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HYGROTHERMAL RESISTANCE OF THE INTERFACE IN HIGH PERFORMANCE POLYMER COMPOSITES

by

Li Zhang

A thesis submitted in conformity with the requirements for the Degree of Master of Applied Science, Department of Chemical Engineering and Applied Chemistry, in the University of Toronto

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ABSTRACT

In this research, the author worked on different approaches to investigate the interfacial behavior in high performance polymeric composite materials including carbon-polyimide and carbon-polyetheretherketone (PEEK). Single fiber pull out test was applied to determine the interfacial shear strength of carbon-polyimide. The interfacial shear strength determined was $16 \pm 6$ MPa. In another case, the transverse test was used to research the environmental effect on the interface in unidirectional carbon fiber reinforced PEEK. Results showed that the interface was unaffected even after 8000 hours of 90°C water immersion. Although the ultimate strength decreased after 4500 hours of water immersion, the stiffness of the material did not change even after 8000 hours of water immersion. Lastly, a simplified model was set up to estimate the transverse elastic properties of composites. More development is still needed to deal with the anisotropic property of carbon fibres.
ACKNOWLEDGEMENTS

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>II</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>III</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>IV</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>VI</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>IX</td>
</tr>
<tr>
<td><strong>1. INTRODUCTION</strong></td>
<td>1</td>
</tr>
<tr>
<td>1.1 Composite Materials</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Polymers</td>
<td>1</td>
</tr>
<tr>
<td>1.3 High Performance Polymer Matrices</td>
<td>2</td>
</tr>
<tr>
<td>1.3.1 Polyetheretherketone</td>
<td>3</td>
</tr>
<tr>
<td>1.3.2 Polyimide</td>
<td>5</td>
</tr>
<tr>
<td>1.4 Interface in Composite Materials</td>
<td>6</td>
</tr>
<tr>
<td>1.4.1 Theories of the interface</td>
<td>7</td>
</tr>
<tr>
<td>1.4.2 Interfacial strength determination</td>
<td>9</td>
</tr>
<tr>
<td>1.5 Environmental Effects on Composite Materials</td>
<td>14</td>
</tr>
<tr>
<td>1.5.1 Hygrothermal effects</td>
<td>15</td>
</tr>
<tr>
<td>1.5.2 Other fluid environmental effects</td>
<td>18</td>
</tr>
<tr>
<td>1.6 Interface in High Performance Polymer Composites</td>
<td>19</td>
</tr>
<tr>
<td>1.7 Objectives of this study</td>
<td>20</td>
</tr>
<tr>
<td><strong>2. EXPERIMENTAL METHOD</strong></td>
<td>22</td>
</tr>
<tr>
<td>2.1 Materials</td>
<td>22</td>
</tr>
<tr>
<td>2.2 Sample Preparation</td>
<td>23</td>
</tr>
<tr>
<td>2.2.1 Samples for pull-out experiment</td>
<td>23</td>
</tr>
<tr>
<td>2.2.2 Laminates and PEEK plates fabrication</td>
<td>27</td>
</tr>
<tr>
<td>2.2.3 Samples for transverse tensile test</td>
<td>28</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

FIGURE 1.1 RELATIONSHIP AMONG THE MAJOR COMPONENTS OF A COMPOSITE 7
FIGURE 1.2 DIRECT TESTING METHODS FOR INTERFACIAL STRENGTH MEASUREMENT 9
FIGURE 1.3 SHORT BEAM SHEAR TEST 13
FIGURE 1.4 IOSIPESCU TEST 13
FIGURE 1.5 TRANSVERSE TENSILE TESTS 14
FIGURE 2.1 A CAPILLARY THREADED WITH A SINGLE FIBRE 24
FIGURE 2.2 A CAPILLARY HOLDER FOR FIBRE THREADING 24
FIGURE 2.3 A CAPSULE HOLDING A DROPLET OF POLY(AMIC ACID) AND AN EMBEDDED FIBRE 25
FIGURE 2.4 CURING CYCLE FOR LARC-PETI-5 25
FIGURE 2.5 SAMPLE FOR TRANSVERSE TENSILE TEST 29
FIGURE 2.6 INSTRON MACHINE SET-UP FOR SINGLE FIBRE PULL OUT TEST 29
FIGURE 3.1 TYPICAL FORCE-DISPLACEMENT PLOTS FOR CARBON PULLED OUT OF POLYIMIDE 35
FIGURE 3.2 DEBONDING FORCE VS. EMBEDDED LENGTH FOR 36
FIGURE 3.3 MOISTURE ABSorption OF PEEK AT 23°C 37
FIGURE 3.4 MOISTURE ABSorption OF PEEK AT 60°C 38
FIGURE 3.5 MOISTURE ABSorption OF PEEK AT 90°C 38
FIGURE 3.6 MOISTURE ABSorption OF AS4-PEEK AT 23°C 39
FIGURE 3.7 MOISTURE ABSorption OF AS4-PEEK AT 60°C 40
FIGURE 3.8 MOISTURE ABSorption OF AS4-PEEK AT 90°C 40
FIGURE 3.9 MOISTURE DESorption FROM AS4-PEEK 41
FIGURE 3.10 FORCE-DISPLACEMENT CURVES FOR PEEK 42
FIGURE 3.11 EFFECT OF 90°C WATER IMMERSION ON THE BREAKING STRAINS OF PEEK 42
FIGURE 4.3 FORCE OF THE SECOND SLOPE CHANGES VS. EMBEDDED LENGTH

FIGURE 4.4 MAXIMUM FRICTIONAL FORCE VS. EMBEDDED LENGTH PLOT

FIGURE 4.5 ARRHENIUS PLOT FOR DIFFUSION CONSTANTS FOR PEEK AND AS4-PEEK

FIGURE 4.6 MOISTURE ABSORPTION OF PEEK AT DIFFERENT TEMPERATURES

FIGURE 4.7 MOISTURE ABSORPTION OF AS4-PEEK AT DIFFERENT TEMPERATURES

FIGURE 4.8 MOISTURE ABSORPTION OF PEEK AND AS4-PEEK AT 23°C

FIGURE 4.9 MOISTURE ABSORPTION OF PEEK AND AS4-PEEK AT 60°C

FIGURE 4.10 MOISTURE ABSORPTION OF PEEK AND AS4-PEEK AT 90°C

FIGURE 4.11 STRESS - STRAIN CURVES FOR PEEK

FIGURE 4.12 STRESS - STRAIN CURVES FOR AS4-PEEK

FIGURE 4.13 COMPARISON OF STRESS-STRAIN CURVES OF PEEK AND AS4-PEEK

FIGURE 4.14 SCHEMATIC ILLUSTRATION OF A) A CROSS SECTION OF A UNIDIRECTIONAL COMPOSITE, B) A SMALLEST REPEATING UNIT, C) REGION 1 AND REGION 2 IN THE REPEATING UNIT

FIGURE 4.15 COMPARISON BETWEEN MODELS FOR ESTIMATION OF TRANSVERSE MODULUS USING $E_F = 233$ GPA, $E_M=3.9$ FOR PEEK, AND $\xi = 2.0$ FOR HALPIN-TSAI'S MODEL

FIGURE 4.16 COMPARISON BETWEEN MODELS FOR ESTIMATION OF TRANSVERSE MODULUS USING $E_{FL} = 13$ GPA, $E_M=3.9$ FOR PEEK, AND $\xi = 2.0$ FOR HALPIN-TSAI'S MODEL

FIGURE 8.1 GEOMETRY OF THE SPECIMEN FOR MOISTURE ABSORPTION MEASUREMENT
LIST OF TABLES

TABLE 1.1 TYPICAL MECHANICAL CHARACTERIZATION OF PEEK AT 23°C    4
TABLE 4.1 MEAN SHEAR STRESSES FOR PULL-OUT TESTS               59
TABLE 4.2 DIFFUSIVITIES OF PEEK AND AS4-PEEK                     62
1. INTRODUCTION

1.1 Composite Materials

A composite material can be defined as a material composed of two or more physically and/or chemically distinct, randomly or orderly arranged phases with an interface separating them.

We can say that the idea of composite material comes from nature. There are lots of naturally occurring composites in this world. Wood is a well-known example: lignin matrix reinforced with cellulose fibres. Bone is an example of a natural composite that supports the weight of the body. It is composed of collagen fibres and apatite matrix.

The history of man-made composite materials can be traced back to several thousand years ago. People used reed reinforced pitch to make composite boats in the Middle East in 5,000 B.C. Wood laminated with shellac was produced in Thebes and India over 3,000 years ago [1]. Today a lot of kinds of composite materials are being used in our daily life. Their applications vary from tennis rackets to aircraft wings, and from bicycle frames to bullet-proof armour materials.

From the examples mentioned above one can see that composite materials normally consist of two major components: reinforcement and matrix. Among various kinds of matrix materials, polymers are no doubt one of the most important and frequently used in composite materials.

1.2 Polymers

A polymer is an organic compound which has a large molecular weight (from several thousands to several millions). The molecule of a polymer is a long chain composed of large numbers of atoms joined together by covalent bonds. These molecules have similar structures which are composed of lots of repeating units. Numerous polymer molecules gather together to make the polymer material.
Polymers can be categorized into two types: thermoplastics and thermosets. The molecules of thermoplastic polymer are linear in structure and there is no chemical linkage between them. Thus the molecules may move or slide when the material is heated up. After the polymer is cooled down, the molecules are "frozen" in their new shape at their new place. As a result, thermoplastics can be melted and reshaped as many times as we want. The following are some commonly used thermoplastics for composites:

- Nylons
- Thermoplastic polyesters
- Polycarbonate
- Polyacetals
- Polyamide-imide
- Polyetheretherketone
- Polysulphone
- Polyphenylene sulfide
- Polyether imide

On the other hand, the case of thermosetting polymer is totally different. The structure of the polymer looks like a three dimensional network. Molecules are linked together at different points by short molecular chains formed during the curing process. So when heated up the molecules cannot move around. Thermosetting polymers cannot be melted and reshaped once they are synthesized. The following are common thermoset matrices for composites:

- Polyesters and vinyl esters
- Epoxy
- Polyimide

1.3 High Performance Polymer Matrices

In recent years advanced composites have been used widely in commercial and military applications. The term "advanced composite" refers to the combination of high performance fibres such as boron, carbon and aramid, and thermally stable matrices. The
most common characteristics of these high performance polymers is that they contain aromatic or heterocyclic rings (or in combination) in the main chain backbone. Among the commercially available high performance polymers, polyetheretherketone and polyimides have attracted great interest in research and development.

