons Ltd.</td>
<td>4600</td>
<td>16 x 287</td>
<td>13</td>
<td>Treated with size MSS4628, a PVAc sizing incorporating a chromium complex adhesion promoter compatible with Nylon.</td>
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<tr>
<td>&quot;</td>
<td>FGRE 5</td>
<td>P</td>
<td>&quot;</td>
<td>2400</td>
<td>--</td>
<td>13</td>
<td>Treated with MSS301, a size designed to be specifically compatible with polypropylene.</td>
</tr>
<tr>
<td>&quot;</td>
<td>LM 698</td>
<td>M</td>
<td>&quot;</td>
<td>3060</td>
<td>16 x 190</td>
<td>13</td>
<td>Treated with a cationic polyelectrolyte epoxy derivative film former incorporating a proprietary silane coupling agent.</td>
</tr>
<tr>
<td>&quot;</td>
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<td>N</td>
<td>&quot;</td>
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<td>16 x 107</td>
<td>10</td>
<td>As for M.</td>
</tr>
<tr>
<td>&quot;</td>
<td>LM 901</td>
<td>L</td>
<td>&quot;</td>
<td>1710</td>
<td>16 x 107</td>
<td>10</td>
<td>As for M but with the omission of the silane.</td>
</tr>
<tr>
<td>&quot;</td>
<td>-</td>
<td>G</td>
<td>Vitrofil SpA.</td>
<td>3600</td>
<td>16 x 225</td>
<td>12</td>
<td>Treated with a polyurethane film former, stearic acid lubricant, but silane omitted.</td>
</tr>
<tr>
<td>&quot;</td>
<td>-</td>
<td>H</td>
<td>&quot;</td>
<td>3600</td>
<td>16 x 225</td>
<td>12</td>
<td>As for G but with the addition of a silane (AllCO)** coupling agent.</td>
</tr>
<tr>
<td>&quot;</td>
<td>-</td>
<td>J</td>
<td>&quot;</td>
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<td>20 x 180</td>
<td>16</td>
<td>As for G.</td>
</tr>
<tr>
<td>&quot;</td>
<td>-</td>
<td>K</td>
<td>&quot;</td>
<td>3600</td>
<td>20 x 180</td>
<td>16</td>
<td>As for H.</td>
</tr>
<tr>
<td>&quot;</td>
<td>-</td>
<td>HC</td>
<td>&quot;</td>
<td>4600</td>
<td>16 x 228</td>
<td>13</td>
<td>As for F but heat cleaned.</td>
</tr>
</tbody>
</table>

*The roving "make up" is the number of strands and the approximate tex of the strand.

**Union Carbide Designation
Fig. 3.1  Flow diagram of processing route used in this work
Fig. 3.2  (a) Schematic of crosshead die construction and
(b) Die in position on the extruder
Fig. 3.3. Coextrusion apparatus for producing polymer coated fibre rovings.
Fig. 3.4 (a) Coated roving
(b) Good moulding granules
(c) Bad moulding granules (note protruding fibres)
Fig. 3.5 (a) Schematic of chopping machine blade arrangement.
(b) Actual equipment
Fig. 3.6  Schematic of fibre heat cleaning apparatus

Fig. 3.7  The BOY 15 screw preplasticizing injection moulding machine
Fig. 3.8 Four branch testpiece moulding, (a) creep (b) & (c) unnotched and notched impact, (d) tensile.

Fig. 3.9 Two branch moulding (a) end gated, (b) side gated.

Fig. 3.10 Impact test sample (machined from large tensile specimen)
Fig. 3.11 Schematic of punch shear test apparatus.

Fig. 3.12 Ring down counting
Fig. 3.13 Schematic diagram of the acoustic emission data acquisition system.

Fig. 3.14 Acoustic emission guard apparatus (a) instrumentation (b) counter (c) digital/analogue converter (d) signal pre-amplifiers (e) transducers.
Fig. 3.15 Tensile specimen in Instron ready for testing
(a) extensometer  (b) guard transducers
(c) signal transducer.

Fig. 3.16(a) Micro-straining rig used for 'in-situ' tensile tests.
(b) Rig in position on microscope.
4. RESULTS

The mechanical properties of injection moulded fibre reinforced plastics are determined principally by the fibre volume fraction, the fibre aspect ratio and fibre orientation distributions, and the state of the fibre-matrix interface. The volume fraction may be controlled by the fabricator within limits dictated by the requirements for adequate flow during processing. The aspect ratio and orientation distribution are however largely controlled by the flow history of the material during the compounding and moulding operations. The practical consequence is that mouldings contain a dispersion of short fibres of variable length with a complex orientation distribution dictated by the flow behaviour of the molten charge into the mould.

The presentation of results obtained during mechanical testing has been divided into two sections for clarity. This is because the majority of fibre types used were not available at the start of this investigation and, in addition, for the reason previously outlined, a larger tensile test piece was required in the latter stages. Microscopical observations for all fibre types and specimen sizes have however been combined, as have the characterisation of materials results. The contents of each section are outlined schematically in Fig. 4.1.

4.1. Mechanical Testing

4.1.1 Small tensile specimens (reinforced with fibres F and P only)

Tensile tests were performed as described on filled and unfilled nylon 6 specimens. The results; in the form of fracture stress, $\sigma_{uc}$, 0.5% secant Modulus, $E_c$, and fracture strain $\varepsilon_{uc}$, are presented as a function of volume fraction of fibres, $V_f$, in Figs. 4.1.1-3. Strength enhancement over the unfilled polymer is reasonably good, but
little difference was observed between the fibre types, the nylon compatible fibre F material showing only slightly superior strengths. The stiffness \( V_f \) relationship coincides for the two fibres and is approximately linear as would be expected from the application of a simple rule of mixtures theory. Failure strain is reduced from 20-30\% for the unfilled polymer to approximately 3\% for the high \( V_f \) material, which is of the same order as the fibre failure strain. The failure strains of the fibre P materials were however approximately 1\% greater than the fibre F materials for all \( V_f \)'s tested. Typical stress-strain curves for the tested materials are given in Fig. 4.1.4.

Acoustic emissions were monitored during tensile testing and a similar trend observed in all cases. In the early stages of a test very little output was recorded, then at some threshold strain the emissions commenced and increased exponentially until specimen failure occurred. The emissions during testing were plotted either as count rate (counts per second) versus strain or cumulative count versus strain. It was observed that the count rate at failure and the total count recorded generally decreased with increasing \( V_f \) and that emissions from the testpieces reinforced with fibre P were the higher. (Fig. 4.1.5.) The \( V_f \) effect is attributed to the higher failure strains at low \( V_f \)'s and thus more relative accumulated damage. This is also true for the P fibre specimens since failure occurred at higher strains. There was no evidence of appreciable fibre fracture so it can be assumed that composite damage, and thus the source of the acoustic emissions, was confined to fibre debonding and matrix cracking. It might be expected that the predicted weaker interfacial bond in the fibre P reinforced materials would result in relatively more fibre debonding and matrix damage and thus a higher emission level, there is however
no additional evidence to support this assumption. And in the later work an opposite effect was observed. A linear relationship between failure strain and total cumulative acoustic count for all the filled specimens tested was recorded and this is shown in Fig. 4.1.6. Acoustic activity during the testing of un-filled specimens was minimal and it may be concluded that matrix flow contributes virtually nothing to the counts recorded from composite specimens.

It was observed during testing that as the load was increased; strain bands, visible as narrow milky white areas, formed across the samples. The onset of this phenomena was gradual and its severity increased with strain until final fracture occurred in a sudden and brittle manner partially through one of the most severe bands. Fig. 4.1.7. Initial examination revealed that the bands were confined to the bulk material (ie. not a surface phenomena) and were inclined at approximately $55^\circ \pm 5^\circ$ to the principal stress axis. Such an angle is characteristic when considering localised deformations, the bands lie along the direction of zero extension and thus no excess strain is imposed on adjacent material. (130). Photographs of failed testpieces reinforced with both fibre types showing the strain banding phenomena are given in Fig. 4.1.8. It is interesting to note that the number of bands appears to increase with $V_f$, but that the individual bands are more pronounced at low $V_f$'s. The formation of the bands is attributed to localised fibre debonding and associated matrix flow, their milky white appearance being due to scattering and refraction of light. The damage is initiated by stress concentration points such as fibre ends or crossover points; since there are a relatively larger number of such initiators in the high $V_f$ materials, the number of bands formed will be greater. However, in low $V_f$ materials the increased failure strains observed allow a greater degree of band development. Extensive examination of
samples using scanning and optical microscopy tends to support these assumptions, the results of which will be discussed later. It should be noted that, although large plastic deformations apparently occur in the bands, the effect is localised and overall elongation remains very low.

In the moulding of the first series of specimens, the criteria for a 'good' test piece was the complete absence of the fibre clumps, ie. a well distributed fibre phase. To consistently achieve this it was necessary to use high screw back pressures, since low back pressures gave insufficient melt shear to adequately disperse the heavily sized fibre strands. Subsequent determination of the fibre length distributions of the mouldings revealed that considerable fibre attrition had occurred, the average fibre lengths being reduced from 6mm in the moulding granules to <0.3mm in the test pieces.

As a result of the short fibre lengths obtained in the first series, a second batch of material was compounded, using only fibre F, in an attempt to retain long fibres in the testpieces and also incorporate higher volume fractions of fibres. The maximum \( V_f \) attainable in this case is limited by two factors, the first is the maximum \( V_f \) of the coaxial moulding granules and the second, the maximum available injection pressure, since the greater the \( V_f \), the higher the injection pressure required. Special care was exercised during extrusion to ensure the polymer coating was as thin as possible and the maximum \( V_f \) obtained was \( \sim 0.4 \). This is approaching the maximum a relatively small machine like the BOY 15 can handle due to its limited injection and mould locking pressures.

An investigation into the effects of back pressure on fibre dispersion and breakage was conducted; the average fibre lengths
obtained at different volume fractions as a result of back pressure variation are given Table 4.1.1. From these figures it is apparent that increased back pressure results in a reduced average fibre length and that this effect is more pronounced at high volume fractions. Although it was found necessary to use high back pressures to remove all signs of clumping, specimens of reasonable quality were obtainable using low back pressures. Also included in Table 4.1.1. are calculated values of critical fibre length, $L_c$, (see literature) along with the proportions of fibres exceeding this length, (data obtained by reference to cumulative length distribution curves, see section 4.2.1). It will be apparent that the average lengths exceed the critical lengths at low volume fractions and that this trend is reversed at high volume fractions. The differences are however not large and since a wide range of lengths exists in the mouldings a considerable percentage of fibres exceed the critical length. In addition, it should be noted that the critical length values were calculated using the estimated fibre failure strain (3%) and the composite failure strain was less than this in all cases.

The results of tensile tests performed on the second series of specimens, recorded as a function of volume fraction, are given in Figs. 4.1.9 - 11 (marked series 2), also plotted for comparison are the series 1 curves. The curves marked 'heat cleaned' will be discussed later. It is seen that, in all cases, the series 2 properties are a marked improvement over the series 1. The failure stresses are considerably higher, as are the moduli, a linear relationship with $V_f$ still being apparent for the latter. Failure strain is reduced, this being consistent with previous observations of improved reinforcement efficiency.
Heat Cleaned Fibre Samples

The third stage of the investigation was to modify the fibre surface coating in order to determine its effect on processability and the reinforcement potential of the fibres. Initially it was necessary to remove the existing sizing agents since it was not possible to obtain commercially a 'clean' fibre. Consultation with the manufacturers suggested that it should be possible to remove the size by solvent action or heat cleaning. The recommended solvents were Acetone or Butanone (M.E.K).

Initial tests using a Stanton Redcroft Thermal Balance, calibrated with a large zero offset to increase sensitivity, revealed that a significant proportion of the size was removed in the 200 - 600°C range, this oxidation process was however fairly slow. The average weight loss was 1.0% for fibre F and 0.75% for fibre P, the difference was expected since the fibre F tows were much stiffer indicating a greater size loading.

Some fibre tows were washed repeatedly in the recommended solvents and others were heat cleaned, in order to determine the most effective method of size removal. Fibres treated in both ways were examined in the scanning electron microscope and photomicrographs of these are shown in Fig. 4.1.12. It is apparent that the size is only distinguishable by its irregular formation on the fibre surfaces and that heat cleaning was the most successful method of size removal.

Tensile specimens, fabricated from the cleaned fibres (designated HCl and SC) were tensile tested and the results are presented in Fig. 4.1.13. The ultimate strengths obtained reflect the microscopical examination in that virtually no difference was observed for the solvent 'cleaned' (SC) material while a marginal strength reduction is apparent for the heat cleaned fibres. (HCl)
The heat cleaned fibres used in the above tests were obtained by winding fibre tows onto metal frames and placing these in an electric muffle furnace at 250°C for several hours. Since the extrusion coating process requires continuous fibre tows the method is not practical for fabricating larger batches of material. The apparatus described in section 3.2 was used at a temperature of 450°C to ensure the maximum level of size removal. The resulting fibre tows were still relatively stiff and also discoloured, indicating that the removal of the size was incomplete. It was also noted that ease of fibre dispersion was not significantly improved during the moulding operation.

Tensile specimens containing these heat cleaned fibres (designated HC2) were moulded and tested as described previously. The properties, as a function of volume fraction, are presented in Figs. 4.1.9 - 11. It is apparent from comparison with the series 1 and 2 results that the degree of reinforcement afforded by the heat cleaned fibres was much lower. The failure stress of the 0.1 Vf specimens was approximately equal to that of the unfilled matrix and an increased Vf resulted in only a slight strength improvement. The difference between the actual and expected strength levels is too great to be explained by loss of fibre-matrix adhesion (due to size removal) and therefore indicates a probable change in the failure mechanism. The stiffness suffered a similar reduction and, contrary to previous observations, appears to deviate from a linear relationship with Vf at low fibre loadings. The failure strains show an increased ductility at low Vf's approaching that of the unfilled matrix but reduced ductility relative to the unmodified fibre specimens at increased loadings.

Comparison of typical stress-strain curves of the series 2 tests and the heat cleaned series (HC2), Fig. 4.1.14, reveals the considerable
difference in their relative behaviour at similar fibre loadings. The acoustic emissions follow the previously observed behaviour, a higher output being observed with decreasing $V_f$. The exception is the $0.1\ V_f$ heat cleaned samples where the observed count rate reaches a maximum value and then decreases with increasing strain while the stress remains virtually constant. This effect has been observed previously but only at very low fibre loadings ($V_f << 0.1$).

The properties of each series of specimens tested are summarised in Table 4.1.2 which gives mean values of fibre length, 0.5% secant modulus, tensile strength and failure strain. The values of interfacial shear strength and orientation factors in Tables 4.1.1 and 2 will be discussed later (Section 4.1.3).

The assumption of a change in failure mechanism for the heat cleaned fibres is further supported by reference to the average fibre length figures in Table 4.1.2. Although it has been shown that fibre length exerts a considerable influence over the mechanical properties, it is apparent that the relatively short lengths obtained with the heat cleaned material can not fully account for their reduced properties. This is especially evident when the similarity between the series 1 and HC2 series average lengths, and the considerably inferior properties of the latter are taken into account. It is seen from Tables 4.1.1 and 2 that increasing fibre volume fractions result in reduced average lengths. The variations are most consistent in the heat cleaned materials and the 'as received' fibre materials moulded with high back pressures, and are attributed to the increased degree of fibre attrition resulting from the greater number of fibres present. The low back pressure series 2 results show an inconsistency in that the $0.38V_f$ material possesses a higher average length than the $0.3V_f$ material. The reason for this is not known but is probably due
### TABLE 4.1.1

Variation of Material Parameters with Screw Back Pressure (Fibre F)

<table>
<thead>
<tr>
<th>Nominal $V_f$</th>
<th>Actual $V_f$</th>
<th>Back Pressure (Bars)</th>
<th>Vol. Average Fibre Length $L$ (µm)</th>
<th>Interface Shear Strength $\tau$ (MPa)</th>
<th>Orientation Factor $C$</th>
<th>Critical Length $L_c$ (µm)</th>
<th>Proportion of Fibres Exceeding $L_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.22</td>
<td>&lt; 10</td>
<td>440</td>
<td>35</td>
<td>0.59</td>
<td>384</td>
<td>56</td>
</tr>
<tr>
<td>0.2</td>
<td>0.19</td>
<td>&gt; 30</td>
<td>400</td>
<td>40</td>
<td>0.63</td>
<td>336</td>
<td>65</td>
</tr>
<tr>
<td>0.3</td>
<td>0.31</td>
<td>&lt; 10</td>
<td>350</td>
<td>38</td>
<td>0.66</td>
<td>353</td>
<td>46</td>
</tr>
<tr>
<td>0.3</td>
<td>0.30</td>
<td>&gt; 30</td>
<td>320</td>
<td>45</td>
<td>0.66</td>
<td>298</td>
<td>58</td>
</tr>
<tr>
<td>0.38</td>
<td>0.38</td>
<td>&lt; 10</td>
<td>360</td>
<td>32</td>
<td>0.67</td>
<td>420</td>
<td>44</td>
</tr>
<tr>
<td>0.38</td>
<td>0.38</td>
<td>&gt; 30</td>
<td>290</td>
<td>40</td>
<td>0.68</td>
<td>336</td>
<td>37</td>
</tr>
</tbody>
</table>

*Critical length $L_c = \frac{\sigma_f r_f}{\tau}$ where $\sigma_f =$ fibre strength $= 2.1$ GPa

$r_f =$ fibre radius $= 6.4$ µm (sect 4.2.2)

$\tau =$ Interface shear strength
Table 4.1.2
Tensile test data for Injection Moulded Glass Reinforced Polyamide 6
(Small specimens, series 1,2 and heat cleaned)

<table>
<thead>
<tr>
<th>Material</th>
<th>Fibre Volume Fraction $V_f$</th>
<th>Tensile modulus $E_c$ (GPa)</th>
<th>$C_V^*$ (%)</th>
<th>Tensile strength $\sigma_{uc}$ (MPa) (%)</th>
<th>$C_V^*$ (%)</th>
<th>Failure strain $\varepsilon_{uc}$ (%)</th>
<th>$C_V^*$ (%)</th>
<th>Average fibre $\bar{L}$ (µm)</th>
<th>Interfacial shear strength $\tau$ (MPa)</th>
<th>Orientation factor</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>SERIES 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fibre F</td>
<td>0.1</td>
<td>4.8</td>
<td>7.3</td>
<td>87.4</td>
<td>8.1</td>
<td>3.8</td>
<td>7.9</td>
<td>280</td>
<td>30</td>
<td>0.56</td>
<td>High back Pressure Used</td>
</tr>
<tr>
<td>Series F</td>
<td>0.2</td>
<td>7.8</td>
<td>7.0</td>
<td>121.2</td>
<td>7.6</td>
<td>3.1</td>
<td>9.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Low back Pressure Used</td>
</tr>
<tr>
<td>0.3</td>
<td>10.5</td>
<td>5.2</td>
<td>130.7</td>
<td>2.0</td>
<td>2.7</td>
<td>7.5</td>
<td>185</td>
<td>47</td>
<td>47</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>SEPES 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fibre F</td>
<td>0.2</td>
<td>9.7</td>
<td>4.8</td>
<td>152.7</td>
<td>2.2</td>
<td>2.5</td>
<td>3.6</td>
<td>440</td>
<td>35</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>13.7</td>
<td>11.0</td>
<td>193.4</td>
<td>13.0</td>
<td>7.6</td>
<td>1.9</td>
<td>13.0</td>
<td>350</td>
<td>38</td>
<td>0.66</td>
<td></td>
</tr>
<tr>
<td>0.38</td>
<td>17.0</td>
<td>1.0</td>
<td>219.7</td>
<td>2.1</td>
<td>1.7</td>
<td>7.5</td>
<td>360</td>
<td>32</td>
<td>32</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td>Heat G</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cleaned (HC2)</td>
<td>0.2</td>
<td>7.1</td>
<td>5.2</td>
<td>74.2</td>
<td>5.0</td>
<td>1.6</td>
<td>11.0</td>
<td>260</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Fibre F</td>
<td>0.3</td>
<td>9.6</td>
<td>6.7</td>
<td>83.4</td>
<td>2.2</td>
<td>1.7</td>
<td>9.5</td>
<td>240</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Unfilled P.A.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*$C_V = \text{Coefficient of variation}$
to the reduced melt plasticization times resulting from the use of low back pressures.

It was originally intended to further modify the surfaces of the heat cleaned fibres by the addition of lubricants and/or coupling agents in order to assess the effects on the composite fracture mechanisms. However, due to the obvious detrimental effects of heat cleaning on the fibre strength, such treatments were considered impractical.

4.1.2 Large Tensile Specimens.

The constitution and mechanical properties of the materials tested are summarised in Tables 4.1.3 - 6. Tensile testing was initially confined to specimens reinforced with a single \( V_f \) (nominally 0.25) only of each type of fibre, excluding fibre P for the reasons previously outlined. Additionally, specimens containing \( V_f \)'s of 0.1 and 0.3 of fibre F were tested for comparison with the small specimen results. This batch of tests is designated Series 4. Both side and end gated specimens were tested and the results are presented in Table 4.1.3. It is apparent that the alternative gates produce little difference in properties, the side gated specimens possessing slightly improved strength and stiffness properties. This is attributed to the elimination of "jetting" at high injection rates with a consequent more uniform flow of the charge into the mould.

It was noted that there was a significant difference in the behaviour of materials from different manufacturers. Considering fibres G, H, J and K, the coupled versions H and K showed significantly superior strengths compared to their uncoupled counterparts, this trend was reflected to a much lesser extent by their moduli, which is to
be expected since only the low strain behaviour is considered.
Comparison of fibres L and N (different manufacturer) reveals little variation in their properties despite the absence of coupling agent on the former. The smaller diameter fibres did not appear to confer superior properties although this might be expected when their relatively larger surface areas are considered. The strain to failure of all samples was low at 1.2-3.0%, the uncoupled specimens, suprisingly, having the low values (<1.3%) with the exception of material L, which had failure strains comparable to the coupled samples. It should be noted that the estimated strain to failure of the fibres is <3%, so that all batches except K fail at much lower strains. The implication of the low strain to failure of the uncoupled materials is that the embrittlement is a result of the presence of the fibres rather than the strength of the interfacial bond as previously surmised.

The large specimens reinforced with fibre F possessed similar properties to the small F specimens, falling between the series 1 and series 2 values. The difference is attributed to fibre length variation since the series 1 and 2 samples can be broadly described as containing short and long fibres respectively.

The differences in tensile properties are illustrated by the comparative stress-strain curves (Fig. 4.1.15) which show the inferior properties of the uncoupled batches G and J, compared to their coupled counterparts H and K, and the similarity between L and N which incorporated a different sizing system.

The acoustic emissions, monitored during all tensile tests, showed a similar trend to that previously described (Section 4.1.1).
Very little output was recorded during the initial stages of the test but at some threshold strain the emissions commenced and the rate increased exponentially until failure. It was however noted that in the uncoupled materials G and J, the total acoustic count was much lower than for the coupled materials H and K as is shown in Fig. 4.1.16. This is partially a result of the slightly higher failure strains of the coupled materials but is also due to the different behaviour of the fibres under load which will be discussed in more detail in section 4.3.1.

The mouldability of the different fibre types was not significantly affected by the type of size present but it was noted that the uncoupled materials G and J were dispersed slightly more easily. The lowest possible back pressures were used during moulding but some fibre clumps were inevitably retained in the testpieces. During testing, final failure often occurred through any fibre clumps that were present, but these specimens did not necessarily possess consistently lower strengths. Indeed some samples fracturing in this manner attained the highest strengths in the particular batch under test. It appears therefore that the presence of such clumps is not significantly detrimental to the mechanical properties.

The fibre volume fractions were determined for each specimen tested and all were found to lie within ±2% of the nominal $V_f$ of 0.25 (0.1 and 0.3 for fibre F), and as such are only a minor source of scatter in results.

