INFLUENCE OF THE FIBRE/MATRIX INTERFACE ON THE
PHYSICAL AND MECHANICAL BEHAVIOUR OF E-GLASS
REINFORCED THERMOPLASTICS

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ABSTRACT

The performance of a composite is not only dependent on the properties of the constituent elements, the fibre, the size and the matrix, but also on the interface between them. Good interfacial bonding is essential for the effective transfer of stress from the matrix to the fibre. Two methods of improving the interfacial adhesion in E-glass reinforced thermoplastics have been studied, namely by coating the fibre with a size specific to the matrix, or by using an in-situ reactive processing technique to activate the matrix itself. The size modification and the matrix modification systems were evaluated in E-glass reinforced thermoplastics with matrices of polyamide 6.6 and polypropylene, respectively.

The elements which constitute the composite, namely the fibre, the size and the matrix, were characterized both individually and when combined in the composite.

Both polymers presented spherulitic structures, however, the nature of these crystallites was shown to be dependent on both the processing conditions and the chemical modification, for the polypropylene. The physical properties of the unreinforced matrices were examined by tensile testing and by viscoelastic analysis, and were shown to be structure-related.

The characterization of the size coating on the fibres proved difficult due to the small dimensions of the fibre, the very thin size layer and the insulating nature of the specimens which resulted in charging with electron microscopy techniques. However, by employing a wide range of experimental methods the polymer of the size and the fibre/size interface were successfully characterized. The behaviour of the size was found to be dependent on the type of matrix reactive polymer added to the silane coupling agent.

The composite materials, of both systems, were characterized structurally, by employing image analysis to examine the fibre length and orientation distributions, and transmission optical microscopy to observe the matrix. The fibre length and orientation distributions were found to be dependent on the processing conditions employed, but independent of the interfacial modification, of both systems. The mechanical properties of the composites were measured by tensile testing and viscoelastic analysis.
Three methods were developed to evaluate the strength of the fibre/matrix bonding in the injection moulded composites:

Viscoelastic analysis, with a torsion pendulum was shown to be sufficiently sensitive to detect variations resulting from the type of size applied to the fibres, or the addition of small quantities of modifying agents to the matrix polymer. The composite was characterized, in its bulk form, by comparing the damping properties of the material.

An adhesion efficiency model was developed to rank the composites with respect to their interfacial bond strength. This method was found to be an effective tool for comparing the different adhesion enhancement systems.

The third method employed was the microdrop test which provided a direct measurement of the interfacial shear stress in each system.
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CHAPTER I
INTRODUCTION
I INTRODUCTION

Fibre reinforced thermoplastics possess several advantages over thermosetting matrix composites, which are already widely employed for applications in many engineering fields, including the aeronautical, transport, marine and chemical industries (e.g. as automobile bumpers, boat hulls and chemical containers). These advantages include easy storage and the possibility of recycling, the latter feature being of both economic and enviromental importance, and desirable characteristics such as good specific strength and stiffness, toughness to resist impact and ability to dampen shock and vibration. Additionally, complex forms can be manufactured at high production rates by injection moulding, rendering these materials industrially viable. However, thermoplastic composites are not limited to the injection moulded form, and there is growing interest in other reinforcement types from long fibres, to continuous, unidirectional filaments. Opportunities to tailor the material properties of a product are provided through processing technology and by reinforcement of specific areas (1).

Unidirectional carbon fibre reinforced thermoplastics such as PEEK (polyetheretherketone) and PPS (polyphenylene sulphide) laminates have been well characterized in recent years (2,3). These materials are high performance thermoplastic composites, however, their high cost restricts their use to a relatively small market i.e. that of the aerospace industry.

A much larger market is available for commodity or bulk composites, reinforced with glass fibres and based on thermoplastics, such as polypropylene and polyamide 6.6 (PA66). The former matrix is a widely available commodity polymer and, when combined with glass fibres, it produces an inexpensive composite. This material is employed for pipelines, a use which also takes advantage of the hydrophobic nature of polypropylene.

PA66 is an engineering thermoplastic which has good high temperature behaviour and is resistant to grease and oils. These properties render it particularly suitable for mechanical parts in domestic appliances.(4,5)

Industrial mass production of both polypropylene and PA66 glass fibre reinforced polymers produces composites with good performance combined with low cost. In addition their ability to provide corrosion protection and to operate with little or no maintance makes these materials particularly suitable for the automotive industry.
The performance of a composite is not only dependent on the intrinsic properties of the constituent elements, the fibre and the matrix, but also on the interface between them. Good interfacial bonding is essential for the effective transfer of stress from the matrix to the fibre. However, E-glass reinforced thermoplastics tend to have limited interfacial bonding as the inorganic (fibre) and the organic (matrix) materials are mutually unreactive. Interfacial adhesion must therefore be improved. This may be achieved by two methods:

1) coating the fibres with a size specific to the matrix

2) using an in-situ reactive processing technique to graft functional groups to the polymer backbone in order to activate the macromolecular chains of the matrix.

These two different approaches to enhancing fibre/matrix adhesion are shown schematically in Figure 1.1.

The subject of this thesis has therefore been the evaluation of both approaches to improving fibre/matrix bonding. Both systems, size modification and matrix modification, were examined within the framework of two contracts, one with the French glass fibre manufacturer, Vetrotex and the other as part of a BRITE EURAM program, with the University of Aston and the Institut Français de Petrole (IFP). This study involved the close collaboration of these partners as detailed in Figure 1.2. Specimen manufacture was undertaken by Vetrotex for the size modified samples, and is the subject of another thesis (6), and by the University of Aston for the matrix modified specimens, employing a novel chemical system (7). Involvement in all stages of the fabrication of the latter sample type gave an understanding of the in-situ reactive process. The work presented in this thesis concerns the characterization of the matrix and composite samples performed at the Ecole Nationale Superieure des Mines de Paris and at the University of Surrey. The results obtained by the other partners have been utilised, as necessary, to explain further the structural and mechanical behaviour of the composite materials.

As this study was financed by these contracts, the materials employed were imposed by the manufacturers. Both systems were reinforced with E-glass fibres, but, size modification was studied in polyamide 6.6 (PA66) composites, whereas the matrix modification was examined in polypropylene composites. Both these matrices are semi-crystalline thermoplastics. The composite samples were injection moulded and
FIGURE 1.1: Two methods by which interfacial bonding can be enhanced:

1) coating the fibres with a size specific to the matrix
2) using an in-situ reactive processing technique to graft functional groups to the polymer backbone in order to activate the macromolecular chains of the the matrix.
### Establishment Role

<table>
<thead>
<tr>
<th>Institution</th>
<th>Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ecole des Mines</td>
<td>Characterization of Composite</td>
</tr>
<tr>
<td>University of Surrey</td>
<td>XPS-Surface Characterization</td>
</tr>
<tr>
<td>University of Aston</td>
<td>Modified Polymer Processing and Composite Manufacture</td>
</tr>
<tr>
<td>IFP</td>
<td>Chemical Characterization Modified Polymer</td>
</tr>
<tr>
<td>Vetrotex</td>
<td>Glass Fibre Manufacture Size Production</td>
</tr>
</tbody>
</table>

**Figure 1.2:** Interaction of the partners within the framework of the Vetrotex contract and the BRITE EURAM program.
therefore exhibited a short, random fibre distribution. The size-modified composites were also produced with two other fibre distributions, short, oriented fibres and unidirectional fibres, which permitted the behaviour of the composite to be characterized for a relatively simple distribution, and subsequently for more complex arrangements of fibres.

In order to better understand the behaviour of these composites a comprehensive study of the interface was necessary. Interfacial properties were assessed by six distinct routes:-

**Chemical -** Microprobe Analysis, Transmission Electron Microscopy

**Surface -** Glancing X-ray Diffraction, X-Ray Photoelectron Spectroscopy


**Micromechanical -** Microdrop Test

**Mechanical -** Tensile Testing

**Dynamic mechanical -** Viscoanalyseur (DMTA), Torsion Pendulum

Each approach was integrated into the project by employing the experimental techniques indicated.

Chapter 2 summarizes the relevant previous research on the behaviour of the reinforcement and the matrices, as well as for the composite materials. Particular reference to the fibre/ matrix interface is made and the methods for interfacial adhesion enhancement are highlighted. The third and fourth chapters detail the materials and the wide range of experimental techniques employed, which include the methods described above. The results obtained are given in the fifth chapter and are discussed in Chapter 6 and 7. A model has been developed to rank the specimens with respect to their adhesion efficiency or their ability to form strong fibre/matrix bonding, and the physical nature of this interfacial bonding has been considered.
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CHAPTER II
LITERATURE SURVEY
II. LITERATURE SURVEY

2.1. INTRODUCTION

The mechanical properties of a fibre-reinforced composite are not only dependent on the intrinsic characteristics of the fibre and the matrix, but also on the interface between these constituents. In the following literature survey the relevant previous research on the behaviour of E-glass fibre-reinforced thermoplastics (Polypropylene (PP) and Polyamide 6.6 (PA66)) is considered with particular reference to the fibre/matrix interface. The requirement for an improvement in fibre-matrix adhesion and some methods for approaching this objective are highlighted.

II.2 GLASS FIBRE-REINFORCEMENT

2.2.1 INTRODUCTION

A high stiffness reinforcement will enhance the stiffness of a more compliant matrix, providing there is good interfacial adhesion, producing a composite with superior properties to those of the individual elements. A wide range of reinforcements are available which may be either particulate (spheres, plates, ellipsoids, irregular, either hollow or solid) or fibrous.

Glass fibres provide the highest volume of fibre reinforcement for plastics. In 1987 the utilisation of glass fibre reinforced plastics (GFRP) exceeded 2.5 million tonnes in the major world markets (U.S.A, Europe and Japan)(1). The continuing and increasing demand for GFRP is due to the good mechanical properties (particularly of specific tensile strength, and specific modulus) per unit cost of glass fibre reinforcement as compared with other engineering materials,(2) The current commercial price for E-glass fibre of the French glass fibre manufacturer Vetrotex is £1.00 to £1.50/kg.

Although there are several types of glass fibre commercially available, 99% of the continuous filaments used are of E-glass, which is based on the eutectic SiO$_2$ - Al$_2$O$_3$ - CaO at 62.0%, 14.7%, and 23.3% respectively (3). The composition of commercial E-glass is given in Table 2.1.
### TABLE 2.1: Composition of E-glass (2)

<table>
<thead>
<tr>
<th>CONSTITUENT</th>
<th>% WEIGHT</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>52 - 56</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12 - 16</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>8 - 13</td>
</tr>
<tr>
<td>CaO</td>
<td>12 - 25</td>
</tr>
<tr>
<td>MgO</td>
<td>0 - 6</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0 - 1</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0 - 0.4</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.05 - 0.4</td>
</tr>
<tr>
<td>F₂</td>
<td>0 - 0.5</td>
</tr>
</tbody>
</table>

### 2.2.2 MANUFACTURE

Continuous glass fibres are fabricated by feeding molten glass, at 1300°C, through platinum bushings, 1 to 2mm in diameter. The exuding glass is drawn into fibres by pulling downwards at speeds up to 60m/s, coated with a protective size and then wound on to a drum. From this process the diameter of the resulting filaments may be varied between about 5 and 24 µm by altering the pulling speed. Other fabrication parameters which influence the fibre diameter are the head of glass in the tank, the viscosity of the glass, which is dependent on both its composition and temperature and the diameter of the bushings. Rapid cooling of the fibre with a water mist occurs at the exit point of the bushing. The fibre cooling rate is shown (4,5) to increase with decreasing fibre diameter and hence increasing drawing rate, in Table 2.2.

### TABLE 2.2: Cooling rate of E-glass fibres

<table>
<thead>
<tr>
<th>FIBRE RADIUS (µm)</th>
<th>PULLING SPEED (m/s)</th>
<th>COOLING RATE(°C/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>---</td>
<td>1.18 . 10⁶ (4)</td>
</tr>
<tr>
<td>6.35</td>
<td>25.88</td>
<td>7.28 . 10⁴ (5)</td>
</tr>
<tr>
<td>10.00</td>
<td>---</td>
<td>4.20 . 10⁴ (4)</td>
</tr>
<tr>
<td>12.7</td>
<td>12.95</td>
<td>1.93 . 10⁴(5)</td>
</tr>
</tbody>
</table>
Figure 2.1 is a schematic representation of the Vetrotex fibre manufacturing process.

**FIGURE 2.1 : Fibre fabrication**

2.2.3 STRUCTURE

Glass is an amorphous material consisting of tetrahedra of SiO₄ organised in three-dimensional short range order as shown in Figure 2.2.

![Structure of bulk glass](image)

**FIGURE 2.2**: Structure of bulk glass (6)

Bulk glass has an open network structure which can be attributed to:
1) the rapid increase in the viscosity of the glass in a narrow temperature range. An increase of 5544 Poise has been measured by Tiede(7) for E-glass after reducing the temperature by 380°C from 1480°C. Viscosity is hence inversely proportional to temperature as described by a Flucher-Vogel type relationship:

\[
\eta(T) = \eta(0) \exp \left( \frac{A}{T - T_c} \right)
\]  \[2.1\]

where: \(\eta(T)\) = glass viscosity at temperature \(T\)
- \(\eta(0)\) = constant of viscosity equation (at \(T\) infinity)
- \(A\) = Flucher-Vogel constant
- \(T\) = Temperature
- \(T_c\) = Constant in Fulcher-Vogel equation

This equation is equivalent to the Williams, Landel and Ferry (WLF) equation which is widely used to describe the characteristic period for a given polymeric relaxation phenomenon, as a function of temperature. (8)
log(A_T) = \frac{-C_1 (T - T_0)}{(C_2 + T - T_0)} \quad [2.2]

where \( T_0 \) = reference temperature
\( A = 2.3C_1C_2 \)
\( C_1 \) and \( C_2 \) = numerical constants for a given system.

2) the rapid cooling of the glass during fibre manufacture, as shown in Table 2.2. The cooling rate of fibres is greater than that of bulk glass giving rise to a lower density of glass in filament form. Typical density values are 2.54 kg m\(^{-3}\) and 2.56 kg m\(^{-3}\) for the fibres and bulk respectively.