1.3.1 Polyetheretherketone

In 1981 a range of polyetheretherketone (PEEK) resins were introduced into the commercial market by ICI under the trade name of Victrex. PEEK is a linear aromatic polymer which has the following repeating unit in its molecules:

\[
\begin{align*}
\text{Staniland} & \text{ reviewed the polymerization chemistry for the class of polymers known as poly(aryl ether ketone). The systematic name of polyetheretherketone is} \\
\text{Poly(oxy-1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-phenylene).} \\
\text{This polymer is produced commercially by a nucleophilic process in a dipolar aprotic solvent, in which hydroquinone, 4,4'-difluorobenzophenone and potassium carbonate are reacted together in diphenylsulphone in the temperature range 150-300°C to form PEEK, potassium fluoride, carbon dioxide and water:}
\end{align*}
\]

\[
\begin{align*}
\text{HO-} & \text{-OH} + \text{F-} & \text{-C} & \text{-F} + \text{K}_2\text{CO}_3 & \xrightarrow{\text{DPS}} & \text{150-300°C} \\
\text{[O-} & \text{-O} & \text{-C} & \text{-]} + 2\text{KF} + \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]
PEEK is a semicrystalline polymer. Amorphous PEEK can be produced by quenching the polymer melt. Increasing crystallinity increases both the modulus and the yield strength of PEEK but reduces its strain to failure [3]. Due to its crystalline structure as well as the aromatic chemical structure, PEEK exhibits excellent environmental resistance compared with other thermoplastic resins. Some mechanical properties of PEEK are listed below:

Table 1.1 Typical mechanical characterization of PEEK at 23°C [4]

<table>
<thead>
<tr>
<th></th>
<th>Modulus (GPa)</th>
<th>Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uniaxial tension</td>
<td>3.6</td>
<td>92</td>
</tr>
<tr>
<td>Uniaxial compression</td>
<td>3.6</td>
<td>119</td>
</tr>
<tr>
<td>Simple shear</td>
<td>1.3</td>
<td>~60</td>
</tr>
<tr>
<td>Poisson's ratio</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>Fracture toughness</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_{IC}$</td>
<td></td>
<td>4.8 MN/m$^{3/2}$</td>
</tr>
<tr>
<td>$G_{IC}$</td>
<td></td>
<td>6.6 kJ/m$^2$</td>
</tr>
</tbody>
</table>

PEEK has a glass transition temperature of 143°C and a melting point of 334°C [5]. The maximum continuous-use temperature of PEEK is 250°C, which makes it an ideal material to replace epoxies in many aerospace structures. Another outstanding property is its high fracture toughness, which is 50-100 times higher than that of epoxies.

Other properties of PEEK such as creep, fatigue and tribological properties have been studied by some researchers [6, 7, 8]. Their results show that compared with other thermoplastic resins PEEK has superior properties.
1.3.2 Polyimide

Compared to PEEK, polyimides have a rather long history. Research on the synthesis of polyimides began in the 1960s due to an increasing demand for high temperature polymer matrices. Polyimide is a general name for the polymers containing the following cyclic imide groups in the main macromolecular chain.

![Cyclic imide group](image)

One of the polyimide synthesis methods is the reaction of a tetracarboxylic acid dianhydride and a diamine in a polar aprotic solvent at 15 to 75°C [9]. The generated polyamic acid is then cyclodehydrated to the corresponding polyimide by extended heating at elevated temperatures or by treatment with chemical dehydrating agents.

Depending on the types of the radicals attached to the imide group and the polymerization process, polyimides can be linear or three dimensional in structure. Thermosetting polyimides are obtained by addition polymerization. Types of thermosetting polyimides include

- Bismaleimides (BMIs)
- PMR-polyimides (Polymerization of Monomeric Reactants)
- Acetylene terminated polyimides
- Benzocyclobutene imides
- Bis(allylnadic) imides

Thermoplastic polyimides are linear polymers produced by condensation polymerization of a polyamic acid and an alcohol. They include

- Polyetherimide ($T_g=217°C$)
- Polyamide-imide ($T_g=280°C$)
LaRC-TPI (Langley Research Center thermoplastic imide) \(T_g=265^\circ C\)

The LaRC-TPI polyimide is produced by the following procedure [10]:

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\text{n} & \quad \text{n} \\
\text{H}_2\text{N} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\text{NH}_2 & \quad \text{C} \\
\end{align*}
\]

\[
\text{O} \quad \text{N} \quad \text{O} \\
\text{C} \quad \text{C} \quad \text{N} \\
\text{O} \quad \text{O} \\
\text{n} \\
\]

Polyimides are used widely in temperature-resistant applications because they possess some unique properties. These include excellent physical property maintenance at high temperatures and in wet environments, almost constant electrical properties over a wide range of temperatures and non-flammability properties.

1.4 Interface in Composite Materials

As we may see from the definition of the composite, the composite material consists of two major components: matrix and reinforcement. Since these two components are different in nature, there is an interface existing between them. It is now well accepted that the overall performance of the composite materials depends not only on the mechanical properties of the matrix and reinforcement but also on the bond strength of the interface. It has been said that "the interface is the heart of a composite" [11]. This is because the role of the interface in the composite is transferring the load
from the matrix to the reinforcements. The interface is so important that it is now widely considered as the third component of the composite.

Research on the interface began with the modification of glass fibres used to reinforce plastics in 1942 in order to improve the performance of fibreglass plastic composites [12]. The term "interphase" can also be seen frequently in the research publications. Figure 1.1 shows the relation among these components in a composite.

![Figure 1.1 Relationship among the major components of a composite](image)

1.4.1 Theories of the interface

Although systematic studies on the interface began in 1963 [12], the interfacial behaviour in composites is still not well understood. Many theories have been developed to explain the interface phenomena but none of them is totally successful in interpreting experimental results.
The chemical bonding theory was developed from a series of experiments in which glass fabric and mat were treated with various chloro silanes to investigate the effect of fibre surface treatment on the strength of glass/polyester composites [12].

This theory proposed that the coupling agent used to treat glass fibres contains different chemical functional groups, some of which could react with silanol groups on the glass and others could react with the matrix resin during curing. The coupling agent thus acted as a vehicle to bond the glass to the resin with covalent bonds.

The mechanical or "hooking" theory proposed that the surface roughness determined the bond strength of the interface. Hooking or interlocking happened at rough or porous surfaces of the reinforcement thus provided good adhesion between filler and resin.

Proposed by Deryagin and his coworkers [13], the electrostatic theory assumed that the filler and the matrix formed a capacitor at the interface, which was charged due to the contact of the two materials. The joint strength came from the electrical double layer at the interface.

Voyutskii [14] developed a diffusion theory to explain the experimental results of breaking strength of adhesive joints, which was considered to vary as a function of time of contact, temperature, polymer type, molecular weight, and viscosity. The author suggested that like a diffusion-controlled process, the interfacial bond strength was determined by the extent of diffusion of polymers across the interface.

The rheological theory proposed by Bikerman [15] claimed that the strength of an adhesive joint was determined by the mechanical properties of the materials comprising the joint and the local stresses in the joint, not by interfacial forces.
1.4.2 Interfacial strength determination

Since the interface plays an important role in the overall performance of the composite, a great deal of effort has been devoted to determining the capacity of the interface to transfer the load from the matrix to the fibres. In order to understand the stress transfer mechanism, researchers developed various mechanical testing methods to characterize the interfacial bond strength. These methods include direct testing methods and indirect testing methods.

Direct testing methods use model composites, i.e., single fibre composites. These methods include the fragmentation test, pull-out test, microtension test, and microcompression test, see Fig. 1.2 [16].

![Figure 1.2 Direct testing methods for interfacial strength measurement [16]](image)
In the fibre fragmentation test, a single fibre is totally embedded in a piece of polymer and a tension load is applied on the specimen in the fibre direction. When the fibre failure strain has been reached the fibre breaks into fragments. Laser Raman spectrometry is used in this test to determine the fibre strain when the composite is stretched [17].

By measuring the critical length of the fragment, \( l_c \), the mean interfacial shear strength \( \tau \) can be calculated as follows

\[
\tau = \frac{\sigma_f}{2} \left( \frac{d}{l_c} \right)
\]

(1-1)

where \( d \) is the fibre diameter and \( \sigma_f \) is the tensile strength of the fibre at a gauge length equal to \( l_c \). Although determining \( l_c \) (less than 1 mm) is not a problem [18, 19], it is difficult to measure the single fibre strength \( \sigma_f \) at such a short length. Researchers normally examine the fibre mean strength and strength distribution data at longer gauge lengths and obtain \( \sigma_f \) by the means of Weibull distribution analysis [20]. Lots of work has been done on the fibre fragmentation test [21-28] to study the interfacial behaviour of a composite. Evidence from fragmentation experiment done by Figueroa et al. [21] indicates that the fibre/matrix interaction in a carbon/polycarbonate system is governed by micromechanical locking, which reflects the residual fibre surface roughness. Their result is consistent with observations by Drzal [22] for a carbon/epoxy system.

For the determination of fibre strain in single fibre composites using Raman spectrometry [31-34], a load is applied to a single fibre composite. The fibre strain is determined by recording the Raman spectra of the fibre at different points \( x \) along this fibre. The shear stress \( \tau_x \) can be calculated at each point \( x \) by a force balance equation on an element of the fibre:

\[
\tau_x = \frac{B d \delta e}{4 \delta x}
\]

(1-2)
where $\varepsilon$ is the level of strain for a given $x$.

In the microindentation test [29, 30], the fibre is compressively loaded on one end and pushed into the matrix causing interface failure under shear. The advantage of the technique is that real composites can be used, so that the effect of neighbouring fibres can be taken into account. The problems of this method are (i) the difficulty of applying the load exactly at the centre of the fibre, (ii) avoiding splitting of the fibre and (iii) measuring the load at debonding.

Among the direct test methods, the pull-out test is perhaps the most widely used one. A tensile load is applied on a single fibre which is partially embedded in a block of resin.

During the fibre pull-out process, the load-displacement change is recorded to determine the debonding force. Assuming the shear stress is uniformly distributed along the embedded length, the mean shear strength of the fibre-matrix interface is given by:

$$
\tau = \frac{F_{\text{max}}}{\pi dl_e}
$$

where $d$ and $l_e$ are the diameter and the embedded length of the fibre respectively, and $F_{\text{max}}$ is the maximum force corresponding to the pull-out process.

Since the pull-out test is direct and straightforward, it was the favourite of many researchers. Piggott and Xiong [35] studied the debonding process in single fibre pull-out test using glass fibre reinforced epoxy. They observe two slope changes in the early part of the force-displacement curve, which are identified as yielding and debonding initiation force respectively, and are independent of embedded length if the embedded lengths are great enough. The experimental results appear to fit the theoretical model proposed by Piggott [36] very well. Gent and Liu [37] proposed an energy analysis when only friction forces are involved at the fibre-matrix interface during pull-out test.
Another type of pull-out technique, the microbond test [38-42], is also used in the interfacial strength determination. Using this method, a very short embedded length can be achieved by putting a tiny drop of resin onto the fibre. First proposed by Miller and co-workers [38], the microbond test uses the same theoretical approaches as the pull-out test to interpret the experimental results.