In order to confirm the property variations observed between coupled and uncoupled materials and to assess the effect of fibre volume fraction, a second batch of material (designated series 5) was compounded and moulded, the testpieces having $V_f$'s of 0.1 and 0.25. The mechanical properties are given in Table 4.1.4 and are
seen to follow the same trends as the series 4 materials. The uncoupled materials, G and J, have inferior properties to their coupled counter-parts at both volume fractions, while fibre L has similar properties to the coupled fibre N. It should be noted that the L material contained fibre volume fractions of 0.17 and 0.25, the low volume fraction results are therefore not directly comparable with the other materials, extrapolated values have however been included in the Tables for comparison. The failure stress, strain, and modulus are presented as a function of volume fraction in Figs. 4.1.17 - 19, also plotted for comparison are the series 4 values. It is apparent from these curves and from Table 4.1.4 that the properties of the series 5, 0.25 $V_f$, specimens are inferior to those of the initial series 4 batch. In all cases the failure stresses and moduli are lower and the failure strains higher. The effect is most pronounced in the case of failure strain and moduli, the only appreciable difference in failure stress occurring in the H and L samples. All samples were tested using the same apparatus and procedures, and, since the magnitude of the variations between batches was not consistent, it is unlikely that experimental error or apparatus malfunction was the cause. The moulding conditions were essentially similar for both batches but it is probable that the lack of a fully interactive control system resulted in machine variations which led to significant differences in fibre orientation and fibre length. Variations in fibre volume fraction were within $\pm$ 2% of the nominal value, as previously observed. Fibre length distributions were available for the series 4 batch of materials only and it was therefore not possible to make quantitative comparisons and thus determine if length variations were the course. It has been shown however, (Section 4.1.1) that variations in fibre length considerably influence the mechanical properties and it is to this that the observed differences are
Tensile test data for injection moulded glass reinforced polyamide 6

(Series 4, large tensile specimens)

<table>
<thead>
<tr>
<th>Material Code</th>
<th>Fibre Volume Fraction $V_f$</th>
<th>Gate Position</th>
<th>Tensile modulus $E_c$ (GPa)</th>
<th>$C_V^*$ (%)</th>
<th>Tensile Strength $\sigma_{uc}$ (MPa)</th>
<th>$C_V^*$ (%)</th>
<th>Failure Strain $\varepsilon_{uc}$ (%)</th>
<th>$C_V^*$ (%)</th>
<th>Interface Shear Strength $\tau$ (MPa)</th>
<th>Orientation Factor $C$</th>
<th>Volume Average Fibre Length $L$ (µm)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>0.1</td>
<td>E</td>
<td>5.4</td>
<td>5.2</td>
<td>103.1</td>
<td>6.7</td>
<td>2.6</td>
<td>7.3</td>
<td>30</td>
<td>0.65</td>
<td>440</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>S</td>
<td>5.4</td>
<td>4.4</td>
<td>107.2</td>
<td>5.7</td>
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<td>8.4</td>
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</tr>
<tr>
<td></td>
<td>0.3</td>
<td>E</td>
<td>12.5</td>
<td>6.2</td>
<td>179.4</td>
<td>3.4</td>
<td>2.1</td>
<td>5.8</td>
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$C_V^*$ = coefficient of variation  
**E** = end gated  
$S$ = side gated
Table 4.1.4
Tensile test data for injection moulded glass reinforced polyamide 6
(large tensile specimens, series 5)

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<th>Fibre Volume Fraction</th>
<th>Tensile Modulus $E_c$ (GPa)</th>
<th>$C_v^*$ (%)</th>
<th>Tensile Strength $\sigma_{uc}$ (MPa)</th>
<th>$C_v^*$ (%)</th>
<th>Failure Strain $\varepsilon_{uc}$ (%)</th>
<th>$C_v^*$ (%)</th>
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$C_v^*$ = coefficient of variation

+ Estimated values for $\nu_f = 0.1$
attributed. Average fibre length values have been given in Table 4.1.3, these and the full length distributions will be discussed in Section 4.2.1. The effect on the properties of fibre orientation variation could not be determined as no quantitative assessment of this was conducted.

The strain banding phenomena associated with failure in the small tensile specimens was again evident in the larger specimens but was generally not as pronounced. This is attributed primarily to the lower failure strains exhibited which do not allow the bands to develop to such an appreciable extent. Generally the uncoupled materials exhibited more banding despite their low failure strains but it was material K, which showed an unexplained high strain to failure, in which the phenomena was most pronounced.

The acoustic emission data obtained from the series 5 tests was found to be unreliable due to an apparatus malfunction which unfortunately could not be corrected in time to preserve the length of the pre-test specimen conditioning period. Consequently, no acoustic emission results are presented for the second batch of material.

Effect of Moisture

The role of a coupling agent is not only to improve properties in the dry condition, it serves also to improve property retention under adverse conditions such as a high moisture environment. Samples of each material (series 5 mouldings) were treated by boiling in distilled water for 48 hours to artificially raise their water content, these were cooled, superficially dried and tested immediately. The tensile test data is given in Table 4.1.5 along with the water uptake values. It is seen that the water absorbed during the boiling treatment
is lower for higher $V_f$ materials and greater in the uncoupled materials. This indicates that the major amount of water is absorbed by the hygroscopic nylon matrix and also that the interface of the uncoupled materials suffers relatively more deterioration. There is a dramatic reduction of strength and stiffness of all materials, but it is in this condition that the effect of the coupling agent is most evident, even in the L and N batches which showed little difference in the dry condition. In the wet condition all the uncoupled materials exhibit poor properties, as does F, which uses a non-silane coupling agent. However, the size and coupling agent system employed in H and K appears to confer superior wet properties over that used in M and N, this is shown in Table 4.1.5 by the % of original strength and modulus figures. It is apparent that in the coupled materials the strength retention is greater with increasing $V_f$ while the converse is true for the uncoupled materials, thus also indicating increased interfacial bond deterioration. It is interesting to note that the coupled materials H, K, M and N, are still comparatively brittle even in the wet condition. Furthermore, the materials M, N and F at high volume fractions actually possess lower failure strains than in their dry state, at low volume fractions however their failure strains are high. There is little difference in the properties of the wet unfilled nylon and the uncoupled batches G, J and L at both $V_f$ levels thus indicating the virtual ineffectiveness of the fibres in a reinforcing role. This is further supported if the failure strain of the fibres ($\sim 3\%$) is considered, it must be assumed that the interfacial bond has completely degraded and the matrix flows around the fibres during extension.

Differences in the tensile properties are illustrated in the comparative stress-strain curves (Figs. 4.1.20 - 21) which show the behaviour of the series 5 materials at both $V_f$'s in the wet and 'dry' conditions. It is seen that the behaviour in the wet condition is
very different and that M and N (0.1 \( V_f \)) exhibit yield points at \( \sim 2.5 \% \) strain.

The acoustic emission was drastically reduced after the boiling water treatment with the uncoupled grades giving virtually zero output. This is consistent with previous observations that the unfilled polyamide gave no acoustic output and the conclusion that output sources were fibre debonding, matrix cracking and fibre fracture. In the uncoupled material the fibres are already debonded prior to testing or debond at lower strains with consequent reduced acoustic output and in addition the incidence of any fibre fracture is reduced. In the wet samples, the matrix flows around the fibres and no acoustic events are recorded. The coupled materials H and K exhibited some acoustic output but at a comparatively reduced level, it was noted that when the stress levelled off with increasing strain, so did the acoustic emission with little increase being apparent prior to failure. The M and N materials showed an even lower initial output which reached a maximum at the respective yield points and then declined to approximately zero.

The incidence and the extent of development of the strain banding phenomena in the wet materials appeared to be dependent on the fibre volume fraction and the sizing system employed. For the uncoupled materials G, J and L, the banding was extensive and evenly distributed at both volume fractions (Fig. 4.1.22a). In the coupled materials H and K; the banding took a different form, similar to that exhibited by the 'dry' materials, the incidence of the bands being more isolated but also more developed (Fig. 4.1.22b). For all of the above, the comments are valid at both \( V_f \)'s but generally the banding was not as pronounced at the high \( V_f \)'s. The M, N and F materials however behaved differently; at the low \( V_f \) the banding was extensive but more developed and angular than in the uncoupled materials (Fig. 4.1.22c).
while at the high $V_f^*$ the incidence of banding was very isolated. This
is attributed to the vastly different failure strains exhibited by
these materials at the two $V_f^*$'s, the reasons for these large
differences are however not understood. If it is assumed that the
bands consist of areas of debonded fibres and localised matrix flow
then their physical appearance is a reasonable indication of the
strength of the interfacial bond. For example; the low interface
strength of the uncoupled materials, especially in the wet condition,
results in extensive debonding at low strains, thus the banding is
even and well distributed. Conversely, the higher interfacial strength
of the coupled materials means that debonding will occur at higher
strains, at points of high stress concentration, this in turn induces
localised debonding in the surrounding areas due to the transferrence
of load. Thus, the incidence of strain banding is more isolated but
the bands tend to be more intense.

The strain banding phenomena is magnified when the materials are
in the wet condition since the effectiveness of the interfacial bond
is reduced by the presence of moisture, considerably more bond
deterioration and thus strain banding being apparent when no coupling
agent is present. Additionally, if the sizing system contains a
coupling agent, its ability to preserve the interfacial bond under
adverse conditions is indicated by the appearance of the strain bands.
Comparison of the specimens a and c in Fig. 4.1.22 (materials H and
M respectively) and reference to the percentage strength retention
figures in Table 4 adequately support this observation, the M and N
materials exhibiting more banding and retaining considerably less
strength than the other coupled materials H and K.

It should be noted that the strain bands in the wet materials,
especially in the uncoupled versions, were not confined to the central
or bulk regions of the testpieces but were also visible at the surface.
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<th>Material Code</th>
<th>Fibre Volume Fraction</th>
<th>Tensile Modulus $E_c$ (GPa)</th>
<th>$C_V^*$ (%)</th>
<th>Tensile Strength $\sigma_{uc}$ (MPa)</th>
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+ note high $V_f$

$C_V^* = \text{coefficient of variation}$
Evidence of this will be presented later in Section 4.3.

Impact Testing

An indication of the toughness of the materials was obtained by means of notched charpy impact tests, these were conducted on materials G, H, J, K, L, M and N in the 'dry' condition only, the specimens being machined from the gauge portions of the large tensile specimens. The results are given in Table 4.1.6 and the quoted specific energy is on the basis of the net projected area of fracture, ie. the area of both fracture surfaces. The results show an interesting trend in that the stronger materials give higher energy values in all cases. This is clearly shown in Fig. 4.1.23 which shows the simple correlation between tensile strength and charpy fracture energy. It might be expected that energy absorbing processes such as fibre pull-out would be more dominant in the uncoupled materials due to the lower interfacial bond strength, thus resulting in tougher materials. This does not appear to be the case, and, since such processes appear to be ineffective in this mode of testing, the implication is that the only parameter of significance is the stress necessary to initiate fracture at the notch tip.

Impact tests of this type are notoriously inaccurate since the results obtained are a measure of the total energy absorbed and give no indication of the contribution of separate events. For example, some energy is absorbed in the form of kinetic energy since the fractured samples travel considerable distances from the apparatus. The magnitude of this energy loss can be estimated:

$$v_s = (1 + \eta) \frac{v_h}{(1 + M_s/M_h)}$$

Where \(v\) = velocity, \(M\) = mass and subscripts \(s\) and \(h\) refer to sample and hammer respectively. \(\eta\) is the coefficient of restitution. If \(\eta\) is assumed to be 1 (elastic collision) and \(M_h \gg M_s\) then:
\[ v_s \approx 2 v_h \]

Now hammer impact velocity = 3ms \(^{-1}\)

\[ \text{Kinetic energy of sample} = \frac{1}{2} M_s v_s^2 \]
\[ \approx 0.04 J \]

This represents approximately 5% of the total energy absorbed. In addition, the results are strongly dependent on the test conditions and on material variations, since the critical stress condition is induced in only a relatively small volume of material.

Despite these drawbacks, the results are useful in a comparative context since they give an indication of the behaviour trends of such materials under impact conditions. For example, in the systems considered, there appears to be no benefit in toughness from the lower interfacial bond strength of the uncoupled materials.

A further indication of the toughness can be obtained by assessment of the areas under the stress-strain curves. This has been done on typical plots from each batch of materials the results are presented in Table 4.1.7. and represent the total energy input per volume. Similarly to the impact tests, the actual numerical values are of little practical value except in a comparative context to indicate trends in the materials investigated. It is evident that the stronger materials are the toughest, but that increasing the \( V_f \) of the uncoupled fibres results in an apparent reduction in toughness whilst the converse is true for the coupled materials. Overall there is a reasonably good correlation between the toughness indicated by these and by the impact results.

In the reporting of mechanical test data an indication of scatter of results has been given in each case by values for the coefficient of variation \( C_v \), where:
### Table 4.1.6

**Notched Charpy Impact Test Data**

<table>
<thead>
<tr>
<th>Material Code</th>
<th>V&lt;sub&gt;f&lt;/sub&gt;</th>
<th>Fracture Energy ( \gamma_{NC} ) (KJm(^{-2}))</th>
<th>Coefficient of Variation ( CV ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>0.1</td>
<td>13.0</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>16.0</td>
<td>15.6</td>
</tr>
<tr>
<td>H</td>
<td>0.1</td>
<td>14.6</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>19.7</td>
<td>16.8</td>
</tr>
<tr>
<td>J</td>
<td>0.1</td>
<td>13.0</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>14.9</td>
<td>8.3</td>
</tr>
<tr>
<td>K</td>
<td>0.1</td>
<td>16.5</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>26.4</td>
<td>8.2</td>
</tr>
<tr>
<td>L</td>
<td>0.1</td>
<td>25.4</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>26.4</td>
<td>13.1</td>
</tr>
<tr>
<td>M</td>
<td>0.1</td>
<td>15.3</td>
<td>14.6</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>25.6</td>
<td>9.2</td>
</tr>
<tr>
<td>N</td>
<td>0.1</td>
<td>16.8</td>
<td>21.2</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>27.9</td>
<td>8.4</td>
</tr>
</tbody>
</table>
Table 4.1.7

Areas Under Stress-Strain Curves

<table>
<thead>
<tr>
<th>Material Code</th>
<th>Fibre Volume Fraction $V_f$</th>
<th>Energy input to fracture $\gamma_{ss}(\text{MJm}^{-3})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>0.1</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.80</td>
</tr>
<tr>
<td>H</td>
<td>0.1</td>
<td>1.87</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>2.35</td>
</tr>
<tr>
<td>J</td>
<td>0.1</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.99</td>
</tr>
<tr>
<td>K</td>
<td>0.1</td>
<td>1.97</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>3.49</td>
</tr>
<tr>
<td>L</td>
<td>0.17</td>
<td>2.29</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>1.90</td>
</tr>
<tr>
<td>M</td>
<td>0.1</td>
<td>1.93</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>2.16</td>
</tr>
<tr>
<td>N</td>
<td>0.1</td>
<td>1.72</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>2.38</td>
</tr>
</tbody>
</table>
The number of samples tested in each group was generally five, this was however increased if the results scatter was large to give a more representative mean value. The impact test data are mean values for eight tests.

To summarise briefly the extent of the mechanical testing programme: The effect on composite properties of incorporating a number of different fibre types has been examined. In their 'as received' condition, the fibres possessed various surface coatings and were of different diameters. The effectiveness of the interfacial bond was reduced by a boiling water treatment and the fibre strength was reduced by a heat 'cleaning' operation. Property assessment was mainly by tensile testing supported by acoustic emission monitoring, and by impact testing.

4.1.3 Calculation of the interfacial shear strength and fibre orientation parameter.

The interfacial shear strength, $\tau$, and the fibre orientation factor, $C$, were evaluated using a slightly modified version of the theory due to Bader and Bowyer (100) which has been described in detail in Chapter 2. The technique fits a modified "rule of mixtures" expression to the experimental stress-strain curve using $\tau$ as a disposable constant. The equation is of the form:

$$
\sigma_c = C \left[ \sum_{i} V_i R_i \tau_i + \sum_{j} V_j E_f \varepsilon_C \left( 1 - \frac{E_f \varepsilon_C}{4\tau R_j} \right) \right] + E_m \varepsilon_c (1-V_f) \quad (4.1.1)
$$

Where $V$ is the volume fraction of fibres of aspect ratio $R$ in each fibre length distribution group and the subscripts $i$ and $j$ refer to subcritical and supercritical fibres respectively.
The data required for each calculation was; four corresponding values of stress and strain determined from the experimental stress strain curves, measured values of R and V and five assumed values of \( \tau \). The calculation was conducted using a Texas TI 59 programmable calculator, the programme for which is given in Fig. 4.1.24. For each stress/strain pairing, the programme completes 5 loops, one for each assumed \( \tau \) value and calculates 5 corresponding C values. Thus, 4 curves of \( \tau \cdot v \cdot C \) can be plotted and their point of intersection is taken as the correct value of \( \tau \) and C. The principle being that C must be a constant at all strain levels while \( \tau \) appears to vary with strain. A typical group of curves is given in Fig. 4.1.26 for a 0.25 \( \frac{V_f}{f} \) fibre J sample.

Substitution of the calculated values into equation 4.1.2 enables a theoretical stress-strain curve to be plotted.

\[
\sigma_{ci} = C \left[ \sum V_i R_i \tau + \sum \varepsilon_i E_f V_j \left( 1 - \frac{\varepsilon_i E_f}{4R_f} \right) + \varepsilon_i E_m (1-V_f) \right]
\]  

(4.1.2)

The equation can be written schematically as:

\[
\sigma_{ci} = C \sigma_x + \sigma_y + \sigma_z
\]  

(4.1.3)

The programme is given in Fig. 4.1.25 and the results consist of; the subcritical fibre contribution \( \sigma_x \), the supercritical fibre contribution \( \sigma_y \), the matrix contribution \( \sigma_z \) and the total stress \( \sigma_{ci} \) for each specified strain value, \( \varepsilon_i \).

Values of \( \tau \) would be expected to remain constant for the same batches of material, reference to Tables 4.1.1-3 reveals that this is however not the case. From Table 4.1.1, it appears that \( \tau \) increases with screw back pressure and decreasing fibre length. A reduced fibre length should be reflected by the mechanical properties to an extent
that the $\tau$ values (calculated from the experimental stress strain curves) would be unchanged. Since this is obviously not the case, the variation must result from the back pressure increase and is therefore attributed to improved fibre wetting and distribution due to longer residence times. There is however no additional evidence to substantiate this assumption. Comparison of the series 1 and 4, $\tau$ values (Tables 4.1.2 and 3 respectively) for the F material indicate a significant volume fraction effect. The 0.1 $V_f$ and the 0.3 $V_f$ values are similar for both series, the difference in $\tau$ being \~18 MPa. This difference is not reflected in the series 2 results and is therefore again attributed to a back pressure effect (high for series 1, low for series 2 and medium for series 4).

The orientation factor, $C$, showed no significant trends for the series 1 and 2 tests with values ranging between 0.51 and 0.68 which indicate reasonably good fibre alignment. ($C=1$ for fully aligned fibres, 0.33 for random in-plane and 0.167 for a 3-D random array).

The calculated $C$ and $\tau$ values for the series 2 samples were used to calculate theoretical stress-strain curves and the results are presented in Fig. 4.1.27. It is seen that correlation is excellent at low strains and is generally better at high $V_f$'s. The discrepancies may be attributed to plastic flow in the matrix and to "damage" which accumulates at the higher strains. This damage may be debonding and/or matrix cracking both of which reduce the stiffness of the material.

Reference to Table 4.1.3 shows that for the G, H, J and K materials, the coupled samples possess the higher $\tau$ values which is as expected when the mechanical properties are considered. This trend
is not followed by the L and N pair however which have similar
τ values despite the absence of silane on the L fibre (again, this
is a reflection of the mechanical properties).

Fig. 4.1.28 gives experimental and theoretical stress-strain
curves for each coupled/uncoupled fibre pair. It is apparent that
the correlation is excellent at lower strains but the plots diverge
at higher strains as previously noted.

Fig. 4.1.29 shows the effect of varying τ and C on the calculated
stress-strain curve compared to an experimental fibre K curve (K data
used for C, τ calculation). It is evident that, while considerable
variation is possible, the shape of the final part of the experimental
curve cannot be accurately modelled. The high failure strain of the
K material is atypical and thus the comparison represents an extreme
case, nevertheless it is useful in highlighting the inaccuracies of
this model.

An attempt was made to estimate τ and C values for the boiled
series 5 samples, since no length distribution data was available
for these mouldings the series 4 values were used. Consideration
of the mechanical properties of the boiled samples indicates a very
large decrease in bond strength for the uncoupled materials and a
significant reduction for the coupled materials. The results,
presented in Table 4.1.8, show this to be the case. The extremely
low C values however indicate erroneous results since previous
figures have not been less than 0.5 irrespective of fibre length, and,
the boiling operation can in no way effect the fibre orientation.
Calculations using series 4, C values, showed no correlation with
τ whatsoever and it must be assumed that the equations cannot ade-
quately predict all types of behaviour.
Table 4.1.8

Interfacial shear strength, $\tau$, and orientation parameter, $C$, for boiled samples

<table>
<thead>
<tr>
<th>Material Code*</th>
<th>Interfacial Shear strength $\tau$ (MPa)</th>
<th>Orientation Parameter $C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>16.0</td>
<td>0.28</td>
</tr>
<tr>
<td>G</td>
<td>5.0</td>
<td>0.28</td>
</tr>
<tr>
<td>H</td>
<td>35.0</td>
<td>0.23</td>
</tr>
<tr>
<td>J</td>
<td>3.5</td>
<td>0.38</td>
</tr>
<tr>
<td>K</td>
<td>26.0</td>
<td>0.34</td>
</tr>
<tr>
<td>L</td>
<td>4.6</td>
<td>0.39</td>
</tr>
<tr>
<td>M</td>
<td>30.0</td>
<td>0.30</td>
</tr>
<tr>
<td>N</td>
<td>25.0</td>
<td>0.33</td>
</tr>
</tbody>
</table>

*All samples $0.25\ V_f$. 
The maximum calculated $\tau$ value for all samples was 48 MPa, this compares with a measured matrix shear strength of 50 MPa and thus indicates that failure should occur by debonding at the weaker interface.

4.2 Characterisation of Materials

4.2.1 Fibre Length Distribution

In order to conduct a visual comparison of fibre lengths in the mouldings, photomicrographs of fibres released from tensile specimens were examined. Full length distributions were determined on selected samples from each batch moulded to assess the effect on the degree of fibre attrition of moulder back pressure, different sizing compounds and fibre diameter. A typical photomicrograph, from which measurements were taken, is shown in Fig. 4.2.1.

The measured fibre lengths were classified into log intervals of 0.2 and, from these figures, plots of fraction of fibres versus log length $L$, or, cumulative fraction of fibres exceeding length $L$ versus log length $L$ were made. The latter format was the most convenient since the average fibre length, $\bar{L}$, could be taken as the length that half the fibres exceeded (50% on the cumulative scale). Random scatter of the mean value determined on samples taken from the same specimens was in the region of 5-10%, a similar value being obtained from specimens in the same moulding run. The injection moulding process was shown to reduce average fibre lengths by over an order of magnitude although a wide range of lengths was found in the mouldings. The effect of back pressure on the length distribution of a $0.38 V_f$ specimen (Fibre F) is illustrated in Fig. 4.2.2, from which it is apparent that increased back pressure has a pronounced detrimental effect on fibre length. Average fibre lengths for other volume fractions of
fibre F have been given in Table 4.1.1.

To ascertain the extent of fibre fracture during testing, length distribution analyses were conducted on each of two samples cut from tested specimens, one from the gauge length adjacent to the fracture region and the other from an unstrained region in the grip portion. The differences between the two distributions for the strained and unstrained material were minor and within the previously mentioned 5-10% scatter range. Thus, it is evident that gross fibre fracture is not a contributory factor in the failure process. Distributions obtained from heat cleaned specimens however, indicated that significant fibre fracture had occurred prior to failure, the average lengths being 0.32 mm in the grip portion and only 0.17 mm in the gauge portion surrounding the fracture path. (Fig. 4.2.3.) It is apparent therefore that the failure mode of the heat cleaned fibre filled samples was different, due to the reduced fibre strength. It should be noted here that the effectiveness of the length analysis method used is demonstrated by the fact that these differences in the length distributions of the heat cleaned fibres were shown. Reference to Table 4.1.2. shows that the average lengths of the heat cleaned specimens at all volume fractions were low, despite the fact that only medium back pressures were used, thus supporting the assumption of reduced fibre strength.