Metallic oxides additions, listed in Table 2.1, modify and perturb the three dimensional network. \( \text{Al}^{3+} \) ions replace the \( \text{Si}^{4+} \) ions to form \( (\text{AlO}_4)^- \) tetrahedra, and \( \text{Na}^+ \), \( \text{Ca}^{2+} \), and \( \text{Mg}^{2+} \) comprise interstitial lattice modifying entities which break-down the siloxane linkages Si-O-Si to form discontinuous groupings Si-O-Ca-O-Si.(9)

Theoretically the glass surface can be represented by truncated tetrahedrons as shown in Figure 2.3.(3)

![Figure 2.3](image)

**FIGURE 2.3**: The glass fibre surface which consists of truncated tetrahedrons

However this configuration is not stable as the surface is highly reactive and hydrophilic. H\(_2\)O molecules are adsorbed to the glass surface and form hydrogen bonds with the non-hygroscopic oxides SiO\(_2\) and Al\(_2\)O\(_3\). Figure 2.4 shows the glass surface hydrated by a monolayer of water molecules.(10)
Figure 2.4: Monohydrated silica surface.

Water retention on the glass surface is attributed to a combination of binding mechanisms: physical adsorption, hydrolysis of the surface network to form silanols, and hydration of the metal cations present in the glass. Glass adsorbs thick water films which become alkaline by leaching alkali ions from the glass.

2.2.4 Surface Chemistry

Several authors (11,12,13,14,15,16) have shown that the surface composition of the fibre is different from that of the bulk material. As summarized in the following table, it can be seen that the E-glass surface has an appreciably higher atomic concentration of Si and significantly lower values for Ca, Mg and B. The S-glass surface, however, is rich in Mg and Al, whereas the concentration of the Si and O is considerably decreased.
Variations in composition can be induced by the diffusion of the Na, Ca, Mg ions towards the surface, where the structure is more open than that of the fibre core. Sodium ion diffusion from R-glass into the size has been demonstrated by Jones and Pawson (13), and Wang et al. showed that aluminium from E-glass is incorporated into a size of hydrolysed γ-APS(14). This migration is facilitated by the weak forces which bind these ions, and by the high surface energy of the glass surface which acts as the driving force for this process. An increased surface concentration of alkali and alkaline-earth oxides is thermodynamically favourable as it decreases the surface energy of the glass(3). Larner et al. (15) suggested that the use of water during manufacture (for the cooling-spray mist and as a carrier for the size) may be responsible for the presence of calcium ions at the surface. An increase in surface Ca concentration was also measured by Nichols and Hercules (16) on heating E-glass fibres.

As the surface of the fibre plays an important role in the interfacial bonding mechanism the chemistry of the fibres must be considered in the light of these surface compositions rather than that of the bulk material.

### 2.2.5 PHYSICAL AND MECHANICAL PROPERTIES

Glass fibres exhibit the following specific properties:-
The mechanical properties of the glass are primarily determined by its three dimensional structure described in Section 2.2.3. In a tensile test the fibres behave as a classic Griffiths material, with rapid failure following crack initiation at a surface defect. This failure mode is typical of a brittle material.(6) However the Young's modulus, and the chemical durability of the fibre are sensitive to variations in composition, as shown by the special property C and S glasses in Table 2.5.

<table>
<thead>
<tr>
<th>GLASS</th>
<th>COMPOSITION %</th>
<th>Young's modulus GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO2</td>
<td>Al2O3</td>
</tr>
<tr>
<td>C</td>
<td>60-65</td>
<td>2-6</td>
</tr>
<tr>
<td>S</td>
<td>64.3-65</td>
<td>24.8-25.1</td>
</tr>
</tbody>
</table>

**TABLE 2.5**: Composition of C and S speciality glasses

**C - glass**: The addition of K2O and Na2O improve considerably the chemical resistance of the glass. The fibres are more expensive and have lower strength (2.8-3.1 GPa)(2) than the E-glass.(6)
S-glass: The high strength (4.6 GPa) is due to the relatively large quantity of added Al₂O₃. These fibres have greater temperature resistance than E-glass, and are also more expensive. The superior mechanical properties of the S-glass fibres render this reinforcement suitable for applications in the aircraft industry.

Properties of glass such as the expansion coefficient are also subject to variations created by the thermal history of the glass.

II.3 FIBRE/MATRIX INTERPHASE

2.3.1 INTRODUCTION

The properties of a composite are strongly influenced by the interface between the E-glass reinforcement (discussed in Section II.2) and the polymer. As the fibre is much stiffer than the matrix, interfacial stresses develop at the fibre ends when a stress is applied to the material. It is these shear stresses which provide the mechanism by which the load is transferred between the reinforcement and the matrix. However, efficient stress transfer can only occur if there is good interfacial bonding. The extent of composite stressing before debonding is hence dependent on the bonding across the interface.

2.3.2 ADHESION

Interfacial adhesion in a composite can be attributed to five mechanisms:
1. Adsorption and wetting
2. Mechanical adhesion
3. Interdiffusion
4. Electrostatic attraction
5. Chemical bonding

The latter three processes are applicable to composites where there is modification of the interphase region by the addition of a size or the presence of a functionally modified matrix material. Both adhesion improvement techniques are considered: the size adhesion promoter in Section II.4 and matrix modification for adhesion improvement in Sections 2.5.2.5 and 2.5.2.6.
2.4.1 INTRODUCTION

A surface coating typically 0.1 to 10 μm in thickness (18), is applied to the glass during fibre fabrication in order to protect the fragile filaments during subsequent handling. This coating may be either a temporary size, which is removed prior to the application of a finish, or a permanent size, which is different in that it remains on the fibre and may contain a coupling agent which aids adhesion. (18)

The reinforcement and the matrix in glass fibre reinforced thermoplastics are mutually unreactive. To ensure efficient stress transfer between the matrix and the fibre, and to improve the chemical resistance of the interface, especially in aggressive environments, the interfacial adhesion can be improved by coating the fibre with a size specific to the polymer. The size is added as a "intermediate" layer which has the chemical and physical properties needed to create a transitional zone between the dissimilar fibre and matrix materials.

A typical industrial size is applied to glass fibres as an aqueous emulsion containing processing aids, such as an antistatic agent, a lubricant, a wetting agent, a binder, and adhesion promoters, or coupling agents. Adhesion is enhanced by:-

1) wetting which ensures good physical contact between the polymer and the fibre.

2) the adhesion promoter, which ensures a chemical adhesion at the fibre/size interface by covalent bonding, and a reactive polymer which links the coupling agent to the matrix. This latter element often also acts as a film former.

3) copolymerisation at the interphase between the constituents of the size and the matrix.

4) diffusion of the size and matrix polymers to form an interpenetrating network which also strengthens the interfacial region.
The adhesion promoting agents in the size are a coupling agent and additional bridging molecules termed as matrix reactive polymers. The former have been the subject of considerable research.

2.4.2 COUPLING AGENTS

2.4.2.1 Introduction

There are two main categories of coupling agent:-

1) organometallic compounds which are typically complexes of cobalt, nickel, lead, titanium or chromium.

2) organosilanes which are the most widely used chemicals for the surface treatment of glass(10). They are applied to the reinforcement surface in the form of an aqueous solution. An organic based solution may also serve as a solvent and is used for other reinforcement types.(19)

Factors influencing the structure of the coupling agent, and hence its properties, also play an important role in the determination of the characteristics of the final composite. These considerations are the structure of the silane in the treating solution, the organofunctionality of the silane, the drying conditions, the topology of the fibre surface and the chemical composition of the surface.

2.4.3 SILANE COUPLING AGENTS

Commercial silane coupling agents have been developed to bond most polymers to glass or metal surfaces. The associated adhesion mechanisms have been widely studied (10,19,20) and several theories for interfacial bonding have been proposed.

It is generally accepted that the reaction of an organosilane, having the general structure \( X_3\text{SiR} \) (where \( X \) is either an alkoxy or a halogen group and \( R \) is an organofunctional group), with the glass involves the hydrolysis of the alkoxy groups to form silanol groups. These groups then react with the silanol groups on the glass surface creating stable siloxane (Si-O-Si) bonds. This reaction is shown schematically in Figure 2.5.
2.4.4 SURFACE CHEMISTRY OF SILANES AT THE REINFORCEMENT/SIZE INTERFACE (18)

The various adhesion mechanisms proposed for the interfacial bonding between the fibre and the size are discussed in the following sections:

a) Chemical Bonding Theory

This simplistic model considers that the condensation reaction between the -Si(OH)₃ group of the silane coupling agent with the silanol groups on the surface of the glass produces a covalent bond. The surface of the fibre is therefore assumed to be covered by a chemisorbed (the adsorbed species is held on the substrate by chemical forces) monolayer of silane coupling agent, which has a second functional group available for matrix interaction. Plueddemann (18) postulated that this reaction is of a reversible nature hence interfacial shear can be accommodated. Commercially, however, it has been shown that several hundred equivalents of monolayers of coupling agent are required to promote good adhesion (21). Certain silanes have been shown to effectively promote adhesion even though their organofunctional groups appear to be matrix-unreactive, as is the case for amine or methacrylate functions in inert polyolefins, which further underlines the inadequacy of this theory (10).
b) **Deformable Laver Hypothesis (18)**

The presence of a deformable, plastic layer between the fibre and the matrix accommodates interfacial stresses. However as the size layer is generally very thin it is unable to provide sufficient relaxation in a short enough time lapse during composite stressing.

c) **Surface Wettability Hypothesis**

This hypothesis considers that physisorption (physical bonding resulting from localised intermolecular dispersion forces) is the major adhesion mechanism. To achieve complete wetting the size must have a low viscosity and a surface tension lower than the critical surface tension of the glass surface. Glass has a high energy surface, (the surface tension typically exceeds 300 mJ m$^{-2}$), and is hydrophilic, which provides the driving force for the formation of a multilayer coverage of water molecules of low critical surface tension (19.1 to 21.7 mJ m$^{-2}$). Hence the presence of water considerably reduces the surface energy of the fibres rendering wetting by an organic polymer difficult. Glass fibres have highly polar surfaces whereas many matrices are non polar, which also reduces fibre/matrix interaction. This theory is an unsatisfactory explanation as many commonly and successfully used silane coupling agents, such as Union Carbide A1100, give rise to surface energies of less than 35 mJ m$^{-2}$ (24), so reducing the wettability of the reinforcement by the thermoplastic matrices (PP has a critical surface tension of 32 mJ m$^{-2}$ and PA66 has a value of 46 mJ m$^{-2}$). (23)

d) **Restrained Laver Hypothesis (18)**

This theory assumes that the interphase has modulus intermediate between those of the fibre and the matrix, and hence can transfer stress from the high modulus reinforcement to the low modulus matrix. Locally the coupling agent increases the matrix modulus by crosslinking at the interface. Thermal shrinkage, which stresses the interphase, is however not accounted for.
e) **Reversible Hydrolytic Bonding Mechanism**

This mechanism combines elements of the chemical bonding, restrained layer and deformable layer hypotheses.(10) A reversible breaking and making of coupling agent/glass bonds provides stress relaxation at the interface. The silanols of the size compete with water molecules at the glass surface, and preferentially bond, eliminating the surface water.

### 2.4.5 EXAMPLE OF AN ORGANOSILANE COUPLING AGENT

**γ-Aminopropyltriethoxysilane (γ-APS)**

a) **Introduction**

γ-aminopropyltriethoxysilane, (γ-APS), is a widely used coupling agent for both thermoplastics and thermosets as it can chemically bond with the inorganic glass surface and the reactive functionalities of the matrix(25). It is marketed by Union Carbide as A1100.(26)

γ-APS is applied to glass fibres from an aqueous solution, the concentration of which varies typically between 0.1 to 1% by weight. (18) Aminofunctional silanes dissolve instantaneously in water and so facilitate the production of the treating solution.(27)

The chemical formula of γ-APS is given in Figure 2.6.

\[(\text{CH}_3\text{CH}_2\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2\]

**FIGURE 2.6 : γ-APS**

Considerable research has been carried out to establish the bonding mechanisms between γ-APS and glass, and the structure of this interphase.

b) **Bonding**

Chemical bonding of γ-APS with surface glass produces strong, covalent bonds across the interface. The following figure shows the schematic models proposed for glass/γ-APS bonding.
FIGURE 2.7: Bonding between γ-APS and glass (28, 29, 30)

a) Hydrogen bonding between NH$_2$ and SiOH groups
b) Extended open chain, with isolated end amine
c) Adsorbed γ-APS with the amino, NH$_2$ group orientated towards the glass surface.

TOF SIMS and XPS studies on γ-APS on E-glass surfaces have consequently indicated that polysiloxane is probably chemically bonded to the glass at every other silicon atom, with occasionally more dense bonding. (14, 31)

c) Structure

γ-APS has a layered structure on glass fibres, the thickness of which is a function of the concentration of the treating solution. This multilayer formation is attributed to the topography of the surface of the reinforcement rather than variations in surface composition. The smooth glass surface induces a preferential orientation of the silane molecules which encourage the subsequent formation of further layers (21). Johanson et al. (33) showed that a monolayer coverage forms independently of the concentration of the treating solution in the case of powdered silica of high specific surface area, when the surface interferes with organized layer production. Order in the size layer is important for interpenetrating network formation. (19)

Three layer fractions were defined by Schrader (32) for γ-APS on glass fibres, based on the strength of the bond to chemical extraction. An outer, physically absorbed layer accounts for 98% of the γ-APS coating. Easy extraction occurs in water at ambient
temperature. The second layer, of approximately ten molecular layers thick, is chemisorbed. After several hours in boiling water this fraction is partially extracted leaving an island type structure on a smooth silane film. Only the latter remains after long periods of extraction. The adhesion of the second layer is attributed to the formation of some siloxane linkages which connect the γ-APS oligomer to the glass. The final and innermost layer is extensively bonded, forming a tight network structure at the glass surface (as shown in Figure 2.7), as confirmed by recent work by Wang et al.(14).

Hence a coupling agent specific to the matrix material promotes adhesion. Adhesion may be further improved by the addition of a linking or bridging molecule which forms strong bonds with both the silane and the matrix polymer. The behaviour of a matrix reactive polymer/silane mixture is generally not well understood.

II.5 PLASTIC MATRICES FOR COMPOSITES

2.5.1 INTRODUCTION

The composite matrix serves the dual purpose of protecting the reinforcement from damage, transferring stress away from fibre breaks in long fibre reinforced composites and for load transfer in short fibre reinforced materials. It also inhibits crack propagation through the brittle phase by ensuring fibre separation. Plastic matrices utilised for composites include both thermosets and thermoplastics.

Thermosets are heavily cross-linked polymers formed by curing a prepolymer to produce a dense three dimensional molecular network. This structure gives rise to a stiff, brittle plastic which is stable to relatively high temperatures with good strength. The polymer degrades rather than melts on heating.