Although the test methods mentioned above provide direct measurement on the interfacial strength, researchers found that these methods produce different results for the apparent interfacial shear strength when testing the same composite system [43, 44]. Piggott [45] reviews these single fibre testing methods and points out the defects of them. For the pull-out test, the author explained, the problem was the difficulty of determining the friction accompanying the debonding of the fibre from the matrix and the high stress concentration present at the fibre entry point and at the embedded end. Since polymers fail in tension rather than shear [46, 47], some of the results produced by single fibre tests are too high to be trusted. The author concludes that direct test methods cannot be used to obtain the true interfacial strength. The alternative test recommended by the author is the 90° off-axis test.

The indirect test methods measure the shear and tensile properties of real composites, normally unidirectional composites. They include: short beam shear test, Iosipescu test and, transverse and off-axis tensile tests.

The short beam shear test uses three point bending method to determine the interlaminar shear strength (ILSS) by choosing the appropriate span-to-width ratio of the beam.
The interlaminar shear strength is given by [17]:

\[ \tau_{ILSS} = 0.75 \frac{F}{A} \]  \hfill (1-4)

where \( F \) is the applied load at failure and \( A \) is the cross sectional area of the specimen. The problem of this method is that the failure process always involves tensile and shear failures. So it is not considered as a precise measurement of the interfacial strength of the composite.

In the Iosipescu test, a device was designed to obtain pure shear condition in the measurement, which is shown in figure 1.7. The shear strength can be calculated by the maximum force divided by the cross-sectional area between the two notch tips.

As we have mentioned above, polymers do not fail in shear. It appears therefore that the methods used to determine the interlaminar shear strength such as three point bending and Iosipescu test are invalid.
Other alternatives for interfacial strength determination are the off-axis and transverse tensile tests. Materials are subjected to tensile forces at an angle $\theta$ to the direction of the fibres. $\theta$ can be small angles like 10-15° or ±45°. Transverse tensile tests ($\theta = 90^\circ$) are also used. Piggott [45] points out that the transverse tensile test is more sensitive to the interface than shear testing. However, the problem of the off-axis tests is that the results are affected by the fibre misalignment in the composite, which leads to fibre failure across the fracture surface.

![Figure 1.5 Transverse tensile tests](image)

1.5 Environmental Effects on Composite Materials

Since most of the advanced composite materials are for outdoor use, the influence of environmental effects, such as temperature, moisture, solvents and chemical fluids, and even ultraviolet rays, on the performance of composites, are of concern in many applications. The physical and mechanical properties of polymer composites may deteriorate under some environmental conditions for the following reasons:

1. Due to their chemical characteristics, polymer matrices may suffer degradation (chemically or physically) when placed in a corrosive environment. For example, swelling of the polymer will happen because of fluid sorption; chemical bonds in the polymer molecules can be attacked by chemicals and ultraviolet light in the sunlight.

2. Moisture or other fluids absorbed by the material may penetrate into the interface of fibre/matrix and thus affect the interfacial bond strength.
3. Diffusion of water or other small chemical molecules may reduce the strength of the fibres and so affect the overall performance of the composite. For example, it is known that moisture absorbed by Kevlar 49 fibres can reduce their tensile strength and modulus [48]. It was also demonstrated that it is degraded by ultraviolet light. A strength loss of 50% is reported for a light fabric (75 g/m²) after 5 weeks exposure in Florida sunshine [48].

1.5.1 Hygrothermal effects

Both moisture and temperature can affect the mechanical and chemical properties of a polymer matrix composite. When polymeric composites are placed in a humid environment, the polymer matrices will absorb water through the surface. Researches show that the higher the temperature, the faster the diffusion process takes place and the shorter time it takes to reach equilibrium. The largest amount of moisture that can be absorbed varies, depending on the chemical structure of the polymers.

A great deal of researches have been conducted to investigate the effect of moisture uptake on properties of composite materials. The results from moisture absorption experiment for epoxy and polyester matrix composites show that the moisture content in the composites increases with time and reaches equilibrium after several days of exposure to humid environment [49]. Some researchers find that water uptake results in reduction of glass transition temperature and mechanical properties of polymers[50]. At a moisture content of 4%, the glass transition temperature can be reduced to 75% of its original value; at a moisture content of 1.5%, flexural strength can be reduced to 50% of its original value. Shen and Springer [51, 52] investigated the effect of moisture and temperature on the mechanical properties of carbon/epoxy angle ply laminates. They found that for [0]ₙ and [0/±45/90]ₕ laminates, effects of temperature change from 200K to 380K on the ultimate tensile strength are negligible; effects of moisture at moisture contents below 1% are also negligible. At moisture contents above 1% the tensile strength decreases with increasing moisture content. The maximum decrease is about
20%. For 0/90° angle ply laminates, both temperature changes and moisture contents have significant effect on the tensile strength of the composite. The reduction in strength can be as high as 60 to 90 percent depending on the temperature and moisture content. Their results also showed that for [0]_s and [0/±45/90]_s laminates a change of temperature from 200K to 450K has a negligible effect on the elastic moduli of the material. Moisture content does not affect the elastic moduli even if the composite is saturated. For 0/90° laminates the temperature change of 150°C results in the decrease of moduli from 50 to 90%. The moduli also decrease significantly with increase in the moisture content. This can range up to 50 to 90% depending on the moisture content and the temperature.

The interlaminar shear strength of composite laminates is also affected by moisture absorption [53]. Joshi [54] reported that short beam shear tests of a unidirectional carbon/epoxy laminate indicated a decrease of 10% in interlaminar shear strength at a moisture content of 1.2%.

Jones et al. [55] reported the effect of moisture on the fatigue properties of [0/90]_s cross ply epoxy matrix composites reinforced with E-glass, HTS carbon and Kevlar 49 fibres. The composites were treated with humid air and boiling water immersion. It was found that neither treatments affected the fatigue resistance of carbon/epoxy composites. Humid air does not affect the fatigue behaviour of E-glass/epoxy either. However, the fatigue resistance of this material is significantly reduced by boiling water immersion as a result of damage of glass fibres in the boiling water. On the other hand, the moisture absorption improves the fatigue resistance of Kevlar 49/epoxy laminate, although at high cycles a rapid deterioration was observed.

Selzer et al. [56] investigated the influence of moisture on the interlaminar fracture energies \( G_{IC} \) and \( G_{IIIC} \) of three kinds of carbon fibre-reinforced polymers: carbon fibre/epoxy, carbon fibre/modified epoxy and carbon fibre/PEEK. They used two crack-opening modes to determine the influence of moisture on crack propagation. For Mode I tests, the results show that the saturated epoxy composites exhibit higher \( G_{IC} \) values than the dry materials. But moisture does not have any effect on the \( G_{IC} \) values of
carbon/PEEK. For Mode II tests, values of \( G_{IIc} \) of all three composites decrease with increasing moisture content. The authors conclude that the reduction of \( G_{IIc} \) is a result of the weakening of the fibre/matrix interface. In their experiment, the maximum moisture content of PEEK composite obtained is 0.3 wt %, compared with 1.6-2.5 wt % for epoxy composites.

Dickson et al. [57] studied the hygrothermal effect on the fatigue behaviour of [0/90]_s carbon fibre reinforced PEEK cross-ply laminates. The preconditioning treatments used were oven drying at 60°C, holding at 23°C and 65% RH, and immersion in boiling water. Their results showed that hygrothermal ageing treatments had no effect on the tensile fatigue resistance of PEEK composite and the fatigue response of carbon/PEEK was much better than that of carbon/epoxy composites. The authors detected an equilibrium water uptake of 0.45% in carbon/PEEK after about 3 weeks in boiling water.

Pritchard et al. [58] researched the effect of thermal spike and moisture on the mechanical properties of [±45]_s carbon/epoxy and carbon/PEEK laminates. The conditioning treatment was 72°C, 96% R.H. environment and the samples were subject to 44 cycles of 135°C thermal spiking. It was found that at the highest moisture content of 0.45% the ultimate tensile strength of carbon/PEEK decreased about 10%.

Hartness [59] reported a similar reduction in transverse flexural strength of the PEEK matrix composite. Other researchers [60-63] reported that moisture had no significant effect on a range of properties including open hole tension and compression, fracture toughness, and standard flexural properties.

Tucker and Brown [64] investigated the moisture absorption properties of a vinyl ester carbon fibre composite under 2000 feet of seawater pressure. The study showed that although higher moisture content was obtained by samples under pressure, the diffusion coefficients were the same as those tested at atmospheric pressure. The high pressure employed resulted in a reduction of about 15% in flexure strength and stiffness, whereas
samples immersed in seawater at atmospheric pressure for six months did not show any loss in strength or stiffness.

1.5.2 Other fluid environmental effects

Besides the good water resistance, PEEK matrix composite also showed excellent organic fluid resistance. The excellent performance of PEEK composites was no doubt due to the outstanding environmental resistance of the PEEK matrix. Hartness [64] tested environmental effects of various reagents (including hydraulic fluids and paint strippers) on PEEK resin and found that the effect was insignificant. Cogswell and Hopprich [65] reviewed other researchers' work in which common solvents, aircraft fluids and paint stripper were used to treat carbon/PEEK composites. Common solvents were found to have no significant effect on the mechanical properties of the composite. After being immersed in aircraft fluids for one month, the composites were found to have only 5% and 10% loss in flexural stiffness and flexural strength respectively. The results of the paint stripper tests showed that one month of immersion did not create any difference in the flexural properties of the carbon/PEEK composites.

Stober et al. [63, 66] investigated the fluid sorption and desorption behaviour of PEEK resin and carbon/PEEK composites. The fluids used included some normal solvents like acetone, methylene chloride, and an aviation hydraulic test fluid-Skydrol, as well as deionized water. The authors found that PEEK and its composites showed very good resistance to water and Skydrol with small amount of absorption. However, the results showed that PEEK resin could absorb large amount of methylene chloride. Depending on the initial crystallinity, the weight gain of the exposed resin could be as high as 20.8%. The absorption of methylene chloride resulted in plasticization and additional crystallization.
1.6 Interface in High Performance Polymer Composites

High performance polymer composites have attracted great interest in recent years because of their outstanding features. Polymers used in these kinds of composites included various kinds of polyimides and PEEK. However, studies on the interface of these composites were few because of the difficulties involved and the interfacial behaviour in these composites have not been fully understood.

Sawada et al. [67] studied the interfacial adhesion in a carbon fibre/polyimide composite using fibre fragmentation test. Their results showed that the surface roughness and active surface area of the fibre determined the interfacial shear strength. The authors found that the interfacial bond strength depended upon chemical bonding.