Full length distribution analyses for the large tensile specimens were conducted on the 0.25 $V_f$ samples only, except in the case of fibre F where 0.1 and 0.3 $V_f$ samples were examined. (Series 4 mouldings). The cumulative plots obtained for fibres L, M, N and F are given in Figs. 4.2.4-5, and for fibres G, H, J and K in Fig. 4.2.6. It is seen that in the case of fibres G, H, J, K, the distributions are wider for larger diameters and for silaned fibres. The converse
is true for fibres L, M and N where the unsilaned smaller diameter fibre L has the wider distribution. Examination of Fig. 4.2.4., shows that the 0.3 $V_f$ material has the narrower distribution which is in agreement with previous observations on the smaller specimens.

Average fibre length values for the series 4 specimens have been presented in Table 4.1.3 and it is evident from a comparison with the series 2 results (Table 4.1.2) that they are generally shorter. This is attributed to the extended melt plasticization times required for the larger tensile specimens, owing to their increased shot weights. The only indication of volume fraction effects is given by the F material which shows a large decrease in $L$ with increasing $V_f$, this is consistent with the series 1 and 2 results, the actual values falling between the two, which is again attributed to extended melt plasticization times.

It is seen from Table 4.1.3 that in the case of materials G, H, J and K; longer fibres are retained by the coupled materials and that the average fibre lengths of the large diameter fibres are considerably greater. The converse is however true for materials L, M and N.

During the moulding operation, the fibres are reduced in length principally by the bending and shearing action of the polymer melt. If we assume the worst possible case, that of a fibre constrained at one point so that the melt is forced to flow perpendicularly round it (Parratt, ref. 4). The load per unit area on the fibre surface is taken as the yield stress of the polymer melt, $\sigma_{my}$. Then if the fibre is treated as a cantilever in bending:
Maximum bending = 16 \sigma_{my} \left( \frac{L}{d} \right)^2 (4.2.1)

At fibre fracture, the maximum bending stress will equal the fibre strength. If two fibres of different diameters \textit{a} and \textit{b} are considered, then the maximum bending stress will be equal:

\[
\frac{16 \sigma_{my}}{\pi} \left( \frac{L_a}{d_a} \right)^2 = \frac{16 \sigma_{my}}{\pi} \left( \frac{L_b}{d_b} \right)^2
\]

Therefore \[
\frac{L_a}{d_a} = \frac{L_b}{d_b}
\]

Thus, the equations predict that the resultant aspect ratios will be equal. Reference to the average aspect ratios given in Table 4.2.1 shows that, experimentally, this is virtually the case. In addition, since the viscosity and therefore the yield stress of the melt increases with fibre content the resulting fibre aspect ratio will be reduced according to equation 4.2.1. Thus increasing \textit{V}_f will result in a shorter fibre length as experimentally observed.

4.2.2 Fibre diameter distributions

The diameters of the fibres used in this investigation were nominally 10, 12, 13 and 16 microns. However, during examination of fracture surfaces it was observed that the actual diameters appeared to vary quite considerably. The extent of these variations was assessed by measurement of individual filament diameters from photomicrographs of two or three strands extracted at random from each batch of glass. The results should therefore be considered as typical values rather than overall averages. A typical photomicrograph is shown in Fig. 4.2.7 and the diameter distribution curves for each
fibre type are shown in Fig. 4.2.8, as plots of cumulative probability versus fibre diameter. Average filament diameters (arithmetic means of all measurements) are given in Table 4.2.1. and it is apparent that, in most cases, these differ significantly from the manufacturers quoted values. In all cases the silaned fibres appeared to have a larger average diameter $d$, than their unsilaned counterparts, the difference being $\pm 0.5\mu m$, which is certainly too large to be accounted for by the silane component of the size alone. An indication of the extent of the diameter variations is given by values for the coefficient of variation in Table 4.2.1, and it is seen that these are generally in excess of 10%. From the distribution curves (Fig. 4.2.8) it is evident that, with the exception of fibres K and M, the distributions are not significantly biased either way. In addition fibres K and M have the widest distributions, the difference between their respective maximum and minimum values being 9.2 and 8.4 microns.

The importance of fibre diameter is principally reflected in the surface area available for sizing compound application. For example a 10\mu m diameter fibre has a 60% greater surface area than a 16\mu m diameter fibre and would therefore be expected to reinforce more effectively over the same length. It is therefore evident that, when comparing the reinforcing potential of a number of different diameter fibres, a critical aspect ratio is a more meaningful concept than critical fibre length. A fibre strength dependent critical aspect ratio for a fibre aligned along the principal stress axis is given by:

$$ R_c = \frac{\sigma_f}{2\tau} \quad (4.2.2) $$

clearly $R_c$ will be smaller for higher values of the interface strength $\tau$.

The reinforcement efficiency of aligned short fibres compared to that of continuous fibres is 0.5 at $R_c$ rising to 0.9 at $5R_c$ and 0.95 at $10R_c$. It is therefore desirable that the average fibre aspect ratio in the
### Table 4.2.1
Fibre Diameter and Aspect Ratios for Series 4 Test-pieces

<table>
<thead>
<tr>
<th>Material Code</th>
<th>Nominal Fibre diameter (µm)</th>
<th>Average fibre diameter $\bar{d}$ (µm)</th>
<th>$C_V$ (%)</th>
<th>Average Aspect Ratio $\bar{R}$</th>
<th>Calculated Critical Aspect Ratio $R_c$ **</th>
<th>Proportion of Fibres $&gt;R_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>13</td>
<td>12.8</td>
<td>7</td>
<td>21</td>
<td>22</td>
<td>49</td>
</tr>
<tr>
<td>G</td>
<td>12</td>
<td>9.49</td>
<td>15</td>
<td>25</td>
<td>30</td>
<td>38</td>
</tr>
<tr>
<td>H</td>
<td>12</td>
<td>10.0</td>
<td>11</td>
<td>26</td>
<td>24</td>
<td>57</td>
</tr>
<tr>
<td>J</td>
<td>16</td>
<td>14.1</td>
<td>8</td>
<td>25</td>
<td>30</td>
<td>35</td>
</tr>
<tr>
<td>K</td>
<td>16</td>
<td>14.7</td>
<td>10</td>
<td>25</td>
<td>26</td>
<td>47</td>
</tr>
<tr>
<td>L</td>
<td>10</td>
<td>10.4</td>
<td>11</td>
<td>31</td>
<td>26</td>
<td>58</td>
</tr>
<tr>
<td>M</td>
<td>13</td>
<td>12.1</td>
<td>13</td>
<td>22</td>
<td>23</td>
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<td>N</td>
<td>10</td>
<td>10.9</td>
<td>13</td>
<td>25</td>
<td>26</td>
<td>45</td>
</tr>
</tbody>
</table>

* $C_V$ Coefficient of variation for diameter measurements

** $R_c = \sigma_f/2\tau$

*** F values from 0.3 $V_f$ testpieces, all others from 0.25 $V_f$
moulding should be as high as possible and since the actual aspect
to control this is best approached by ensuring that
portion of fibres which exceed that
to be noted that $R$ is reasonably close to $R_c$ and that
the fibre lengths were reduced in the
more of smaller
diameter fibres.

2.3 Constitution of the sizing components

Size loading.

The size loadings on each fibre type, as determined by a burn off
percentage weight loss and temperature obtained from the micro
thermal balance is shown in Fig. 4.2.9. It is apparent from the
results that fibre F has the heaviest application of size, this
being consistent with the very stiff nature of the F rovings. The
loadings on the remaining fibre types fell within a narrow band of
0.67 to 0.81% ww. The exception was fibre G which showed a 0.9%
weight loss which is surprising when the soft pliable nature of the
rovings is considered, since this would normally indicate a low sizing
level. A direct comparison between all fibre types would be misleading because of the variation of surface area with fibre diameter, an indication of which is also given in Table 4.2.2. As a result of the much larger surface area of the small diameter fibres it might be expected that their weight losses would be relatively larger. This is obviously not the case (Table 4.2.2) and can probably be attributed to the use of lower size levels to preserve the bulk density of the rovings. Comparison of similar diameter fibres shows that; in the case of fibres G, H, J and K, the unsilaned fibres have the greater size loadings, whilst the converse is true for fibres L, M, and N (different manufacturer and sizing system). The reasons for these discrepancies are however not known but, it has been reported (99), that whilst heat cleaning is an effective method of removing the organic components of the size, a small residue of inorganic material from the silane coupling agent remains on the fibre surface. It is possible therefore that this might account for the larger weight losses of the unsilaned fibres G and J.

In this investigation no attempt has been made to measure the thickness of the fibre coating, however by simple calculations it is possible to obtain a rough estimate from the magnitude of the weight loss during heating.

If the following figures are assumed:

Fibre diameter \( d = 16 \times 10^{-6} \) m  
Fibre length \( L = 5 \times 10^{-3} \) m  
E glass density \( \rho_f = 2.55 \times 10^3 \) Kg m\(^{-3}\) (since no figures for the actual size density are available the density of polyurethane has been used)

Fibre volume \( V = \pi r^2 L = 1.0053 \times 10^{-12} \) m\(^3\)
Fibre mass \( M_f = \rho_f V = 2.5635 \times 10^{-9} \) Kg
Now if weight loss = 0.8% then the fibre mass $M_f$ constitutes 99.2% of the total fibre/size combination, mass $M_{fs}$

$$M_{fs} = 2.5842 \times 10^{-9} \text{ Kg}$$

Mass of size $M_s = 0.02067 \times 10^{-9} \text{ Kg}$

Vol. of size $V_s = M_s/\rho_s = 1.8791 \times 10^{-14} \text{ m}^3$

Vol. of size $V_s = \pi L (r_{fs}^2 - r_f^2)$ where $r_{fs} = \text{fibre & size radius}$

$r_f = \text{fibre radius}$

$$r_{fs} = 8.07442 \times 10^{-6} \text{ m}$$

thickness of size $= r_{fs} - r_f = 744.2 \AA$

This figure is of the same order as reported average size thicknesses of 700 Å (65).

Table 4.2.2

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Weight loss %</th>
<th>Surface area of fibres $m^2 g^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0.76</td>
<td>0.12</td>
</tr>
<tr>
<td>F</td>
<td>1.00</td>
<td>0.12</td>
</tr>
<tr>
<td>G</td>
<td>0.90</td>
<td>0.13</td>
</tr>
<tr>
<td>H</td>
<td>0.68</td>
<td>0.13</td>
</tr>
<tr>
<td>J</td>
<td>0.81</td>
<td>0.1</td>
</tr>
<tr>
<td>K</td>
<td>0.79</td>
<td>0.1</td>
</tr>
<tr>
<td>L</td>
<td>0.67</td>
<td>0.16</td>
</tr>
<tr>
<td>M</td>
<td>0.79</td>
<td>0.12</td>
</tr>
<tr>
<td>N</td>
<td>0.73</td>
<td>0.16</td>
</tr>
</tbody>
</table>
Fibre Surface Examination.

Fibres selected at random from each roving type were examined in order to determine the fibre surface topography. Typical photomicrographs are shown in Fig. 4.2.10 (i-ix). In all cases the coating appears to be continuous but excess size is present in the form of isolated islands and areas of preferential deposition in the capillaries between the fibres. This is the reason for the experimentally determined size loadings being more than an order of magnitude greater than the 0.02-0.04% required for the theoretically desirable monomolecular layer. Comparing the fibres, little difference is apparent between types P, F, L, M and N despite the use of very different sizing compounds. Fibre P does not exhibit, in the example given, the longitudinal ridges of size that result from broken capillary buildups, these were however observed during examination of the fibres but not to such a great extent as the other fibre types. Considering the remaining fibre types, which were from a different manufacturer, the size appears more ductile and this would account for the softer 'feel' of the fibre rovings. The unsilaned fibres G and J have a smooth finish interrupted in places by agglomerations of size resulting from fracture of the preferential capillary buildup, their ductile appearances however contrasts with the brittle looking irregularities on the surfaces of the other fibre types. The fibres J and K, while preserving the characteristic ductile or softer size appearance have a considerably rougher general surface topography which can only be attributed to the presence of the silane coupling agent. If the roughness is preserved through compounding it will obviously be a contributory factor to the higher observed failure stresses of the silaned fibres by increasing the fibre matrix frictional forces. This is probably not the case however, since the thermoplastic coating will melt during compounding and disperse in the matrix material.
Also shown in Fig. 4.2.10(ix) are heat cleaned type H fibres and it is evident that size removal, whilst being extensive, is incomplete, since ridges of size are still discernable on the surfaces.

It is apparent from these results that electron microscopy provides little quantitative information concerning size formulation and thickness and thus serves only to enable a general comparison of the fibres to be made.

Size Analysis by ESCA.

Results obtained from the mechanical testing of 'dry' specimens revealed that there was little difference between the properties of composites filled with fibre L and those incorporating fibres M and N despite the manufacturers assurance that the L size contained no coupling agent. An analysis of the size components was therefore conducted using ESCA (Electron Spectroscopy for Chemical Analysis) in an attempt to determine the presence of silane in the size. The results obtained for each fibre type are presented in Table 4.2.3 and a typical plot of percentage intensity versus binding energy is given in Fig. 4.2.11. It can be assumed that the analysis accurately reflects the true constitution of the size and is not influenced by the presence of the glass fibres themselves since the estimated electron escape depth of \( \approx 20\text{\textmu A} \) is more than an order of magnitude less than the estimated size thickness (\( \approx 700\text{\textmu A} \)). This assumption is supported by the work of Wong (131) who examined E and S-Glass fibres by Auger spectroscopy and observed that the surface compositions were very different from the bulk glass compositions. Comparison of Wongs results (Table 4.2.4) with the experimental results shows no correlation, the atomic percentages of oxygen and silicon being much greater for the former, while Mg, Al, F and B are absent from the latter.
The high carbon levels observed are a result of airborne contamination in the system and are seen even on 'clean' surfaces. The presence of calcium in this type of analysis is usually attributed to the use of impure water at some stage in the samples history, in this case it may result from the aqueous size application stage.

It is apparent from the results that silicon is present in all of the coatings but that the level is higher for the silaned materials, as would be expected. This is true for the L and N materials which tends to indicate that the former was indeed unsilaned as specified. The reason for the presence of silicon in the unsilaned coatings is not known but it is improbable that the glass surface is the source. The results, in the form of bar charts are given in Fig. 4.2.12, and from these it is apparent that an increase in silicon content is accompanied by a corresponding increase in the oxygen content, this is attributed to the presence of a silane. Examination of the deconvoluted silicon peak (from Fig. 4.2.11) which is shown in Fig. 4.2.13, reveals that the Si-O component is approximately three times the intensity of the Si-C component, thus, there are three Si-O bonds to each Si-C bond (as intensity is related to the number of atoms present). This is expected if the silane formula, \([\text{H}_2\text{N(CH}_2\text{)}_3\text{Si(OC}_2\text{H}_5\text{)}_3]\), is examined since each silicon atom is bonded to one carbon and three oxygen atoms. It is highly probable therefore that the silicon present originates from the silane coupling agent component of the size.

It is known that the silane employed on fibres H and K is a Union Carbide A100 or its equivalent (γaminopropyltriethoxy silane) and that the film former and lubricant on fibres G, H, J and K are a polyurethane and stearic acid respectively. However, the exact formulae and percentages of those compounds is not known, it is therefore
not possible to correlate the experimental results with the size constituents in a quantitative manner. The situation is worsened when considering fibres L, M and N, since the actual compounds employed in the size are not known except that it is a "cationic polyelectrolyte epoxy derivitive" and that the silane is "similar to, but not the same as, Al100".

The results presented, while not conclusive, do give a reasonable indication as to the presence or absence of a silane coupling agent and support the data obtained from the tensile testing of the boiled samples.

**Table 4.2.3**

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>18.5</td>
</tr>
<tr>
<td>H</td>
<td>25.1</td>
</tr>
<tr>
<td>J</td>
<td>18.6</td>
</tr>
<tr>
<td>K</td>
<td>25.0</td>
</tr>
<tr>
<td>L</td>
<td>25.8</td>
</tr>
<tr>
<td>N</td>
<td>32.1</td>
</tr>
</tbody>
</table>

**Table 4.2.4**

<table>
<thead>
<tr>
<th>Composition of E Glass Fibres (After Wong)</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>Ca</td>
</tr>
<tr>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Bulk</td>
<td>4.5</td>
</tr>
<tr>
<td>Surface</td>
<td>3.4</td>
</tr>
</tbody>
</table>
4.2.4 Fibre Strength

An indication of the respective strengths of the heat cleaned fibres (HC2) and the 'as received' fibres (F) was obtained by tensile testing specimens of an epoxy resin containing unaxially aligned fibres of each type. The stress-strain relationship was linear in each case up to failure but the actual failure behaviour differed significantly. Considering the 'as received' fibre specimens, the load increased until some audible fibre fractures occurred, the specimens then failed completely with extensive splintering in the longitudinal direction. The acoustic emission showed an initial increase, which can be attributed to noise from the grips (unguarded detection system used), and then dropped away to almost zero until failure, which was accompanied by a massive increase in output. The HC2 fibre specimens failed at much lower load/strain levels and failure occurred by longitudinal splitting and transverse cracking. The acoustic emission output was similar in that an initial peak, which dropped away, preceded the massive increase associated with failure. Typical examples of failed specimens are shown in Fig. 4.2.14.

The mechanical test data is given in Table 4.2.5 along with the fibre volume fractions. Also tabulated are the respective coefficients of variation to give an indication of the results scatter. It is apparent from the comparatively low values of failure stress and failure strain of the HC2 specimens that heat cleaning has considerably degraded the fibre strength. The scatter of results is much greater for these fibres, a coefficient of variation of 28 and 24% being obtained for $\sigma_{uc}$ and $\varepsilon_{uc}$ respectively. The moduli, measured at 1.0% strain (extrapolated for HC2 specimens) were the same, which would be expected from the low strain measurements.
An indication of the strength and moduli of the fibres can be obtained by the application of a simple rule of mixture approach whereby:

\[
E_f = \frac{E_c - E_m (1-V_f)}{V_f} \quad (4.2.3)
\]

\[
\sigma_{uf} = \frac{\sigma_{uc} - \sigma_{um} (1-V_f)}{V_f} \quad (4.2.4)
\]

Where \( E, \sigma, V \) refer to Modulus, strength and volume fraction respectively and the subscripts \( f,c,m \) and \( u \) refer to fibre, composite, matrix and ultimate. Using the experimental data and assuming the matrix modulus and strength are 3.01GPa and 56MPa respectively (matrix data from ref. 132) the following results are obtained.

<table>
<thead>
<tr>
<th></th>
<th>( E_f ) (GPa)</th>
<th>( \sigma_{uf} ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibre F</td>
<td>69.1</td>
<td>1.40</td>
</tr>
<tr>
<td>Fibre HC2</td>
<td>71.2</td>
<td>0.44</td>
</tr>
</tbody>
</table>

The calculated fibre moduli are approximately equal and are in agreement with published values for E glass of around 70 GPa (5,8). The strengths however show a considerable difference, the heat cleaned fibres having \( \sqrt{\frac{1}{3}} \) the strength of the 'as received' fibres. The strengths of brittle fibres, such as glass, are highly dependent upon their lengths, diameter and handling history. Virgin, defect free fibres have strengths of \( \sqrt{3.5} \)GPa whilst values of the order of 2GPa or less are common for industrially produced fibres, the reduction being due to damage or inherent defects at the fibre surface (5,6,8,9). These figures are statistical averages and a range of fibre strengths exists in any particular composite system. Fibre fracture will occur
at the most severe flaw when stress is applied to the composite, this initial break may be accommodated by debonding or matrix flow thus permitting further increases in applied load until final composite failure is initiated by fibre fractures at less severe flaws. Alternatively, catastrophic matrix cracking may be initiated by the first fibre fracture and the composite failure stress is then determined by the weakest fibre flaw.

From the noted observations it appears that the 'as received' fibre composites fail in the former manner whilst the HC2 composites follow the latter mechanism. The low failure stresses of the 'as received' fibres compared to reported values are a result of crack initiators such as voids and misaligned fibres causing premature failure of the composite.

Table 4.2.5

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Failure Stress $\sigma_{uc}$ (MPa)</th>
<th>Coeff. of Variation $C_V$ (%)</th>
<th>Failure Strain $\varepsilon_{uc}$ (%)</th>
<th>Modulus at 1% Strain $E_c$ (GPa)</th>
<th>$C_V$ (%)</th>
<th>Volume Fraction Fibres $V_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>970</td>
<td>6</td>
<td>2.0</td>
<td>48</td>
<td>6</td>
<td>0.68</td>
</tr>
<tr>
<td>HC2</td>
<td>312</td>
<td>28</td>
<td>0.6</td>
<td>48</td>
<td>6</td>
<td>0.66</td>
</tr>
</tbody>
</table>

5 Fibre Orientation Distribution

The degree of fibre alignment is important in determining the mechanical properties. Aligned fibres result in maximum stiffness and strength in the alignment direction with minimum properties normal to this direction, i.e. the greatest degree of anisotropy. At the opposite end of the scale a fully random orientation gives an isotropic material with a stiffness of about an order of magnitude less than the aligned material. Fibre filled thermoplastics generally show a pronounced fibre orientation in the flow direction and are therefore markedly anisotropic.
The fibre distribution is however, very complex, often consisting of a laminate type structure with a random skin layer, flow aligned intermediate layers and a transversely oriented central layer.

A partial quantitative assessment of the fibre orientation distribution was conducted on a single specimen only, in order to check the calculated orientation constants (Sect. 4.1.3). The photomicrographs from which measurements were made are shown in Fig. 4.2.15, this is of the area adjacent to the fracture surface, ~0.6mm below the specimen surface i.e. in the flow aligned layer. The orientation distribution is shown graphically in Fig. 4.2.16 and it is apparent that approximately 80% of the fibres lie within 25° of the injection direction. An orientation coefficient, \( C_m \), was calculated using an equation proposed by Krenchel (97) which is of the form:

\[
C_m = \sum_{1}^{n} a_k \cos^{4} \theta_k
\]  

(4.2.5)

Where \( a_k \) is the fibre fraction at the orientation angle \( \theta_k \) to a reference axis (the injection direction) and \( n \) is the number of angle intervals into which the fibre orientation distribution is divided. The calculated coefficient, \( C_m \), was 0.84 which is high compared to predicted values of 0.55-0.65 (sect. 4.1.3), but it must be remembered that this value accounts for only one part of the flow aligned layer and does not consider the misoriented skin and core 'layers', whereas the predicted values are averages for the whole specimen.

6.6 Differential Scanning Calorimetry (D.S.C)

A DSC investigation was conducted to determine any physical or chemical differences that existed between the mouldings since it was noted that distinct colour variations were apparent with a change of fibre type. The matrix material, nylon 6, was a natural unpigmented
grade and thus white in colour. Reinforcement with fibres G, H and J retained the whiteness at low fibre fractions but a slight 'greying' was apparent at increased fibre loadings. This discolouration was more evident with the fibre K material despite its similar origin and processing conditions. Fibres F, P, L, M and N however, caused a distinct yellow colouration which was more pronounced at higher fibre fractions especially in the F materials.

The discolouration is attributed to the different sizing systems employed by the manufacturers which may react differently at the interface and with the bulk polymer. Assuming the fibres are coated with 1% of a sizing material, then in a typical composite containing 50% by weight \( (0.3V_f) \) of reinforcement, the size will constitute approximately 1.0% of the matrix. During compounding the polymeric coatings will melt, or even degrade if the temperature is sufficiently high, and be dispersed throughout the molten matrix with possible adverse effects on its properties. For example, a polyvinyl acetate film former is known to degrade at 250°C and generate acetic acid which produces chain scission of the polyamide at the elevated temperatures used during compounding. The resulting reduction in molecular weight will be reflected in the crystallinity and mechanical properties of the polymer.

The DSC scans enabled information on the nature and degree of crystallisation of the unfilled Nylon and composites to be obtained. All of the traces were linear until just prior to melting when a small positive crystallisation peak marking additional crystallisation was observed. This was followed by a much larger negative peak due to the polymer melting. Unfilled polymer samples showed a single melting peak whilst the filled materials exhibited multiple peaks, typical examples of thermograms obtained are shown in Fig. 4.2.17. The presence of multiple peaks indicates that some form of degradation process such
as chain scission had occurred, resulting in distinct polymer forms with different melting points. Reference to Table 4.2.6 reveals that, in all cases, the melting points, $T_m$, were approximately $224^\circ C$, the curves for the composites being extrapolated to obtain a single value.