Thermoplastics are linear or branched polymer systems, which derive their mechanical properties from the intrinsic characteristics of the monomer units and the high molecular weight of the polymer, as they do not form a three dimensional network. These polymers can be melted and remelted and so have the advantage of being remouldable. This thesis is concerned with two thermoplastic matrices, namely polypropylene (PP) and polyamide 6.6 (PA66), which are discussed in the following sections.
2.5.2 POLYPROPYLENE (PP)

2.5.2.1 INTRODUCTION

Polypropylene is a commodity or bulk thermoplastic, and constitutes, with the other major materials of this type (polyvinylchloride (PVC), polystyrene (PS) and polyethylene (PE)), 70% of the thermoplastics market. The production of PP composites is attractive as the matrix is widely available and relatively cheap (typically £0.45 to £0.55/kg).

Polypropylene presents certain advantages over HDPE and PVC, the thermoplastic leaders in terms of commercial tonnage, in that it is more rigid and resistant than the former, and is more easily worked than the latter.(34) In addition PP has the lowest density of these thermoplastics (900 kg m$^{-3}$) which contributes to its good specific properties. This combination of desirable characteristics gives an excellent compromise between performance and cost. The translucence and glossy appearance of PP may also be considered as desirable by manufacturers.

Polypropylene, however, contains a high content of secondary hydrogen atoms and so is susceptible to oxidative attack. The addition of antioxidants and stabilizers is therefore necessary to protect the macromolecule against scission by heat and/or oxygen.

2.5.2.2 STRUCTURE

a) Introduction

Polypropylene is a semicrystalline polymer, (100% isotatic polypropylene has a crystallinity of approximately 68% (37)) which can be considered as a rubbery matrix reinforced by spherulitic crystals. The "matrix" consists of amorphous zones which at ambient temperature, are above their glass transition temperature. Many of the characteristics of polypropylene can be explained by considering its structure on both a molecular and macroscopic scale.
b) Molecular Structure

Polypropylene is a linear polymer, consisting of a backbone of C - C bonds with lateral methyl groups, as shown in Figure 2.8.(35)

\[-(-\text{CH}_2\text{-CH}-)_n\text{-CH}_3\]

**FIGURE 2.8:** Polypropylene formula (PP)

Three types of polypropylene are produced: isotactic, syndiotactic and atactic, though most commercially exploitable polypropylene is based on the isotactic form. Hence it is this configuration which will be further discussed. The atactic form is an undesirable side product in the formation of isotactic polypropylene and is considered as an impurity, however it is used as a hot melt adhesive, especially for bookbinding.

c) Isotactic Polypropylene

The macromolecular polymer chain adopts a trans/gauche or gauche 3-1 helical conformation, corresponding to the minimum potential energy position and hence the most stable polypropylene form. Each turn of the chain occupies an equivalent geometric position, at 0.65nm intervals, along the axis of the helix, as shown in Figure 2.10.

**FIGURE 2.9:** Planar schematic of isotactic Polypropylene

**FIGURE 2.10:** 3-1 helix conformation adopted by Polypropylene
The crystalline structure of polypropylene is built up from the previously described 3-1 helices. Four polymorphs $\alpha$, $\beta$, $\delta$ and $\gamma$ exist, their differences induced by variations in the stacking geometries of this basic microstructural unit. Table 2.6 compares these four structures.

<table>
<thead>
<tr>
<th>POLYMORPH</th>
<th>STRUCTURE</th>
<th>UNIT CELL PARAMETERS</th>
<th>CONDITIONS FOR FORMATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>monoclinic</td>
<td>$a = 0.665$ nm, $b = 2.096$ nm, $c = 0.66$ nm, $\beta = 99^\circ 20$, 4 chains/unit cell crystal density $= 936$</td>
<td>most widely occurring polymorph thermodynamically stable</td>
</tr>
<tr>
<td>$\beta$</td>
<td>hexagonal</td>
<td>$a = 1.908$ nm, $c = 0.649$ nm, 9 chains/unit cell crystal density $= 922$</td>
<td>meta stable minority constituent of the bulk thermal gradients shearing certain nucleating agents quenching below $130^\circ$C</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>triclinic</td>
<td>$a = 0.638$, $c = 0.633$, 1 chain/unit cell crystal density $= 939$</td>
<td>high pressure slow cooling low molecular weights</td>
</tr>
<tr>
<td>$\delta$</td>
<td></td>
<td></td>
<td>high percentage amorphous material</td>
</tr>
</tbody>
</table>

**TABLE 2.6** : Polypropylene crystalline polymorphs (36, 37) crystal density in kg m$^{-3}$
e) Lamella Structure

The zones of parallel helices form lamella (35) the thickness of which depends on the thermal history of the polymer (38) and corresponds to a fold in the macromolecular chain consisting of several monomer units. Typically these lamella are 10nm thick. The lamella exhibit a regular twist about their b axis.

![Figure 2.11: Lamella structure](image)

f) Macromolecular Structure

Lamella microstructural units combine to form a spherulitic superstructure.(38) The fibrous crystals fan out, growing by a dendritic mechanism.(39)

![Figure 2.12: Spherulitic superstructure](image)

Spherulitic size has been shown to be a function of undercooling and melting temperature(40). Nucleation increases with increasing undercooling below the melt
temperature, and hence produces a reduction in spherulite diameter. The spherulite size however increases with an augmentation of the melt temperature.

A filler also influences the structure (41) as the surface energy of the reinforcement may suppress or accelerate the formation of crystallites or affect the type and dimensional distribution of spherulites.

Spherulites can be classified by their appearance between crossed polars(38). For isotactic polypropylene the spherulites display a Maltese cross pattern. Four distinct spherulitic types are present in polypropylene, the characteristics of which are given in Table 2.7.

<table>
<thead>
<tr>
<th>SPHERULITE TYPE</th>
<th>CRYSTAL LATTICE</th>
<th>CRYSTALLISATION TEMP. (°C)</th>
<th>BIREFRINGENCE</th>
<th>EXTINCTION PATTERN</th>
</tr>
</thead>
<tbody>
<tr>
<td>I monoclinic</td>
<td>Below 134</td>
<td>+0.003</td>
<td>Simple Maltese cross</td>
<td>predominant form</td>
</tr>
<tr>
<td>MIXED</td>
<td>134 - 138</td>
<td>0.002 (+ve and -ve)</td>
<td>coarse fibrous mixture</td>
<td></td>
</tr>
<tr>
<td>II monoclinic</td>
<td>Above 130</td>
<td>-0.002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III hexagonal</td>
<td>Below 128</td>
<td>-0.007</td>
<td></td>
<td>Very small volume fraction</td>
</tr>
<tr>
<td>IV hexagonal</td>
<td>128 - 132</td>
<td>negative</td>
<td></td>
<td>Ringed spherulite</td>
</tr>
</tbody>
</table>

TABLE 2.7 :PP spherulitic types (39, 42)

Type I and III are widely observed, although many bulk samples are of a mixed nature. The former spherulitic types are distinguished by both differences in birefringence and growth rate. The β phase, although nucleating at a lower rate than the Type I and II structures, grows 20 to 70% faster than the α phase.(43) β spherulites are sporadic, large structures often truncated by impingement.
g) Amorphous Region (35, 44)

The crystal lamella, that make up the spherulitic superstructure, are separated by amorphous zones. The origin of these areas can be attributed to:

1) loose folds between successive elements of folds of the chain in the lamella.
2) very loose folds, between non successive elements of the same lamella.
3) tie chains
4) cilia
5) fully included free chains

FIGURE 2.13: Interlamella amorphous zones

The tie chains are particularly important as they determine the mechanical continuity of the system, and hence control the Young's modulus, E, and also affect the yield strength. The properties of the amorphous region are dictated by the relative percentages of the five phenomena and their interaction.

2.5.2.3 PHYSICAL AND MECHANICAL PROPERTIES

Polypropylenes physical and mechanical characteristics, given in Table 2.8, are structure dependent.

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>UNIT</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>DENSITY</td>
<td>kg m$^{-3}$</td>
<td>905</td>
</tr>
<tr>
<td>MELTING TEMPERATURE</td>
<td>°C</td>
<td>165 - 170</td>
</tr>
<tr>
<td>YOUNGS MODULUS</td>
<td>GPa</td>
<td>1.0 - 1.4</td>
</tr>
<tr>
<td>YIELD STRESS</td>
<td>MPa</td>
<td>25 - 38</td>
</tr>
<tr>
<td>ELONGATION TO BREAK</td>
<td>%</td>
<td>300</td>
</tr>
<tr>
<td>LINEAR EXPANSION COEFFICIENT</td>
<td>10$^{-6}$ °C$^{-1}$</td>
<td>175</td>
</tr>
</tbody>
</table>

TABLE 2.8 : Mechanical and physical properties of PP(45)
The melting temperature of polypropylene is a function of its crystallinity, with an increase in the crystalline phase from 40 to 100% giving an increase in melting point of $9\degree C$ to $171\degree C$.(37)

### 2.5.2.4 DYNAMIC-MECHANICAL PROPERTIES

Mechanical relaxations in semi-crystalline homopolymers result from the superposition of spectra from three phases: "free" amorphous, crystalline (which has a noticeable affect on melting as described in Section 2.5.2.3), and crystallite constricted amorphous. The latter region may induce a second glass transition peak, at higher temperatures, as the macromolecular chains are immobilized by interactions with the surrounding crystal lamella. This phenomena is observed in polyethylene where the free amorphous phase glass transition temperature, $T_g$(free)$=195K$ and $T_g$(constricted)$=220K$. (46)

Three major transitions characterize the viscoelastic behaviour of polypropylene, these being $\beta$, $\alpha$ and $\alpha^c$ at -80, 5 and $90\degree C$ respectively. Additional relaxations, $\gamma$ and $\alpha^{c'}$, have been reported at -253 and $170\degree C$. The position and amplitudes of these relaxations are a function of the microstructure of the polymer and may be interphase related in the composite. The characteristics of the $\beta$, $\alpha$ and $\alpha^c$ transitions are examined in the following section.(47, 48)

**$\beta$ transition**

This secondary transition is attributed to localized movements in the amorphous phase

**$\alpha$ transition**

The $\alpha$ relaxation is the glass transition of the amorphous phase, which corresponds to the onset of long range motion of the macromolecular chains in the amorphous region.

Both tacticity and temperature influence the position of this peak. Increasing tacticity provokes an increase in the transition temperature.(49) The amplitude of this relaxation is also dependent on these factors and increasing crystallinity (and increasing transition temperature) are accompanied by a diminishing $\alpha$ peak height.

**$\alpha^c$ transition**

This is a crystalline phase dependent transition, the exact origin of which has been the subject of some controversy. As the $\alpha^c$ relaxation does not exist in atactic
polypropylene (100% amorphous) the influence of the crystalline zones is hence confirmed.

Several hypotheses have been advanced to explain the occurrence of this transition:—
1) purely crystalline dependent
2) purely amorphous dependent, due to molecular movements in the constricted amorphous zones of the polymer.
3) dependent on an interaction between the phases.
Considerable work carried out by Jourdan(47) established that this relaxation results from movements of defects within the crystalline phase, which induce accommodating deformations in the strongly interacting amorphous phase.

2.5.2.5 ADHESION

Polypropylene is relatively unreactive due to the non-polar nature of the molecule. To improve adhesion the polymer must be modified. This may be achieved by:—

1) using a plasma treatment which affects the surface of the polymer without altering its bulk characteristics. This particular method is suitable for preparing the surfaces of adhesively bonded joints or treating surfaces prior to printing or painting, however is of little interest in the case of fibre reinforced composites.(50)

2) modifying the structure of the macromolecule by grafting functional groups to its backbone, rendering the chain more reactive and hence facilitating adhesion. An in-situ reactive processing technique is widely employed for the production of glass fibre reinforced polyolefins, and leads to improved bonding without the aid of a polymer specific size. In the following section this second method of interfacial adhesion promotion is considered:—

2.5.2.6 MATRIX MODIFICATION FOR ADHESION IMPROVEMENT

a) Introduction

Polypropylene is an inert hydrocarbon which is non-polar and lacks functionality. This polymer therefore does not adhere strongly to E-glass fibre reinforced composites. However by grafting functionalized groups to the polymer backbone, a modified or
activated plastic is produced which is a suitable substrate for a composite material. Polyolefins may be modified either alone or in the presence of a reinforcing agent.

**b) Reactive Process Grafting**

Short fibre composite manufacture involves high shear stresses on the high viscosity melt at high temperature. A mechanical degradation of the base polymer occurs, which is dependent on both processing parameters: oxygen partial pressure (trapped or dissolved in the polymer feed), processing temperature and the rate of application of mechanical stress, and the structure of the polymer itself. Hence processing of polypropylene results in the chain scission of the macromolecule, creating radicals as shown in Figure 2.14.

\[
\begin{align*}
\text{CH}_3 \quad \text{CH}_3 \\
-\text{CH} \cdot \text{CH}_2 \quad \text{CH}_2 \cdot \text{CH}_2 \\
\text{ROOR} \quad \text{N}_2 \\
\text{CH}_3 \quad \text{CH}_3 \\
-\text{CH} \cdot \text{CH}_2 \cdot \text{CH} - \text{CH}_3 \\
\text{FM} \\
\text{O}_2 \quad \text{RH} \\
\text{CH}_3 \quad \text{CH}_3 \text{OOH} \\
\text{CH} \cdot \text{CH}_2 \text{OOH} + \text{R'} \\
\text{ROOH} \\
\text{OH} + \text{CH} \cdot \text{CH} - \text{CH} - \text{CH}_3 \\
\text{FM} \quad \text{OH} \\
\text{O} \quad \text{O} \\
\text{CH}_3 \quad \text{CH}_3
\end{align*}
\]

**FIGURE 2.14:** Oxidative and targeted reactions of polypropylene during processing

a. Mechanical scission of carbon-carbon bonds, b. Formation of reactive macroalkyl radicals during processing, c. Reaction of radicals with functionalized modifier (FM), d. Macroalkyl hydroperoxides (formation is a function of oxygen concentration), e. and f. Oxidation, initiated by the macroalkyl hydroperoxide, which leads to a decrease in molecular weight, g - i Competing undesirable reactions.
Many thermoplastics polymers show a high rate of mechanical degradation in the initial stage of the processing operation, hence antioxidants are used to stabilize the melt. It has been established however that mechanochemical addition or grafting of various functional groups is possible by exploiting the radical formation during processing.