The influence of fibre matrix adhesion on the mechanical properties of high strength carbon fibre/PEEK composites was discussed by Fife et al. [68]. The authors compared the mechanical properties of two unidirectional composites with the same components: one was prepared with optimised interface adhesion and another had poor adhesion between fibre and matrix. Their results showed that the fibre-matrix adhesion level did not significantly influence the fibre dominated properties such as $0^\circ$ tension and compression of the composites. However, the non-fibre directional properties of the composite such as transverse flexural strength and interlaminar fracture toughness were significantly affected by the interfacial adhesion.

Hodge et al. [68] studied the fibre-matrix adhesion in carbon fibre reinforced PEEK composite with a fibre surface energy approach. The authors assumed that the total surface free energy across an interface could be split into a non-polar or dispersive interaction and a polar interaction. Their results indicated that the polar component of the fibre surface energy is the major factor in influencing the fibre-PEEK adhesion.

As we have mentioned before, PEEK is a semi-crystalline thermoplastic. The crystalline structure formed at the fibre-matrix interface during composite processing also
influences the physical properties of the composite. Peacock et al. [69, 70] studied the crystalline texture of the PEEK matrix in APC-2 composite. They found that the carbon fibre surface was a nucleation centre that caused the formation of spherulites and there was no evidence of transcrystallinity. Although the "on-fibre" spherulite initiation could also be found in other two non-optimised carbon/PEEK system, HS/PEEK and HM/PEEK, it appeared that the APC-2 composite had the highest interfacial adhesion represented by transverse flexural strength which was 2-3 times higher than that of the other two composites. However, other researchers [71, 72] claimed they found transcrystallinity in the matrix close to fibre surface. The crystal texture depended primarily on the crystallization condition. Lower crystallization temperature resulted in spherulite formation and higher temperature resulted in transcrystalline formation.

Researches on environmental effect on carbon/PEEK interface were few. Chen [73] investigated the hygrothermal effect on carbon/PEEK interface through single fibre pull-out test. The results indicated that the interface strength might be reduced by 90°C water immersion but the effect was small.

1.7 Objectives of This Study

High performance polymer matrix composites such as carbon/polyimide and carbon/PEEK are gaining wide use in aerospace applications. Although great amount of work has been done to study the mechanical properties of these composites, the interfacial behaviour has not been fully understood.

Environmental effects on the performance of composite materials is a critical issue in composite study, especially for the materials to be used for engineering purposes. Although some work has been done to research the environmental effect on PEEK composites, the detailed investigation on the environmental effect on the interface has not been reported except Chen's work [73], which was carried out using a single fibre pull-out approach. As single fibre test could be misleading [45], other approaches should be tried to study the interfacial behaviour in composite materials.
The purpose of this study is to investigate the interfacial strength of high performance polymer matrix composites through different approaches. In the first part of this study, we were trying to study the interfacial strength of the carbon fibre reinforced polyimide using single fibre pull-out test.

Another objective is to study the influence of environmental effect on the interface of PEEK/AS4 composites. The methodology used in this study was the transverse tensile test.
2. EXPERIMENTAL METHOD

2.1 Materials

Two kinds of polymers were used in the experiment. One was polyimide and the other was polyetheretherketone (PEEK). The polyimide was LaRC-PETI-5, manufactured by Imitec Inc. The product was a viscous brown liquid containing 70% of N-methyl-pyrrolidinone (solvent) and 30% of poly(amic acid).

The PEEK was Victrex (Grade 151G), produced by ICI, which was in the form of extruded pellets.

The prepreg used in the experiment was APC-2 prepreg manufactured by ICI. The APC-2 prepreg was a melt impregnated tape containing unidirectional continuous AS4 carbon fibres and PEEK. The grade of the PEEK resin used in this prepreg was unknown. The tape was 12" (305mm) wide and about 0.16 mm thick.

The carbon fibres used in the experiment were Hercules AS4 carbon fibres.

The release agent used in laminate fabrication was Frekote 44-NC Release Interface supplied by The Dexter Corporation.

The epoxy resin used in sample preparation for image analysis was Epon 815 manufactured by Shell Limited. The curing agent for the epoxy was triethylene tetramine (TETA).
2.2 Sample Preparation

2.2.1 Samples for pull-out experiment

Single fibres were threaded in the capillaries before fibre embedment (Figure 2.1). The threading procedures were as follows:

1. A tow of carbon fibres were placed straight on a clean sheet of paper. The capillaries were placed one after one in a straight line on a holder (Figure 2.2).

2. As the carbon fibre was too thin to be grasped by hand, a piece of stainless steel wire was used as a lead. A small droplet of cyanoacrylate glue was put at one end of this wire to adhere one end of the carbon fibre. Then the fibre was pulled out of the tow and threaded through the capillaries following the wire. The threaded fibre was cut using a pair of scissors leaving about 1 cm long outside each end of a capillary.

3. The fibre end at the bottom of the capillary was bent to 90° and secured by a piece of masking tape with a piece of paper covering the side facing the fibre so that the fibre was not adhered to the tape. The prepared capillaries were placed on a carousel which can hold 39 capillaries and 39 capsules with the other fibre end heading downward.

The polyimide reagent received from the supplier was a mixture of poly(amic acid) and solvent. To minimize the amount of volatile matter that may be produced during curing reaction, a small amount of resin was used in the sample preparation. A small droplet of resin was placed on the concave surface of the top of the screw inside a capsule for fibre embedment (Figure 2.3). The capsules holding the resin were placed in the holes underneath the capillaries with the resin facing the hanging down fibres for fibre embedment.
Figure 2.1 A capillary threaded with a single fibre

Figure 2.2 A capillary holder for fibre threading
Figure 2.3 A capsule holding a droplet of poly(amic acid) and an embedded fibre

Figure 2.4 Curing cycle for LaRC-PETI-5
The fibre embedment procedures were as follows:
1. The fibre-threaded capillary was pushed toward the resin droplet in the capsule using a micrometer and the process was observed using a microscope.
2. When the fibre reached the resin surface, the advancement was carefully controlled to ensure that a range between several dozen to several hundred μm of embedment was made.

After one carousel of samples were prepared, the carousel was put into an oven with a programmable temperature controller for curing. In order to dry the N-methylpyrrolidinone solution of the PETI-5 slowly to get the solvent out, the curing process was carried out as follows:
1. The oven temperature was raised to 290°C from room temperature at the rate of 2°C per minute.
2. The temperature was held at 290°C for 2 hours.

These two steps were to drive out the solvent in the poly (amic acid) mixture.
3. Then the temperature was raised to 370°C at the rate of 2°C per minute. During this period the condensation reaction happened and the polyimide was formed.
4. After reaching 370°C the temperature was held for 30 minutes.
5. Then the oven was cooled down at a rate of 2°C per minute.

The above two steps were to get rid of the volatile matter produced during the polyimide forming reaction. The following diagram shows the above mentioned procedures.

After the oven was cooled down to room temperature, the carousel was removed. At this time the successfully prepared samples for pull-out test would have fibres standing on the resin surface. The fibres were cut at the end of the capillaries leaving about 1cm of fibre sticking out of the resin. The capsules having embedded fibres were used for the pull-out test.
2.2.2 Laminates and PEEK plates fabrication

AS4-PEEK laminates and PEEK plates were fabricated by compression moulding. The APC-2 prepreg was cut into pieces of 304×304 mm size. To make each piece of laminate, 18 plies of prepreg were laid up symmetrically and balanced to avoid warping due to differential thermal contraction on cooling.

The laid-up prepregs were placed between two sheets of aluminum of 1 mm thick each and the size of 305×305 mm which were sprayed with Frekote 44-NC release agent on the surfaces facing the prepregs. The whole sandwich was then placed in a steel mould with a 305×305×10 mm cavity, for consolidation.

Consolidation was performed using a Wabash 30 ton hot press with programmable temperature controllers by the following procedures.
1. The designated platen temperatures were set at 395°C before consolidation.
2. When the platen temperature was reached, the mould was placed between the two platens and a pressure of 70 psi was applied. This pressure was sufficient to ensure good heat transfer without doing damage to the fibres before the PEEK matrix is soft enough to be compliant. The temperature of the mould was monitored using a digital thermocouple thermometer.
3. When thermal equilibrium had been reached, a pressure of 200 psi was applied for 5 minutes.
4. After consolidation the pressure was increased to 250 psi and the mould was cooled down at about 30°C/minute which is the maximum cooling rate that could be performed by the machine.

Laminates produced by this procedure had a thickness of about 2-3 mm.

The PEEK plates were manufactured by the following procedure. The PEEK (Grade 151G), which is in the form of extruded pellets, was put in a stainless steel mould with a 150×150×10 mm cavity, whose inside surfaces had been sprayed with Frekote 44-NC release agent. About 90 grams of PEEK were used to mould each plate. The mould
temperature was monitored using a digital thermocouple thermometer. The moulding process is as follows:

1. A 200 psi pressure was applied and the mould was heated from room temperature to 340°C.
2. The pressure was released and the mould was heated to 380°C.
3. The mould was kept at 380°C for 10 minutes and then cooled by air to 330°C.
4. A 30 psi pressure was applied and the mould was cooled to 290°C.
5. The pressure was increased to 70 psi while the mould was cooled to 165°C.
6. The pressure was released and the mould was cooled to room temperature, and the plate was removed from the mould.

The PEEK plates produced by this procedure had a thickness of about 3mm.

### 2.2.3 Samples for transverse tensile test

The size of the composite specimen for tensile testing recommended by ASTM standard was 25×170 mm. Because the laminates were in sizes of 305×305 mm, to save materials, the PEEK/AS4 laminates were cut into coupons in sizes of 25×150 mm with the fibre direction normal to tensile force direction, using a diamond saw. Both edges of each sample was smoothed with silicon carbide grinding paper of up to 800 grit. The coupons were glued to aluminum tabs of 25×25 sizes at each end before tensile testing (Figure 2.5).

Coupons from each laminate were divided into three sets. One set of specimens was tested without treatment. The other two sets of samples were immersed in 90°C water for the desired period of time to test the environmental effect. After water immersion, one set of the water-conditioned specimens were tested on the MTS machine right away while they were still "wet". The other set of specimens were baked in an oven at 80°C before mechanical testing. The specimens which had been immersed in water for 500 to 2500 hours were baked for 30 hours. Other specimens were baked for 300 hours.
Figure 2.5 AS4-PEEK composite sample for transverse tensile test

Figure 2.6 The Instron machine set-up for single fibre pull out test
The PEEK plates were in sizes of 150×150 mm. Since PEEK is a very tough plastic, the PEEK plates could not be cut by the diamond saw. They were cut into coupons by the size of 15×150 mm using a band saw. Because of the toughness of the PEEK, it was difficult to grind the specimens into dumb-bell shape which was recommended for pure polymer tensile testing. Both edges of the coupons were polished with SiC grinding paper of up to 800 grit. The specimens were tested in rectangular shape without aluminum tabs.