The enthalpy of crystallisation was measured by determining the melt and crystallisation peak areas, subtracting them and converting this area to a $\Delta H$ from knowledge of the machine calibration, characteristics and sample weights. In each case the mass of the polymer was used, the fibre mass being subtracted from the total. The equation given (4.2-6) was used, where $A$ was the peak area, $M_p$ the polymer mass, $B$ the chart setting divided by the heating rate, $E$ the cell calibration coefficient and $A_{qs}$ the $Y$ axis range.

$$\Delta H_x\text{ (cal/g)} = \frac{A}{M_p} \left[ \frac{60 BE A_{qs}}{} \right]$$ \hspace{1cm} (4.2-6)

The $\Delta H$ for a 100% crystalline polyamide 6 is approximately 45 cal/g (34) thus division of calculated values, $\Delta H_x$, by this figure allowed percentage degrees of crystallisation to be determined. These are presented for the materials examined in Table 4.2.6. It is apparent that, with the exception for material H, the filled materials possess higher degrees of crystallinity and that materials K and L are the highest. The general effect of increasing the degree of crystallinity on the mechanical properties of unfilled polymers is that; modulus and yield stress increase and elongation to yield and to fracture decrease (14). The presence of fibres will obviously complicate this and, it is apparent from comparison of the mechanical properties (Table 4.1.4) with the percentage crystallinities that no consistent pattern emerges.

Thus, from the results obtained, it can be assumed that variations in the matrix resulting from the presence of dispersed sizing compounds
are not a significant contributory factor in the observed composite property variations. However, it should be noted that it has been shown (65) that reaction with PVAc and cationic sizes can cause embrittlement of the polymer although such an effect is not evident in this investigation.

Table 4.2.6

Differential Scanning Calorimetry Data

<table>
<thead>
<tr>
<th>Sample*</th>
<th>Melting Point $T_m$ (°C)</th>
<th>Enthalpy of Crystallisation $\Delta H_x$ (cal g$^{-1}$)</th>
<th>Crystallinity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfilled</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P.A.6</td>
<td>223.5</td>
<td>21.0</td>
<td>46.7</td>
</tr>
<tr>
<td>G</td>
<td>224</td>
<td>23.2</td>
<td>51.5</td>
</tr>
<tr>
<td>H</td>
<td>224</td>
<td>18.8</td>
<td>41.7</td>
</tr>
<tr>
<td>J</td>
<td>224</td>
<td>20.8</td>
<td>47.0</td>
</tr>
<tr>
<td>K</td>
<td>224</td>
<td>24.0</td>
<td>53.4</td>
</tr>
<tr>
<td>L</td>
<td>224</td>
<td>23.9</td>
<td>53.2</td>
</tr>
<tr>
<td>M</td>
<td>224</td>
<td>22.8</td>
<td>50.7</td>
</tr>
<tr>
<td>F</td>
<td>223.5</td>
<td>22.5</td>
<td>49.9</td>
</tr>
</tbody>
</table>

*All filled samples are 0.1V$^*_f$ with the exception of material L which is 0.17V$^*_f$. 
4.3 Microscopy and Fractography

3.1 Optical Microscopy

Examination of polished sections of tensile specimens under the optical microscope revealed useful information concerning; the fibre orientation, the strength of the interfacial bond and the mechanisms operating during failure. The positioning of the sections examined and the terminology used to describe them in the text is illustrated schematically in Fig. 4.3.1.

It will be apparent from the photomicrographs shown, that there is little contrast between the glass fibres and the nylon matrix, this being due to the relatively high percentage of light transmitted by both materials. This effect is advantageous when samples are viewed in the transmission mode since microstructural damage such as fibre debonds show up as dark lines around the fibres due to the inability of the failed interface to transmit as much light. In addition, in the reflection mode, debonded fibres at or near the polished surface are highlighted by bright white lines since the incident light is internally reflected by the fibres. The lack of contrast is disadvantageous in that it is often difficult to distinguish fibres from the matrix and also it is not possible to see clearly small scale damage effects such as fibre fractures. It was however noted during specimen preparation that washing the freshly polished surface with acetone etched the nylon matrix slightly while not affecting the glass fibres, the contrast was thus enhanced.

Fibre Orientation

In the specimens examined the variation of fibre alignment was analogous to a laminated structure. The individual 'laminae' comprised; a thin skin of random in-plane orientation resulting from chilling of the molten charge by the cold mould surface, thick intermediate layers
of highly axially aligned fibres, and a central or core region of fibres with a pronounced transverse bias. (Fig. 4.3.2) This multilayer structure was apparent in all the sections examined, however, it was noted that the axial alignment improved with increasing fibre length and fibre volume fraction and also that the misaligned core region was not as pronounced in the smaller tensile specimens.

The highly uniform fibre distribution achieved in the mouldings is illustrated in Fig. 4.3.3 for different volume fractions of fibres, from this it is also apparent that a \( V_f \) of 0.38 is approaching the maximum quantity of fibres that can be incorporated if their separation is to be maintained. The influence of fibre orientation on the fracture behaviour is indicated in Fig. 4.3.4 which shows that the fracture path tends to follow the fibre alignment of the core region.

**Matrix cracking and fibre fracture.**

The incidence of matrix cracking was not extensive and, if observed at all, was confined to regions adjacent to the fracture path. An example of typical matrix cracking is given in Fig. 4.3.5 the sample being viewed under both reflected and transmitted light. The crack formation results from one or two probable mechanisms. Either; a number of fibres have debonded due to the applied stress and have subsequently been linked by matrix cracks or alternatively, a propagating matrix crack has been successively blunted by debonding at the fibre-matrix interface. The latter is most likely since the crack appears to originate at the specimen fracture surface and little other major debonding is apparent. It should be noted here that, in Fig. 4.3.5 b, a considerable number of debonded fibre ends are visible (isolated black lines), the importance of these will be discussed later.
Major matrix cracking was observed on only a few isolated occasions in low $V_f$ specimens, although such behaviour is atypical. Close examination serves to illustrate some interesting points about the fracture mechanisms encountered in composite materials. An example of extensive matrix cracking is given in Fig. 4.3.6, this is considered to be a result of the failure process rather than the cause, since no progressive crack growth was observed during testing. The specimens failed in a brittle manner and it appears that the rapid propagation of the final fracture was impeded and diverted, by the presence of the fibres. Fig. 4.3.6b, shows the same area viewed under transmission and, clearly visible either side of the cracks, are debonded fibres and sockets left by fibres in the process of pulling out. Higher magnification micrographs of an area of cracking enables a closer examination of these phenomena to be conducted Fig. 4.3.7. It is apparent that the socket length is of the same order as the crack width and, despite the massive nature of the crack, only two fibre fractures are readily seen (Marked $F_1$ and $F_2$).

In most cases, as would be expected, the shape of the sockets conforms to that of the ends of the pulling out fibres (Fig. 4.3.7, $S_3-S_6$). This is not the case for those sockets designated $SM_1$ and $SM_2$ which have rounded ends, this is attributed to infiltration of the mounting resin during specimen preparation, the 'negative meniscus' shape resulting from resin shrinkage during curing. Since the crack dimensions are insufficient to allow such long pullouts it must be assumed that the fibres were partially pulled out at the fracture surface. Examination of Fig. 4.3.8. confirms this assumption, the fibres being 0.8 and 0.9mm long respectively. If 0.9mm is taken as the semi-critical fibre length (see literature), then knowledge of the fibre strength and dimensions and using equation (2.2.21) enables a value for the bond strength $\tau$, to be estimated. A result of 15 MPa is obtained, which is very low when compared to
previously calculated values (Sect. 4.1.3).

None of the materials examined exhibited fibre fractures to any significant extent, both surface and subsurface fibres being considered. In addition, for the isolated surface fractures observed it was generally not possible to distinguish between stress damage and specimen preparation damage as the cause. An exception to this observation is visible in Fig. 4.3.7a (F1) where it appears that the advancing crack has fractured the fibre.

When a matrix crack intercepts a fibre its behaviour is primarily dependent on the strength of the interfacial bond. In strongly bonded systems, fibre fracture will generally occur with little associated debonding. If the interfacial bond is weak, the crack will be blunted by debonding at the interface, as the crack opens the fibre debonds more until either the end is reached, the fibre failure strain is attained, or the fibre fractures at a flaw. If the fibre end is within a semi-critical length of the crack plane and no flaws are present, the fibre will gradually pull out leaving a socket in the matrix. The latter mechanism is apparently operative in the systems under investigation (Figs. 4.3.6-8), the actual behaviour is however not so simple. Reference to Fig. 4.3.9 shows clearly that matrix cracks usually propagate around the fibres without fracturing them. Rather than initially blunting the cracks by debonding, the fibres appear to arrest the cracks which are then temporarily diverted either side of the fibres, eventually intercepting and progressively debonding or possibly fracturing the fibres as described. The crack forks may intercept on the same plane or, more likely will grow out of the original plane leaving a matrix step indicating the crack propagation direction. Such behaviour is evident in Fig. 4.3.9. and is indicated by arrows, it is also shown schematically in Fig. 4.3.10. The fibre fracture visible in Fig. 4.3.7. (F2) has obviously occurred at a fibre flaw since its distance from the crack plane is much less than the semi-critical length.
The behaviour of misaligned fibres is well illustrated by the photomicrograph in Fig. 4.3.11a (same area as 4.3.9, lower focus point) and schematically in Fig. 4.3.11b. The crack intercepts and circles the fibre in a similar manner to that described, the debonding is however most severe on the edge of the fibre bisecting the crack with the greatest angle. As the crack opens, the fibre is subjected to large bending stresses at points A and B in Fig. 4.3.11b, these are initially accommodated by matrix deformation and debonding but will eventually lead to premature fibre failure at the point of maximum stress. Thus, misaligned fibres with long pullout lengths were generally not observed during S.E.M fracture surface studies.

Inter-facial bond strength

It was observed during specimen preparation that the ease of polishing appeared to be related to the strength of the interfacial bond. The coupled materials (H,K,M,N) suffered relatively little fibre displacement or ripout during the polishing stage. Whereas, in the uncoupled materials G and J (and to a lesser extent L), a considerable number of fibres were ripped out. This effect is shown in Fig. 4.3.12 for similar planar sections of materials G and H, the cavities left by the displaced fibres being visible as black areas. Subsurface examination of the uncoupled materials revealed extensive interfacial debonding throughout the specimens (Fig. 4.3.13), unlike the coupled materials where debonding was generally confined to areas surrounding strain bands or matrix cracks. It was initially considered that the debonding and associated ripout was, induced by the straining; subsequent examination of untested specimens however, showed that they behaved similarly, in that considerable ripout occurred during polishing. Fig. 4.3.14. Further examination of the uncoupled samples in the transmission mode revealed significant fibre debonding prior to testing.
although this was generally confined to the core region. (Fig. 4.3.15)

Such pre-test damage is considered due to thermal stresses induced on cooling the injection moulded samples, which are of sufficient magnitude to debond the uncoupled but not the coupled materials. This is obviously a contributory factor in the observed lower failure strains of the uncoupled materials and will be discussed later.

Strain Bands

Microscopical examination of the strain banding phenomena observed during tensile testing showed that the bands consisted of regions of intensely debonded fibres, the surrounding areas having suffered little damage apart from debonded fibre ends. There was an absence of matrix cracking within the bands, despite the extensive debonding, and the bands themselves appeared to be confined to the misaligned core regions of the samples. Detailed examination was best performed in the transmission mode. However, if the sample thickness was too great to allow sufficient light passage, other modes of illumination such as polarised light and dark field proved informative despite their relatively limited depth of penetration. Fig. 4.3.16 shows strain bands viewed in the dark field mode in which the debonding can clearly be seen, these are visible as bright areas against a dark background since the failed interface reflects the incident light. The planar section is approximately half way through the specimen in the misaligned core region as can be seen from the reflection micrograph. The transverse section shows the whole thickness of the sample and it is apparent that the damage is located principally in the core region.

It was noted during examination of the polished surfaces using reflected light that polishing damage was often confined to
certain areas (coupled materials only), subsequent subsurface examination of such areas revealed they were sites of strain banding. Fig. 4.3.17. In addition, the matrix was occasionally preferentially removed in these areas resulting in a 'relief' effect, the fibres standing proud from the surface. These facts thus indicate that some form of matrix damage, probably ductile flow, had occurred in conjunction with the observed debonding.

Fig. 4.3.18 shows a strain banded area under reflection and transmission, the bands being visible as areas of shadow in the latter. An interesting point to note is the fibre fracture in photomicrograph b at the point where two fibres cross over, the unfractured fibre being bent. In addition, a large number of isolated debonded and partially pulled out fibres are visible with no associated matrix cracking, if the sample were loaded further these would coalesce to form well defined bands such as in Fig. 4.3.17. A further example of the isolated nature of the debonding is given in Fig. 4.3.19, the debonds are situated in a band and the surrounding area is virtually damage free. The low magnification (and hence greater depth of field) photomicrograph given in Fig. 4.3.20 shows the well defined nature of the bands in a thicker section and this should be compared with the bands in the failed samples of Fig. 4.1.18.

Fig. 4.3.21 gives a series of photomicrographs which are considered to be of a strain banded area in an advanced stage since the matrix appears to have torn apart in a ductile fashion rather than cracked. Debonded fibres just below the surface are clearly visible in both the polarised and dark field modes.

In-situ tensile testing

In order to examine closely the order of events leading to failure, particularly strain banding, on a microscopic scale; a
number of specially prepared specimens were strained in-situ under the microscope. Both coupled and uncoupled materials were tested and significantly different behaviours observed.

The coupled specimens showed very little debonding prior to straining and, on application of the load, the order of events was as follows: Fibre ends debonded initially, this occurred rapidly with whole ends debonding instantaneously. Debonding next occurred at fibre crossover points. On increasing the applied load the debonds progressed along particular fibres thus reducing their reinforcing capability. Excess load was therefore transferred to surrounding fibres causing them in turn to debond, resulting in localised areas of deformation or 'bands' of debonded fibres. Final failure occurred through one of the most severe bands with the debonded fibres being pulled out at the fracture surface. This behaviour is shown by the series of photomicrographs in Fig. 4.3.22 which are of a coupled fibre H material (0.1 V_f). The area shown is to the right of the main band through which the sample failed, the formation process of the bands is however clearly illustrated by the minor band in photomicrographs (iv-viii). Photomicrograph (ix) is of the failed sample and some of the debonds have apparently disappeared while some have shrunk in size, the former is due to oil (see Chapter 3) seeping down the interfaces and the latter is due to specimen relaxation on failure. The whole failed sample is shown in photomicrograph (x) in which the strain bands are clearly visible.

The uncoupled fibre material exhibited relatively extensive interfacial debonding prior to testing as previously observed. On application of the load, the existing debonds progressed rapidly along the fibres with other fibres also debonding. The behaviour contrasted with the coupled materials in that debonding did not generally initiate at fibre ends, being principally observed in transversely oriented fibres. The debonding appeared to be more
extensive than in the coupled materials and additionally was not so localised, i.e., the banding effect was not so pronounced. This behaviour is illustrated in Fig. 4.3.23.

To summarise briefly. In the large number of specimens examined, the incidence of matrix cracking was small and generally confined to areas surrounding the fracture plane. Extensive cracking was observed in a few low $V_f$ samples but this is considered to be a result of, rather than a cause of the failure. Fibre fractures were rarely seen and were often difficult to distinguish from polishing damage. Strain bands appear to consist of areas of debonded fibres in the absence of matrix cracks, the debonds initiating at points of high stress concentration such as fibre ends or cross-over points. A volume fraction effect was noted in that the debonding appeared to be most severe in lower $V_f$'s which is attributed to the higher strains involved. The coupled and uncoupled materials behaved differently, the latter exhibiting a significant degree of debonding prior to testing and relatively more dispersed bonding on post test examination. In addition, the extent of fibre rip-out during polishing was greater in the uncoupled materials. Thus, an appreciably lower bond strength is indicated for the uncoupled materials, this applying to materials G and J specifically since material L exhibited an intermediate behaviour.

4.3.2 Scanning Electron Microscopy

Using this technique the fracture surfaces of all types of specimen were examined. It was noted that the fracture path tended to be more irregular at higher $V_f$'s and that this effect was more noticeable in the large tensile specimens.
The nylon matrix demonstrated a predominantly brittle behaviour with extensive fibre pullout and little fibre fracture evident in the crack plane. Despite the general brittle appearance however, the majority of samples exhibited regions of ductile matrix flow. Such regions were exclusively confined to the misaligned core areas of the samples and were observed at all $V_f$'s. The incidence and extent of the ductile behaviour was however dependent on $V_f$, being more pronounced in the low $V_f$ samples which can be attributed to their higher failure strains. Fig. 4.3.24 depicts ductile and brittle matrix regions observed in the same specimens. The clean, misaligned fibres in the former and the aligned fibres with adhering matrix in the latter should be noted. The majority of fracture surfaces were of the general form illustrated in Fig. 4.3.25. It was observed that the ductile regions tended to be present on surfaces at an angle to the principal stress axis while the brittle matrix regions were on surfaces perpendicular to the stress axis and also in the areas of good fibre alignment surrounding the sample core. (Fig. 4.3.26.)

The condition of the pulled out fibre surfaces is generally considered indicative of the strength of the fibre matrix interfacial bond, clean fibres indicating poor bonding and 'dirty' fibres indicating a strong bond. In the samples examined however, both types of surface were seen (Fig. 4.3.24), clean in ductile regions and 'dirty' in brittle regions. A further example is given in Fig. 4.3.27 which is of a fibre L specimen. Initial examination of the fibres in the brittle area shows apparently clean fibres, but closer examination at high magnification (micrograph c) reveals that a considerable amount of matrix is still adhering to the fibre. The ductile regions observed are considered to be a result of the relatively slow strain banding phenomena, while the brittle areas result from the fast final brittle failure. It thus appears that the actual region at which the fibres debond is dependent on the fracture
speed; if slow, then debonding occurs at the interface (as observed optically) and if fast, then 'debonding' occurs within the matrix or at an interphase region.

Despite the obvious difference in bond strength, indicated by the mechanical properties and optical examination of the coupled and uncoupled materials, the condition of their respective fibre surfaces was not significantly or consistently different. Clean fibre, ductile regions were observed with both forms of sizing, as were brittle areas containing fibres with adhering matrix. Fig. 4.3.28 shows matrix adhering to both coupled K fibres and uncoupled J fibres. Such clear evidence of matrix presence was generally only visible at high magnifications and this serves to highlight an inherent drawback in the technique, i.e., the lack of contrast between different materials.

In an attempt to determine if ductile matrix flow was occurring in the strain bands prior to final failure, sections were cut through a strain banded region using an ultramicrotome. The area of matrix deformation shown in Fig. 4.3.29 is assumed to be part of a strain band, it is unlikely to be a result of the preparation technique since the slice was obtained by one cut and the surrounding area has been left 'smooth'. It is apparent that some form of matrix flow has occurred within the region and fractured fibre ends are clearly visible.

The photomicrograph given in Fig. 4.3.30 is of a typical brittle matrix region of a 0.1 $V_f$, fibre F sample and shows a number of interesting points. The fracture initiation point is a broken fibre or fibre end, the direction of crack propagation being indicated by the characteristic striations in the matrix. The crack has forked round a fibre altering its plane and leaving a 'step' in the matrix (cf. Fig. 4.3.9). Sockets from which fibres have pulled out are visible and the remaining fibres have debonded to a certain extent, as indicated by the interfacial gaps at their bases.
A fracture initiation point in a brittle area is shown in Fig. 4.3.31, the circular crack front which initiated at a fibre end has radiated outwards and the main fracture path has then deviated from the crack plane. An example of a fibre break initiating a matrix crack is given in Fig. 4.3.32 the crack has propagated in a brittle manner for a small distance and has then been accommodated by matrix flow.

It was rare that a propagating matrix crack fractured fibres in its path though some isolated cases were observed, an example of which is given in Fig. 4.3.33 where the fibre, which has fractured while being strained, has receded into its socket. Since such phenomena were infrequently observed it can be assumed that the few fractures seen are a result of flaws in the fibres. Further evidence of the ability of the fibres to withstand crack propagation is given in Fig. 4.3.34 where it is apparent that the crack has passed round fibres without damaging them.

Extensive fibre pullout was apparent in all cases but the actual pulled out fibre lengths did not appear to follow expected trends. The pullout length should depend on the interfacial bond strength according to equation (2.2.21), thus, the higher \( \tau \), the shorter the pullout length. Experimental observations however revealed no major differences in pullout length between the coupled and uncoupled material pairings. Overall, pullout lengths were reasonably short indicating a high interfacial bond strength, it was however noted that longer fibres were apparently present in the ductile regions and the misaligned core regions. The series 2 samples were however atypical since they exhibited significantly longer pullout lengths, but, it must be remembered that their average fibre length was also greater. Fig. 4.3.35 shows the long pulled out fibres in a 0.38 \( V_f \) series 2 sample and also serves to illustrate the misalignment in the central region and the
well aligned intermediate region, which confirms optical observations.

As previously stated, if any fibre bundles were present, final fracture often occurred through one of the bundles, an example of this is given in Fig. 4.3.36 from which it is apparent that, despite the lack of fibre dispersion, the bundle has been impregnated by the matrix and that the matrix has then behaved in a ductile fashion on failure. This was generally the case with transversely oriented fibre bundles, longitudinally aligned bundles however usually exhibited brittle characteristics, behaving similarly to a very large single fibre.

Heat Cleaned Fibre Samples

The heat cleaned samples (HC2 series) demonstrated considerable matrix ductility, this was most pronounced in the 0.1 $V_f$ samples which showed no brittle behaviour at all. Increasing $V_f$ reduced the extent of the ductility, the 0.4 $V_f$ samples demonstrating approximately equal proportions of ductile and brittle matrix despite their very low failure strains. The extensive ductility at low $V_f$ is depicted in Fig. 4.3.37, from which it is also apparent that the sample has necked prior to failure. Little fibre pullout is evident and it appears that final failure occurred at the edges of the specimen, which is probably due to the improved fibre alignment in those regions. The fibre surfaces in all cases were fairly clean, with little matrix adhering, even in the brittle areas.

An interesting point to note is the shape of the fibre ends (Fig. 4.3.38) in the HC2 materials, these tended to be perpendicular to the fibre axis in contrast with the generally observed angular ends of the 'as received' fibre materials (see Fig. 4.3.32). In order to determine the shape of fibre ends produced in tensile failure, a sample of epoxy resin containing continuous aligned fibres was fabricated and tested. Part of the resulting fracture surface is shown in Fig. 4.3.39, from which it is
apparent that the majority of fibre ends are perpendicular to the fibre axis. Thus, it is reasonable to assume that any perpendicular ends seen in the short fibre materials are a result of tensile failure. The angular ends generally observed are assumed to result from flexural failure during the compounding and moulding operations.

The fibre-end shape in the heat cleaned fibre materials therefore indicates that the significant fibre fracture which occurred during testing was the result of reduced fibre strength. This supports a similar conclusion reached from the length distribution data presented in section 4.2.1.

**Boiled Samples**

The principal points to emerge from this part of the investigation were an overall increase in matrix flow and a significant increase in fibre pullout length. The latter point is important in that the samples subjected to the boiling treatment were from the same batches of mouldings tested in the 'dry' condition (Series 5). Thus, if pullout lengths are greater for the boiled samples then a certain amount of fibre fracture must have occurred in the 'dry' specimens, though no real evidence of this was obtained during their examination or from length distribution data. Fibres having perpendicular ends were noted, in small numbers, in the 'dry' samples and it must be assumed that these have fractured and pulled out.

The coupled materials H and K which exhibited slightly increased failure strains demonstrated both brittle and ductile matrix areas, Fig. 4.3.40, the fibre surfaces being 'dirty' in the former and 'clean' in the latter. This was also the case for the coupled M and N materials despite their lower failure strains ($0.25V_f$) compared to the dry condition.

The uncoupled materials showed considerably more matrix ductility which might be expected from their much higher failure strains, Fig. 4.3.41.
It is worth at this point considering the actual process by which the matrix material draws in a ductile manner in the presence of fibres. This is shown schematically in Fig. 4.3.42 and it is apparent that in the fracture surface, a large proportion of the fibre will be obscured by the drawn matrix giving an impression of short pullout lengths. The fibre surfaces of the uncoupled materials were generally clean with very little matrix adhering to them.