Initial grafting work involved the stabilization of polymers using reactive antioxidants. The in-situ reactive process was found not only to be effective on unsaturated thermoplastics such as ABS but also, and surprisingly so, in the case of polypropylene which has a saturated macromolecule. Binding occurs in two stages, during the first macroalkyl radicals are formed by the mechanical scission of the polymer chain. The presence of an radical initiator will further initiate the radical process, as shown in Figure 2.15.

\[
\begin{align*}
R^0 + CH_2=CHR_1 & \rightarrow RCH_2CHR_1^0 \\
\end{align*}
\]

**FIGURE 2.15:** Reaction of an initiator radical, \(R^0\), with a polyolefin monomeric unit, \(CH_2=CHR_1\) (53)

An adduct is then produced by grafting a modifier or functionality group to the activated chain. The modifier must be bifunctional, with one end-group to react with the size and the other with the polymer. Commercial modifying agents include acrylic acid and maleic anhydride, the formulae of which are given in the following figure.

\[
\begin{align*}
CH_2=CHCOOH & \quad \text{1.} \\
\end{align*}
\]

**FIGURE 2.16:** Commercial modifying agents: 1. acrylic acid, 2. maleic anhydride

"Traditional" reactive processing gives rise to an improvement in interfacial adhesion and hence composite properties. An injection moulded, glass-reinforced unmodified polypropylene, with a short, random fibre distribution, has a tensile strength of 41MPa, whereas in the version modified with maleic anhydride and peroxide the strength is improved to 70MPa. (54)
However the grafting reaction is hindered by undesired side reactions such as homopolymerisation of the additive or cross-linking of the polymer, which reduce the efficiency of the process and can lead to the loss of molecules such as antioxidants. Work by Munteanu (55) involved grafting monomeric antioxidants, containing polymerisable groups, to polymers in the presence of free radical generators during processing. The grafting level achieved was of only 20 - 30%, the inhibition of the targeted reaction being largely attributed to the homopolymerisation of the antioxidant. An alternative grafting method (56), which results in binding levels inferior to 80%, uses non-polymerisable antioxidants and shear as the only initiator. The major disadvantage of this system is the formation of a by-product which is easily lost from the polymer under aggressive conditions.

This problem has been overcome by the incorporation of a novel "functional monomer" which increases the efficiency of the grafting process, in some cases, to 100% and immobilizes the modifier in the polymer, preventing any losses (54). This reactive processing technique hence produces a modified polymer, free of toxicity problems associated with migration of modifiers, which should exhibit good adhesion with the reinforcement and therefore enhance composite properties even in aggressive enviroments.

2.5.3 POLYAMIDE 6.6. (PA66)

2.5.3.1 INTRODUCTION

PA66 is defined as an engineering thermoplastic. This particular classification refers to thermoplastics which offer some of the following properties: high strength, stiffness, toughness and resistance to chemical attack, and/or heat.(57)

PA66 is one of the highest melting point commercial polyamides (m.pt is 264 °C), which at ambient temperature exhibits good chemical resistance to petrol, oils and grease. This renders this polymer particularly suitable for light engineering applications such as fans and door handles in cars and domestic uses such as curtain fittings, which also takes advantage of PA66's low coefficient of friction. As a glass-reinforced composite it is widely used in and around engines due to its excellent fuel resistance and stiffness retention with increasing temperature.
This matrix material is however sensitive to water, oxidation and concentrated mineral acids, phenols and chlorinated solvents. On absorbing water, the polymer swells and typically a 1wt.% uptake in water results in a 0.3% increase in volume. Water uptake is dependent on the moulding wall thickness, the relative humidity of the atmosphere, and the composition of the moulding compound. Generally PA66 reaches saturation for an uptake of water of approximately 8wt%.

2.5.3.2 STRUCTURE

a) Introduction

Polyamide 6,6, like polypropylene, is a semi crystalline thermoplastic, ranging from 25 to 50% crystallinity. Its nomenclature indicates the dyadic nature of this nylon, i.e. both the diamine and dicarboxylic acid components of the molecular unit have equal numbers of carbon atoms.

b) Molecular Structure

The linear macromolecules which constitute PA66 are obtained by step growth polymerisation between diamines and dicarboxylic acids, or by dehydration of a salt crystallized from a mixture of hexamethylene diamine and adipic acid monomers. Its general formula is given in Figure 2.17.

\[- \begin{array}{c}
\text{NH} \\
\text{(CH}_{2}\text{)}_{6} \\
\text{NH} \\
\text{(CO)} \\
\text{(CH}_{2}\text{)}_{4} \\
\text{CO}
\end{array} \text{n} \] -

FIGURE 2.17: PA66 formula (59)

The molecules form extended planar zigzags.

c) Crystalline Region

Hydrogen-bonding between the macromolecular chains controls packing as shown in Figure 2.18.
The two types of H-bonded sheets formed give rise to the polymorphs of PA66.

**α-polymorph:** successive planes are displaced in the c direction

**β-polymorph:** hydrogen-bonded sheets have alternating up and down displacements

Both polymorphs have a triclinic unit cell, which undergoes a phase transformation (termed the Brill transition) at 160°C to form a pseudo hexagonal structure. A decrease of 20°C in the Brill transition temperature is produced by the presence of water, when as a vapour.
Table 2.9 compares the afore described polymorphs.

<table>
<thead>
<tr>
<th>POLYMORPH</th>
<th>STRUCTURE</th>
<th>UNIT CELL PARAMETERS</th>
</tr>
</thead>
</table>
| α         | triclinic     | a = 0.49nm  
            |               | b = 0.54nm  
            |               | c = 1.72nm  
            |               | α = 48.5°  
            |               | β = 77°    
            |               | γ = 63.5°   
            |               | 1 unit/cell  
            |               | crystal  
            |               | density = 1240 |
| β         | triclinic     | a = 0.49nm  
            |               | b = 0.80nm  
            |               | c = 1.72nm  
            |               | α = 90°    
            |               | β = 77°    
            |               | γ = 67.5°   
            |               | 2 units/cell  
            |               | crystal  
            |               | density = 1248 |
| γ         | pseudo--hexagonal | γ = 67.5°  |

**TABLE 2.9: PA66 crystalline polymorphs (62)**

Unit cell parameters for α and β polymorphs measured at ambient temperature  
Crystal density in kg m⁻³

These parameters are temperature dependent (63), an increase in temperature induces an increase of the unit cell parameters a and b (at 120°C a = 0.491 nm and b = 0.554 nm) and a diminuation of c (c(120°C) = 1.698 nm).

d) Macromolecular Structure

PA66, similarly to PP, exhibits a spherulitic macromolecular structure. Four types of spherulites have been observed (64) the characteristics of which are summarized in the following table.
<table>
<thead>
<tr>
<th>SPHERULITE TYPE</th>
<th>CRYSTAL LATTICE</th>
<th>CRYSTALLISATION TEMP. (°C)</th>
<th>BIREFRINGENCE</th>
<th>EXTINCTION PATTERN</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>triclinic</td>
<td>265</td>
<td>positive</td>
<td>Simple Maltese cross predominant form</td>
</tr>
<tr>
<td>II</td>
<td>triclinic</td>
<td>258-265</td>
<td>negative</td>
<td>germination from large crystalline germs</td>
</tr>
<tr>
<td>III</td>
<td>triclinic</td>
<td>Temp.1. 260&lt;br&gt;Temp.2. 265&lt;br&gt;Temp.3. 260</td>
<td>non-birefringent</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>triclinic</td>
<td>mixed</td>
<td>fibrous</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 2.10: PA66 spherulitic types**

### 2.5.3.3 PHYSICAL AND MECHANICAL PROPERTIES

The physical properties of polyamides are dominated by the intermolecular N-H--O=C hydrogen bond.

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>UNITS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>DENSITY</td>
<td>kg m⁻³</td>
<td>1140</td>
</tr>
<tr>
<td>MELTING TEMPERATURE</td>
<td>°C</td>
<td>264</td>
</tr>
<tr>
<td>YOUNGS MODULUS</td>
<td>GPa</td>
<td>1.4 - 2.8</td>
</tr>
<tr>
<td>YIELD STRESS</td>
<td>MPa</td>
<td>60 - 75</td>
</tr>
<tr>
<td>ELONGATION TO BREAK</td>
<td>%</td>
<td>40 - 80</td>
</tr>
<tr>
<td>LINEAR EXPANSION COEFFICIENT</td>
<td>10⁻⁶°C⁻¹</td>
<td>90</td>
</tr>
</tbody>
</table>

**TABLE 2.11:** Mechanical and physical properties of PA66
2.5.3.4 Dynamic Mechanical Properties

The dynamic mechanical behaviour of PA66 is characterized by three transitions $\gamma$, $\beta$ and $\alpha$ at -130, -60 and 75°C respectively\(^\text{(64)}\). A further transition at 250°C has been observed and is attributed to a crystalline induced relaxation.

$\gamma$ transition
A similar relaxation is observed in both polyethylene and polyamide 12 at -140°C, and has been ascribed to the localized crankshaft motion of the aliphatic groups present in all these polymers in the amorphous phase. \(^\text{(17)}\)

Water modifies the mobility of the -CH\(_2\)- functionalities and so affects this transition.

$\beta$ transition
As for the previous case this relaxation is due to molecular movements within the amorphous regions of the polymer. The $\beta$ transition is highly water dependent, as it is assigned to complex movements of water molecules linked to the amide grouping in the polyamide macromolecule, as shown in the following figure.

\[ \text{FIGURE 2.19: Insertion of a water molecule in a PA66 chain(48)} \]

$\alpha$ transition
Again this is an amorphous phase transition as has been demonstrated by the $\gamma$ irradiation of the polymer which provokes a decrease in crystallinity and results in an augmentation of the intensity of the relaxation\(^\text{(66)}\). Boyd\(^\text{(67)}\) measured a decrease of the transition amplitude after inducing cross linking of the chains by electronic bombardment which confirms the previous result. The transition disappears completely when the cross linking points are separated by less than fifteen repeat

\[ \text{FIGURE 2.19: Insertion of a water molecule in a PA66 chain(48)} \]
monomer units. It can therefore be concluded that this transition is produced by the movement of a group of adjacent molecular groups, and is a pseudo glass transition. Owen\(^{(68)}\) confirmed that for PA12 200 mobile entities (aliphatic or amide groups) which is equivalent to 16 repeat units are required for relaxation.(48)

II.6. GLASS FIBRE-REINFORCED COMPOSITES

2.6.1 INTRODUCTION

Three phases constitute a composite, the reinforcement, the matrix and the interphase. Each of these elements controls certain of the characteristics of the composites. A fibrous reinforcement determines the longitudinal mechanical properties and the coefficient of thermal expansion in a unidirectional composite. The matrix ensures that the fibres act in a cooperative manner, and plays an important role in the shear and transverse properties of the composites. Chemical and thermal stability are also dictated by the intrinsic characteristics of the matrix. Micromechanical processes occurring during fracture, and transverse, shear and compressive properties are greatly influenced by the interphase. However efficient interfacial adhesion is essential for good composite characteristics.

2.6.2 FIBRE/MATRIX INTERPHASE

a) Stress Transfer Between The Fibre And The Matrix

As the fibre is much stiffer than the matrix, interfacial shear strains are developed at the fibre ends when a stress is applied to the reinforcement. These shear strains provide the mechanism by which the load is transferred between the fibre and the matrix. Several models for stress transfer have been proposed:-

b) Cox Model

Cox\(^{(69)}\) considered a single, short elastic fibre in an elastic matrix, subjected to strain \(\varepsilon\), parallel to the fibre. Assuming that there is perfect bonding at an infinitesimally thin interface, he suggested a proportionality between the shear stress at the interface
and the difference in longitudinal displacement between the fibre and the matrix. This classic shear lag analysis assumes homogeneous matrix strain, the matrix in proximity to the interface having the same characteristics as the bulk material. Stress transfer is described by the following equation:-

$$\sigma = Ef \varepsilon_f \left\{ 1 - \frac{\cosh \beta (L/2 - x)}{\cosh \beta L/2} \right\} \quad [2.3]$$

where

$$\beta = \left( \frac{2G_m}{Ef r^2} \ln \left( \frac{R}{r} \right) \right)^{1/2} \quad [2.4]$$

and $\sigma =$ composite stress

$Ef =$ Young’s modulus of the fibres

$\varepsilon_f =$ fibre strain

$x =$ distance from fibre end (figure 2.20)

$\beta =$ rate of stress build-up from the fibre ends

$G_m =$ shear modulus of the matrix

$r =$ fibre radius

$2R =$ interfibre spacing

$L =$ fibre length

The tensile stress predicted by this model is minimal at the extremities of the reinforcement, however the shear stress is at its maximum value as shown in Figure 2.20.

**FIGURE 2.20: Stress transfer according to COX**
A deficiency of the Cox analysis is that the maximum shear stress is predicted to occur at the fibre-ends. In fact it must drop to zero at the extremities of the fibre. Additionally the interfacial strength is not considered, as the Cox analysis assumes both perfect elasticity and perfect interface bonding. Thermoplastic matrices however often have a shear yield strength which is lower than the shear stress predicted by the Cox model, as the matrix behaves plastically. Kelly and Tyson (70) described this behaviour.

c) Kelly - Tyson Model

This model assumes a constant interfacial shear stress along the fibre over the transfer zone which determines load build-up. An interfacial shear stress with the value of the interfacial strength $\tau_i$ results in the maximum rate of increase of stress, $\sigma$, and hence the maximum average stress carried by the fibre.

The linear build up is described by a simple equilibrium of forces:

$$\sigma \pi r + \tau_i 2 \pi r \; dx = (\sigma + d\sigma) \pi r^2$$  \[2.5\]

where $r = $ fibre radius

At the fibre end, $x=0$ and $\sigma=0$, therefore this expression can be rearranged and integrated to give an equation of the form:-

$$\sigma = 2 \tau_i x / r$$  \[2.6\]

A critical length, $l_c$, exists when the maximum load transferred into the fibre is equal to its breaking stress. Stress build up occurs from both extremities of the fibre so $l_c=2x_c$. Hence for this critical case:-

$$l_c = r \sigma_{fu} / \tau_i$$  \[2.7\]
FIGURE 2.21: Stress transfer according to Kelly-Tyson

In this model the interfacial shear stress is constant over the shear transfer length and is independent of the applied strain, which is not a realistic concept. The shear modulus of the matrix and the strength of the bond are not featured in this model.

Neither the Cox nor the Kelly-Tyson models address all the relevant parameters in composite behaviour prediction however both give reasonable qualitative understanding of reinforcement.