2.2.4 Samples for moisture absorption measurement

The specimens used in the moisture absorption studies were 1 inch square (25×25 mm) with the thickness of 2-3 mm. The composite used for this was cut from one molded laminate. Similarly the PEEK samples were cut from one molding to ensure the same experimental condition. These laminates and PEEK plates were moulded using the procedures described in section 2.2.2.

2.2.5 Samples for image analysis

Sections within about 1 cm distance from the fracture surface of the tested composite coupons were cut using a diamond saw. The surface normal to fibre direction was polished using a rotational grinder equipped with sand paper. To save labour and time, several pieces of specimen were embedded in a block of epoxy resin so that they could be polished at one time. The embedding procedures were as follows:
1. Six pieces of samples were adhered on the double side tape which was adhered to the bottom of a polysiloxane rubber mould, with the surfaces to be polished facing down.
2. The mould was then filled with liquid epoxy which was premixed with TETA (1: 0.12 wt.).
3. The assembly was put into the oven for curing at 80°C for 2 hours.

The finest polishing medium used was 0.3 μm alumina powder.
2.2.6 Samples for SEM observation

Portions of the tested broken laminates that had the fracture surfaces were cut using the diamond saw. Then the fracture surface was gold sputtered for scanning electron microscopic observation.

2.3 Sample Testing

2.3.1 Fibre pull-out test

Fibre pull-out test was carried out on an Instron machine which was equipped with a 500g load cell. The cross head speed was set at 0.5 mm/min. by selecting the appropriate gear wheel combination. The machine was equipped with a pen recorder. The data of voltage changes of the load cell versus time during testing were also collected by a data acquisition board and recorded by a computer. The data acquisition rate was 5 points per second.

A capsule holding a single fibre sample was secured in a fixture and hung on the load cell with the fibre pointing downward; see Fig. 2.6 in page 29. After the capsule was in place, the machine was calibrated and the voltage-force relation was obtained using a digital multimeter.

Using cyanoacrylate glue, the fibre was then glued to the surface of an upright copper plate which was fixed to a block of metal placed on the base of the Instron machine. The surface of the copper plate was lightly abraded before mounting. The gluing process was carefully carried out to ensure that (i) the free length (the distance between resin surface and the upper edge of the copper plate) was less than 1 mm; (ii) the fibre was vertical.
After the fibre was glued, the machine was turned on and the cross head moved upward. The voltage data obtained by the computer were converted to force, based on the calibration before testing, and the force-displacement curve was plotted.

2.3.2 Hygrothermal exposure

The specimens were totally immersed in water for environmental aging. Samples for tensile tests were exposed to distilled water in a bath, the temperature of which was controlled within $\pm 1.0^\circ$C by a thermocouple temperature controller. After different periods of time, the specimens were taken out of the bath and subjected to mechanical tests. Moisture absorption studies were carried out at three different temperatures: 23$^\circ$C (room temperature), 60$^\circ$C, and 90$^\circ$C. Before water immersion, samples were dried in an oven at 80$^\circ$C until no weight change was observed. Samples were taken out periodically and weighed. Before weighing, water on the sample surface was carefully wiped off using tissue paper. The weight gain as a function of time were recorded.

The specimens that had been immersed in water for 4500 hours were tested for moisture desorption. Specimens were taken out periodically and weighed while they were being baked. The changes of moisture content as a function of time were recorded.

2.3.3 Transverse tensile test

This test was carried out on a Model 810 Material Testing System (MTS). The maximum load selected for all specimens was 10 KN and the cross head speed was 2mm/min. The strain was measured by an extensometer.

Before testing, one end of the specimen was clamped in the upper grip. During the clamping procedure the specimen was carefully aligned to make sure that it was vertical. Then the lower grip was raised and the other end of the specimen was clamped.
The modulus of each specimen was measured first. An extensometer was secured at the middle of the clamped specimen using two rubber bands. When the load had reached about 1 KN, the testing was stopped to avoid inelastic deformation. After the moduli of one batch specimens were measured, the specimens were loaded on the machine again to measure the ultimate tensile strength.

2.4 Image Analysis

Samples obtained by the method described in section 2.2.5 were used to determine the fibre volume fraction of the composite and the interfacial strength contribution to the transverse tensile strength of the composite.

2.4.1 Fibre volume fraction determination

The polished surfaces of the composite samples were observed under an OLYMPUS light microscope which was equipped with a digital camera connected to a computer. For each sample six pictures were taken randomly at different positions. These images were stored in the computer for analysis.

The images taken by the digital camera were scaled with the fibres white and matrix gray. Using a computer program the gray scale pictures were turned into black and white in a process called thresholding. At this time the cross sections of the fibres were black and the resin matrix was white. The whole picture was then split into 48 frames to calculate the volume fraction of each frame, which was equal to the number of black pixels divided by the number of total pixels in the frame. The volume fraction of the sample was taken as the average of the volume fractions calculated from the six pictures taken on the same sample.
2.4.2 Determining the interfacial strength contribution to the transverse tensile strength of the composite

The cross section of the fracture profile of the samples prepared using the method described in section 2.2.5 was recorded on 8-9 consecutive gray scale pictures, depending on the thickness of the samples. Then each picture was analysed by the following procedures:

1. Using the pen tool of the image analysis program a line was drawn on the picture tracing the profile of the interface failure surface. The line was a discontinuous line composed of incomplete circles, called "interface profile". This edited picture was saved as a file.

2. Then, using the pen tool, a line was drawn tracing the crack surface in the matrix on the fracture surface of the sample. This connected the incomplete circles drawn previously. This line, which represented the fracture surface of the sample, was called "fracture profile".

3. The pictures were then turned into black and white images, which contained only the drawn lines, and were saved as new image files.

4. Using the computer program, the number of pixels on the interface profile and fracture profile were calculated separately.

5. The contribution of the interfacial strength to the transverse tensile strength of the composite $A_i$ was calculated by the following equation:

$$A_i = \frac{\text{Pixels on the interface profile}}{\text{Pixels on the fracture profile}} \quad (2-1)$$
3. EXPERIMENTAL RESULTS

3.1 Fibre Pull-out Test

Fig. 3.1 shows four typical pull-out curves obtained with carbon in polyimide. It appears that the force does not normally increase linearly to a maximum, but instead have a premature peak (Fig. 3.1a), or a change in slope (Fig. 3.1c and d). After the force reaches its maximum, it drops perpendicularly to about 0.02 N followed by long-lasting zigzag curve.

Figure 3.1 Typical force-displacement plots for carbon pulled out of polyimide
Fig. 3.2 shows the force maximum plotted as a function of embedded length (The embedded lengths were assumed to be equal to the displacements at zero load).

The maximum force vs. embedded length data are rather scattered. However, it can be seen that the debonding force increased monotonically with embedded length.

From the data shown above, the mean shear strength of fibre-matrix interface was calculated using the following equation

$$\tau = \frac{F}{\pi dl} \quad (3-1)$$

where $F$ was the debonding force, $d$ was the diameter of the fibre and $l$ was the embedded length.
The mean shear strength of the carbon fibre/polyimide interface was 16±6 MPa.

3.2 Moisture Effects on PEEK and the AS4-PEEK Composite

3.2.1 Moisture absorption

When the weight-gain of the PEEK was plotted vs. square root of time, a linear increase was observed initially at 23°C. Saturation was observed after about 1600 hours; and the moisture content at saturation was about 0.42%; see Fig. 3.3. Similar results were observed at 60°C (Fig. 3.4) and 90°C, Fig. 3.5, except that the times to saturation were reduced, and the water absorption at saturation was increased. At 60°C, saturation was reached after about 400 hours of immersion with the maximum moisture content of about 0.48%. When samples were immersed in 90°C water, it took only about 100 hours for the samples to reach saturation. The moisture content at equilibrium was about 0.4% at 23°C and about 0.5% at 60°C and 90°C.

![Figure 3.3 Moisture absorption of PEEK at 23°C](image-url)
Figure 3.4 Moisture absorption of PEEK at 60°C

Figure 3.5 Moisture absorption of PEEK at 90°C
Figs. 3.6-3.8 show the moisture absorption of AS4-PEEK. The initial linear increase was also observed in these curves. However, compared to those of PEEK, the initial linear parts of the curves were shorter. The composites did not appear to saturate. The absorption curves, plotted vs. $\sqrt{\text{time}}$, had two approximately linear regions, and the moisture still appeared to be being absorbed after 2500 h.

Figure 3.6 Moisture absorption of AS4-PEEK at 23°C
Figure 3.7 Moisture absorption of AS4-PEEK at 60°C

Figure 3.8 Moisture absorption of AS4-PEEK at 90°C
Fig. 3.9 shows the moisture desorption of the composite which had been immersed in 90°C water for 4500 hours. During the first 100 hours at 80°C, the moisture content dropped quickly from 0.2% to 0.05%. Then the moisture content dropped slowly to almost zero after 200 more hours of drying.

3.2.2 Moisture effects on mechanical properties

Fig. 3.10 compares the force-displacement curves for PEEK under two conditions: without treatment and treated with 90°C water for 3000 h. Because of different sample sizes used, the water treated sample had much lower breaking force.
Figure 3.10 Force-displacement curves for PEEK at different immersion time

Figure 3.11 Effect of 90°C water immersion on the breaking strains of PEEK
Fig. 3.11 shows the effect of water immersion on the breaking strains of PEEK. The results showed that the ultimate strain of the material decreased as the time of immersion increased.

Fig. 3.12 shows the moisture effect on the tensile strength of PEEK. No loss of strength was observed until samples had been immersed in water for 3000 hours. After 3000 hours, the strength decreased by about 15%. Fig. 3.13 shows that after drying at 80°C for 300 hours, the strength could not be recovered.

![Figure 3.12 Effect of water immersion on the strength of PEEK](image)

Figure 3.12 Effect of water immersion on the strength of PEEK
Figure 3.13 Effect of drying after water immersion on the strength of PEEK

The modulus of PEEK increased by about 10% after 1500 hours of immersion, see Fig. 3.14. When the samples were dried at 80°C for 300 hours after immersion, the moduli of the samples which were treated with water for 1500 and 3000 hours were lower than that of the wet samples, see Fig. 3.15.