It was noted previously that, in some of the boiled samples, the strain banding phenomena was not confined to the core region and was visible on the test piece surface. In order to elucidate this, a number of failed specimen surfaces were examined. Fig. 4.3.43 shows strained and unstrained regions of a fibre J testpiece and banding, in an advanced stage, is clearly evident on the surface of the former. One area of banding is shown in Fig 4.3.44 and it is apparent that the matrix has parted in a semi-ductile fashion leaving fibres bridging the gap. The unstrained region shows no such behaviour and the indentations visible are outlines of fibres close to the surface. In addition, failed 'dry' samples containing severe strain bands were examined but no sign of the bulk deformation was visible on the specimen surface. It is therefore apparent that the boiling treatment has in some way altered the matrix material to allow strain bands to propagate to the surface regions.

Impact Samples

The fracture surfaces of the impact test samples were similar in appearance to the tensile samples, fibre pullout was extensive with the pullout lengths being relatively short. The shape of the fracture surfaces varied, depending on the $V_f$. In low $V_f$ materials, the fracture tended to propagate directly across the samples in the plane of the notch while, in the high $V_f$ samples, the crack deviated from the notch.
plane quite considerably, the fibres obviously having a much greater effect. This is illustrated in Fig. 4.3.45, from which it is apparent that in the high $V_f$ materials the initial fracture path tends to follow the fibre alignment direction.

The matrix demonstrated predominantly brittle behaviour except at the compressive edge of the samples where ductile matrix flow was observed in all cases, Fig. 4.3.46. Since the flow direction is normal to the notch plane, it is apparent that the samples have finally parted with a shearing action. In addition, the width of the ductile region was generally greater in the high $V_f$ materials. The behaviour of the matrix under shearing forces is also illustrated in Fig. 4.3.47 where two crack planes have crossed and the matrix has sheared perpendicularly to the cracks, leaving a step which is ductile in appearance.

The condition of the fibre surfaces follows previous trends, clean in the ductile regions and having adhering matrix in the brittle regions. The amount of matrix adhering to the fibres however tended to be greater in the coupled materials and also more evenly distributed over the surface.

To summarise briefly the observations made during fracture surface examination. The fibre pullout length appeared to bear some relationship to the average length of fibres present and did not appear to be significantly affected by the presence of coupling agents. The condition of the pulled out fibre surfaces was dependent on the fracture behaviour of the matrix, being clean in ductile regions and retaining matrix in brittle regions. All samples demonstrated brittle and ductile regions, the latter being confined to the core regions of the tensile samples and the compressive faces of the impact samples. This phenomenon is assumed to be a result of fracture propagation rate, slow speeds resulting in ductile regions and fast giving brittle regions.
The final fracture behaviour is fast and brittle and appears to be initiated by matrix cracking at fibre fractures and fibre ends in the well aligned intermediate regions. The shape of the fibre ends is indicative of their mode of failure, if perpendicular to the fibre axis then failure is tensile and, if angular, then failure was in bending. The high incidence of perpendicular ends in the heat cleaned sample substantiates previous assumptions of considerable fibre fracture as a result of reduced fibre strength. The presence of moisture has the effect of increasing matrix ductility and reducing the effectiveness of the interfacial bond as indicated by the overall increase of fibre pullout lengths in the boiled samples. In addition, these increased pullout lengths indicated that some fibre fracture had occurred in the 'dry' samples since mouldings from the same batches were used for each series of tests.
Fig. 4.1 Schematic outline of results chapter.
Fig. 4.1.1 Fracture stress as a function of $V_f$ for Series 1 samples (fibres F and P).

Fig. 4.1.2 0.5% secant modulus as a function of $V_f$ for Series 1 samples (fibres F and P).
Fig. 4.1.3 Fracture strain as a function of fibre volume fraction for fibres F and P

Fig. 4.1.4 Comparative stress-strain curves for fibres F and P
Fig. 4.1.5 Relationship of acoustic emission total output (a), and count rate (b), with fibre volume fraction for materials F and P.

Fig. 4.1.6 Correlation between total output and tensile failure strain.
Fig. 4.1.7. Strain band formation with increasing strain for a small, $0.1 \ V_f$, fibre F sample
Fig. 4.1.8 Strain banding in failed samples.

a, c, e = Fibre P; 0.1, 0.2, 0.3 $V_f$ respectively

b, d, f = Fibre F; 0.1, 0.2, 0.3 $V_f$ respectively

Fig. 4.1.9 Fracture stress as a function of $V_f$ for Series 2 and HC2 samples.
Fig. 4.1.10 0.5% secant modulus as a function of $V_f$ for Series 2 and HC2 samples.

Fig. 4.1.11 Fracture strain as a function of $V_f$ for Series 2 and HC2 samples.
Fig. 4.1.12  S.E.M. micrographs showing condition of fibre surfaces

a) Fibre F, untreated
b) Fibre F, heat cleaned
c) Fibre F, solvent cleaned
Fig. 4.1.13 Fracture stress v. $V_f$ for solvent cleaned and heat cleaned fibres (HCl) compared to the untreated fibre.
Fig. 4.11.14  
Typical tensile stress-strain curves and acoustic emission behaviour for  
(a) Series 2 samples and (b) heat cleaned (HC2) fibre samples, at different  
fibre volume fractions.
Fig. 4.1.15 Comparative stress-strain curves for Series 4 tests ($V_F=0.25$, except where indicated).

Fig. 4.1.16 Typical acoustic emission behaviour for coupled and uncoupled materials.
Fig. 4.1.17 Fracture stress as a function of $V_f$ for Series 4 and 5 samples.
(coincident points displaced for clarity)
Fig. 4.1.18 0.5% secant modulus as a function of $V_f$ for Series 4 and 5 samples. (Coincident points displaced for clarity)
Fig. 4.1.19 Fracture strain as a function of $V_f$ for series 4 and 5 samples.

(Coincident points displaced for clarity)
Fig. 4.1.20 Typical stress-strain curves for Series 5 tensile test specimens in the wet and dry conditions $V_f = 0.1$

Fig. 4.1.21 Typical stress-strain curves for Series 5 tensile test specimens in the wet and dry condition $V_f = 0.25$
Fig. 4.1.22 Form of strain banding in boiled samples
a) uncoupled materials G and J
b) coupled materials H and K
c) materials M, N and F

Fig. 4.1.23 Correlation between tensile strength and Charpy impact energy.
**Fig. 4.1.24. TI59 programme for calculating τ & C**

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Fig. 4.1.25 TI-59 Programme for calculating stress strain curves
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**Fig. 4.2.10 - Continued**
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F1, indicates fibre fracture.
S1, S2, indicate sockets left by pulling out fibres.

(b) Area in, and adjacent to (a), transmitted light,
S3-6, sockets left by pulling out fibres
SM1, SM2, sockets with meniscus shaped ends
F2, fibre fracture.
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F, Sample (planar section)
(a) reflected, (b) transmitted light, same focus point.
Arrows indicate crack forking round fibre.
Note also bright white lines in (a) which indicate debonding.

n.b., The line across the fibre (see diagram)
is not a fracture but the shadow of the crack
behind the fibre. No line is visible connecting
the upper crack since the matrix has been polished away.
Fig. 4.3.10 Crack propagation around fibres, the 'b' alternative represents the case cracks growing out of the original plane.
(a) Debonding of misaligned fibres. 
(\(E \approx 0.1 V_f \))

Fig. 4.3.11

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Sample (planar section)
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Fig. 4.3.22 (pages 226-227) Series of photomicrographs showing the initiation and propagation of fibre debonding with increasing strain during the 'in-situ' tensile testing of a coupled fibre H sample.

Micrograph No.

(i) Unstrained sample with reference grid.

(ii) End debonds visible as black marks as specimen strained.

(iii) More end debonds visible, note broken fibre and edge debond at fibre crossover point in area A2.

(iv) Some end debonds have propagated along fibres, more of 'edge debonded' fibre in A2 has debonded.

(v) 'Edge debonded' fibre has broken in area A3, debonds have propagated further. The black mark to the left of the debond in C2 is not a fibre break but the shadow of another end debond.

(vi) Debonds have propagated further from fibre ends and also either side of break in A3. Debonded region is seen to form a band across B 1 to 3.

(vii) Further debond propagation. Black regions are shadows of more debonding out of focal plane.

(viii) Debonding more severe. Note that single debond visible in area D1 in micrograph (v) has caused surrounding fibres to also debond through transference of load.

(ix) Sample has failed to the left of the area visible. Note that some debonds have apparently disappeared while others have shrunk, this is a result of oil seeping down the debonds, and, relaxation of the sample, respectively.

(x) Showing the failed sample, the strain bands are clearly visible.

Fig. 4.3.23 (page 228) photomicrographs of uncoupled fibre J sample during 'in-situ' tensile testing.

The micrographs are the same scale as Fig. 4.3.22 but show more contrast due to the use of a green filter during microscopy. It is apparent that more fibres are debonded prior to testing (micrograph i) and the debonding during testing is more extensive.
Fig. 4.3.23.
Fig. 4.3.24  Ductile and brittle matrix areas in the same specimen.  
($F$, $V_f=0.2$). Note the clean fibres in the ductile region 
and the matrix adhering to the fibres in the brittle areas.

Fig. 4.3.25  Schematic diagram of the general shape of the fracture 
surfaces showing areas where brittle and ductile matrix 
is found.
Fig. 4.3.26  Brittle and ductile regions in the same sample (F, 0.1 V_f) following the format shown in Fig. 4.3.25.
Fig. 4.3.27 (a) and (b) Brittle and ductile areas in a $0.1 V_{\epsilon}$, L, sample showing fibre surface condition. (c) Matrix adhering to surface of fibre which is indicated by arrows on micrograph (a).
Fig. 4.3.28 Matrix adhering to the surfaces of pulled out fibres. (a) coupled K sample, (b) uncoupled J sample.

Fig. 4.3.29 Surface of microtomed section (transverse) showing appearance of strain band.
Fig. 4.3.30  Brittle matrix area showing pulled out fibres and fibre sockets, note: characteristic surface markings indicating crack propagation direction
F=fracture initiation point
M=matrix step
D=debonded fibres
(sample: F, 0.1V_f)

Fig. 4.3.31  Radial matrix crack initiated at a fibre end (F, 0.1V_f).
Fig. 4.3.32 Matrix crack initiated at a broken fibre ($F, 0.1V_f$)

Fig. 4.3.33 Brittle area in a $0.1V_f, N$, sample. The arrows indicate a fibre broken by the propagating matrix crack.
Fig. 4.3.34 Matrix crack (arrowed) passing round fibres without fracturing them. 
\( F, 0.38V_f \)

Fig. 4.3.35 Long pulled-out fibres in a \( 0.38 V_f \) sample showing good fibre alignment towards specimen edge and misalignment in central core region.
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Fig. 4.3.45 Comparison of the fracture behaviour at the notch in (a) $0.1V_f$ and (b) $0.25V_f$, impact samples.
Fig. 4.3.46  Typical appearance of the compressive edge of the impact specimens.

Fig. 4.3.47  Ductile appearance of matrix fractured in shear.
5. DISCUSSION OF RESULTS

5.1 Mechanical Properties

The improvements in mechanical properties that can be achieved by the incorporation of short glass fibres into a thermoplastic matrix are dependent on the complex interaction of several variables. These are principally; the fibre concentration, the fibre length and orientation distributions, and the strength of the interfacial bond. Optimum composite properties will result from long aligned fibres which are well bonded to the matrix. The actual length and orientation distributions obtained however, will be dictated by the processing route used and this results in considerable anisotropy of properties. The interfacial bond strength can be controlled by the application of coupling agents which are designed not only to improve the bond in ideal situations, but also to enhance strength retention under adverse environmental conditions. The sizing system employed can also have indirect consequences in that, it can exert considerable control over fibre length distributions by effecting the mouldability of the materials.

Previous work on glass and carbon filled nylon 66 (1,104,105) has shown that increases in fibre concentration, fibre length and interfacial bond strength result in improved stiffness (especially at higher strains), higher strength and reduced ductility. In this investigation, similar property trends are observed with $V_f$ and fibre length variation, the effect of the interface is however, more complex. The behaviour of the interface and its effect on mechanical properties was assessed by examination of fibres coated with two silanes and two film forming compounds. Samples were tested after a short environmental conditioning period and also after a boiling water treatment which highlighted the ability of the silane to retain bond integrity under adverse conditions.
It was apparent that bond strength is affected by both the silane and the other components of the size, good adhesion being possible in the 'dry' state without a coupling agent while in the wet condition, the silane is a necessary requirement to maintain property levels. Low bond strengths resulted not only in reduced stiffness and tensile strength, as would be expected, but also caused a reduction in ductility and impact strength. In addition the interfacial bond strength appeared to vary with the processing conditions and fibre loadings.

In the initial investigation there was little difference in the properties of materials F and P, which indicates no significant variation in the behaviour of their respective coupling agents, although one was designated nylon compatible (F) and the other, polypropylene compatible. The fracture mode as assessed by fractography and length distribution analysis leads to similar conclusions. This does not of course imply that the converse would be true, since the F and P fibres may well give quite different properties in a polypropylene matrix. It is generally considered that the nylons, with their ability to form hydrogen bonds, develop reasonably strong interfaces with glass fibres without the need for elaborate coupling agents.

Overall, the F material compared well in performance with the other materials, despite its obsolete size specifications. The other two sizing systems represent commercially available formulations from two different manufacturers, their behaviour was however significantly different. In one system, the omission of a coupling agent produced no detrimental effects (in the 'dry' condition) whereas for the other system, such an omission resulted in considerably inferior properties.

**Composite Stiffness**

In all of the materials examined, the low strain modulus was observed to increase with $V_f$ and mean fibre length as would be expected
from a rule of mixtures analysis, a linear relationship with \( V_f \) being apparent. Figs. (4.1.2, 4.1.10). The presence of a coupling agent in the GHJK group of materials resulted in a slight modulus increase; in the L and N pair however, no difference was apparent. The fibre diameter was observed to have no significant effect in the less well bonded G and J materials but for the H,K,L,M and N batches, an increased diameter gave reduced stiffness, this phenomenon being more pronounced at higher strains. It is, therefore, indicated that, where a good interfacial bond exists, significant improvements in composite stiffness may be obtained by the use of small filament diameters, such an effect being attributed to the increase in interface area.

In the wet condition, all of the materials exhibited a drastic reduction in stiffness which was of the order of 50% for the coupled materials and 70% for the uncoupled batches. The silane is therefore reasonably effective at retaining bond strength in such detrimental environments.

**Composite Strength**

The tensile strengths exhibited similar, but more marked, trends to the moduli. The L,M and N materials showed comparable strengths to the coupled H and K materials despite the lack of a coupling agent on L. The remaining uncoupled materials however showed considerably inferior properties, attaining only 60-70% of the strengths of their coupled counterparts. The relationship of failure stress to volume fraction was non-linear, tending to level off at higher \( V_f \)'s. Other workers have observed that, at very high \( V_f \)'s, strength passes through a maximum, subsequently declining quite rapidly (108). The fibre loadings employed in this investigation were however insufficient to cause such behaviour.

The boiling treatment caused a dramatic reduction in strength
compared to the 'dry' materials, the samples without coupling agents exhibiting an almost total loss of reinforcement efficiency. (Table 4.1.5). In addition, it is of interest to note that the fibre F material with the outdated non-silane size showed a greatly inferior 'wet' performance compared to the currently used silane formulations employed on M and N (from the same manufacturer).

**Composite Ductility**

The failure strains of all the materials examined (including the heat cleaned material which will be discussed later) showed a decrease with increasing volume fraction and fibre length, attaining levels which were generally less than the estimated fibre failure strain of 3.0%. (Figs. 4.1.3., 4.1.11). It is noteworthy that, in the 'dry' condition, the elongations to failure of the uncoupled materials G and J are actually less than their coupled counterparts, while for materials L and N the values are similar. In the wet condition, the reverse trend is apparent, an absence of coupling agent resulting in increased ductility compared to the coupled materials.

If the interface is less well developed the relevant theories (see literature) predict reduced composite modulus and strength, which is indeed the case here. In considering the ductility however, it might be expected that a reduced bond strength would reduce the constraining effect of the fibres, thus allowing greater elongations. Since this is contrary to the observed behaviour for the 'dry' materials the implication is that, in the absence of a coupling agent, the fibres are acting as internal stress concentrators. An additional factor concerning the higher elongation to failure of the coupled materials is the ability of the better interfacial bond to restrain the coalescence of any cracks and debonds which may arise during straining. Similar conclusions are indicated by fractography since
the coupled material do not exhibit such extensive pre- and post-test debonding as the uncoupled materials.

The trend reversal in the wet state, i.e. the greater failure strains of the uncoupled materials, is due principally to the increased ductility of the water plasticized matrix, and the virtual complete degradation of the interfacial bond. The latter reduces the interfacial shear stress and thus the constraining effect of the fibres on the matrix, and the former means that stress concentrations caused by the debonded fibres (cf 'dry' material) can be accommodated by matrix flow. The complexity of the situation is however increased when the very low ductilities of the 0.25 \( V_f \), M, N and F materials are considered, these failing at strains below their 'dry' levels. Since the equivalent 0.1 \( V_f \) samples failed at very high strains, the implication is that, for F, M and N, there exists a critical volume fraction at which the fracture mechanism alters. This will be influenced by the bond strength, the extent of matrix plasticization and by any size-matrix reaction that has occurred, the precise form of this influence is however not known. This complex and contrary behaviour will be discussed further in Section 5.3 with reference to the observed failure mechanisms.

The results presented clearly demonstrate the beneficial effects of silane coupling agents. In the 'dry' condition, some composites exhibited a 30% strength reduction on omission of the silane, but in others this caused very little variation. In the wet state however, silane treatments produced far superior properties in all cases.

The L and N materials showed a similar stress-strain behaviour to that observed by Berry and Stanford (112) in an investigation of coupled and uncoupled glass fibres in nylon 66. These materials demonstrated very little difference in the dry state but when wet, the coupled materials exhibited superior properties.
The Sizing Systems

The similarity in properties of the L, M and N materials in the dry state was in contrast to the behaviour of the G, H, J and K batches which is principally due to the different sizing systems employed, the materials originating from different manufacturers. It is considered that the cationic film former employed on fibres L, M and N will bond readily with the anionic glass surface thus competing with the silane for bond sites, and possibly reducing the density of silane bonds actually formed. In the dry condition, such behaviour will be advantageous as good interfacial bonds develop directly, via the film former, even in the absence of a coupling agent. In the presence of moisture however, the water soluble cationic film former alone cannot protect the interface from water attack which accounts for the drastic property reduction observed for the L material. Such an effect is also responsible for the different behaviour of the silaned materials in the wet condition. Since the ionic nature of the size allows for the formation of relatively fewer silane bonds, the interfacial degradation will be correspondingly greater than in the non-cationic sized materials. (Table 4.1.5).

Attempts to highlight the exact nature of the size formulation using scanning electron microscopy (Section 4.2.3) were inconclusive since the technique enables only topographical features to be examined. It was apparent that excess size was present as a result of interfibre capillary buildups and as random surface agglomerations, similar observations being reported by other workers (e.g. 21). The polyurethane based sizing system used on fibres G, H, J and K was more ductile in appearance and differed from the other materials in that the silaned variations possessed a generally rougher surface topography, this being due to the method of application. For the H and K materials, the silane is in solution and the film former in emulsion, with submicron
sized particles. It is considered that the silane coats the emulsion particles and in so doing reduces the wettability of the size. This results in the globular appearance on the fibres. The size components of the L,M and N batches however are both in solution which, on application to the fibres, results in a 'smooth' surface finish.

Measurements of the size loadings did not reveal a great deal of useful information, the amount of size present being less than one per cent in all cases. The two groups of materials however exhibited different characteristics, the G,H,J and K batches demonstrated higher weight losses for the unsilaned fibres whereas the reverse was true for the L,M,N group. The former behaviour can probably be explained by incomplete removal of the size as observed by Sawyer (99). The latter behaviour, i.e. reduced weight loss for the uncoupled L material may be due simply to a lower level of size loading. Alternatively, if the reduced degree of silane bonds as a result of the ionic bonding mechanism is considered, removal of the size will be easier, giving relatively greater weight losses.

The data obtained from the ESCA analysis (Section 4.2.3) shows that more silicon is present in the size of the coupled materials for both groups and that the silicon is derived from the silane coupling agent. The results comprise the only direct evidence of the lack of coupling agent on the L material (although indirect evidence was obtained by its wet behaviour) and thus support the assumption of some form of ionic bonding mechanism. All of the uncoupled materials showed some silicon present, the actual reason for this is not known, but it is unlikely to have originated from the actual glass surface since the results of Wong (131) and the known composition of E-glass would require a much greater silicon level.
The matrix discolourations observed, particularly at high $V_f$'s, are attributed to size-matrix interaction (Section 4.2.6). Such behaviour has been reported elsewhere (65), the interaction also causing matrix embrittlement. The latter was attributed by the author to molecular weight reduction and a consequent increased degree of crystallinity. Reductions in failure strain with increased crystallinity have also been noted by other workers (15-18). For the materials examined here, D.S.C. experiments indicated that some polymer degradation had occurred with the introduction of the fibres, crystallinities ranging from 41-53% and multiple melting peaks being observed.

Material K possessed the highest degree of crystallinity but also the highest failure strain at high $V_f$'s which is contrary to behaviour that might be expected (i.e. high crystallinity embrittles). Evidence of matrix embrittlement in the form of matrix cracking was not generally observed during microscopical examination and it is concluded that, while discolouration was apparent, it caused no obvious detrimental effect on the properties.

Heat cleaned material

Samples fabricated using the heat cleaned material (see Section 4.1.1) were observed to possess significantly inferior properties, the stiffness and strength being much lower than even the 'short' fibre series 1 materials. Although it was apparent that the material was quite useless for any practical application, a number of interesting points emerged from the investigation.

The extent of the property deterioration is certainly too great to be accounted for only by loss of interfacial adhesion as a consequence of the size removal. Indeed, microscopy revealed that size removal was incomplete, a factor also indicated by the discolouration of the fibres after the heat cleaning treatment. Additionally the fibre lengths,
although short, were not too dissimilar from the 'short fibre' series 1 samples.

The available evidence points to a fibre fracture controlled failure process due to reduced fibre strength, since, a significant reduction of fibre lengths was found after the material had been strained in tension. In addition, it has been shown that tensile fracture of glass fibres result in perpendicular end shapes (Fig. 4.3.3a) and a large number of such ends were observed on the HC2 series fracture surfaces. Positive evidence of reduced fibre strength was obtained from the testing of the uniaxially aligned fibre composites, a 70% decrease being recorded.

Temperature induced fibre strength losses have been reported by a number of workers (eg. 8) being attributed to such diverse causes as surface contamination and alkaline corrosion. Adams et al (133) have noted strength losses in excess of 60% for glass fibres heated at 500°C for 15 minutes. The authors suggest that this behaviour is due to an ion exchange mechanism at the glass surface inducing tensile stresses with consequent strength reductions, Na⁺ ions are considered to exchange with smaller H⁺ ions present as hydroxyl groups on the glass surface.

At low volume fractions, the composite is weaker than the unfilled matrix but failure strains are high, extensive matrix ductility and little fibre pullout being evident on the fracture surfaces. At \( V_f \)'s > 0.1, strength increases to a maximum value and the failure strains decrease dramatically to levels lower than the 'long' fibre (Series 2) samples. The fracture surfaces still exhibited considerable matrix ductility, but fibre pullout lengths were longer (though still short in comparison to the untreated fibre materials).

If fibre fracture is assumed to be the controlling failure mechanism, it is apparent that a critical \( V_f \) exists. Below this level,
the matrix is capable of accommodating the additional loads imposed by the fractured fibres. At high $V_f$'s however, the increased constraining effect of the fibres allows greater loads to be attained until, when the strain is sufficient, extensive fibre fracture occurs. The matrix is unable to sustain this excess load and composite failure at low strains results.

The results indicate that there is an embrittlement effect as a result of the mere presence of the fibres, regardless of the degree of reinforcement, an assumption supported by the low strain to failure of the dry uncoupled materials.