Galiotis et al. (71) has shown that the tensile stress measured in a fibre embedded in a matrix has a stress profile similar to that predicted by Cox. However, when the applied strain is increased above a threshold failure value of the interface the stress profile changes dramatically. Failure is assumed to be due to shear debonding at the fibre/matrix interface or yielding of the matrix. Failure is initiated at the extremities of the fibre and propagates along the interface. Even in the debonded region there appears to be some capacity for stress transfer. The stress build-up is linear, followed by an exponential profile predicted by the Kelly-Tyson and Cox models respectively. When strong bonding exists across the interface the system will behave in a Cox-like
manner under increasing applied strain until the shear stress at the fibre end exceeds the strength of the bond. Debonding then occurs resulting in a dramatic decrease in the shear which can be carried across the interface. Stress transfer still remains, but this is due to bonding of a mechanical or frictional nature only. A shallow stress gradient is established at the fibre-end with a transition to a steeper slope at the end of the debonded region. This explains why the debond does not grow over the entire fibre length. A combination of the Cox and Kelly-Tyson analyses hence has been shown to give a realistic understanding of short-fibre composites.

Outwater (72) suggested that a resin matrix behaves as a metal matrix, as the load is transferred to the fibres by frictional forces induced at the interface.

The above described models are applicable to uniaxially aligned short fibre composites.

2.6.3 MECHANICAL PROPERTIES OF POLYMER COMPOSITES

a) Long Fibre Composites

Uniaxial continuous fibre systems are anisotropic, with Young's modulus greater along the fibre direction than that measured when the load is applied at 90° to the reinforcement axis.

The Young's modulus of a unidirectional composite, when loaded parallel to the fibres, can be predicted using the rule of mixtures, assuming perfect fibre-matrix bonding, and that the strains in fibre, matrix and composite are equal. Stiffness is hence given by:

\[ E_c = E_f V_f + E_m (1 - V_f) \]  \[2.8\]

where \( E_c \) = Young's modulus of the composite
\( E_f \) = Young's modulus of the fibres
\( V_f \) = volume fraction of fibre
\( E_m \) = Young's modulus of the matrix
\( 1-V_f \) = \( V_m \) = volume fraction of the matrix
However if the fibre volume fraction is low the fibres are too widely spaced to permit load transfer and reinforcement. Hence the fibre volume fraction must attain a critical value, as demonstrated in Figure 2.22.

![Critical fibre volume fraction diagram](image)

**FIGURE 2.22: Critical fibre volume fraction**

This approach is considered to be too simplistic for a real composite, as tensile failure involves a complex interaction of fibres and matrix through the interphase as reviewed by Bader (73). Nevertheless the rule of mixtures is a reasonable predictor for the modulus of a continuous fibre unidirectional composite in the fibre direction.(74)

b) Short Fibre Composites

The theoretical evaluation of the mechanical characteristics of an injection moulded short fibre reinforced thermoplastic is highly complex, as they contain fibres with a range of lengths, which are oriented in different directions. These reinforcement variations are created during composite manufacture: the fibre length distribution is dependent on screw speed, injection rates (75), back pressure and sprue, runner and gate dimensions (high melt shear results in shorter fibres), whereas the orientation distribution is dependent on melt flow.
Complex flow orientation patterns form in injection moulded parts as shown by the cross-section of a simple edge gated plaque in Figure 2.23.


Orientation has a considerable affect on tensile properties of composite materials as shown in Table 2.12.

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>ULTIMATE TENSILE STRENGTH (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RANDOM IN PLANE</td>
</tr>
<tr>
<td>POLYETHYLENE</td>
<td>42.13</td>
</tr>
<tr>
<td>POLYCARBONATE</td>
<td>61.36</td>
</tr>
<tr>
<td>PA12 (PA66 FIBRES)</td>
<td>45.78</td>
</tr>
</tbody>
</table>

**TABLE 2.12**: Tensile properties of glass reinforced composites of the same volume fraction, but with differing orientation distributions

Bright and Darlington (77) highlighted the effect of the moulding material on fibre orientation. Glass fibre reinforced PP and PA66 were studied, with the former tending to favour a random-in-plane orientation in the outer layers of a simple moulding where as the outer layers of the latter favoured orientation parallel to injection, even with strongly divergent flow geometry.
As has been shown, fibres are rarely aligned in injection moulded composites. Krenchel (78) evaluated an orientation efficiency factor, $\eta_0$, in order to account for this distribution. Composite stiffness is calculated as:

$$E_c = \eta_0 V_f E_f + (1 - V_f) E_m$$  \[2.9\]

where

$$\eta_0 = \sum a_k \cos^4 \Theta_k$$  \[2.10\]

where $a_k$ = fibre fraction oriented in angular increments away from the applied load $\Theta_k$

when $\eta_0$=1 the load is applied parallel to the fibre axis and $\eta_0$=0 if it were perpendicular.

Injection moulded parts additionally exhibit a fibre length distribution. The contribution to composite strength arising from subcritical and supercritical length fibres (critical length, $l_c$, calculated using Kelly's model, Section 2.6.2c) must therefore also be considered. Bader and Bowyer (79) hence predicted composite behaviour using:

$$E_c \varepsilon_c = \sigma_c = \eta (X+Y) + Z$$  \[2.11\]

where $c$ = total composite stress

$X$ = sub-critical fibre contribution

$$\Sigma_{\text{(sub-critical)}} l_i V_i/2rf$$

$Y$ = super-critical fibre contribution

$$\Sigma_{\text{(super-critical)}} E_f \varepsilon_c (1-E_f \varepsilon_c rf/2 l_j) V_j$$

$Z$ = matrix contribution

$$E_m \varepsilon_c (1-V_f)$$

$\eta$ = Krenchel factor

Calculation involves the summation of the contribution of fibres of different lengths to the composite stress. Assumptions employed by the authors are that the interfacial shear stress is constant at all values of composite strain and that the Kelly-Tyson model is applicable for all fibre orientations. Mittal and Gupta (80) have shown however that at a constant value of $\tau$, at low composite strains, gives rise to a variable
They described the relationship between interfacial shear stress and composite strain as a linear function, \( \tau = K \sigma_c \). Recent work by Hill et al. (81) has established that the Bader-Bowyer model is suitable for high composite strains whereas the Mittal-Gupta model is appropriate for the low-strain case. It has been postulated that the interfacial shear stress follows an empirical power law relationship, of the base polymer response, of the following form:

\[
\tau = \tau_{\text{max}} \left( \frac{\sigma_{PP}}{\sigma_{PPy}} \right)^y
\]

where: \( \tau_{\text{max}} \) = maximum interfacial shear stress (measured from a fragmentation test)

\( \sigma_{PP} \) = stress in base polymer at any composite strain

\( \sigma_{PPy} \) = stress in the composite at matrix yield

\( y \) = power law function

Exact solutions for evaluating the elastic properties of short fibre composites have been suggested by Christensen (82). For predictive work, and for practical use, a reasonable estimation can be made using the following formula (83):

\[
E_c = C V_f E_f \left[ \int_0^{L_c} \frac{L}{2L_c} Q(L) \, dL + \int_{L_c}^{L_{\text{max}}} (1-L/L_{\text{max}}) Q(L) \, dL \right] + V_m E_m
\]

where \( E_c \) = Young's modulus of the composite

\( C \) = fibre orientation distribution function

\( V_f \) = volume fraction of fibres

\( E_f \) = Young's modulus of fibres

\( L_c \) = critical fibre length

\( Q(L) \) = normalized function of fibre length distribution

\( V_m \) = matrix volume fraction

\( E_m \) = Young's modulus of the matrix
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CHAPTER III
MATERIALS
III. MATERIALS

3.1 INTRODUCTION

The necessity for good fibre/matrix adhesion in composites, and the methods of achieving this objective, have been discussed in the previous two chapters. An improvement in interfacial adhesion can be produced by coating the fibre with a matrix-specific size or by the modification of the matrix itself using functional groups. Both systems have been examined.

Although fibre coating is widely used and binding at the interface created using silane coupling agents is well documented, little work has been done previously to establish the role of all the elements which make up this coating. This study considers simplified sizes consisting of two important elements in a commercial size: a γ-aminopropyltriethoxysilane coupling agent and a matrix reactive polymer. The size-modification method requires the tailoring of the size to produce adequate adhesion with a given matrix. For example, a polar matrix interacts effectively with a polar size to produce strong interfacial bonding, as is the case of fibres, coated with a polyurethane based size, used to reinforce a PA66 matrix. A non-polar size, such as a polypropylene-based coating, will partially bond with the silane, but will not react with a polar matrix. This size can, however, form an interpenetrating network with non-polar polymers, which strengthens the size/matrix interphase.

The second method by which interfacial adhesion can be enhanced is by matrix modification. A size is still a necessary element at the interface, however its chemistry can be greatly simplified, and a unique size is suitable for all types of matrices. A modified polyolefin matrix, polypropylene, has been examined. This particular matrix is unreactive due to its molecular structure, and hence requires effective activation by modification to induce good fibre/matrix adhesion. Many of the established modifying systems have serious shortcomings, such as low efficiency of the chemical reaction with the polymer macromolecule and competition between undesirable side reactions (e.g. homopolymerisation of the modifier or cross-linking), and the desired binding reaction. Recent studies (1) have developed a process by which the efficiency of the melt reactions between the polymer and the modifying agents can be improved. Thus, there is a greater probability of stronger subsequent adhesion between the polymer matrix and the fibre.
The fibre, size, matrix and composite materials, as well as their fabrication, are described, for both of the modification systems, in the following chapter.

III.2 SIZE MODIFICATION

3.2.1 REINFORCEMENT

E-glass fibres, manufactured by Vetrotex, and of diameter of approximately 17\mu m, are the reinforcement of the "size modified" composites. The composition and the fabrication of the reinforcement are discussed in Section 2.2.

3.2.2 SIZE

Four simplified sizes were applied to the fibres, during fabrication. Each size contains the Union Carbide \( \gamma \)-aminopropyltriethoxysilane coupling agent, A1100 (except for Size 4), and a matrix reactive polymer which acts as a bridging molecule between the size and the matrix. A titanium compound marker was added to all but Size 2, to facilitate observation in the early stages of this study. The nature of the marker was not revealed by the size and glass fibre manufacturer, Vetrotex. The sizes are shown in Table 3.1:

<table>
<thead>
<tr>
<th>SIZE CODE</th>
<th>COUPLING AGENT</th>
<th>MATRIX REACTIVE POLYMER</th>
<th>OTHER ADDITIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A1100</td>
<td>Epoxy</td>
<td>Ti</td>
</tr>
<tr>
<td>2</td>
<td>A1100</td>
<td>Polypropylene (PP)</td>
<td>-----</td>
</tr>
<tr>
<td>3</td>
<td>A1100</td>
<td>Polyurethane (PU)</td>
<td>Ti</td>
</tr>
<tr>
<td>4</td>
<td>-----</td>
<td>Polyurethane (PU)</td>
<td>Ti</td>
</tr>
</tbody>
</table>

**TABLE 3.1**: Composition of simplified sizes

In addition model films of the simplified sizes, both with and without the A1100 coupling agent, were produced by Vetrotex. Film fabrication, for specimens containing A1100, involved an initial step to hydrolyse the silane (1 part silane to 9
parts water). The matrix reactive polymer was added after 15 minutes stirring and the solution was then mixed for a further 15 minutes. Preliminary films were produced by drying the mixture in Teflon coated aluminium dishes. Finally the specimens were compression moulded, between Teflon sheets, to a thickness of 0.5mm, at the temperature indicated in the Table 3.2.

<table>
<thead>
<tr>
<th>MATRIX REACTIVE POLYMER</th>
<th>% SILANE</th>
<th>HEAT TREATMENT TEMPERATURE (°C)</th>
<th>MOULDING TEMPERATURE (°C)</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPOXY</td>
<td>_____</td>
<td>80</td>
<td>100</td>
<td>sticky liquid covers solid film</td>
</tr>
<tr>
<td>EPOXY</td>
<td>50</td>
<td>80</td>
<td>100</td>
<td>sticky liquid covers solid film</td>
</tr>
<tr>
<td>PP</td>
<td>_____</td>
<td>50 - 60</td>
<td>200</td>
<td>very fragile</td>
</tr>
<tr>
<td>PP</td>
<td>50</td>
<td>50 - 60</td>
<td>200</td>
<td>very fragile</td>
</tr>
<tr>
<td>PU</td>
<td>_____</td>
<td>50 - 60</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>PU</td>
<td>10</td>
<td>50 - 60</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 3.2 :Size film fabrication conditions

3.2.3 MATRIX

Polyamide 6.6 (Maranyl A100), produced by ICI, has been used as the matrix for the size modified composites. The structure and behaviour of this semicrystalline polymer are described in Section 2.5.3 of the literature survey.

Size/PA66 interaction was studied with polymer alloys, consisting of mixtures of the PA66 matrix and various quantities (3, 5, 7 and 12%) of a commercial size, termed Size B. An additional sample containing 12% of Size A (a simplified size) was produced. The compositions of the sizes are:-

Size B - commercial size comprising of a polyurethane, a silane coupling agent and other constituents
Size A - pure polyurethane which acts as a matrix-specific polymer in the commercial size

3.2.4 SIZE-MODIFIED COMPOSITE

Composite material, made from the above described individual elements, has been supplied by Vetrotex in various forms, with:-

1. Continuous fibre reinforcement
2. Short oriented fibre reinforcement
3. Short randomly orientated fibre reinforcement

A constant nominal weight of 50% fibres was chosen for all composite specimens. The real percentage weight of fibres has been measured for each sample type as described in Section 4.2.1.2.

3.2.4.1 Composite Manufacture

Each of the above composites has its own specific fabrication route.

a. Continuous reinforcement

The continuous fibre specimens were compression moulded from rods or ribbons, which consist of continuous fibres pultruded in a coating of polymer using the "hot melt" procedure (Figure 3.1). Moulding cycle time was limited to 50 minutes (2) to avoid polymer degradation. A typical compression cycle consisted of six steps:-

1. Mould was preheated to 280°C (25 minutes)
2. Rods were aligned in the mould
3. Preheating of the rods for 1 minute 45 seconds (for 2mm thick specimens)
4. Pressure of 100 bars applied for 15 seconds
5. Accelerated cooling (using oil) to 100°C (25 minutes)
6. Ejection of specimens from the mould at 100°C
FIGURE 3.1: Hot melt process
b. Short Oriented Fibres

Granules produced from the pultruded rods were directly injection moulded to ensure that the reinforcement remained essentially parallel to the flow direction. The resulting specimens contained short oriented fibres.

c. Short Randomly Oriented Fibres

Composite granules were manufactured by incorporating a fibre roving in the PA66 polymer with a twin screw extruder. The screw action results in the melting of the polymer, chopping of the fibres and separation of the individual filaments from the initial roving. The granules obtained were injection moulded to produce the final composite.