Figure 3.14 Effect of water immersion on modulus of PEEK
Figure 3.15 Effect of drying after water immersion on modulus of PEEK

Figs. 3.16 shows some typical force-distance plots for transverse tests of the AS4-PEEK composites. Comparing the curves in each plot, curves obtained from water treated samples were almost the same as their no-treatment counterparts, except that the breaking forces were lower. Sometimes the two curves in one plot were almost overlapped, see the curves for samples treated for 2500 h and 6000 h.
Figure 3.16 Force-displacement curves for AS4-PEEK
Figure 3.17 Effect of 90°C water immersion on the breaking strains of the composites

The breaking strain vs. time plot (Fig. 3.17) shows that as the immersion time increased, the ultimate strain of AS4/PEEK deceased. Strains of the dried samples had the similar trend as time of treatment increased, see Fig. 3.18.

Figure 3.18 Effect of drying after water immersion on the breaking strains of the composites
For AS4-PEEK composite, both wet strength, Fig. 3.19, and strength after drying out at 80°C for 300 hours, Fig. 3.20 showed a loss of about 20% after 4000 h, followed by no further change up to 8000 h. The modulus was not significantly affected.

Figure 3.19 Effect of water immersion on $\sigma_{2u}$ of AS4-PEEK

Figure 3.20 Effect of drying after water immersion on $\sigma_{2u}$ of AS4-PEEK
Figure 3.21 Effect of water immersion on $E_2$ of AS4-PEEK

Figure 3.22 Effect of drying after water immersion on $E_2$ of AS4-PEEK
3.3 Image Analysis Results

Figure 3.23 shows the projected area fraction of interface normal to the stress, $A_i$, from samples with different time of water immersion. The results showed that, although the variations are large, the values of $A_i$ remained at about 0.04-0.05.

![Graph showing the effect of moisture on interface in PEEK/AS4](image)

**Figure 3.23 Effect of moisture on interface in PEEK/AS4**

Fig. 3.24 and 3.25 show the composite cross sections of the area near the fracture surface with the fibres normal to the observer. From the pictures taken under light microscope we can also see most of the fibres at the fracture surface are covered with resin. The failure happened at the matrix where is very close to the fibre surface. Picture 3.25a is the part of the fracture profile of the composite without water treatment. Picture 3.25b is part of the fracture profile of the composite treated with water for 2500 hours.
Figure 3.24 Cross section area at the fracture surface of AS4-PEEK immersed in water for 1500 hours
Figure 3.25 Cross section area at the fracture surface of AS4-PEEK. a) No treatment; b) Immersed in 90°C water for 2500 hours
3.4 Microscopic Observations

Scanning electron microscopic pictures taken from the fracture surfaces of composite samples showed that water immersion did not affect the fracture characteristic of the composite. No matter how many hours the samples were treated with water, fibres at the fracture surface looked the same: they were well coated with a layer of resin. The interface appears to be as strong as, or stronger than the polymer matrix. No bare fibre was visible in the SEM; the pictures shown are typical of the surfaces viewed.

Figure 3.26 SEM pictures taken from the fracture surfaces of AS4-PEEK
Figure 3.26 SEM pictures taken from the fracture surfaces of AS4-PEEK (cont.'d)
4. DISCUSSION

4.1 Pull-out Test With Carbon/Polyimide

From the pull-out curves we can see that the fibre pull-out procedure is always accompanied by a sudden drop of force, which indicates the interface failure. Although the polyimide used in this study was a thermoplastic, we can noticed that the major peaks of the pull-out curves are rather sharp, indicating brittle failures.

Another characteristic of the force-displacement plots is the slope changes occurring at the uphill slope before the summit. As pointed out by other researchers [74], these changes were the results of transitions occurring in the pull-out process. In this experiment, several possible regions on a force-displacement curve could be identified that may be associated with different interfacial phenomena: an elastic region, a plastic deformation region and a region where frictional forces dominate the process after fiber debonds. All pull-out plots had at least one slope change. But, unlike the case of carbon/PEEK pull-out observed by Chen [73], the most obvious slope change happened near the half way of the slope. The second slope change near the summit was sometimes not clear. In Chen's case, the second slope change was the most obvious one. It appears that the reason of the difference is the dutility of PEEK and the brittleness of the polyimide.

The lower slope change, $F_y$, was considered to be the yielding point of the polymer near the interface. The upper slope change, $F_{ds}$, corresponded to the beginning of the debonding failure. The maximum force, $F_{dc}$, was considered to correspond to the completion of the interface failure process [74].

For each of the pull-out tests which was successfully performed, i.e., fibres were pulled out rather than broken, the embedded length of each fibre was determined by two ways. First, the pulled-out fibres were observed under the light microscope and the length
between the embedded fibre end and the meniscus formed at the fibre entry point was measured. Second, the embedded length was also estimated by the displacement shown in the pull-out curve when the force dropped to zero. Results showed the embedded length determined by both methods have good agreement, see Fig 4.1.

Figure 4.1 Plot of embedded length estimated from the pull-out curve versus embedded length estimated from light microscope observation
Figure 4.2 Force of the first slope changes vs. embedded length

Figure 4.3 Force of the second slope changes vs. embedded length
Fig. 4.2, 4.3 and 4.4 show the relationship between $F_y$, $F_{ds}$, the maximum frictional force, $F_f$, and the embedded length. Great scatter was observed in these results. However, the monotonically increasing trend could still be seen for $F_{ds}$ and $F_f$, see Fig. 4.3 and Fig. 4.4. From these plots we can determine the mean shear stresses $\tau_y$, $\tau_{ds}$, $\tau_{dc}$. For example,

$$\tau_y = \frac{1}{n} \sum_{i=1}^{n} \frac{F_{yi}}{\pi d L_i}$$  \hspace{1cm} (4-1)$$

where $n$ is the number of results and $F_{yi}$ is the value of $F_y$ for an embedded length $L_i$.

Table 4.1 lists the results from the calculation above.
Table 4.1 Mean shear stresses for pull-out tests

<table>
<thead>
<tr>
<th>(\tau_y)</th>
<th>(\tau_{ds})</th>
<th>(\tau_{dc})</th>
</tr>
</thead>
<tbody>
<tr>
<td>27±39</td>
<td>13±5</td>
<td>16±6</td>
</tr>
</tbody>
</table>

Again, large variations are observed in these results. We could not find any plateau in these plots, which were observed in the AS4-PEEK case by other researcher [73]. The scattering of the results is partly due to the limited number of successful tests, but mainly because of the nature of the pull-out test. In the pull out test, the embedded length has a significant effect on the interfacial shear strength values. As the embedded length decreases, the value of \(\tau\) increases. As a result, the wider range of embedded length measured, the more confidence we can have on the pull out test results. Actually what happened in the pull out process is more complicated than we assumed here, where the stress concentration around the fibre and the frictional forces were not taken into account. All these factors combined together resulted in the great scattering of the pull out test result.

4.2 Moisture Absorption

Among all the environmental factors affecting the performance of polymer-matrix composites, temperature and moisture are always the major concerns. The mechanical, thermal, and chemical properties of polymeric composite are degraded by the combination of elevated temperature and moisture absorption level. The fundamental properties of the components of the composite which have primary influences on the response of the material to the hygrothermal environment are coefficients of thermal expansion, thermal conductivities, moisture diffusion coefficients, and moisture saturation levels.
The experimental results showed that for both PEEK and AS4-PEEK, higher temperature resulted in shorter time for the materials to reach moisture absorption equilibrium. It appeared that the maximum moisture content is different at different temperatures; the higher the temperature, the higher the moisture content the material can absorb. It was also noticed that it took much longer time for the composite to reach the maximum moisture content than for the polymer. As pointed out by other researchers, when dealing with moisture absorption problems, Fickian diffusion is a reasonable approximation for many materials[75]. When exposed to a moist environment, the percent moisture content M (percent weight gain) of the material varies as a function of time t

\[ M = \frac{\text{Weight of moist material} - \text{weight of dry material}}{\text{Weight of dry material}} \times 100 \]  \hspace{1cm} (4-2)

To calculate the percent weight gain, we can calculate the moisture concentration c first. The moisture concentration distribution is described by the Fick equation

\[ \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} D_x \frac{\partial c}{\partial x^2} \]  \hspace{1cm} (4-3)

where \( D_x \) is the mass diffusivity along the x direction (laminate thickness direction).

It was observed that the diffusivity changes very little with the moisture content [76]. As the specimens used in the experiment are thin (2mm thick), we assume that the temperature inside the material approaches equilibrium much faster than the moisture concentration and hence the temperature inside the material can be taken to be the same as the ambient temperature. With the temperature and the diffusivity being constant inside the material the problem is described by the equations

\[ \frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} \]  \hspace{1cm} (4-4)

with the boundary conditions
\[ \frac{c - c_i}{c_m - c_i} = 1 - \frac{4}{\pi} \sum_{j=0}^{\infty} \frac{1}{2j + 1} \sin \left( \frac{(2j + 1)\pi x}{h} \right) \exp \left[ - \frac{(2j + 1)^2 \pi^2 D_c t}{h^2} \right] \] (4-6)

The total weight of the moisture \( m \) in the material is obtained by integrating equation (4.6) over the plate thickness

\[ m = \int_{0}^{h} c \, dx \] (4-7)

The result of this integration is [77]

\[ m = m_i + (m_m - m_i) \left( 1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{\exp[-(2j + 1)^2 \pi^2 (D_c t/h^2)]}{(2j + 1)^2} \right) \] (4-8)

\( m_i \) is the initial weight of the moisture in the material (i.e. the weight prior to exposure to the moist environment) and \( m_m \) is the weight of moisture in the material when the material is fully saturated. Shen and Springer [75] approximated Jost's solution with

\[ m = m_i + \{(m_m - m_i) \times [1 - \exp(-7.3(D_c t/h^2))]\}^{3/4} \] (4-9)

The diffusivity \( D \) is obtained from the initial slope of the \( m_m \) versus \( \sqrt{t} \) curve (see Appendix) [75]

\[ D = \pi \left( \frac{h}{4M_m} \right)^2 \left( \frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2 \] (4-10)
Based on the above equations, we can now calculate diffusivities of PEEK and AS4-PEEK from the initial slopes of the absorption curves. Since the composite had not reached the saturation level, the maximum moisture content of the composite was estimated by multiplying the maximum moisture content of the polymer by the volume fraction of the polymer in the composite. The diffusivity values are listed below, with the p and c subscript referring to the polymer and composite respectively.

Table 4.2 Diffusivities of PEEK and AS4-PEEK

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>D_p (μm²s⁻¹)</th>
<th>D_c (μm²s⁻¹)</th>
<th>D_c / D_p</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>0.46 ± 0.12</td>
<td>0.06 ± 0.02</td>
<td>0.13</td>
</tr>
<tr>
<td>60</td>
<td>2.31 ± 0.04</td>
<td>0.49 ± 0.09</td>
<td>0.21</td>
</tr>
<tr>
<td>90</td>
<td>6.45 ± 0.82</td>
<td>2.13 ± 0.72</td>
<td>0.33</td>
</tr>
</tbody>
</table>

The diffusivities were plotted by lnD vs 1/T shown in Fig. 4.5.