**Interfacial shear strength and orientation parameters**

The calculated values of the interfacial shear strength, $\tau$, exhibited significant variations with screw back pressure, fibre length and fibre volume fraction (see tables 4.1.1, 4.1.2). These parameters are however interdependent since reduced fibre length is a direct consequence of the extended melt plasticization times associated with increased back pressure. Higher fibre loadings require increased back pressures to adequately disperse the fibres. The principal variable affecting $\tau$, thus appears to be the screw back pressure, an increase of which results in higher interfacial shear strengths. This is attributed to the improved fibre 'wetting' and dispersion. Such variable behaviour is also indicated by the work of Richards and Sims (72) who observed that the strength of coupled (Silane Al100) glass reinforced nylon.6. was dependent on the degree of mixing, improved values being obtained with long mix times despite consequent fibre length degradation. Reference to table 4.1.1 shows that, at each $V_f$ level, $\tau$ increased with back pressure. The actual values of the 0.38 $V_f$ material were however inferior, this is again attributed to a mixing effect, since dispersion will be inhibited by the relatively greater number of fibres present. Additionally, a $V_f$ of
0.38 is approaching the maximum amount of fibres that can be practically incorporated and the relative increased severity of fibre-fibre interactions could adversely effect the ability to form good interfacial bonds.

Values of $\tau$ calculated for the series 4 tests followed expected trends with the uncoupled materials exhibiting lower values. Material L is the exception however, but this is considered due to the ionic bonding mechanism which operates even in the absence of a coupling agent, the $\tau$ values reflecting the mechanical behaviour.

The $\tau$ values obtained for the boiled samples are considered to be unreliable because of the unrealistically low orientation parameter results obtained simultaneously (Table 4.1.8). Despite this however, the magnitude of the shear strengths fairly accurately represents the behaviour of the materials, a virtual loss of bond integrity being predicted for all of the uncoupled batches, which is the case. Of the coupled materials, F exhibited the weakest bond strength which is expected when its non-silane coupling agent is taken into account. The water soluble sized M and N materials possessed inferior $\tau$ values compared to the hydrophobic sized H and K materials which also showed the best mechanical properties. The results obtained for L and N showed similar trends to those of Berry and Stanford (112) who also used an analysis based on the Bader-Bower equation (100-102), comparison of the actual results is not possible however, since different materials were used.

The calculated orientation parameters for the 'dry' materials all fell in the range 0.51-0.68 indicating reasonably good fibre alignment. This is in agreement with microscopy observations which showed the fibres to be preferentially oriented along the specimen axis. In addition, the values obtained show good correlation with the results of other workers (1, 65, 100-102, 112).
The theoretical stress-strain curves (Figs. 4.1.27, 28) showed excellent correlation with experimental curves at low strains, the plots however tend to diverge at high strains and this effect is more pronounced in the low $V_f$ materials. Such behaviour is attributed to inadequacies in the equation which only considers the reduced reinforcing efficiency of the fibres with increasing strain (i.e. more fibres become subcritical in length). It takes no account of the viscoelastic nature of the matrix or the level of accumulated composite damage such as fibre debonding and fracture, matrix cracking and matrix flow, all of which will contribute to the observed stiffness reduction with increasing strain. Additionally, the equation only utilises a single orientation parameter which cannot possibly account for the inhomogeneous orientation distribution and its effect on composite behaviour. The predicted curves for the coupled and uncoupled materials show a better correlation for the latter which is a result of their lower failure strains ($0.25V_f$ only), which do not allow as much accumulated composite damage. (Fig. 4.1.28).

Attempts have been made by other workers to predict the behaviour of SFRT by summing fibre contributions over both length and orientation, having measured these distributions experimentally, but poor agreement with experiment was obtained (68). Even this approach is inadequate due to the interdependence of both fibre length and orientation (1) and, additionally, these are also a function of positional variation in the mouldings. (69, 77). In an ideal situation, fibre lengths should be summed over every fibre angle, but, there is little point in conducting such a time consuming analysis if it is not possible to consistently and accurately reproduce fibre length and orientation distributions in successive mouldings. The work of Bright et al (82) has shown that it is possible to exert some degree of control over orientation by varying injection moulding conditions. Until such
techniques are fully developed however, the rather simplistic
approaches similar to those advocated by Bader and Bowyer (100-102) are
preferable to other more complex analyses for predicting composite
behaviour.

Impact Behaviour

The charpy impact tests (Section 4.1.2) showed similar trends
to the tensile tests in that, the uncoupled materials G and J gave lower
impact energies than their coupled counterparts H and K, while there
was little difference in the L and N pair. Increasing the $V_f$ also gave
higher impact strengths, the strongest materials were therefore the
toughest, a good correlation with tensile strength being apparent
(Fig.4.1.23). Other workers (1,60,65,113) have observed an initial
decrease in impact strength with the addition of fibres, followed by
an increase with $V_f$. Since, in this case, no results are available
for the unfilled material and only two $V_f$'s were examined it is not
possible to confirm this behaviour. Seiler et al (107) have observed
a similar impact behaviour during an investigation of glass reinforced
nylon 6, showing that an increase in both interfacial bond strength and
$V_f$ result in higher impact strengths.

The Charpy test does not in fact measure the fracture energy but
rather the total energy absorbed during the fracture process. In brittle
materials this will be equal to the stored elastic strain energy when
the fracture initiates, but in SFRTP there may be contributions from
many sources. The energy required to initiate fracture (stored elastic
strain energy) is dependent on the strength and stiffness of the
materials. Essentially the tensile strength of the material must
be reached at the notch tip. Thus, in SFRTP, increasing the $V_f$ and
interfacial bond integrity would require a higher stress to initiate
failure, this being the observed behaviour. It might be expected that
energy dissipative mechanisms such as fibre pull-out would be enhanced
by reductions in the bond strength, thus giving tougher materials. This is contrary to the experimental results indicating that the strengthening effect of a stronger interface is more dominant than the effect of these secondary energy dissipating mechanisms. Examination of the fracture surfaces reveals that fibre pullout is extensive in all cases and apparently independent of interfacial bond strength, although no actual quantitative assessment was made. The matrix exhibited a predominantly brittle behaviour and the pulled out fibres generally had matrix material adhering to them. This indicates that the resistance to pullout was not simply a function of the friction between the glass and nylon. It is therefore logical to assume that those materials having a higher bond strength would require more energy to pull-out the fibres, resulting in an increase in toughness.

Considering the experimental behaviour, Table 5.1.1 gives values of the measured impact energies, $U_c$, also tabulated are calculated values of the stored elastic strain energy, $U_s$ (obtained using equation 5.1.1, which is the energy stored in a beam when the maximum surface stress is $\sigma_n$) and the difference between the two terms, $U_x$.

$$U_s = \frac{1}{18} \sigma_n^2 \frac{E_c}{L_s b_s d_s}$$  \hspace{1cm} (5.1.1)

Where; $\sigma_n$ = stress at the notch tip (assumed to be equal to the composite tensile strength), $E_c$ = composite modulus and $L_s, b_s, d_s$ refer to the length, breadth and depth of the impact sample respectively.

It is apparent from Table 5.1.1 that the elastic strain energy term accounts for only a small part of the total energy measured. Equation 5.1.1 is strictly applicable only to unnotched configurations, it could be modified to account for the effect of a notch by the inclusion of a stress concentration factor. This, however, would reduce
the strain energy term to an even lower level, thus, \( U_x \) may be regarded as a lower bound value. The term \( U_x \) represents energy absorbed by mechanisms such as fibre pull-out, formation of new surfaces, kinetic energy and acoustic energy. The energy due to fracture surface formation in the glass, matrix, and by debonding at the interface is likely to be quite small, as are the contributions from kinetic energy (see Section 4.1.2) and acoustic energy. If it is therefore assumed that all this energy may be due to fibre pullout, then it is possible to calculate a frictional fibre pullout term:

\[
\text{Pullout force, } F_{po} = \pi d_f L_{po} \tau_{po} \quad (5.1.2)
\]

\[
\text{Pullout work, } W_{po} = \frac{F_{po} \times L_{po}}{2} \quad (5.1.3)
\]

where \( d_f \) = filament diameter, \( L_{po} \) = pullout length and \( \tau_{po} \) = frictional 'bond strength'.

\[
\text{Number of fibres/unit area } N = 4 \frac{V_f}{\pi d_f^2} \quad (4.1.4)
\]

\[
\text{Pullout work/unit area } = W_{po} N = 2 \frac{L_{po}^2 V_f \tau_{po}}{d_f} \quad (5.1.5)
\]

If the 'excess' energy term, \( U_x \), is divided by the projected fracture area (ie. \( 2 \times \) cross sectional area), a 'fracture energy' term \( \gamma_x \) is obtained, this will be a measure of the energy absorbed by the fibre pullout. Reference to Table 5.1.1 demonstrates that, as assumed, more energy is absorbed by the coupled materials and the high \( V_f \) materials.

By equating \( \gamma_x \) to the pullout work/unit area and rearranging equation (5.1.5) it is then possible to calculate values for the frictional 'bond strength', \( \tau_{po} \).
The average pullout length, $L_{p0}$, was estimated to be \( \approx 200\mu m \) from S.E.M. micrographs, little difference between materials being apparent, although only a visual comparison was made.

The $\tau_{p0}$ values given in Table 5.1.1 suggest that the coupled fibres possess a higher frictional resistance against pullout and that the contribution from pull-out is greater at higher $V_f$, in spite of a reduction in the estimated value of $\tau_{p0}$. This is compatible with the observation that the pre-debonding interface shear strength, $\tau$, also decreased at high $V_f$. The estimated values of $\tau_{p0}$ are all lower than $\tau$ (see Section 4.1) and are considered to fall into a range which suggests the model is realistic.

The results therefore indicate that it is possible to increase the toughness of SFRTP by actually increasing the interfacial bond strength. A limiting value however would be the matrix shear strength, at $\tau$ values less than this, fibre pullout is the dominant fracture and energy absorbing mechanism while, at greater $\tau$ levels, fibre fracture would probably dominate with a consequent reduction in toughness.

\[ \tau_{p0} = \frac{\gamma_x d_f}{2L_{p0}^2 v_f} \] (5.1.6)
### Table 5.1.1

Impact Test And Fibre Pullout Data.

<table>
<thead>
<tr>
<th>Material Code</th>
<th>$V_f$</th>
<th>Charpy Energy $U_c$ (J)</th>
<th>Strain Energy $U_s$ (J)</th>
<th>$* = U_c - U_s = U_x$ (J)</th>
<th>$** = \gamma_x$ (KJm$^{-2}$)</th>
<th>$*** = \tau_{po}$ (MPa)</th>
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</thead>
<tbody>
<tr>
<td>G</td>
<td>0.1</td>
<td>0.75</td>
<td>0.096</td>
<td>0.65</td>
<td>10.83</td>
<td>16.3</td>
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<td>0.25</td>
<td>0.96</td>
<td>0.079</td>
<td>0.88</td>
<td>14.67</td>
<td>8.8</td>
</tr>
<tr>
<td>H</td>
<td>0.1</td>
<td>0.87</td>
<td>0.13</td>
<td>0.74</td>
<td>12.33</td>
<td>18.6</td>
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<td></td>
<td>0.25</td>
<td>1.15</td>
<td>0.16</td>
<td>0.99</td>
<td>16.50</td>
<td>9.9</td>
</tr>
<tr>
<td>J</td>
<td>0.1</td>
<td>0.78</td>
<td>0.09</td>
<td>0.69</td>
<td>11.50</td>
<td>22.9</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.85</td>
<td>0.07</td>
<td>0.78</td>
<td>13.00</td>
<td>10.3</td>
</tr>
<tr>
<td>K</td>
<td>0.1</td>
<td>0.90</td>
<td>0.16</td>
<td>0.74</td>
<td>12.33</td>
<td>24.5</td>
</tr>
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<td></td>
<td>0.25</td>
<td>1.56</td>
<td>0.18</td>
<td>1.38</td>
<td>23.00</td>
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<tr>
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<td>1.24</td>
<td>20.60</td>
<td>15.14</td>
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<td>0.14</td>
<td>1.41</td>
<td>23.50</td>
<td>11.75</td>
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<td>M</td>
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<td>0.90</td>
<td>0.15</td>
<td>0.75</td>
<td>12.50</td>
<td>20.20</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>1.31</td>
<td>0.18</td>
<td>1.13</td>
<td>18.80</td>
<td>12.18</td>
</tr>
<tr>
<td>N</td>
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<td>0.12</td>
<td>0.89</td>
<td>14.80</td>
<td>18.50</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>1.65</td>
<td>0.17</td>
<td>1.48</td>
<td>24.60</td>
<td>12.3</td>
</tr>
</tbody>
</table>

* $U_x = \text{measured charpy energy} - \text{calculated strain energy}$

** $\gamma_x = U_x / A$ where $A = (2 \times \text{cross sectional area})$

*** $\tau_{po} = \text{frictional 'bond strength'}$
5.2 Processing Conditions

Most authors agree that to obtain optimum composite properties, the fibre lengths in the mouldings must be as high as possible, and the fibres should be well dispersed. The injection moulding operation can therefore exert a considerable influence over the mechanical properties, principally by controlling the degree of fibre attrition and hence the fibre length distributions in the final mouldings. The actual moulding of the materials used in this investigation produced no practical problems although, with the equipment used, volume fractions of 0.4 represented an upper limit.

During the initial moulding programme (Series 1), the criteria for a 'good' testpiece was the absence of any fibre bundles and to achieve this high screw back pressures were required. This resulted in excellent fibre dispersion but at the expense of fibre length, reductions of over an order of magnitude being observed. (Table 4.1.1, 4.1.2). Subsequent mouldings obtained using low back pressures (Series 2), retained longer fibres but the dispersion was not as good, fibre bundles frequently being observed. The significant property improvements resulting from increased fibre lengths are illustrated by reference to Figs. (4.1.1-3), (4.1.9-11) and by Table (4.1.2). The detrimental effect on fibre length of increased screw back pressures, which are a result of the higher degree of melt shear, have been noted by a number of other authors (59, 68-70). The effect was more pronounced at higher \( V_f \)'s which can be attributed to increased melt viscosities resulting from the greater number of fibres present and the consequent higher shear stresses, although the magnitude of these will depend on the shear rate (72). The presence of fibre clumps or bundles was found to have no significantly adverse effect on the properties, which is contrary to the observations of Lunt (65). Fractography however revealed that the bundles were quite well impregnated by the nylon matrix and that small bundles appeared to behave as large single fibres.
Lunt makes no comment on the bundle appearances, so it is possible that their behaviour and effects are different, particularly since he used the more brittle nylon 66 as a matrix.

It was not possible to gauge a volume fraction effect on fibre length for all of the materials examined since length distributions were only assessed for a single $V_f$ (0.25 series 4), with the exception of the F material for which $V_f$'s of 0.1 and 0.3 were analysed. These samples exhibited similar fibre length trends to the series 1 and 2 tests, reduced values being apparent at the higher volume fraction. The magnitude of the average lengths was between the series 1 and 2 values and this was reflected by the intermediate mechanical properties obtained.

For the G, H, J and K batches, longer fibres were retained by the coupled materials, which also possessed the wider distribution of lengths, the converse was however true for the L, M and N group of materials. Such behaviour is attributed to melt viscosity variations induced by reaction of the nylon with the sizing compounds and/or, the melting point of the film forming components affecting the dispersability of the fibres. Considering the former; at the same shear rates (ie screw speeds) a viscosity increase will produce higher shear stresses and consequent fibre length reductions (cf. volume fraction effect on viscosity). Lunt (65) has observed, experimentally, size induced viscosity variations in nylon 6.6 where, increasing the concentration of a P.V.Ac. based size (similar to fibre F) resulted in a viscosity decrease while increasing the concentration of a cationic size (similar to that on fibres L, M and N) produced the reverse effect. Obviously the different sizing system on the G, H, J, K group of fibres will also affect the viscosity in some undetermined way, as will the presence or absence of a coupling agent, thus influencing the fibre length. For the latter effect, an increase in the melting point of the film former will reduce the degree of melt shear experienced by the individual filaments by preventing dispersion
of the fibres at lower temperatures, thus increasing the retained lengths. Since the different film former/coupling agent combinations used will possess various melting points, such behaviour will also contribute to influencing the fibre length distributions.

It might be expected that the smaller diameter fibres would confer improved properties due to their relatively larger surface areas. It is apparent however from Table 4.2.1 that the compounding and moulding operation reduced fibre lengths to give aspect ratios of the same order, so that no such benefits were derived. The average aspect ratios in the moulded materials were generally less than the calculated critical values, indicating that improved properties would result from increased aspect ratios.

Reasonably high back pressures are generally required during the moulding operation to give sufficient melt shear to overcome the cohesive effects of the film forming component of the size (which functions in this way to protect the fibres from abrasive damage). It seems probable therefore, that the effect of the size on melt viscosity combined with the binding properties of the film former exerts more influence on composite properties indirectly; by controlling fibre length, than does the direct advantage of the enhanced bonding produced by a coupling agent. Thus, to obtain optimum composite properties, careful selection of the sizing compounds is of paramount importance.

There was no discernable difference in fibre orientation arising from variations in moulding conditions, although such effects have been reported elsewhere (82). Some specimen to specimen variation was noted, but it was not possible to attribute this to any specific moulding parameter, this probably being due to viscosity variations resulting from slightly different machine cycle times. Fibre alignment was generally pronounced along the testpiece axis which is expected when the long linear flowpath from the gate through the constricted gauge
length portion of the cavity, is considered, this having the effect of constraining long fibres in the flow direction. Slightly improved alignment was observed at higher $V_f$'s which is due to the physical constraints imposed by the greater volume of fibres present. In common with many other workers (see section 2.3.1) the observed orientation distribution was analogous to that of a laminated system, misaligned fibres in the sample core regions being sandwiched between well aligned outer layers. The reasons for such behaviour have been discussed previously (Sect. 2.3.1).

The large tensile samples were moulded using both end and side gating with no significant advantages accruing from either method. There was a slight property improvement in the side gated specimens which was attributed to improved fibre orientation resulting from the elimination of jetting, no actual physical evidence of this was however obtained.

It has been shown (65) that differences in fibre lengths produced at the extrusion stage of the melt compounding production route are maintained, albeit at a reduced level, in the final mouldings. Thus, it is apparent from this fact and the results presented, that, to retain long fibres in the mouldings, the degree of fibre attrition prior to the moulding operation must be kept to a minimum. Of the processing routes available, the coextrusion technique represents the most promising since the pre-moulding fibre length can be controlled. In its present form however, the technique suffers some drawbacks; the fibres are not pre-dispersed in the moulding granules and, to ensure minimum mixing times in the injection moulding machine, low size loadings must be employed which may be insufficient to adequately protect the fibres in the harsh moulding environment. Significant improvements will however accrue if a method of ensuring impregnation of the polymer into the roving can be found, thus coating the individual filaments and consequently reducing the required degree of melt plasticization.
5.3 Failure Behaviour

The failure mechanisms operating in any particular composite system will be determined by many variables which include: the fibre and matrix failure strains, the interface strength, the fibre orientation, and the fibre volume fractions. In the case of SFRTP, the stress concentrations known to exist at fibre ends may be accommodated by fibre debonding, matrix cracking or ductile matrix flow, these may lead to fibre fracture or alternatively the fibres may still be able to support the applied load. Whatever the operative mechanisms, if the stress concentration at the fibre end is diffused into the matrix, the composite may then be loaded to a failure point which may be initiated by fibre fracture or matrix cracking.

In an ideal situation, one single mechanism may be sufficient to account for composite failure but, in 'real' materials which possess a range of fibre lengths, strengths and orientations, many of the pertinent mechanisms may actually contribute to the failure process.

One failure model proposed by Curtis et al (1, 104, 105) for SFRTP, is based on experimental observations of glass and carbon fibre reinforced nylon 66. These authors propose that the failure sequence is initiated by matrix cracks which form first at the ends of long better aligned fibres, where the strain concentration in the matrix is greatest. Further cracks are then formed at shorter, less well aligned fibres, as strain is increased. Final failure occurs when the accumulation of matrix cracks so weakens a critical cross section of the testpiece that catastrophic failure occurs. A formal theory was proposed by the authors and subsequently refined by Bader et al (140), which is really only applicable to long aligned fibres, this relying on the load shed by the matrix cracks being accommodated.
by adjacent fibres which 'bridge' the cracked zone. Failure then occurs when the extent of cracking in a localised critical zone causes the bridging fibres to be loaded to their failure stress.

An alternative model could be constructed on similar lines but with fibre fracture as the initiating mechanism. In such a case the strain concentration in the matrix in the region of a fibre end causes a stress concentration in the fibres bridging that zone. (Fig. 5.3.1). It is thus possible to conceive a condition in which aligned fibres could fail at macroscopic strains significantly lower than the normal fibre failure strain. It has been suggested (141) that the stress concentration in a fibre under such conditions is in the order of 15%, thus, fibre failure would occur at \( \approx 85\% \) of the normal failure strain of E-glass fibres, which is not too far removed from the values recorded. On the other hand the post failure fibre length analyses failed to reveal any significant fibre fracture prior to catastrophic failure of the composite, which would tend to rule out this hypothesis. The failure model proposed for the materials in this investigation is based on the observed 'layered' fibre orientation distribution, and, the assumption that there are residual stresses in the specimens which are compressive at the sample surface and tensile in the misaligned core region.

On application of a load, the failure sequence is initiated by the debonding of fibres in the pre-stressed core region. This occurs at the ends of aligned fibres and along the length of misaligned fibres (but since the alignment is generally transverse the latter would predominate). As strain is increased, the debonds propagate along the fibres and the load shed causes adjacent fibres also to debond. Such areas of localised debonding materialise on a macroscopic scale as strain bands which are confined to the core region. The number and size
of these bands increases with strain, with consequent localised matrix flow, voiding and fibre pullout. Then, at some point which is dependent on fibre concentration, interfacial bond strength and matrix moisture content, one band attains critical dimensions and catastrophic brittle failure is initiated.

As such, this represents a basic failure model for which evidence will be presented and, with slight modifications, it can account for all of the experimentally observed behaviour.

Evidence that the fracture process does not involve cumulative fibre fracture or matrix cracking is provided respectively by the pre-and post-testing length distribution analysis, and the small incidence of matrix cracking as observed from microscopy.

The residual stresses that are assumed to exist in the specimens are considered to originate from two sources. Russell and Beaumont (16-18) have shown that, in injection moulded nylon 6, there are residual parabolic stress distributions which result from non-uniform volume changes due to differential cooling rates. These are compressive stresses at the surface and tensile stresses in the core. The second source is due to thermal strains which arise from the layered orientation distribution. Shrinkage on cooling in an aligned composite system is anisotropic, being greater in the direction normal to the fibres. This results from the greater thermal expansion coefficient of the matrix material and the higher relative proportion of matrix in this (normal) direction. If we consider the testpiece as a sandwich (Fig. 5.3.2) then on cooling through ΔT, the aligned layers will shrink less in the x-direction and more in the y-direction, than the misaligned core layer. This will induce longitudinal thermal stresses which are compressive in the outer layers and tensile in the core region, and therefore additional to the stresses arising from non-uniform cooling. Russell and Beaumont have shown that the
magnitude of the latter stresses varies with mould temperature, the
maximum compressive stresses being of the order of 7 MPa and the
tensile stress approximately half this value for a 3mm thick moulding.