All the specimens were heat treated at 160°C, for a period dictated by the thickness of the specimen, prior to testing. ICI recommends a heat treatment of 15 minutes per 0.32 centimetres thickness, to stabilize the polymer and effectively fix the crystallinity of the PA66 matrix. As PA66 is particularly sensitive to water the specimens were stored in a desiccator containing silica gel.

III.3 MATRIX MODIFICATION

3.3.1 REINFORCEMENT

Chopped E-glass strands, produced by Owens Corning, were used in this study, having been coated with a commercial size, A1100 (Union Carbide). The initial fibre length was 4.5mm and fibre diameter was 15μm.

3.3.2 MATRIX

Unstabilized, isotactic polypropylene (ICI Propathane HF26) powder was used as the basis for the modified matrix. Modification was produced during an in-situ reactive processing technique (1), in the presence of various combinations of three chemical
additions: an initiator (peroxide), a modifying agent and a trifunctional co-agent. Four modifying agents employed are designated:

1. AA  
2. MA  
3. PM  
4. PA

Modifying agents 1 and 2 are acrylic acid and maleic anhydride, respectively. Both of these modifying agents are commercially available. Their chemical formulae are given in Section 2.5.2.6 Although both are effective functionalized chemicals they exhibit the following disadvantages:

1. Toxicity  
2. Corrosiveness  
3. Volatility

Manufacture with these modifying agents hence requires the use of special machinery which prevents the release of irritant vapour into the workplace.

To overcome these difficulties two compounds (with code names PM and PA) (1) were synthesized, both of which are derivatives of maleic anhydride (MA), and which contain a thermal antioxidant. These compounds present the following advantages:

1. Safe handling  
2. Little material loss  
3. Non volatile  
4. Non hydrolysable  
5. Thermal stability

Three of the modifying agents are considered in this work: MA (ex. Aldrich) PM and PA. MA, which is less toxic than AA and is a widely available, cheap compound, was employed as a commercial comparison for the synthesized PM and PA.

The classical MA system was examined at each stage of the modification process, as described by Figure 3.2. The base material was a processed polypropylene to which a peroxide initiator, Triganox 101, was added. This activates the polypropylene by
FIGURE 3.2: MA modification of the polypropylene matrix
forming functional groups on the polypropylene macromolecule. However, without the presence of a modifying agent, a PP + I (polypropylene/initiator) mixture may promote some interaction between the polypropylene and the size coating the fibre, but the improvement of the properties of the composite will be limited. The PP + MA (polypropylene/maleic anhydride) mixture will not give rise to enhanced interfacial adhesion as these elements are mutually inert, and require activation of the polymer backbone to promote their interaction. The combination of MA and peroxide (PP + MA + I) produces a modified polymer suitable for composites and may be the basis of commercial modified polypropylene composites such as ICI grade HW60. This system has been improved upon (1) by the addition of a functional monomer. Each of the various chemical reactions are given schematically in Figure 3.3.

3.3.3 MATRIX-MODIFIED COMPOSITE

The E glass reinforcement was added to the matrix to produce nominal fibre fractions of 30% by weight of the final compound. The true percentage fibre weight for each of the composite samples was measured using the method described in Section 4.2.1.2.

3.3.4 MODIFIED POLYMER AND COMPOSITE MANUFACTURE

Both the polymer and composites were produced by reactive processing, followed by injection moulding.

3.3.4.1 Reactive processing

Polymer modification by reactive processing was achieved using three methods:-

a. Internal mixer

Small-scale modification was achieved using a BRABENDER torque rheometer.
**FIGURE 3.3:** Chemical modification of polypropylene to enhance fibre/matrix bonding.
b. Buss-Ko kneader

Processing was performed on a single screw extruder, a Buss-Ko kneader (model PR46). The ingredients (modifier, initiator and coagent) were mixed in the combinations given in Table 3.3, with the polypropylene and the mixture introduced in the feeder of the extruder. Granules of the modified polymer were premixed with chopped glass fibre and reprocessed in the same extruder at higher temperatures and lower shear, to form modified polymer-composite granules.

c. Twin screw extruder

A final series of samples were produced by reactive processing in a BTS 30 intermeshing co-rotating twin screw extruder (TSE), which has two major advantages. First, the quality of the product can be improved, as the modifying reaction can be controlled by commutation of the various sections of the intermeshing, self-wiping screw, and the addition of fibres at the end of the processing cycle limits reinforcement degradation. Second, the reactive processing is potentially an industrially-viable using this technique as the output of modified material is dramatically increased.

3.3.4.2 Injection moulding

Injection moulded test specimens of modified polymer and composite were produced on a VICTOR 110 (FORTUNE MACHINERY LTD.) machine, using a specially designed mould (Figure 3.4). The latter forms ASTM standard tensile test, charpy, three-point bend test and hardness specimens in a single shot.

The moulding conditions employed were:-

Barrel temperature profile

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>nozzle</td>
<td>220°C</td>
</tr>
<tr>
<td>zone 1</td>
<td>200°C</td>
</tr>
<tr>
<td>zone 2</td>
<td>190°C</td>
</tr>
<tr>
<td>zone 3</td>
<td>170°C</td>
</tr>
</tbody>
</table>
FIGURE 3.4: Mould employed for the injection moulded test specimens.
Figure 3.5 is a schematic representation of the polymer and composite manufacturing route.

Polymer property variations due to processing condition modification have been studied. The scheme presented in Figure 3.6 details the fabrication routes of the pure polypropylene specimens used to establish the effect of this type of modification on the behaviour of the matrix.
3.3.4.3 Compression moulding

In order to examine the effect of processing conditions on polypropylene, a limited number of polymer samples were compression moulded using a 100 TON DANIEL press with electrically heated plattens. Processed polymer was held at 180°C, with no applied pressure, followed by one minute at full pressure, after which the specimen was cooled to room temperature (cooling time ca. 15 minutes), under full pressure, by passing cold water through the plattens.

The film thickness was controlled by the initial weight charge, for example a 8g polymer charge gave rise typically to a film of approximately 200µm thick. Steel spacers were employed to obtain a uniform thickness.

Films 200µm thick were produced for dynamic mechanical analysis, while thinner films, from 20 to 50µm, were used for optical microscopy.
By varying the chemical composition during processing, a number of grades of polymer and composite were produced. Table 3.3 details the code names and the composition of the specimens.

<table>
<thead>
<tr>
<th>CODE NAME</th>
<th>MODIFYING AGENT</th>
<th>FUNCTIONAL MONOMER</th>
<th>PEROXIDE %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SERIES 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ICIHW60F</td>
<td></td>
<td></td>
<td>30</td>
</tr>
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<td>MA000</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>MA00F</td>
<td></td>
<td></td>
<td>30</td>
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<td>MA</td>
<td>X</td>
<td></td>
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<tr>
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<td>MA</td>
<td>X</td>
<td>30</td>
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<td>PM</td>
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<tr>
<td>BT05F</td>
<td>PM</td>
<td></td>
<td>30</td>
</tr>
</tbody>
</table>

**TABLE 3.3** : Specimen code names and compositions

SERIES 1 = Buss-Ko Kneader processed
SERIES 2 = Buss-Ko Kneader processed
SERIES 3 = Twin screw extruder processed
The first two letters of the code name of Series 1 and 2 indicate which of the modifying agents was employed: the maleic anhydride and two synthesized functional monomers are represented by MA, PM and PA, respectively. Series 3, which uses the PM modifier only, however, is represented by BT (these specimens having been processed in the BTS 30 twin screw extruder). A number code follows; 000 for unprocessed pure polypropylene, 00 for processed pure polypropylene and 01 to 303 for modification ranging from the addition of one to all the chemical modifiers. Finally a F is added to the end of the code for all composite samples.

ICIHW60F is a commercial modified polypropylene composite, which was injection moulded at Aston University from composite granules supplied by ICI.

The MA101 and MA103 polymer modifications were exploited as the basis of composite materials as both these systems have good grafting potential. MA101F was considered as analogous to the ICIHW60F commercial sample, as both are modified systems and contain 30% glass fibres. MA103F differs from these samples as it contains an additional functional monomer, which should further enhance fibre/matrix adhesion.

3.4 CONCLUSION

A wide range of sample types including sized fibres, model size films, and modified polymer have been examined. Information produced for each of these specimens has provided a comprehensive background to the behaviour of the composite material.
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CHAPTER IV

METHODS
IV. METHODS

4.1 INTRODUCTION

Both the macroscopic and microscopic aspects of the "adhesion enhanced" composites and their constituents have been studied with a wide range of complimentary experimental techniques. Each method provides essential information about the nature of the material, necessary in the prediction of the specimen properties.

The mechanical properties of the injection moulded fibre reinforced thermoplastics are principally determined by the fibre-volume fraction, the fibre length and fibre orientation-distribution, as well as the fibre/matrix interphase. All these elements are considered.

IV.2 STRUCTURAL CHARACTERIZATION

Composite structure is determined by the matrix polymer, the adhesion promoter, the presence of fibres and the fabrication process. The structural nature of the specimens has been established with the techniques described in Sections 4.2.1 and 4.2.2.

4.2.1 STRUCTURAL CHARACTERIZATION

4.2.1.1 Transmission Optical Microscopy

Polarized light microscopy was used to study the structure of both the polymer and the composite. This technique has been employed to compare the effect of different modifiers and processing variables, as well as the presence of fibres, on the spherulitic structure typically observed for the semicrystalline matrices, PA66 and polypropylene.

a. Specimen preparation

Film specimens of both the matrix polymer and the composite, of 10 to 50μm thickness, were prepared for observation. Although compression-moulded polymer samples can be pressed to the appropriate thickness, the injection-moulded polymer has to be microtomed to procure the required thin films. Composite specimens are more difficult to obtain due to the different intrinsic characteristics of the fibres and
the matrices. Microtoming was found to be inappropriate, as the hard inorganic fibres damaged the diamond knife, and tended to be extracted from the soft polymer matrix, destroying the interfacial region. Hence mechanical polishing has been employed. The composite was mounted on the polishing head of the polisher (see Figure 4.1) using double sided adhesive tape. This apparatus ensured parallel polishing. By grinding, with a series of grinding discs, a polished thin film of approximately 25μm thick was produced.

![Diagram of specimen, polishing head, and polisher](image.png)

**FIGURE 4.1: Thin film preparation**

The thin film was mounted on a glass slide by securing the edges using adhesive tape.

b. Experimental conditions

The thin films were observed with an AXIOVERT 405M light microscope (ZEISS) equipped with crossed polars. The microscope was used in the transmitted light mode.

4.2.1.2 Percentage Weight of Fibres

The percentage weight of fibres, in the composite, is an important factor when considering the mechanical properties of the material. Its value was ascertained using the following methodology.

a. Specimen preparation

Reinforcement material contained in the central section of a tensile test specimen was considered as representative of the percentage weight of fibres of the composite. Having been cut from the sample, this central part was pyrolysed in a preheated oven (400°C) for 45 minutes to remove the polymer. Each specimen was weighed before
and after complete removal of the polymer to evaluate the relative proportions of reinforcement and matrix. The average specimen weight was 3g.

b. Experimental conditions

Weighing was performed using a METTLER AT250 balance with an accuracy of 0.0001g. Each value is an average of three measurements.

c. Calculation

From the percentage weight fibre results, the volume fraction, $V_f$, of the reinforcement can be calculated using:

$$ V_f = \frac{\rho_m}{\rho_m - \rho_f + (\rho_f / W_f)} \quad [4.1] $$

where $\rho_m =$ matrix density = $\rho(PP) = 0.90$g cm$^{-3}$

$\rho_f =$ fibre density = $\rho(PA66) = 1.14$g cm$^{-3}$

$W_f =$ weight fraction of fibres

Hence, assuming there is no porosity, the matrix volume fraction, $V_m$, is obtained as:

$$ V_m = 1 - V_f \quad [4.2] $$

4.2.1.3 Fibre Length Distribution

Fibre length is a primary controlling factor of the mechanical behaviour of the composites. An injection moulded composite contains fibres of various lengths, the distribution of which must be ascertained for theoretical mechanical properties calculation. The fibre length distribution was established for both the composite granules, after reactive processing (in the Buss-Ko kneader or in the twin-screw extruder) and for the injection moulded samples. Fibre length was measured by image analysis. Histograms of fibre length as a function of frequency were produced as a result of this analysis.
a. Specimen preparation

The basis for the measurement was the filaments obtained from the pyrolysis of the tensile test specimen (as described in Section 4.1.2.1) or from pyrolysed composite granules. The fibres were distributed, as a single layer, on a glass slide. Two slides were prepared for each specimen and twenty images were obtained for each slide.

b. Experimental conditions

Video images of the fibre were obtained using a TRACOR NORTHERN TN8502 image analyser, coupled to a NACHET optical microscope. The acquired images were analysed with a Tracor Northern "FIBRE ANALYSIS" program.

4.2.1.4 Fibre diameter distribution

The fibre diameter also plays a role in the determination of the mechanical behaviour of the composite, and was assessed with a Watson Image Shearing Eyepiece (W.I.S.E.). An average of 30 fibres were measured for each result.

a. Specimen preparation

Single fibres mounted on card frames were directly measured.

b. Experimental conditions

The W.I.S.E was mounted on a ZEISS optical microscope. This method involves the splitting of the normal image of the fibre into two components, one green and one red. The diameter of the specimen was measured by the rotation of the setting head, necessary to shear the normal image to the point where the two component images touch, as shown in Figure 4.2.

4.2.1.5 Fibre Orientation Distribution

Injection moulded composite samples exhibit a fibre orientation related to the flow of the material into the mould, as described in Section 2.6.3.2. The strengthening
FIGURE 4.2: Watson Image Shearing Eyepiece
efficiency of these short fibres is dependent on their orientation distribution, the reinforcement at 0° to the loading direction providing the maximum load bearing capabilities. The fibre orientation distribution of the composite samples was evaluated by image analysis. Histograms of fibre orientation as a function of frequency were obtained.

a. Specimen Preparation

The injection moulded test-piece was ground before polishing with 1µm grit on an automatic polisher to half its thickness. This process is schematized in Figure 4.3.