Figure 4.5 Arrhenius plot for diffusion constants for PEEK and AS4-PEEK
The straight lines in Fig. 4.5 show that the diffusivities fitted the Arrhenius equation

\[ D = D_0 e^{-E/kT} \]  

(4-11)

where \( D_0 \) is a constant, \( E \) is the activation energy for diffusion, \( k \) is Boltzmann's constant, and \( T \) is the absolute temperature.

For a composite with fibres square packed the diffusivity of the composite can be calculated from the polymer's diffusivity by [78]

\[ D_c = D_p \left\{ \frac{2}{\sqrt{1-c^2}} \tan^{-1} \sqrt{\frac{1+c}{1-c}} - \frac{\pi}{2} + 1 - c \right\} \]  

(4-12)

for fibres which are impervious to water, and with

\[ c = \sqrt{\frac{4V_f}{\pi}} \]  

(4-13)

For \( V_f = 0.61 \), the value for the composite, \( D_c/D_p \) should be 0.24, whereas the experimental results here give 0.13, 0.21, 0.33 for 23°C, 60°C, and 90°C respectively. The average of these three numbers gives 0.22, which is very close to the number expected.

The following figures compare the experimental results and the estimation by Fick's Law based on the diffusivities and maximum moisture content calculated from experimental work. The dots are experimental data and the solid lines were computed by Fick's Law.
Figure 4.6 Moisture absorption of PEEK at different temperatures

Figure 4.7 Moisture absorption of AS4-PEEK at different temperatures
Figure 4.8 Moisture absorption of PEEK and AS4-PEEK at 23°C

Figure 4.9 Moisture absorption of PEEK and AS4-PEEK at 60°C
The water absorption results of the polymer are generally in agreement with Fick’s Law. However, deviations were found in some of the experiments. The experimental data of PEEK at 60°C and 90°C, the initial part of AS4-PEEK at 90°C fit the calculated curves very well. The initial absorption data for PEEK and AS4-PEEK at 23°C and 60°C are higher than the moisture content calculated by Fick’s Law. The reason is that the formula we used to calculate the Fickian absorption is

\[ m = \left[1 - \exp(-7.3)(Dt/h^2)\right]^{3/4} \]  

(4-14)

in which the initial moisture content of the materials was not taken into account, because it is difficult to determine. In the case of PEEK 90°C water immersion, a good fit was observed between the experimental results and Fick’s Law. The reason might be that the sample was completely dried before immersion.

It should be noticed that even though the initial moisture content is taken into account, the moisture absorption of the composite did not obey the Fick’s Law at the later
part of the experiment, see Fig. 4.7. The moisture content kept increasing, which is well above the level we estimated from the polymer volume fraction of the composite. It was already shown that carbon fibres absorbed relatively little water by other researchers (only about 0.018% after 500 h at 98% RH)[79]. It appeared that something might have happened in the absorption process, in which the interface might play an important role, because in the above calculations we did not consider the contribution of the interface in the absorption process and we didn’t know the diffusivity of the interface. The longer time it took for the composite to reach saturation also indicates that the reinforcement acted as barrier of the diffusion process.

4.3 Mechanical Properties
4.3.1 Moisture effect

The force-displacement curves of PEEK were converted into stress-strain curves and showed in Fig. 4.11. After water aging, both the ultimate strength and strain of PEEK decreased. However, the slope changes indicated that modulus increased.

![Figure 4.11 Stress-strain curves for PEEK](image)
The stress-strain curves for AS4-PEEK (Fig. 4.12) show that water aging had little effect on the mechanical properties of the material. There is not much difference between the curves for the no-treatment samples and the water treated samples, sometimes these curves overlapped, except that lower strength was observed for water treated samples. This means that the overall mechanical properties of the composite were not affected by the adverse environment.

Figure 4.12 Stress - strain curves for AS4-PEEK
Figure 4.12 Stress - strain curves for AS4-PEEK (cont.’d)

Figure 4.13 Comparison of stress-strain curves of PEEK and AS4-PEEK
Fig. 4.13 compares the stress-strain curves of polymer and composite from transverse test. The stress at failure are about the same, but the strains are reduced when fibres are present.

The experimental results showed that water absorption did not affect the mechanical properties of both polymer and composite until after 3000 hours of treatment.

It’s well accepted that significant stresses can be introduced inside the composite during the processing of the material. This is because of the significant difference in coefficients of thermal expansion between the filaments and matrix materials. For example, epoxy resin has a coefficient of thermal expansion of approximately $25 \times 10^{-6}$ ($^\circ$F$^{-1}$) while typical filaments such as glass, boron, and carbon have a value somewhere near $2.7 \times 10^{-6}$ ($^\circ$F$^{-1}$) [80]. This order of magnitude difference can introduce large stresses even during cooling of the composite from processing temperature to room temperature. It’s well known that polymer absorbs water. Moisture absorption will result in the swelling of the matrix. Therefore it is possible that after long term hygrothermal treatment of the composite, the residual stress inside the composite will be somewhat relieved. The matrix strength reduction by water attack might be offset by the stress relief effect. When the treating time is longer, the effect of deterioration of the polymer might overwhelm the stress relief effect and the composite strength began to decrease. This is the reason we observed decrease of polymer strength after 3000 hour immersion but the strength of composite did not decrease until after 4500 hours of treatment.

### 4.3.2 Interface strength

The composite transverse strength, $\sigma_{2u}$, was very reproducible, with coefficients of variation of 2-3%. The polymer strength, $\sigma_{mu}$, was even less variable, with cv’s of 1-2%. This is to be expected, since both the polymer and the composite are moderately tough [4].
The composite transverse strength is equal to the polymer strength, so we conclude that the interface strength, $\sigma_i$, is at least as great as that of the polymer. This is confirmed by the micrographs, which show no interface failure.

This result is much more clear cut from that obtained from the pull-out experiments, in which AS4 carbon fibre and PEEK were used [81]. These suggested that the mean shear stress at the interface when the fibre debonded was $85 \pm 29$ MPa. This was reduced to $57 \pm 19$ MPa after 3000 h in 90°C water. The large coefficients of variation, i.e. 33-34% and the overlapping of the results made it difficult to judge whether or not water was affecting the interface. In contrast, the transverse test shows clearly that it was not. It is also noticed that the pull out test with carbon fibre and polyimide gave results with large coefficient of variation. All these support the case of phasing out the pull out test.

4.3.3 Elastic properties

The inverse rule of mixtures (IROM) given by

$$\frac{1}{E_2} = \frac{V_f}{E_f} + \frac{V_m}{E_m}$$  \hspace{1cm} (4-14)

has been used to estimate the transverse modulus, $E_2$, of a unidirectional composite [82]. The IROM is also referred to as the "Equal stress model" because it assumes that the stress of the matrix and the fibres are the same as the stress applied on the composite. Here $V_f$ and $V_m$ are the matrix and fibre volume fractions, and $E_f$ and $E_m$ their respective Young's moduli. For $V_f = 0.61$ and using $E_m = 3.9$ GPa, and with $E_f = 233$ GPa we obtain $E_2 = 9.7$ GPa, i.e. within the experimental range of results. The model used for this is somewhat crude, with all the fibres lumped together so that the stress is the same in both fibres and matrix. Perhaps because of this, Halpin-Tsai is often preferred [83]. This may be written
with

\[ \eta = \frac{\frac{E_f}{E_m} - 1}{\frac{E_f}{E_m} + \xi} \]  \hspace{1cm} (4-16)

This gives \( E_2 = 20.1 \) GPa for this composite with \( \xi = 2.0 \), the preferred value for this curve fitting parameter. Clearly, Halpin-Tsai is not useful in this case.

A better approach may be to refine the assumption used for the inverse rule of mixtures. Consider square packed fibres, and assume that we can approximate the fibre by giving it a square section; see Fig. 4.14. The square OABC represents the smallest repeating unit of the composite and this can be further subdivided into regions 1 and 2, with some fibre and without any. If we assume that applying a stress \( \sigma_2 \) does not change the geometry significantly, i.e. straight lines remain straight, then BC moves to B'C'. Let this displacement be \( v \). The strain in the all-polymer region 2, \( \varepsilon_2 \), is given by

\[ \varepsilon_2 = \frac{2v}{R} = \frac{\sigma_2}{E_m} \]  \hspace{1cm} (4-17)

the strain in region 1 is also \( \varepsilon_2 \), but with \( v \) given by

\[ v = \frac{r \sigma_{v1}}{E_f} + \left( \frac{R}{2} - r \right) \frac{\sigma_{v1}}{E_m} \]  \hspace{1cm} (4-18)
Figure 4.14 Schematic illustration of a) a cross section of a unidirectional composite, b) a smallest repeating unit, c) region 1 and region 2 in the repeating unit
The stress, $\sigma_2$ is obtained by a force balance:

$$\frac{R\sigma_2}{2} = r\sigma_y + \left(\frac{R}{2} - r\right)\sigma_y$$

so that, eliminating $\sigma_y$ and $\sigma_1$ using equations (4-17) and (4-18), we have

$$\sigma_2 = \frac{2v}{R} \left\{ \frac{r}{E_f} + \frac{R}{E_m} \frac{1}{\frac{R}{2} - r} \right\}$$

Writing $V_f = \frac{4r^2}{R^2}$ and using $\varepsilon_2 = \frac{2v}{R}$ this simplifies to

$$E_2 = \frac{\sigma_2}{\varepsilon_2} = \frac{\sqrt{V_f}}{E_f} + \frac{1 - \sqrt{V_f}}{E_m}$$

This is better than Halpin-Tsai, but less good than IROM for estimating $E_2$ in this case; it gives 14.0 GPa if we use fibre longitudinal modulus $E_f = 233$ GPa. Since the carbon fibres are anisotropic, with a transverse modulus much less than the longitudinal one, it’s more reasonable to use the fibre transverse modulus. However, it’s rather difficult to measure the fibre transverse modulus. Some references only gave out estimation from experiment with composite or just theoretical calculation. If we use the number given by Smith [84], which is $E_{fL} = 13$ GPa, $E_2$ would be 7.6 GPa, which is closer to experimental result than 14.0 GPa. Nevertheless, it gives insight into the stress and strain concentrations that are ignored in the simplest models. Thus, from equation (4.17) and (4.21);

$$\sigma_y = E_m \frac{\sigma_2}{E_2}$$

and from equation (4-19) and (4-22)
which in this case comes to $\sigma_{y1} = 1.20\sigma_2$. We can now calculate the strain in the polymer in region 1. This is $1.2\sigma_2/E_m$, compared with a mean strain of $\varepsilon_2$. So the strain magnification is $1.2E_2/E_m$ which comes to 4.3. For a composite breaking strain of 1.13%, this region of the polymer reached a strain of 4.9%, i.e. close to the breaking strain of the polymer in the absence of the composite: see Fig. 4.13.