The magnitude of the thermal stresses can be estimated by use of
equation (5.3.1) which is due to Bailey et al (142). Strictly this is
only applicable to cross ply laminated systems but if the moulded samples
are treated similarly, due to their 'sandwich' construction, then the
equation can be applied:

\[
\varepsilon_{TL} = \frac{E_L t_L (\alpha_T - \alpha_L) \Delta T}{E_L t_L + E_T (t_T/2)}
\]

(5.3.1)

Where: \(\varepsilon_{TL}\) is the strain in the transversely aligned core in the
longitudinal direction; \(E_L\) and \(E_T\) are the moduli of the layers, parallel
and transverse to the fibre direction respectively; \(\alpha_L\) and \(\alpha_T\) are the
thermal expansion coefficients of the longitudinal and transverse layers
in the longitudinal direction, \(\Delta T\) is the temperature change, and \(t_L\) and
\(t_T\) are the thicknesses of the layers. Previous work (78) has shown that,
for injection moulded samples, \(E_T \approx E_L/2\). Also, from microscopy it is
estimated that \(t_L = t_T = 1\) mm. Thus, for this particular case, equation
(5.3.1) can be reduced to:

\[
\varepsilon_{TL} = \frac{4}{5} (\alpha_T - \alpha_L) \Delta T
\]

(5.3.2)

Bowling (143) has measured thermal expansion coefficients for a
0.25\(V_f\) nylon 6.6, finding that \(\alpha_L = 2.4 \times 10^{-5}\) and \(\alpha_T = 5.9 \times 10^{-5}\)
for the temperature range -60 to 140°C. Using these values and
assuming \(\Delta T = (260-20) = 240°C\) then:

\[
\varepsilon_{TL} = 0.007 = 0.7\
\]
The outer or longitudinal layer strain in the longitudinal direction, $\varepsilon_{\text{LL}}$, can be found by balancing forces:

$$\varepsilon_{\text{LL}} E_L 2t_L = \varepsilon_{\text{TL}} E_T t_T$$

$$\therefore \varepsilon_{\text{LL}} = \frac{\varepsilon_{\text{TL}}}{4}$$

(assuming $E_T = \frac{E_L}{2}$ and $t_L = t_T$)

Therefore $\varepsilon_{\text{LL}} \approx 0.2\%$

Taking material H as an example, at 0.25 $V_F$ for the series 4 samples, the tensile modulus, $E_C$ is 11.1 GPa. If it is assumed that $E_L = E_C$, then the compressive stress induced in the outer layers in the longitudinal direction, $\sigma_{\text{LL}}$, is:

$$\sigma_{\text{LL}} = E_L \varepsilon_{\text{LL}}$$

$$= 22 \text{ MPa}$$

and the longitudinal tensile stress in the misaligned core region:

$$\sigma_{\text{TL}} = E_T \varepsilon_{\text{TL}}$$

$$= E_T/2 \varepsilon_{\text{TL}}$$

$$= 39 \text{ MPa}$$

These values are obviously very high, but, it should be remembered that the extreme situation of longitudinally aligned, continuous fibre, outer layers and a transversely aligned inner layer was considered. The moulded materials however, contain a spectrum of misoriented short fibres in the core and well aligned short fibres in the outer layer. In addition, the use of equation 5.3.2, assumes a constant modulus over the temperature range in question which is not the case, significant reductions occurring at elevated temperatures (113,119). Furthermore,
the treatment assumes a constant buildup of stress with reduction in temperature. For a semicrystalline material such as nylon 6, at temperatures above the glass transition temperature (~50°C, see ref. 14), the amorphous material within, and surrounding, the spherulites can undergo large scale molecular motion which will allow some degree of stress relaxation to occur simultaneously with the thermal stress formation process.

All of these factors will contribute to reducing the level of the thermal stresses below the calculated values. The exercise does however serve to illustrate that the magnitude of these stresses can be significant.

An indication that such stress distributions do in fact exist is obtained when the behaviour of the uncoupled G and J materials is considered, since it was observed that debonding existed in the core layer of untested specimens. The phenomenon was not however apparent in the coupled systems but this is attributed to their higher bond strengths which were capable of withstanding the imposed stress levels.

The consequences of the residual stress distribution in practical terms are that, on application of a tensile load, the stress required to debond fibres will first be reached in the core (tensile stressed) region. Thus, specimen damage will be confined initially to this region, resulting in the experimentally observed strain banding behaviour. Evidence that the strain bands consist of areas of debonded fibres has been presented in Section 4.3.1, and the sequence of events leading to the band development is shown by the in-situ tensile tests (Figs. 4.3.22 and 23). Additionally, there is some indication from the microtomed sections (Figs. 4.3.43 & 4) that matrix voiding and flow occur in conjunction with the debonding.

The fracture models previously described rely on catastrophic
failure being initiated by a critical density of matrix cracks or fibre fractures, the final crack propagating outwards from these damage zones. The model proposed here is essentially similar in concept in that a debonded fibre causes adjacent fibres to also debond, forming a damage zone or strain band. When this band attains critical dimensions and the remaining undamaged material cannot support the applied load, fracture will be initiated in one of two ways. Either a crack will propagate outwards from the band in a brittle fashion (see Fig. 5.3.3a) or brittle cracks are initiated by sporadic failure events in the well aligned surface regions. The first alternative is considered unlikely since it would require that the whole of the characteristically ductile strain banded region be visible on the fracture face. This is generally not the case, the fracture occurring only partially through a strain band (Fig. 5.3.3b). If however, the final failure is initiated by an end debond or fibre fracture in the aligned outer layers, then the resulting crack(s) will intersect with strain bands in an essentially random manner.

At low strain levels, a fibre end debond will be contained due to insufficient energy being available for matrix crack formation. As strain is increased, the shear stresses at the fibre end will cause debonding along the fibre, this being illustrated schematically in Fig. 5.3.4 (route a). At higher strains, an end debond may propagate as a small radial matrix crack (Fig. 5.3.4, route b) of the type shown in Fig. 4.3.3. The crack radiates only a small distance because insufficient energy is available to overcome the constraining effect on the matrix of the surrounding fibres. At still higher strain levels where the core damage zone has attained a critical size, the stored strain energy may be sufficient to allow catastrophic propagation of existing matrix cracks (Fig. 5.3.4 route b) and also to allow catastrophic cracks to initiate from further end debonds (Fig. 5.3.4 route c).
Fractographic evidence tends to support the latter mechanism since fracture occurs only partially through one of the strain bands, and, the characteristic matrix surface markings indicate that the initiation points are in the aligned outer regions. For example see Fig. 4.3.30. In addition, any fibre fractures that occur will behave in a similar manner, i.e. if it is energetically favourable, a fibre fracture will initiate a catastrophic matrix crack.

The majority of the materials investigated failed at strains less than the estimated fibre failure strains, this tends to rule out fibre fracture as the principal failure initiating mechanism, especially in view of the similarity of the pre- and post-test length distributions. However, fractography on the boiled samples revealed apparently longer pullout lengths than had been observed in the dry materials. Since both test series had originated from the same batch of mouldings, the implication is that some fibre fracture must have occurred in the "dry" tested samples. This may be attributed to local stress concentrations, at fibre ends or crossover points, producing fibre fracture at average composite strains lower than the fibre failure strains, the extent of the fractures being insufficient to register in the length distribution analysis.

A critical point in the development of such a model was the condition of the sample fracture surfaces. These showed both "weak" and "strongly" bonded characteristics in different regions of the same fracture surface. Regions of ductile matrix flow containing fibres with clean surfaces were found in the central or misaligned fibre core regions while the matrix in the more aligned outer layers demonstrated brittle behaviour and contained fibres with matrix debris adhering to them.

The ductile regions are considered to be an integral part of the strain banding phenomena which occurs at low deformation rates. They form in the following manner; when the fibres in the core region debond
the surrounding matrix is less constrained, this allows local plastic deformation to occur resulting in molecular chain alignment and cavitation. Thus, when the specimen ultimately fails in a fast and brittle manner the flow aligned regions extend and separate, exhibiting the characteristic fibrillar or 'petal like' morphology observed on the fracture surfaces. Indications of the occurrence of molecular chain alignment was obtained from high magnification examination of the 'petals' which exhibited striations in the flow direction.

Berry (135) makes the comment that it is generally accepted that the tensile component of stress is responsible for brittle failure while ductile yielding occurs under the influence of the shear component. Proof of such behaviour is widespread since brittle fracture surfaces are generally normal to the applied stress while lines of shear (cf. Lüders lines) are often observed in ductile yielding polymers. This type of behaviour is the case here since the ductile regions were generally found on surfaces at an angle to the applied stress while brittle regions were perpendicular to the stress direction (Fig. 4.3.25). The angle of the strain bands (≈55° to the stress axis) is characteristic when considering localised shear deformations since they lie along the direction of zero extension and thus impose no excess strain on the adjacent material (130).

A similar type of bimodal failure behaviour has been noted in glass filled ABS by Dover et al (125). The resulting fracture surfaces possessed the characteristics of good and poor interfacial bonding, this being due to an initially slow crack growth followed by a fast brittle failure. The authors attribute such behaviour to the viscoelastic or strain rate dependent nature of the interface or interphase layer.

Bessell et al (15) have observed brittle and ductile fracture surfaces in nylon 6 which were dependent on the degree of crystallinity
(high crystallinity - brittle fracture). In addition these authors have also noted that matrix modification occurs adjacent to the fibre surface giving a more crystalline structure. These facts may well account for the observed behaviour in the brittle areas, the fibres pulling out with a sheath of matrix adhering to them, but they do not account for the clean fibres in the ductile regions. It must also be noted that Burton et al (136) have shown that the columnar spherulitic growth behaviour observed by Bessell in in-situ polymerised nylon does not exist in injection moulded systems due to the non-establishment of critical conditions.

Controversy still reigns as to the exact form of bonding at the interface and over the existence of an interphase layer (Section 2.1.3). Despite this, it seems reasonable to assume that some kind of matrix modification does occur adjacent to the fibre surface due to reaction with the coupling agent and/or the other sizing components, resulting in an interphase layer which may possess different properties. Some indication of this is obtained when the behaviour of a crack intercepting a fibre is considered (Fig. 4.3.10). The crack front is observed to fork around the fibre without actually intercepting it, leaving a thin layer of matrix, and only reaches the fibre when the crack front has passed, a phenomena also commented on by other workers including Curtis (1). This behaviour may be due to a structurally different interphase layer or it may only be a physical effect of the fibre locally constraining the matrix.

In considering the experimentally observed behaviour, the hypothesis of Dover et al (125) offers the most viable explanation, ie. that the interface (or an interphase layer) is viscoelastic so that the bond strength, \(\tau\), apparently changes with fracture speed. Slow speed deformations, such as those encountered in the formation of the strain bands, allow debonding and ductile behaviour at the fibre surface.
The high rates of deformation that occur during catastrophic failure however, result in 'debonding' between the interphase layer and the matrix in a brittle fashion, leaving pulled out fibres with matrix adhering. The residual stress distribution will aid such behaviour, allowing debonding to occur at lower overall strain levels. In addition, the thermal stresses are imposed at low deformation rates (due to thermal contraction) which will favour interfacial debonding, as observed in the uncoupled materials. A further contributory factor towards debonding in the banded regions is the observation by Bessell et al (32) that the interface is weaker in shear, since a shear deformation mode will be aided by the fibre misorientation.

Changes in the surface condition of pulled out fibres have also been commented on by other workers (eg. 107) this being attributed to a fracture speed effect although no explanation was offered.

Considering the low strain to failure of the uncoupled materials in the dry condition (L excepted due to its different bonding mechanism); since the residual stress distribution and lower interfacial bond strengths cause pre-test debonds, and debonding at lower overall strain levels, the accumulated damage will attain a critical state at lower strains thus resulting in premature failure. Furthermore, the reduced constraining effect of the fibres will mean that less energy is required to propagate catastrophic matrix cracks.

In the wet state, plasticization and hence swelling of the nylon matrix will tend to relieve the residual compressive stresses at the surface, the extent of this depending on the degree of degradation of the interfacial bond. If a reasonably strong bond remains (as in the K and H materials) then the constraining effect of the fibres will maintain the compressive stress, resulting in a failure sequence similar to the 'dry' state. If the bond is completely degraded, as in the uncoupled materials, then such constraints will be removed allowing relaxation of
the residual stresses. This would remove the confinement effect on the strain banding phenomena, allowing debonding to initiate anywhere in the sample. Such behaviour was observed experimentally, the incidence of strain banding in the uncoupled materials being higher and also extending to the surface (Figs. 4.3.43 and 44). A similar surface "crazing" effect has been observed by Lunt (65) in low $V_f$ glass reinforced nylon 6.6 after a boiling water treatment. He comments that the behaviour is consistent with a failure process controlled by fibre debonding and matrix cracking, such effects arising from matrix plasticisation and interfacial bond degradation. The photographic evidence offered however was more consistent with ductile matrix rupture rather than cracking. (It is perhaps useful to comment here that, throughout this investigation, 'matrix cracking' is taken to mean parting of the matrix in a brittle fashion, as opposed to ductile rupture). In addition, Russell and Beaumont (16-18) in their investigation of the residual stresses in unfilled nylon 6 mouldings noted that when subjected to a boiling water treatment, the nature of the residual stress distribution reversed, i.e. became tensile at the surface, this being attributed to inhomogeneous volume changes resulting from water induced crystallisation.

The overall embrittlement effect of introducing fibres into a thermoplastic matrix is due to the constraining effect of the fibres. If this is removed by substantially reducing the interfacial bond strength as in the wet materials, or by fibre fracture resulting from reduced fibre strength, as in the heat cleaned materials, then extensive matrix ductility and higher failure strains will result. This is with the proviso that the matrix material can sustain the additional load without failing, thus such behaviour is generally apparent at low $V_f$'s. At high $V_f$'s, the relatively reduced volume of matrix will not be capable of withstanding the extra load and failure occurs at low strains, such as observed in the heat cleaned material ($V_f > 0.1$) and some of the boiled
samples \(0.25 V_f\), materials F, M and N).

The considerable dependence of the mechanical properties on the absorbed moisture content highlights the need for accurate environmental conditioning of these hygroscopic materials if representative and comparable results are to be obtained. The so called 'dry' samples were pre-test conditioned for 21 days at 20°C and 50% relative humidity to reduce the inherent brittleness of absolutely dry nylon. While it is recognised that such a period is insufficient to allow complete moisture equilibrium, it does allow the material properties to be assessed under conditions more likely to be encountered in service. The boiling treatment represents an environmental extreme, unlikely to be encountered in actual use but serves to accentuate property trends in the presence of moisture.

**Acoustic Emission Analysis**

This technique was used to investigate and monitor the onset and accumulation of composite damage during tensile testing. Since the unfilled polymer produced no acoustic emissions during testing it is assumed that slow matrix deformations do not contribute to the observed acoustic activity during the testing of the composites. Acoustic emissions are transient elastic stress waves generated by the rapid release of stored strain energy, ie. they occur only from sudden events. In composite materials, the principal sources in descending order of energy release are: fibre fracture, matrix cracking, interfacial debonding and fibre pullout, the latter making a significant contribution only if a 'stick-slip' mechanism is operating.

Correlation of results with other techniques, principally optical microscopy and length distribution analysis, in which no significant matrix cracking or fibre fracture was observed (with the exception of the heat cleaned materials), indicates that a major source of acoustic
emission in the initial stages of testing was debonding at fibre ends. The 'in-situ' tensile tests (see Section 4.3.1) demonstrated that the fibre ends debonded in a sudden manner and, since these occurrences are accompanied by the release of stored elastic strain energy, significant acoustic emissions result. The debonding of misaligned fibres along their length did not occur in such a sudden manner, consequently their contribution is smaller.

The observed slow initial increase in output with strain agrees well with the proposed failure model. The debonding mechanism, which is a relatively low energy event, accounts for the initially slow buildup in output and this is followed by higher energy events at increased strains such as matrix crack formation and fibre fracture, which contribute to the exponential increase.

Comparing the different materials, it is apparent that the acoustic emission behaviour is a fairly complex function of volume fraction, type of sizing system and fibre diameter. Table 5.3 lists the approximate acoustic emission 'onset' strains from which it appears that, for the same type of material (i.e. same fibre, different $V_f$, or, same sizing formulation, different diameter), an increase in stiffness results in reduced onset strains. This might be expected, since higher stresses are imposed at lower strains in stiffer materials, thus more energy is available to initiate and propagate composite damage and such events would therefore involve a greater release of stored energy.

The uncoupled materials exhibited lower onset strains and lower total outputs than their coupled pairs. This is due respectively to their lower bond strengths which allow debonding to occur at lower strains and their reduced failure strains which do not allow as much accumulated damage (G and J only). Material K, despite having a high failure strain compared to material H (same size formulation), exhibited a lower total output, this can probably be attributed to the greater
number of fibres in the latter (same $V_f$, smaller diameter) and hence greater number of fibre ends acting as damage sites.

Considering the LMN group of materials, L had the lowest onset strain but its output was comparable with material M which is attributed to the similarity in properties due to the ionic bonding mechanism. Material N, possessed similar onset strains but considerably reduced total outputs compared to M, this despite its higher stiffness and greater number of fibre ends. The reason for such behaviour is not known but is again in all probability due to a sizing system effect.

It must be noted that the Series 2 and HC2 results are not directly comparable with the Series 4 results since an unguarded detection system was used in the former. Thus appreciable emissions can be expected to have originated from the testing machine and the grip portion of the sample. This may however account for the lower onset strains of the Series 2 (Fibre F) samples compared to the Series 4 (Fibre F) values.

The heat cleaned materials exhibited both low onset strains and high outputs, in addition it was noted that the output rate increased much more rapidly. (0.1 $V_f$ excepted). This is attributed to the change in failure mode with its higher incidence of fibre fracture and thus increased output at lower strains. The 0.1 $V_f$ material demonstrated a substantially different behaviour in that the output reached a maximum when the stress-strain curve levelled off, subsequently declining with increasing strain. It is suggested that such behaviour is a result of the high ductility of these materials. At increased strains, high energy events such as fibre fracture are virtually completed, leaving the lower energy debonding and non-contributory matrix flow, the output therefore declines.

The behaviour of the wet materials appeared to be dependent on the extent of interfacial bond degradation. The uncoupled materials
demonstrated virtually zero output which is a result of the complete bond deterioration. The coupled materials however, generally exhibited lower onset strains compared to the dry state, Table 5.3.1 and their outputs reached a maximum when the stress-strain curves levelled off. The emissions declined to zero with increasing strain in the low $V_f$ M and N materials, but maintained an almost constant level in the H and K materials. The difference in behaviour can be attributed to the relatively greater degree of bond deterioration in the former materials. This allows more debonding at lower strains, thus at the yield point, the acoustic events are virtually complete giving a subsequently declining output. The absence of a sharp increase prior to failure can be attributed to both the increased degree of debonding and the increased matrix ductility which, respectively, reduce the extent of fibre fracture and matrix cracking.

Although no literature specific to composites could be found describing the observed output behaviour of the heat cleaned and wet M and N samples (ie. increase to maximum and decline), Liptai (134) describes a similar behaviour for aluminium in tension. The count rate peaks at the yield point and emission activity decreases with increasing strain beyond yielding. This was attributed to the initiation and movement of dislocations accompanying the metal deformation.

It is apparent from the results presented that the properties of the materials are highly dependent on the complex and largely unquantified behaviour of the sizing system employed on the fibres. This is not simply a function of the degree of interfacial bonding (which itself varies with fibre content, moisture content and amount of melt mixing) since the size, by influencing the polymer rheology, exerts a considerable indirect control over composite properties. More work is needed to accurately characterise the effect of the size on the matrix and interface especially in view of a recent paper by Han et al (144) who showed that the type of
coupling agent influences melt rheology, this supplementing the observations by Lunt (65) that the film former also has such effects. Additionally, the failure process in these materials was shown to be a complex function of many variables such as the interface, the fibre parameters and the orientation distribution. It is therefore evident that, if accurate models for predicting SFRTP behaviour are to be formulated, more work is needed to quantify the micromechanisms involved in the failure process.

Table 5.3.1
Acoustic Emission 'Onset' Strains

<table>
<thead>
<tr>
<th>Material Code</th>
<th>$V_f$</th>
<th>Approximate 'onset' Strain, $\varepsilon_{AE}$ (%)</th>
<th>Tensile Modulus $E_c$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>'Dry'</td>
<td>'Wet'</td>
</tr>
<tr>
<td>F</td>
<td>0.2</td>
<td>0.7</td>
<td>-</td>
</tr>
<tr>
<td>Series 2</td>
<td>0.3</td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.38</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Heat Cleaned</td>
<td>0.1</td>
<td>0.8</td>
<td>-</td>
</tr>
<tr>
<td>HC2</td>
<td>0.2</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>F(Series 4)</td>
<td>0.1</td>
<td>1.0</td>
<td>no output</td>
</tr>
<tr>
<td>F</td>
<td>0.3</td>
<td>0.7</td>
<td>no output</td>
</tr>
<tr>
<td>G</td>
<td>0.25</td>
<td>0.8</td>
<td>no output</td>
</tr>
<tr>
<td>H</td>
<td>0.25</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>J</td>
<td>0.25</td>
<td>0.8</td>
<td>no output</td>
</tr>
<tr>
<td>K</td>
<td>0.25</td>
<td>1.4</td>
<td>1.3</td>
</tr>
<tr>
<td>L</td>
<td>0.25</td>
<td>1.4</td>
<td>no output</td>
</tr>
<tr>
<td>M</td>
<td>0.25</td>
<td>1.5</td>
<td>1.4</td>
</tr>
<tr>
<td>N</td>
<td>0.25</td>
<td>1.5</td>
<td>1.4</td>
</tr>
</tbody>
</table>
Fig. 5.3.1. Stress distribution in a short fibre as a result of the stress concentrating effect of a fibre end.

On cooling the testpiece through $\Delta T$, differential thermal shrinkage will induce thermal stresses, $\sigma^t$, in the sample such that:

\[
\begin{align*}
\text{outer} & \quad \begin{cases} 
\sigma_x^t = \text{compressive} \\
\sigma_y^t = \text{tensile} \\
\sigma_z^t = \text{tensile}
\end{cases} \\
\text{inner} & \quad \begin{cases} 
\sigma_x^t = \text{tensile} \\
\sigma_y^t = \text{compressive}
\end{cases}
\end{align*}
\]

Fig. 5.3.2. Schematic illustration of method by which residual stresses are induced.
Fig. 5.3.3. a) Catastrophic crack radiates from strain band of critical size.

b) Catastrophic crack initiated by fibre end debond or fibre fracture, propagates partially through a strain band.

Fig. 5.3.4. Behaviour resulting from a fibre end debond at different stored strain energy levels.
6. CONCLUSIONS

6.1 Mechanical Properties

The mechanical behaviour of short glass fibre reinforced nylon 6 is controlled principally by the fibre concentration, length and orientation. Increasing the fibre volume fraction and length gives an increase in modulus and strength but a decrease in failure strain. In general the impact strength increases in proportion to the tensile strength.

The mechanical behaviour is also strongly influenced by the choice of sizing compounds applied to the glass reinforcement. In this work it has been shown that, in the case of a conventional polyurethane based size, the omission of the silane coupling agent results in a significant deterioration in all of the mechanical properties of the dry material, and, a catastrophic reduction in the case of materials subjected to a boiling water treatment prior to testing. However, in the use of another glass treated with a cationic polyelectrolyte based size, there was little difference in the dry properties, but the wet properties showed an even greater reduction. From this behaviour, it may be concluded that the polyelectrolyte size forms an adequate bond to the glass surface even if no silane is used. This bond however, is not as resistant to moisture induced degradation. The silane component of the size in both cases acts principally to maintain the integrity of the interface against this water induced degradation.

In most of the materials tested, the omission of the silane resulted in not only lower strengths but also lower ductility, and this is also reflected in lower charpy impact performance.

6.2 Failure behaviour

Virtually all of the materials tested in the dry condition and the higher $V_f$ materials tested when wet, failed in tension by a mixed brittle/
ductile fracture mode. The failure process is initiated by the ductile mechanism which, in turn, initiates a catastrophic brittle failure sequence. The earliest failure events appear to be debonding at the fibre matrix interface within the misoriented core of the moulding, which is subject to an internal residual tensile stress. These microscopic debonded regions interlink, inducing localised matrix flow, eventually forming well defined strain bands. The final brittle failure sequence commences in the better aligned outer layers of the mouldings and appears to be initiated by sporadic micro brittle failures which may either be fibre fractures or matrix cracks at fibre ends. Each of the regions possesses a distinct fracture morphology, the ductile regions exhibit clean fibres and extensive matrix flow whilst, in the brittle areas, there is no matrix flow and considerable evidence of matrix debris adhering to the exposed fibres.

6.3 Processing

Although not adequately investigated in this work, it was clear that the processing conditions had a strong influence on both fibre length and orientation distributions in the mouldings. In particular, the higher screw back-pressures necessary to adequately disperse the higher $V_f$ compounds resulted in more fibre breakage. It was also observed that the higher $V_f$ compounds tended to have better fibre alignment.

In order to optimise the mechanical properties of a fibre reinforced thermoplastic it is desirable to maximise the $V_f$ and fibre length. The choice of size for a particular composite system will strongly influence the way in which the fibre strand is dispersed during processing. It is therefore important to select the sizing formulation with regard to the materials used and the method of compounding, quite apart from the primary consideration of the coupling agent function.
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1. Introduction

The mechanical properties of injection-moulded, fibre-reinforced thermoplastics are determined principally by the fibre volume fraction, the fibre aspect ratio distribution, the fibre orientation distribution and the state of the fibre/matrix interface. The fibre volume fraction may be controlled by the fabricator, within the limits allowed by the requirement for adequate flow during processing, but the fibre aspect ratio and orientation is largely dictated by the flow history of the material during compounding and moulding. The practical consequence is that mouldings contain a dispersion of rather short fibres (typically less than 1mm) with a complex orientation distribution dictated by the flow of the molten charge into the mould.