![Specimen Preparation](image)

**FIGURE 4.3**: Specimen preparation for fibre-orientation analysis

A significant contrast between the reinforcement and the matrix is necessary for image analysis. To obtain this contrast the specimens were etched with hydrofluoric acid, which produces dark rings around the glass fibres. For the polypropylene composites the fibres therefore appeared as dark objects in a light background. The PA66 polymer is sensitive to this acid hence, after etching, this sample was lightly repolished with 1µm grit. The fibres, in this case, appeared as bright objects in a dark background.

b. Experimental conditions

A NACHET optical microscope was employed to examine the longitudinal cross-section of the composites. The video images were analysed on a TRACOR NORTHERN image analyser with the Tracor Northern "SIZING" program
X-ray diffraction is a technique which can be used to ascertain the crystallinity of a sample and its crystalline structure. The analysis is performed by measuring the angle and intensity distribution of the X-ray diffraction generated by the focussed high energy X-ray beam. The X-ray diffraction pattern is produced by the reflection of the beam from the flat polymer surface, as shown in Figure 4.4.

**FIGURE 4.4: X-ray diffraction**

Braggs law is given by:-

$$n\lambda = 2d\sin \theta$$  \[4.3\]

where $n =$ order of diffraction

$\lambda =$ X-ray wavelength

$d =$ interplanar spacing

$\theta =$ half angle of deviation of the diffracted rays from the incident X-ray (= Bragg angle)

The results are presented as peaks corresponding to the \{hkl\} reflections, where h,k,l are Miller indices of planes producing diffraction. The area of the peak gives the intensity of the reflection and its position gives the angle $2\theta$. These peaks are
superimposed on a background of diffuse X-ray scatter due to the amorphous zones of the semi-crystalline polymer.

a. Specimen preparation

The specimens were mounted as shown in Figure 4.5.

![Sample preparation for X-ray diffraction](image)

**FIGURE 4.5:** Sample preparation for X-ray diffraction

It is the random orientation of the crystalline and amorphous material within the polymer based specimens which rendered this simple sample preparation technique viable.

b. Experimental conditions

The diffractometer used was a SIEMENS D500 with Kα₁, Kα₂ cobalt source (with λ=1.789Å), with a ELPHYSE linearly proportional counter and DIFFRAC AT (SOCABIM) data treatment software.

For the polypropylene-based materials a counter window angle of 0.1° was used to scan the 2θ range of 13° to 36°, with a test time of 500 seconds. (30kV, 10mA)

The PA66 matrix samples were analysed using a 0.1° counter window angle, with a 2θ range of 12° to 42°. The test time was 600 seconds. (40kV, 10mA)
c. Calculation

Specimens crystallinity, $X$, was evaluated using the following relationship:

$$X = \frac{A_p}{A_a + A_p} \ [4.4]$$

where $A_{a,p}$ = area under amorphous, a, and crystalline, p (peaks), regions respectively.

The two phase concept of polymer structure, i.e. that there exists relatively perfect crystallites interspersed with amorphous regions, has been applied to these results. Although simplistic, not allowing for crystal defects, this theory is widely used as it provides a crystallinity value which can be used as a basis of comparison between the various modifications and can be considered as a quantitative approximation of the true crystallinity.

For the polypropylene matrix samples, the amorphous region was defined by a parabola which just touches the minimum between the fourth and fifth peaks of the spectrum, i.e. the reflections at $d=4.8$ and $4.2\text{Å}$ respectively, as shown in Figure 4.6. This definition of the crystalline region was described by Turner et al.(1).

![FIGURE 4.6: Typical unmodified polypropylene diffraction pattern.](image)
A similar technique was employed for the PA66 matrix samples, where a hypothetical amorphous region was also described by a parabola.

Additionally, the crystal structure of the samples was established from the peak positions. A typical polypropylene spectrum results from the superposition of two spectra, one due to the monoclinic or α phase and the other being attributed to the hexagonal or β phase. The relative proportions of the α and β polymorphs, the most prevalent forms of isotactic polypropylene, are described in terms of the K-value (1) and K'-value (2) where:

\[
K = \frac{I_{\beta} (020)}{I_{\beta} (020) + I_{\alpha} (110) + I_{\alpha} (040) + I_{\alpha} (130)} [4.5]
\]

where \(I_{\alpha,\beta}(h,k,l)\) are the intensities of the \((h,k,0)\) X-ray wide angle reflections of the α and β modifications. The position of these peaks are \(d=6.3, 5.8, 4.8\) and \(4.2\) Å respectively, as shown in Figure 4.6.

The K-value is zero in the absence of the β modification and unity if only the β phase is present. However, Ullmann and Wendorff (2) established that the K-value will not exceed 0.75 as the K-value calculation assumes that the α and β wide angle reflections are separated in the scattering pattern, which is not the case with the exception of the (130) reflection. They evaluated a K'-value which takes into account the superposition of the α and β patterns, and hence gives a better estimate of the true composition of the sample. The K'-value is given by:

\[
K' = 1.33K [4.6]
\]

As the K' value tends to one, the polypropylene becomes the β polymorph i.e. with a hexagonal structure.

4.2.2 MICROSTRUCTURAL CHARACTERIZATION

Structural analysis of the polymer and composite materials is possible using the methods previously described. However, the small diameter of the reinforcement and the thickness of the size coating (typically a few hundred nanometres) render these
"macroscopic" techniques of insufficient resolution for fibre/size interface and fibre/matrix interphase characterization. Hence the study has been extended with a series of surface analysis experiments, in order to examine the microstructure of the interface in greater detail.

Surface Characterization

4.2.2.1. Field Emission Gun Scanning Electron Microscopy (FEGSEM)

The spatial distribution of the size on the fibres was assessed with FEGSEM, which gives good resolution even at low acceleration voltages as a consequence of the design of the electron gun. Figure 4.7 compares the electron gun of a classical scanning electron microscope (SEM) with that of a FEGSEM.

![Electron gun comparison](image)

**FIGURE 4.7**: Electron gun  
- a. SEM  
- b. FEGSEM

SEM electron emission is thermoelectronic, whereas, in the case of FEGSEM, it is produced by the tunnel effect: a negative potential at the anode extracts electrons from the fine point of the tungsten cathode creating a strong electric field (typically 5x10^{-7} V cm^{-1}). The brilliance and the density of the electron beam are extremely high (at $\beta=10.10^{3} Acm^{-2}s^{-1}$ and $J_0=10^{4} Acm^{-2}$ respectively) resulting in an excellent signal/background noise ratio, even at low accelerating voltages. Typical values for the brilliance and the density of the electron beam of a standard SEM are $\beta=4.10^{4} Acm^{-2}s^{-1}$ and $J_0=1Acm^{-2}$ respectively. Improved resolution results from a small
cross-over radius of the probe, of approximately 2.5nm, which is $10^4$ times less than that of a SEM.

The low accelerating voltages used by this system permit insulating materials, such as E-glass fibres to be observed without prior metallisation. Surface features are therefore not masked. A second advantage of the low accelerating voltages is that the electron beam penetrates less deeply than that of a SEM and hence only a superficial surface layer is observed; the size/glass contrast is enhanced.

However, as the electron beam is very sensitive to field variations an ultra vacuum ($10^{-8}$Pa) is required.

a. Specimen preparation

A mesh of fibres was mounted on a stub and directly observed.

b. Experimental conditions

A JEOL SIMUL 300S FEG scanning electron microscope was employed at 1.1kV to observe the mounted fibres.

4.2.2.2 X-Ray Photoelectron Spectroscopy

The chemical state of the size, both on the fibres and in their film form, was investigated using X-ray photoelectron spectroscopy. This method involves the energy analysis of low energy electrons liberated from the specimen as the result of the photoemission process. An X-ray photon, of energy $h\nu$, is absorbed by a single electron in the sample, providing sufficient energy for the latter to escape from its core orbit, with a kinetic energy, $E_k$, where:-

$$E_k = h\nu - E_B - W \quad [4.7]$$

where $h = \text{Plank's constant} = 6.626.10^{-34}\text{Js}$
\[\nu = \text{frequency of radiation}\]
\[h\nu = \text{photon energy}\]
\[E_B = \text{binding energy of the electron}\]
\[W = \text{spectrometer work function}\]
As the incident X-ray energy is known, and the escaping electron energy is measured, the original binding energy of the electron, which is the signature of its atom, can be calculated. The binding energy is plotted as a function of intensity, or number of counts per second.

a. Specimen preparation

Specimens, as received, have been mounted on stubs as shown in Figure 4.8.

b. Experimental conditions

Analysis was performed with a V.G. Scientific ESCALAB MKII coupled to a VGS-5000s datasystem based on a DEC PDP11/73 computer. Al Kα radiation (photon energy, $h\nu=1486.6\text{eV}$) was employed. Glass fibres, coated with Size 2, were further analysed using Mg Kα ($h\nu=1253.6\text{eV}$) radiation, which leads to a shallower sampling depth (approximately 5nm for carbon 1s peak in organic compounds) than the Al Kα radiation (6nm). Survey spectra were recorded at an analyser pass energy of 50eV, together with high resolution spectra of the elemental regions of interest (analyser pass energy of 20eV).
Bulk Characterization

4.2.2.3 Glancing X-ray Diffraction

Classic X-ray diffraction evaluation involves the rotation of both the specimen and the counter during testing. The incident X-ray hence penetrates deep within the sample, which, for the size-coated fibres, gives rise to a spectrum typical of the amorphous glass, as the characteristic signal of the size is masked by that of the fibre. Therefore information about the size on the fibres can not be obtained using this technique. However, by fixing the specimen, and allowing only the counter to rotate, a shallow incident angle can be maintained, hence the diffraction pattern of the size can be measured. These techniques are schematized in Figure 4.9.

![Diagram of classic and glancing X-ray diffraction](image)

**FIGURE 4.9:** Scheme of a. classic and b. glancing X-ray diffraction

a. Specimen preparation

A monolayer of fibres, or the size film were secured across a mount, similar to that shown in Figure 4.5, with adhesive tape.

b. Experimental conditions

All specimens (fibres and films) were analysed using Co Kα radiation, with a fixed incident angle of 10°. The test time was of 600 seconds with a detector 2θ range of 12 to 80°.
Localized Structural Characterization

4.2.2.4 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (PHILIPS EM430, 300kV), with a possible spatial resolution of 0.23nm, is an ideal technique for interfacial studies. This method requires very thin samples, with a thickness of approximately 100nm, as the strong interaction of the electron beam with the examined material in its bulk form results in the absorption of the electrons. However the production of thin foil samples is particularly difficult, due not only to intrinsically different thinning rates of the fibre and the polymer (either size or matrix), but also, in the case of the fibre/size interface, due to problems in handling the small diameter fibres (15-17µm) and also the necessity of retaining the surface layers of the filaments. A successful thin foil fabrication method for small diameter fibres has been developed which enables the soft polymer size and the brittle glass to be imaged and analysed. A microcharacterization of this interfacial area is hence possible.

Images produced by the incident electron beam/ specimen interaction exhibit a range of contrasts which can be attributed to various phenomena:-

1. an absorption contrast, produced by variations in the density and the thickness of the sample. Increasing atomic number results in darker regions, with bright field imaging.
2. a diffusion contrast, due to an angular deviation of the beam induced by the material.
3. a diffraction contrast, which is related to variations in crystallinity and crystalline orientation.
4. a phase contrast, which is attributed to phase change produced by small structures (less than 2nm in diameter) in the specimen

a. Specimen preparation - fibre/size interface

It has been found that small diameter fibres can be directly ion milled without any prior mechanical grinding and hence damage to the fibre/size interface caused by polishing can be avoided. Problems occurred in handling the fibres were overcome using the following methodology (3). A mesh of fibres was stuck across a hole cut into a metal sheet. Fibres were removed until a monolayer, of aligned filaments remained. A copper ring (external diameter of 3mm) was then stuck to the fibres using an epoxy
glue. The ring was then removed from the mount by cutting the fibres along the external edge of the ring. This process is schematized in Figure 4.10(fig.1).

Ion etching with a GATAN ion miller, using inert Ar+ ions at 5kV, was employed to thin the sample. The sample was cooled to cryogenic temperatures (-186°C) before ion milling to inhibit degradation of the polymer coating on the fibres. An ion beam incident angle of 12° was used. Contact between the fibres is essential as the shadow of the fibres prevents the thinning of the edge of the reinforcement. Figure 4.10(fig.2) shows the result of thinning individual fibres where only the glass is available for observation. In Figure 4.10(fig.3) the size is protected from the ion beam, by the adjacent fibres, and so is not destroyed during the thinning process, hence the interfacial region remains intact.

Fig 1

![Diagram](image1)

Fig 2:

![Diagram](image2)
b. Experimental conditions

The thin foil samples were observed in a Philips EM430 transmission electron microscope at 300kV, after metallization with a very fine layer of carbon.

4.2.2.5 Electron Energy Loss Spectroscopy (EELS)

Electron energy loss spectroscopy measures the energy distribution of electrons transmitted through a thin foil sample in the transmission electron microscope. The spectrum obtained gives information on the interaction between the incident electrons and the atoms within the thin foil. The majority of electrons (approximately 80%) traverse the specimen without any energy loss either because no interaction has occurred or that the interactions are of an elastic nature. These electrons produce the zero-loss or elastic peak at $E = 0\text{eV}$, as shown in Figure 4.11. This peak, however, has a finite energy width due to inherent spread of the energy of the incident electrons and due to the generation of phonon mode vibrations which induce electron energy losses of approximately $0.1\text{eV}$ to the material.
FIGURE 4.11: Example of an EELS spectrum
The second peak observed in Figure 4.11 is the low-loss region which results from the direct interaction between the incident electrons and the atomic electrons. This excitation of electrons in the molecular orbital gives an energy loss (of less than 15eV) which is characteristic of the excited molecule. This part of the spectrum is highly complex and difficult to interpret.

The spectrum of a glass presents an additional peak at approximately 20eV due to "plasmon" excitation, i.e. the onset of oscillation of the weakly bonded electron gas, produced by the incident electron. Beyond this peak the electrons excite the valence electrons, with decreasing probability as the energy loss increases. Above 50eV peaks or core-loss edges corresponding to the ionization of the inner atomic shells are superimposed on the continuous background signal. When the incident electron interacts with an atom, an energy, E, equal to the appropriate binding energy, \(E^b\), must be transferred from the incident electron to the atom for some shell to be ionized. Hence when \(E\) is greater than \(E^b\) ionization is impossible, but ionization occurs when \(E=E^b\), and with decreasing probability as \(E\) increases above the \(E^b\) value. The spectrum therefore presents an edge at a given value which then falls off to the level of the continuous background. Each peak is associated with an electronic orbit of an element.