Figures 4.15 and 4.16 compare the predictions of Equations (4-14), (4-15) and (4-21), with Fig. 4.15 using the fibre longitudinal modulus and Fig. 4.16 using the fibre transverse modulus given by Smith [84]. The solid lines are computed from Equation (4-21).

$$\sigma_{y1} = \frac{\sigma_2}{\sqrt{V_f}} \left(1 - \frac{(1-V_f)E_m}{E_2}\right) \quad (4-23)$$

**Figure 4.15** Comparison between models for estimation of transverse modulus using $E_f = 233$ GPa, $E_m = 3.9$ for PEEK, and $\xi = 2.0$ for Halpin-Tsai's model
Figure 4.16 Comparison between models for estimation of transverse modulus using $E_{t_l} = 13$ GPa, $E_m=3.9$ for PEEK, and $\xi = 2.0$ for Halpin-Tsai's model

We can see that the expectation of Equation (4-21) lies between the Halpin-Tsai model and the Inverse Rule of Mixture. In the case of AS4-PEEK, when we use the fibre longitudinal modulus, the equal stress model gives the closest estimation. If we use the fibre transverse modulus, the Halpin-Tsai model performs better. Unfortunately, because of the experimental method used, we cannot obtain AS4-PEEK composite with different volume fractions. It is hard to say which model fits the experimental results well since there was only one volume fraction available. It should also be noticed that the fibre transverse modulus is only a theoretical estimation. The true value is still unknown. Furthermore, the model we developed uses square instead of circle as the fibre cross section to simplify calculation, which is not sufficient in accuracy. However, it is valuable to try out different approach to estimate the transverse elastic properties of composite materials.
5. CONCLUSIONS

1. The pull out test using carbon fibre and polyimide showed that the interface shear strength was $16 \pm 6$ MPa. The values of forces at slope change points did not appear to have plateau values on a statistical point of view. Results were accompanied with large coefficient of variations. The experimental results support the point to phase out the pull out test.

2. Moisture absorption experiment showed that the diffusion process in PEEK generally obeyed Fick’s Law, with minor deviations. The saturation moisture content for the polymer varied with temperature; the higher the temperature, the higher the maximum moisture content. The maximum moisture content for PEEK was 0.51% when samples were immersed in 90°C water. For the composite, the experimental results did not fit the Fick’s Law very well. The material absorbed more water than the expected saturation level. The reason was not clear because of insufficient time for experiment. The diffusivities of both polymer and the composite fitted the Arrhenius equation.

3. Both polymer and the composite were very resistant to moisture. The moisture had little effect on the mechanical properties of the materials even if they were immersed in 90°C water for 100 days. The ultimate strength of the polymer decreased by 15% after 3000 hours of immersion. The transverse strength of the composite decreased by 18% after 4500 hours of immersion with no further change till 8000 hours of exposure. The stiffness of both materials were not deteriorated by water no matter how long the samples were treated with 90°C water.

4. The elastic theory analysis showed that the Inverse Rule of Mixture is a rough approximation although the results it gave were close to experiment results. A different approach needs to be developed because of the anisotropic elastic property of the carbon fibre.
6. REFERENCES

5. ibid., p.29.


65. Hartness, J. T., Polyether etherketone matrix composites, SAMPE Conference (Atlanta, 1982).


### 7. LIST OF NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>c</td>
<td>moisture concentration in the specimen (g mm(^{-3}))</td>
</tr>
<tr>
<td>c(_i)</td>
<td>initial moisture concentration in the specimen (g mm(^{-3}))</td>
</tr>
<tr>
<td>c(_m)</td>
<td>maximum moisture concentration in the specimen (g mm(^{-3}))</td>
</tr>
<tr>
<td>d</td>
<td>diameter of fibre (mm)</td>
</tr>
<tr>
<td>D(_0)</td>
<td>constant in the Arrhenius equation</td>
</tr>
<tr>
<td>D(_c)</td>
<td>diffusivity of the composite (μm(^2)s(^{-1}))</td>
</tr>
<tr>
<td>D(_p)</td>
<td>diffusivity of the polymer (μm(^2)s(^{-1}))</td>
</tr>
<tr>
<td>D(_x)</td>
<td>mass diffusivity along the x direction (μm(^2)s(^{-1}))</td>
</tr>
<tr>
<td>E</td>
<td>activation energy for diffusion (J mole(^{-1}))</td>
</tr>
<tr>
<td>E(_2)</td>
<td>transverse modulus of the composite</td>
</tr>
<tr>
<td>E(_f)</td>
<td>Young's modulus of fibre (Nm(^{-2}))</td>
</tr>
<tr>
<td>E(_fL)</td>
<td>fibre transverse modulus</td>
</tr>
<tr>
<td>E(_m)</td>
<td>Young's modulus of the matrix</td>
</tr>
<tr>
<td>F(_{dc})</td>
<td>maximum force of the pull out process (N)</td>
</tr>
<tr>
<td>F(_{ds})</td>
<td>force of the second slope change in the pull out curve (N)</td>
</tr>
<tr>
<td>F(_{max})</td>
<td>maximum force in the fibre pull out test (N)</td>
</tr>
<tr>
<td>F(_y)</td>
<td>force of the first slope change in the pull out curve (N)</td>
</tr>
<tr>
<td>h</td>
<td>thickness of the specimen for moisture absorption measurement (mm)</td>
</tr>
<tr>
<td>k</td>
<td>Boltzmann's constant (J K(^{-1}))</td>
</tr>
<tr>
<td>l(_c)</td>
<td>critical length of the fibre fragment in fragmentation test (mm)</td>
</tr>
<tr>
<td>l(_e)</td>
<td>embedded length of the fibre in pull out test (mm)</td>
</tr>
<tr>
<td>m</td>
<td>total weight of the moisture in the specimen (g)</td>
</tr>
<tr>
<td>M</td>
<td>percent moisture content (%)</td>
</tr>
<tr>
<td>r</td>
<td>half of the length of each side of the square unit representing the cross section of fibre in the composite</td>
</tr>
<tr>
<td>R</td>
<td>the length of each side of the smallest repeating square unit in a composite</td>
</tr>
<tr>
<td>t</td>
<td>time (hour)</td>
</tr>
<tr>
<td>T(_g)</td>
<td>glass transition temperature (°C)</td>
</tr>
</tbody>
</table>
\( v \) displacement of the smallest repeating unit in a composite when a stress is applied

\( V_f \) fibre volume fraction of the composite

\( V_m \) matrix volume fraction of the composite

\( \varepsilon \) strain (dimensionless)

\( \varepsilon_2 \) strain in the direction normal to fibre

\( \sigma_2 \) stress applied on the composite in the direction normal to the fibre

\( \sigma_f \) tensile strength of fibre (Nm\(^{-2}\))

\( \sigma_{y1} \) stress applied on the region 1 in the smallest repeating unit of the composite in the direction normal to the fibre

\( \sigma_{y2} \) stress applied on the region 2 in the smallest repeating unit of the composite in the direction normal to the fibre

\( \tau \) mean interfacial shear strength (Nm\(^{-2}\))

\( \tau_{dc} \) mean shear strength of the interface determined by pull out test (Nm\(^{-2}\))

\( \tau_{ds} \) mean shear stress calculated from Fdc (Nm\(^{-2}\))

\( \tau_{ILSS} \) interlaminar shear strength (Nm\(^{-2}\))

\( \tau_y \) mean shear stress calculated from Fy (Nm\(^{-2}\))

\( \xi \) adjustable parameter in the Halpin-Tsai model
8. APPENDIX

To calculate diffusivity $D_x$ we refer to equation (4-4)

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2}$$

(4-4)

For a semi-infinite solid ($h \to \infty$) the boundary conditions (equations (4-5a) and (4-5b)) become

$$c = c_i \quad 0 < x < \infty \quad t \leq 0 \quad (8-1a)$$
$$c = c_m \quad x = 0 \quad t > 0 \quad (8-1b)$$

The moisture concentration as a function of position and time in the solid is [77]

$$\frac{c - c_i}{c_m - c_i} = 1 - \text{erf} \left( \frac{x}{2\sqrt{D_xt}} \right)$$

(8-2)

the weight of moisture which enters an area $A$ in time $t$ is calculated by

$$m = \int_{0}^{t} -AD_x \left( \frac{\partial c}{\partial x} \right)_{x=0} \, dt$$

(8-3)

The solution of equation (8-2) and (8-3) was given by Jost [77]

$$m = 2A \left( c_m - c_i \right) \sqrt{\frac{D_x t}{\pi}}$$

(8-4)
Figure 8.1 Geometry of the specimen for moisture absorption measurement
Now we consider the moisture entering the specimen from all six sides (Fig. 8.1). In the early stages of the process we assume that the interaction among diffusion from different sides can be neglected. So the total weight of entering moisture is

\[ m = 4(c_m - c_i)(nl \sqrt{D_x} + nh \sqrt{D_y} + hl \sqrt{D_z}) \sqrt{\frac{t}{\pi}} \]  

(8-5)

where \( n \) is the width of the specimen and \( l \) is the length of the specimen. \( D_x, D_y \) and \( D_z \) are the diffusivities in the \( x \), \( y \), and \( z \) directions. For an initially dry specimen (\( c_i = 0 \) and \( W_d = pg h n l \)) the moisture content as a function of time is

\[ M = \frac{W - W_d}{W_d} \times 100 = \frac{m}{W_d} \times 100 = \frac{4c_m}{\rho gh} \left( \sqrt{D_x} + \frac{h}{l} \sqrt{D_y} + \frac{h}{n} \sqrt{D_z} \right) \sqrt{\frac{t}{\pi}} \]  

(8-6)

Because \( c_m/\rho g \) is the maximum moisture content

\[ M = \frac{4M_m}{h \sqrt{\pi}} \left( \sqrt{D_x} + \frac{h}{l} \sqrt{D_y} + \frac{h}{n} \sqrt{D_z} \right) \sqrt{t} \]  

(8-7)

Equation (8-7) can also be written as

\[ M = \frac{4M_m \sqrt{t}}{h \sqrt{\pi}} \sqrt{D} \]  

(8-8)

where

\[ D = \left( \sqrt{D_x} + \frac{h}{l} \sqrt{D_y} + \frac{h}{n} \sqrt{D_z} \right)^2 \]  

(8-9)
Hence the slope of the initial part of the diffusion curve is

\[
\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} = \frac{4M_m}{h\sqrt{\pi}} \sqrt{D}
\]  \hspace{1cm} (8-10)

Therefore we have equation (4-10)

\[
D = \pi \left( \frac{h}{4M_m} \right)^2 \left( \frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2
\]  \hspace{1cm} (4-10)