The reinforcing potential of a fibre is a function of its aspect ratio, its orientation and the shear strength of the fibre/matrix interface. A strain dependent critical aspect ratio for a fibre aligned along the principal stress axis is given by:

\[ R_{CR} = \frac{\varepsilon_c E_f}{\tau_i} \]  ... 1

The quantity \( \varepsilon_c E_f \) is the stress in a continuous aligned fibre at the strain \( \varepsilon_c \), and clearly the critical aspect ratio, \( R_{CR} \), will be smaller for higher values of the interface strength, \( \tau_i \). The reinforcement efficiency of aligned short fibres compared with that for continuous fibres is 0.5 at \( R_{CR} \), rising to 0.9 at \( R=5 R_{CR} \) and 0.95 at \( R=10 R_{CR} \). It is, thus, highly desirable that the average fibre aspect ratio in the moulding should approach \( 5R_{CR} \) and since the actual aspect ratio is difficult to control this is best approached by ensuring that \( \tau_i \) is as high as possible.

The degree of fibre alignment is also important in determining the mechanical properties. Aligned fibres result in the maximum stiffness and strength in the direction of alignment with minimum
properties normal to this direction, i.e. the greatest degree of anisotropy. At the other end of the scale a fully random fibre orientation gives an isotropic material with a stiffness about an order of magnitude less than in the aligned case. Practical moulded filled thermoplastics usually show a pronounced fibre orientation in the direction of flow. They are therefore anisotropic. The fibre distribution is often very complex, however, and in thin sections a laminated structure with a random skin layer, flow-aligned intermediate layers and transverse oriented centre layer is commonly observed (Fig. 5).

In the present work the influence of coupling agents on the development of the interfacial bond has been studied, together with the effects of processing variables on the stiffness strength and failure behaviour of glass-fibre filled polyamide 6.

2. Experimental

The materials used comprise a single grade of polyamide 6 (Maranyl F 114) supplied by I.C.I. Limited and a range of E-glass fibre rovings some of which were specially prepared by the manufacturers for this investigation. These are described in Table I.

The fibre designated "F" had a poly vinyl-acetate based size incorporating a chromium complex as an adhesion promotor. Fibres G, H, J, and K had a polyurethane based size which in H and K incorporated a proprietary silane coupling agent. L, M and N likewise were treated with a proprietary size, with silane coupling agent in the case of M and N.

It is normal practice to use a relatively heavy application of size to maintain strand integrity during the processes of chopping and dry blending prior to compounding. However, since an alternative compounding process was to be used in this work the level of size application was reduced in the glasses L, M and N. It should be noted that the strands in F, G and H are significantly heavier than in the other rovings. The rovings treated with the polyurethane based size (G, H, J, K) were relatively "soft", whilst L, M and N were significantly "harder", F being the hardest of the range.

The injection moulding compound was prepared by a technique of cross-head die extrusion, whereby the polymer is coated onto a continuous roving of glass-fibre. The co-axial polymer/glass-fibre "lace" is then chopped into pellets suitable for injection moulding (1).
TABLE I
DESCRIPTION OF E-GLASS ROVINGS USED IN INVESTIGATION

<table>
<thead>
<tr>
<th>Designation</th>
<th>Tex</th>
<th>Make up</th>
<th>Nominal Fibre dia (µm)</th>
<th>Size formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>4600</td>
<td>16x 228</td>
<td>13</td>
<td>PVAc size with Cr complex coupling agent</td>
</tr>
<tr>
<td>G</td>
<td>3600</td>
<td>16x 225</td>
<td>12</td>
<td>PU size No coupling agent</td>
</tr>
<tr>
<td>H</td>
<td>3600</td>
<td>16x 225</td>
<td>12</td>
<td>PU size + silane coupling agent.</td>
</tr>
<tr>
<td>J</td>
<td>3600</td>
<td>20x 180</td>
<td>16</td>
<td>PU size No coupling agent</td>
</tr>
<tr>
<td>K</td>
<td>3600</td>
<td>20x 180</td>
<td>16</td>
<td>PU size + silane coupling agent.</td>
</tr>
<tr>
<td>L</td>
<td>1710</td>
<td>16x 107</td>
<td>10</td>
<td>Proprietary size No coupling agent.</td>
</tr>
<tr>
<td>M</td>
<td>3060</td>
<td>16x 190</td>
<td>13</td>
<td>Proprietary size + silane coupling agent.</td>
</tr>
<tr>
<td>N</td>
<td>1710</td>
<td>16x 107</td>
<td>10</td>
<td>Proprietary size + silane coupling agent.</td>
</tr>
</tbody>
</table>

The roving "make up" is the number of strands and the approximate tex of the strand.

This technique has been found to be convenient in that small batches of special compounds may readily be prepared. The moulding pellets are in the form of co-axial cylinders with the fibres in the centre. The length of the cylinders, and hence the fibre may be controlled during the chopping operation. It should be noted that the fibres are not fully wetted and impregnated during the compounding operation. The final fibre dispersion occurs during the injection moulding process itself. This was done on a BOY 15 automatic injection moulding machine incorporating a screw-preplasticization stage. For this work a pellet length of 4mm was found to give the best distribution but even then the average fibre length in the moulding was reduced to the order of 250µm, although a significant proportion of much longer fibres did survive (Table III). The degree of fibre dispersion was controlled by adjusting the screw back-pressure. A higher setting resulted in a greater amount of shear on the material with consequent better dispersion of fibre bundles but relatively more fibre breakage. It was found that longer pellets required a higher back-pressure for adequate dispersion and that the fibre length in the moulding was actually reduced if very long (e.g. >6mm) pellets were used.
Typical length and diameter distributions are shown in Figure 1 and 2. It should be noted that the fibre volume fraction of the extrusion coated moulding pellets was of the order of 0.4. The \( V_f \) of the mouldings was controlled by blending a proportion of unfilled polymer pellets with the compound. This blend was then charged into the injection moulding machine. In this work two nominal fibre fractions of 0.1 and 0.25 were used.

The mechanical test programme was conducted on injection moulded tensile test bars. These test pieces were 150mm long with a
gauge section of 12 x 3mm. Each moulding consisted of two test pieces, one end-gated and the other side-gated. The impact test pieces were cut from the gauge portion of tensile test bars and a notch 2mm deep cut by sawing. The tip of the notch was sharpened by cutting with a scalpel blade immediately prior to testing. After moulding, the tensile test bars were conditioned at a temperature of 20°C and 50% relative humidity for a period of at least 28 days before they were tested. This procedure was to allow a substantial equilibration of moisture content to be achieved. Some test pieces were further treated by boiling in distilled water for 48 hours to artificially raise their water content, they were then cooled to room temperature, superficially dried and tested immediately.
Tensile testing was carried out on an Instron test machine, strain was measured with an electrical resistance strain gauge based extensometer and acoustic emission recorded using a guarded transducer system. Load, strain and acoustic emission rate were recorded autographically. A Charpy type machine was used for impact testing, an impact velocity of 3 ms⁻¹ at a kinetic energy of 5 J was used.

The fibre fraction of each batch of material was determined by using a burn-off technique to separate the fibres from the matrix, and the fibre length distribution was measured by examining these released fibres under the microscope. The fibre diameter distribution was also measured using a microscope technique.

3. Results

The constitution and mechanical properties of all the materials are summarised in Tables II A and B. It should be noted that, except in the case of F, the fibre length distributions were determined only on samples of the 0.25 Vₐ materials.

The fibre diameters were measured on two or three strands taken at random from each batch of glass. These results should, therefore, be taken as typical values rather than overall averages. It was found that both the diameter and length distributions followed a consistent pattern over all the fibre batches (Table III).

The interface shear strength, τᵢ, and the orientation parameter, Cₒ, were estimated using the method described by Bowyer and Bader (2). This technique fits a modified "rule of mixtures" equation to the experimental stress/strain curve using, τᵢ as a disposable constant. The values obtained are consistent with those from previous work (3) and compare with a measured value of shear strength of the unfilled polymer of 50 MPa. It should be noted that, except in the case of L, the materials without coupling agent have the lower τᵢ values.

The tensile modulus values for the "dry" material show some scatter between batches which may be attributed to random differences in orientation, fibre length and volume fraction. The coupled glasses give marginally higher dry modulii than the uncoupled versions (G, J, L). This trend is more marked in the case of the tensile strength comparisons for G and J, although in the 0.25 Vₐ L material there is little difference. The strain at failure of all the dry materials is low at 2.4 - 3.0% for the 0.1Vₐ and 1.3 - 3.0% for the 0.25Vₐ material. It should be noted that the estimated strain in the fibre at failure is about 3%, so that all batches except K fail at much lower strains. The reasons for the higher strains achieved with batch K are not understood.
### TABLE II A

**MECHANICAL TEST DATA FOR INJECTION MOULDED GLASS-FIBRE REINFORCED POLYAMIDE 6 - Vf = 0.1**

<table>
<thead>
<tr>
<th>Fibre Code</th>
<th>Fibre Volume Fraction</th>
<th>Test Condition/ Gate Position</th>
<th>Tensile Modulus E (GPa)</th>
<th>Tensile Strength σc (MPa)</th>
<th>Failure Strain εc (%)</th>
<th>Notched Charpy Impact Energy YCN (kJ/m²)</th>
<th>Notched Charpy Impact Energy Y1 (MPa)</th>
<th>Interface Shear Strength ct (MPa)</th>
<th>Fibre Orientation Parameter co</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>0.1</td>
<td>Dry/E</td>
<td>5.42</td>
<td>103</td>
<td>2.6</td>
<td>-</td>
<td>30</td>
<td>0.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dry/S</td>
<td>5.41</td>
<td>107</td>
<td>2.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wet/E</td>
<td>1.70</td>
<td>33.6</td>
<td>&gt;25</td>
<td>-</td>
<td>12.9</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>0.1</td>
<td>Dry/E</td>
<td>4.79</td>
<td>82.6</td>
<td>2.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>No coupling agent</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wet/E</td>
<td>1.22</td>
<td>31.7</td>
<td>&gt;25</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>0.1</td>
<td>Dry/E</td>
<td>5.10</td>
<td>101</td>
<td>3.0</td>
<td>14.6</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wet/E</td>
<td>2.67</td>
<td>50.8</td>
<td>5.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>J</td>
<td>0.1</td>
<td>Dry/E</td>
<td>4.64</td>
<td>75.3</td>
<td>&gt;25</td>
<td>13.0</td>
<td>-</td>
<td>-</td>
<td>No coupling agent</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wet/E</td>
<td>1.09</td>
<td>31.7</td>
<td>&gt;25</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>0.1</td>
<td>Dry/E</td>
<td>5.40</td>
<td>113</td>
<td>3.0</td>
<td>16.5</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wet/E</td>
<td>2.77</td>
<td>55.8</td>
<td>5.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>0.17 (0.1)*</td>
<td>Dry/E</td>
<td>7.19 (5.05)*</td>
<td>128</td>
<td>2.7</td>
<td>25.4</td>
<td>-</td>
<td>-</td>
<td>No coupling agent</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wet/E</td>
<td>5.20</td>
<td>31.2</td>
<td>15.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>0.1</td>
<td>Dry/E</td>
<td>4.50</td>
<td>100</td>
<td>3.0</td>
<td>15.3</td>
<td>-</td>
<td>-</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wet/E</td>
<td>2.40</td>
<td>32.7</td>
<td>12</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>0.1</td>
<td>Dry/E</td>
<td>4.80</td>
<td>95.4</td>
<td>2.4</td>
<td>16.8</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wet/E</td>
<td>2.38</td>
<td>31.9</td>
<td>9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Estimated values for Vf = 0.1

**E** - end gated

**S** - side gated

"Dry" - 28 days at 20°C and 50% RH

"Wet" - Boiled in distilled water for 48h.

### TABLE II B

**MECHANICAL TEST DATA FOR INJECTION MOULDED GLASS-FIBRE REINFORCED POLYAMIDE 6 - Vf = 0.25**

<table>
<thead>
<tr>
<th>Fibre Code</th>
<th>Fibre Volume Fraction</th>
<th>Test Condition/ Gate Position</th>
<th>Tensile Modulus E (GPa)</th>
<th>Tensile Strength σc (MPa)</th>
<th>Failure Strain εc (%)</th>
<th>Notched Charpy Impact Energy YCN (kJ/m²)</th>
<th>Notched Charpy Impact Energy Y1 (MPa)</th>
<th>Interface Shear Strength ct (MPa)</th>
<th>Fibre Orientation Parameter co</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>0.30</td>
<td>Dry/E</td>
<td>12.5</td>
<td>180</td>
<td>2.1</td>
<td>-</td>
<td>46</td>
<td>0.59</td>
<td>High Vf</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dry/S</td>
<td>13.1</td>
<td>180</td>
<td>2.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wet/E</td>
<td>4.27</td>
<td>33.7</td>
<td>1.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>0.25</td>
<td>Dry/E</td>
<td>10.7</td>
<td>102</td>
<td>1.3</td>
<td>16.8</td>
<td>35</td>
<td>0.56</td>
<td>No coupling agent</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dry/S</td>
<td>10.1</td>
<td>107</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wet/E</td>
<td>2.16</td>
<td>28.8</td>
<td>15</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>0.25</td>
<td>Dry/E</td>
<td>11.1</td>
<td>169</td>
<td>2.2</td>
<td>19.7</td>
<td>44</td>
<td>0.62</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dry/S</td>
<td>12.2</td>
<td>175</td>
<td>2.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wet/E</td>
<td>4.86</td>
<td>86.0</td>
<td>3.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>J</td>
<td>0.25</td>
<td>Dry/E</td>
<td>10.0</td>
<td>106</td>
<td>1.4</td>
<td>14.9</td>
<td>35</td>
<td>0.55</td>
<td>No coupling agent</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dry/S</td>
<td>11.3</td>
<td>106</td>
<td>1.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wet/E</td>
<td>2.12</td>
<td>28.7</td>
<td>15</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>0.25</td>
<td>Dry/E</td>
<td>10.2</td>
<td>164</td>
<td>2.9</td>
<td>28.4</td>
<td>40</td>
<td>0.64</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dry/S</td>
<td>10.7</td>
<td>165</td>
<td>3.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wet/E</td>
<td>5.34</td>
<td>92.9</td>
<td>4.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>0.25</td>
<td>Dry/E</td>
<td>10.8</td>
<td>159</td>
<td>2.2</td>
<td>26.4</td>
<td>40</td>
<td>0.57</td>
<td>No coupling agent</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dry/S</td>
<td>11.1</td>
<td>167</td>
<td>2.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wet/E</td>
<td>4.2</td>
<td>29.1</td>
<td>5.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>0.25</td>
<td>Dry/E</td>
<td>9.78</td>
<td>152</td>
<td>1.7</td>
<td>25.6</td>
<td>45</td>
<td>0.94</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dry/S</td>
<td>9.75</td>
<td>154</td>
<td>1.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wet/E</td>
<td>4.6</td>
<td>60.4</td>
<td>2.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>0.25</td>
<td>Dry/E</td>
<td>11.4</td>
<td>157</td>
<td>2.0</td>
<td>27.9</td>
<td>40</td>
<td>0.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dry/S</td>
<td>11.2</td>
<td>168</td>
<td>2.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wet/E</td>
<td>4.75</td>
<td>62.9</td>
<td>1.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Typical stress/strain curves for all compounds at $V_f = 0.1$ (Fig. 3) and $V_f = 0.25$ (Fig. 4). Tests in "dry" condition - full lines; "wet" condition - chain dotted lines. The broken lines L in Fig. 3 and F in Fig. 4 denote compounds of anomalous $V_f$.

The differences in tensile properties are illustrated in the comparative stress-strain curves (Figs. 3 & 4) which show the uncoupled batches G and J to have far inferior properties than their coupled counterparts H and K. However, there is little difference between L and N which incorporate a different size and, (in the case of M and N) a different coupling agent.

There appears to be very little difference in properties between the end-gated and side-gated, samples. If anything the latter show a marginally higher modulus. This is due to the elimination of "jetting" at high injection rates. It was found that the flow of charge into the mould was more uniform with this side-gated configuration.

The calculated values for the fibre-orientation parameter $C_0$ are similar for all batches falling in the range 0.55-0.65. This
indicates a pronounced fibre alignment along the axis of the test piece and is in agreement with previous observations (3). The orientation of the fibres varies through the specimen thickness (4); there is a thin skin of random in-plane orientation where the charge has been chilled by the cold mould surface. Under this is a region of very highly axially aligned fibres and in the middle a region with a marked transverse bias, Fig. 5. The alignment in the axial region has been measured and gives an orientation parameter of 0.8-0.85. The differences in estimated $C_Q$ values are considered to be mainly due to a variation in the relative thickness of these three principal layers. This arises from variations in the actual flow of the charge into the mould. In principle it could be controlled by the injection moulding machine settings. This, however, was not possible on the machine used in this work. It would be useful to assess the effectiveness of a full interactive control system in this context.

![Photomicrograph of cross section of a typical tensile test bar showing the 6 layer orientation distribution: a - random; b - aligned, c - normal.](image)

The estimated interface shear strengths fall in the range 40-48 MPa for the coupled materials and 35-40 MPa for the un-coupled in the standard "dry" condition. This is a little less than the shear strength of the unfilled polyamide 6 of ~ 50 MPa and indicates that the interface is the weakest point.

In Table III the critical aspect ratio, calculated from the estimated value of $\tau_i$ and the actual failure strain, is given for each batch together with the proportion of fibres (by volume) which exceed that ratio. It will be noted that, with the exception of K
which showed an unusually high failure strain, \( \bar{R} \) is quite close to \( R_c \) and that some 25-40\% of the fibres exceed the critical ratio. From this it is clear that the properties of all these materials are limited by the length of the fibres. An increase in fibre length (or an increase in \( \tau_f \)) would result in higher stiffness and strength with a consequent reduction in strain to fracture.

### Table III

**Fibre Diameter and Aspect-Ratio Distribution from 0.25\( \nu_f \) Moulded Test Pieces**

<table>
<thead>
<tr>
<th>Fibre Code</th>
<th>Nominal Diameter</th>
<th>Average Diameter</th>
<th>Standard Deviation</th>
<th>Coefficient of Variation</th>
<th>Volume Average Fibre Length</th>
<th>Average Fibre Aspect Ratio</th>
<th>Calculated Critical Aspect Ratio</th>
<th>Proportion of Fibres Exceeding ( R_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( d_0 (\mu m) )</td>
<td>( \bar{d} (\mu m) )</td>
<td>( S (\mu m) )</td>
<td>( C_v (%) )</td>
<td>( \bar{t}_v (\mu m) )</td>
<td>( \bar{R} )</td>
<td>( R_c * )</td>
<td>(X)</td>
</tr>
<tr>
<td>F</td>
<td>13</td>
<td>12.8</td>
<td>0.90</td>
<td>7</td>
<td>270</td>
<td>21</td>
<td>30</td>
<td>27</td>
</tr>
<tr>
<td>G</td>
<td>12</td>
<td>9.49</td>
<td>1.43</td>
<td>15</td>
<td>240</td>
<td>25</td>
<td>26</td>
<td>46</td>
</tr>
<tr>
<td>H</td>
<td>12</td>
<td>10.0</td>
<td>1.10</td>
<td>11</td>
<td>260</td>
<td>26</td>
<td>35</td>
<td>37</td>
</tr>
<tr>
<td>J</td>
<td>16</td>
<td>14.1</td>
<td>1.14</td>
<td>8</td>
<td>350</td>
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<td>K</td>
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<td>1.19</td>
<td>11</td>
<td>320</td>
<td>31</td>
<td>40</td>
<td>25</td>
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<tr>
<td>M</td>
<td>13</td>
<td>12.1</td>
<td>1.59</td>
<td>13</td>
<td>270</td>
<td>22</td>
<td>26</td>
<td>39</td>
</tr>
<tr>
<td>N</td>
<td>10</td>
<td>10.9</td>
<td>1.40</td>
<td>13</td>
<td>270</td>
<td>25</td>
<td>38</td>
<td>12</td>
</tr>
</tbody>
</table>

* \( R_c \) calculated at actual failure strain of the composite.

** \( K \) had an anomalously high failure strain of 3.0Z.**

There is a dramatic reduction of strength and stiffness of all materials when tested after the 48 hour boiling in water treatment. It is in this condition that the effect of the coupling agent is most marked, even in the batches L and N, which showed little difference in the dry condition. It is noteworthy that there is a significant reduction in properties attributable to the omission of the coupling agent, in the dry condition, in batches G and J whereas in L there is little effect. In the wet condition all the uncoupled batches show up poorly, as does F, which uses the non-silane coupling agent. However, the size and coupling agent system used in H and K appears to confer superior wet properties over that used for M and N.

It is interesting to note that in the more effectively coupled materials, H, K, M and N, the material is still comparatively brittle even in the wet condition. In the uncoupled batches, G, J and L, there is little difference in properties at the two \( \nu_f \) levels in the wet condition indicating that the fibres are virtually ineffective. The actual water absorption during the boiling...
treatment was measured and results are shown in Table IV. It can be seen that water uptake is lower at higher $V_f$ and greater in the uncoupled materials.

**TABLE IV**
WATER UPTAKE ON BOILING IN DISTILLED WATER FOR 48 HOURS

<table>
<thead>
<tr>
<th>Fibre Code</th>
<th>Water Uptake % WW</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V_f = 0.1$</td>
</tr>
<tr>
<td>F</td>
<td>5.2</td>
</tr>
<tr>
<td>G</td>
<td>6.1</td>
</tr>
<tr>
<td>H</td>
<td>5.7</td>
</tr>
<tr>
<td>J</td>
<td>6.2</td>
</tr>
<tr>
<td>K</td>
<td>5.6</td>
</tr>
<tr>
<td>L</td>
<td>5.3 (0.17$V_f$)</td>
</tr>
<tr>
<td>M</td>
<td>5.8</td>
</tr>
<tr>
<td>N</td>
<td>5.7</td>
</tr>
<tr>
<td>Unfilled PA.6</td>
<td>6.7</td>
</tr>
</tbody>
</table>

The acoustic emission was monitored during all tensile tests and showed a similar general trend in all cases. Very little output was recorded in the early stages of the test but at some threshold strains the emissions started and then the rate built up exponentially until failure. The one noteworthy observation was that in the uncoupled materials G and J the total acoustic count was much lower than in their coupled counterparts H and K as is shown in Figure 6. Acoustic emission was drastically reduced after the boiling water treatment with the uncoupled grades giving virtually zero output. This is consistent with the previous observation (5) that unfilled polyamide gave no acoustic output and we may conclude that the sources of noise are fibre debonding, brittle matrix cracking and fibre fractures. In the uncoupled material the fibres debond at lower strains with consequent reduced acoustic output and the incidence fibre fracture is also reduced. In the "wet" samples the matrix flows around the fibres and no acoustic events are recorded.

The Charpy impact energy was determined using a sub-standard specimen, cut from the gauge portion of a tensile test bar, with a sharpened saw-cut notch. The specific energy quoted is on the basis of the net projected area of fracture, i.e. both fracture surfaces or 2 x net cross-section area. These results show an interesting
Stress/strain curves for compounds G and H showing the reduced acoustic emission associated with the absence of coupling agent.

Correlation between Charpy impact energy and tensile strength.

4. Concluding Remarks

A range of polyamide 6 compounds containing E-glass treated with different size formulations have been evaluated by tensile and impact testing.

The beneficial effects of silane coupling agents are clearly demonstrated. In the dry condition some compounds showed a 20% reduction in strength when the silane was omitted, but in others there was little difference. However, after boiling for 48 hours in distilled water the silane coupled materials were, in all cases, far superior.
The impact strength showed a similar trend to that of the tensile strength, and in the dry condition there appeared to be no benefit in ductility or toughness from the lower interface strength in the uncoupled materials.

Fibre diameters of from 10-16μm were used but in the compounding and moulding operations the fibre lengths reduced to give aspect-ratios of the same order, so that there was no benefit to be gained by using the smaller diameter fibre. In all cases the average aspect ratio of fibre in the moulded material was less than the calculated critical value indicating that improved properties would result if fibre breakage could be reduced and the average aspect-ratio increased.

5. Acknowledgements

We are indebted to Pilkington Brothers Ltd, Research and Development Laboratories and to Vitrofil S.p.A. for supplying special batches of glass-fibre for this project, and one of us (JFC) gratefully acknowledges support by way of a Science Research Council studentship which enabled him to participate in the work.

6. References