An extended energy loss fine structure may also be observed which is related to the environment of the element and is again difficult to interpret.

a. Specimen preparation

Thin foil samples of the sized fibres were prepared with the methodology described in Section 4.2.2.4.

b. Experimental conditions

The fibre and size were chemically analysed with a GATAN 601 EELS mounted on a 430 Philips transmission electron microscope and coupled to a TRACOR datasystem.

4.2.2.6 Microprobe Analysis

Elemental analysis was achieved with a microprobe. The zone to be analysed is bombarded by an electron beam, the penetration depth of which is dependent on the
density of the specimen and the energy of the incoming electrons, as shown in Figure 4.12.

**FIGURE 4.12: X-ray penetration depth as a function of specimen density and electron energy**

The electron/material interaction permits an atomic electron to escape from its atom, leaving a vacancy in an inner orbit. This hole is rapidly filled by an electron from an outer orbit. The energy liberated by the electronic transition, $\Delta E$, is eliminated by a photon, the frequency of which is characteristic of its atom:-
\[ hv = \Delta E = E_1 - E_2 \]  \[4.8\]
where \( h \) = Plank’s constant = 6.626 \times 10^{-34} \text{Js}

\( \nu \) = frequency of radiation

and \( hv \) = photon energy

\( E_1 \) = electron binding energy of inner orbit

\( E_2 \) = electron binding energy of outer orbit

Figure 4.13 shows the principal electronic and X-ray emission which can be produced by electron/sample interaction.

The emitted X-rays are detected in order to identify the chemical composition of the sample, each peak of the X-ray spectrum being characteristic of a particular element. In a bulk composite the interaction volume and hence the volume analysed are considerable (typically 1\( \mu \text{m}^3 \)), as is shown in Figure 4.13. Therefore global information from the fibres, size and matrix is detected. To obtain results from distinct regions of the composite, and to improve the lateral resolution, the interaction volume must be reduced (Figure 4.13). By using specimens, with a thickness of approximately 100nm, the interaction depth is diminished and the spatial resolution of the microprobe is enhanced (the volume analysed is approximately 2.10^{-5} \( \mu \text{m}^3 \)).

a. Specimen preparation

The thin foils previously prepared for observation using transmission electron microscopy were employed. The specimens were coated with a fine layer of carbon.
b. Experimental conditions

A CAMECA SX50 microprobe was employed. Four elements, namely silicon, calcium, aluminium and titanium have been researched to characterize the fibre/size interface and the size itself. The silicon is present in the fibre and the size, the aluminium and the calcium in the fibre only, and the titanium (from the marker) is found in the size only.

4.2.2.7 Fourier Transform Infrared (FTIR) Spectroscopy and FT-Raman spectroscopy

The size coatings on the glass fibres were analysed by FTIR and FT-Raman spectroscopy. These techniques give information on the chemical and physical nature of the polymer. Most polymers absorb electromagnetic radiation in the wavelength range of 1 - 50μm i.e. in the infrared region. This is because the molecules undergo transitions between vibrational states of different energies causing both the absorption and emission of radiation.

The energy, $E$, of a molecule can be separated into four additive terms belonging to various motions of the molecule. In solids two of these terms are neglected (which correspond to the translation of the molecule, a movement which does not lead to any interaction with the electromagnetic radiation, and the rotational energy, as the free rotation of the molecule is restricted) and therefore the energy of such a molecule is determined by the electronic and vibrational energy contributions. Interaction between the molecule and the electromagnetic radiation occurs when the Bohr's relationship is fulfilled:-

$$\Delta E = h\nu \quad \text{with} \quad \Delta E = E_k - E_m \quad [4.9]$$

where $\Delta E$ = energy difference between two energy levels $k$ and $m$

$h = \text{Planck's constant}$

$v = \text{frequency of the absorbed or emitted radiations}$

Both IR and Raman spectroscopies are based on the same physical origin: the vibrations of the atoms of a molecule which correspond to allowed transitions between different energy levels. It is the interaction between the electromagnetic radiation and
the sample which differs between the spectroscopic methods. In IR spectroscopy specific frequencies of radiation are absorbed by the sample. Infrared instrumentation is divided into two classes, dispersive and non dispersive. In non dispersive spectrometers, such as FTIR, the grating or prism found in a standard dispersive infrared instrument is replaced by an interferometer.

FT-Raman spectroscopy is a complimentary technique to FTIR spectroscopy. A powerful laser source, emitting monochromatic visible or infrared radiation is employed to produce the Raman effect (inelastic scattering). This is in contrast to infrared absorption where the incident radiation is polychromatic. The incident radiation is scattered in all directions when it interacts with the sample. During irradiation the spectrum of the scattered radiation is detected at an angle to the incident radiation.

a. Specimen preparation

The fibres, mounted on a metal support, were directly analysed with FTIR and FT-Raman spectroscopy.

b. Experimental conditions

The FTIR spectra were obtained with a NICOLET 800 spectrophotometer coupled with a NIC-PLAN microscope. The spectra were obtained with the parameter settings given in Table 4.1.

<table>
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<tr>
<th>DATA COLLECTION PARAMETERS</th>
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<td>Number of scans</td>
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</tr>
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<td>Electronic gain</td>
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</tr>
<tr>
<td>Velocity</td>
<td>30</td>
</tr>
</tbody>
</table>

**TABLE 4.1**: FTIR spectroscopy data collection parameters
The FT-Raman spectra of the glass fibre samples were recorded with a NICOLET 910 spectrophotometer, which uses a YAG - laser. Scattered radiation was collected and collimated employing a 180° reflective optical geometry. The spectra were obtained using 450mW of laser power, 600 scans and 4cm\(^{-1}\) resolution. Data processing was performed with a NICOLET 680D spectral workstation.

IV.3 PHYSICAL CHARACTERIZATION

4.3.1 Macromechanical Characterization

4.3.1.1 Tensile Tests

The mechanical properties of the injection moulded samples were evaluated by tensile testing. These characteristics are affected not only by the mechanical behaviour of each component, but also by the interface; interfacial failure degrades the overall mechanical properties of the composite. Therefore tensile test results were used to evaluate the efficiency of the different interfacial adhesion modifications.

a. Specimen preparation

Injection moulded dumbell tensile test specimens were used for all tests.

b. Experimental conditions

An Instron machine was utilised, at ambient temperature, using cross-head speeds of 1mm and 5mm per minute for the composite and the polymer respectively. Composite deformation was measured using an extensometer with an accuracy of 3.10^-6m and a deformation limit of 8.1%. The cross-head displacement was used to evaluate the deformation of the polymer as the elongation of the polypropylene matrix exceeded 300% rendering all other available measuring techniques unsuitable.

Specially designed grips were prepared (Figure 4.14) to prevent slipping and to ensure the correct specimen alignment with the axis of the tensile test machine.
FIGURE 4.14: Tensile test grips developed to prevent slipping and to ensure correct specimen alignment with the axis of the tensile test machine.
4.3.2 Micromechanical Characterization

4.3.2.1 Microdrop tests

The mechanical properties of the composite are dependent on the quality of the interface and the strength of the interfacial adhesion. The evaluation of the interfacial shear strength is therefore important for the calculation of the theoretical characteristics of the composite. Although there are numerous methods for the measurement of the interfacial shear strength, the nature of the thermoplastic matrix renders the preparation of many of the required samples particularly difficult. For the microdrop test the matrix is deposited on the fibre in the form of a droplet, which is relatively easy to produce.

a. Specimen preparation

Individual fibres, of a gauge length of 60mm, were mounted on card frames. A small section of the polymer was cut from an injection moulded specimen, then placed on a metal support, in contact with a mounted glass fibre. The polymer was melted with a soldering iron, heated to approximately 430°C, held in close proximity to the specimen. The drop of liquid polymer forms a concentrique ellipsoid around the fibre, as shown in Figure 4.15. The droplet length was measured with an optical microscope with an accuracy of 1µm. Drops of an average length of 350µm were produced.

b. Experimental conditions

The specimens were tested with a Universal fibre tensile test machine at a cross head speed of 1mm/min. Specially developed grips were employed to retain the drop in place while extracting the fibre. A photograph of the grips is displayed in Figure 4.16.

c. Calculation

The interfacial shear stress, \( \tau_i \), was calculated with:-

\[
\tau_i = \frac{F}{\pi dL} \quad [4.10]
\]

where
- \( F \) = fibre pull-out force
- \( d \) = diameter of the fibre
- \( L \) = length of the microdrop
FIGURE 4.15: Droplet of liquid polymer around the fibre
FIGURE 4.16: Grips developed for the microdrop test.
4.3.3 Viscoelastic Analysis

A distinct feature of the mechanical behaviour of polymers is the way in which their response to an applied stress or strain depends upon the rate or time period of loading. This phenomenon, or linear viscoelasticity, can be presented by two parameters: one related to an elastic behaviour, described by Hookes law and characterized by a storage modulus $E'$ and the other due to a viscous behaviour, given by Newtons law and characterized by a loss modulus $E''$. The real and imaginary moduli are schematized in the Argand diagram of Figure 4.17.

$$E^* = E' + iE'' \quad [4.10]$$

**FIGURE 4.17: Linear viscoelasticity**

**Hookes Law**

$$\sigma \propto \varepsilon \quad \text{or} \quad \sigma / \varepsilon = \text{constant} = E' \quad [4.11]$$

At small strains Hookes law holds, as the stress, $\sigma$, is proportional to the strain, $\varepsilon$, for many materials.

**Newtons Law**

$$\sigma = \eta \frac{de}{dt} \quad [4.12]$$

where $\eta = \text{viscosity}$

$de/dt = \text{strain rate}$

This equation describes the linear viscous behaviour of the material, and holds at small strains.
Dynamic mechanical properties of the size coated fibres, the model size films, the modified polymer and the corresponding composites have been tested in the linearly elastic region under a harmonic regime, as shown in Figure 4.18.

\[ \tan \delta = \frac{E''}{E'} \text{ or } \frac{G''}{G'} \] [4.13]

A sinusoidal load is applied to the specimen. The phase difference or lag period, \( \delta \), measured between this applied load and the resulting deformation, is a direct measure of the damping characteristics of the material, and is given by:

\[ \tan \delta = \frac{E''}{E'} \text{ or } \frac{G''}{G'} \] [4.13]

where \( E' \) or \( G' \) = storage modulus and shear storage modulus respectively
\( E'' \) or \( G'' \) = loss modulus and shear loss modulus respectively

Hence thermomechanical spectra consist of the storage and loss functions plotted as a function of temperature. A \( \tan \delta \) spectrum is characterized by a series of peaks each of which can be attributed to the onset of motion of internal structural elements. Hence this particular macromechanical technique can be used to evaluate internal molecular motion and the molecular architecture of the specimen.

4.3.3.1 Dynamic Mechanical Thermal Analysis (DMTA)

A VISCOANALYSEUR (METRAVIB) (Figure 4.19) was employed to establish the dynamic mechanical properties of the material. This apparatus is versatile, adapting to many loading types, with a frequency range of 5 to 1000 Hz and a temperature range of -150 to 400°C. The maximum deformation amplitude is 800\( \mu \)m.
FIGURE 4.19: Viscoanalyseur (Metravib)
a. Specimen preparation

The wide variety of specimen types has necessitated a wide range of mechanical grips and loading modes. These are summarized in Table 4.2.

<table>
<thead>
<tr>
<th>SPECIMEN TYPE</th>
<th>LOADING MODE</th>
<th>GRIPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>POLYMER OR SIZE</td>
<td>TENSION-TENSION</td>
<td>THIN FILM GRIPS</td>
</tr>
<tr>
<td>FILM (upto 1mm thick)</td>
<td></td>
<td>FILM</td>
</tr>
<tr>
<td></td>
<td><img src="image1" alt="Diagram" /></td>
<td></td>
</tr>
<tr>
<td>BULK POLYMER OR COMPOSITE</td>
<td>COMPRESSION - COMPRESSION</td>
<td><img src="image2" alt="Diagram" /></td>
</tr>
<tr>
<td>Parallelepips milled with</td>
<td></td>
<td></td>
</tr>
<tr>
<td>parallelism of the faces</td>
<td></td>
<td></td>
</tr>
<tr>
<td>accurate to 1%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><img src="image3" alt="Diagram" /></td>
</tr>
<tr>
<td>COMPOSITE RIBBON</td>
<td>HORIZONTAL SHEAR</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 4.2**: Mechanical testing configurations
b. Experimental conditions

The dynamic mechanical properties has been measured as a function of increasing temperature at a frequency of 5Hz. Appropriate temperature ranges have been chosen for each specimen type and matrix material:-

<table>
<thead>
<tr>
<th>SPECIMEN TYPE</th>
<th>MATRIX</th>
<th>TEMPERATURE RANGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>POLYMER FILM</td>
<td>PP</td>
<td>-150°C to 160°C</td>
</tr>
<tr>
<td>SIZE FILM</td>
<td>PP</td>
<td>-150°C to 60°C</td>
</tr>
<tr>
<td>BULK POLYMER OR COMPOSITE</td>
<td>PP</td>
<td>-150°C to 160°C</td>
</tr>
<tr>
<td>COMPOSITE RIBBON</td>
<td>PA66</td>
<td>-150°C to 200°C</td>
</tr>
</tbody>
</table>

**TABLE 4.3 : DMTA temperature ranges**

4.3.3.2 Torsion Pendulum

The MICROMECHANALYSEUR (METRAVIB) inverted forced torsion pendulum (Figure 4.20) is a more sensitive technique than the DMTA and has been used to further characterize the polymer and composite and hence the fibre/matrix interphase. Its greater sensitivity results in high resolution spectra, and is related to the low frequencies employed (ranging from $10^{-5}$ to 1Hz) and the capacity to measure accurately modulus decreases of four orders of magnitude, which is essential when testing amorphous polymers in their glass transition region.

The mechanics of the system are described in Figure 4.21.

a. Specimen preparation

Parallelipiped test specimens for the torsion pendulum were milled from the composites and polymers to the dimensions given in Figure 4.22.
FIGURE 4.20: Microméchanalyseur (Metravib)
5. Dynamic mechanical tests- torsion pendulum

The torsion couple is produced by magnetic-like interaction of the two Helmoltz coils (3) through which passes a current I. The twist produced is transmitted to the specimen (5) by a rigid shaft (12). The specimen deformation is measured using the Poggendorff method: a light beam from a regulated source (10), is reflected by a mirror, fixed to the moving grip (11) by way of the rigid shaft, towards a differential photo voltage cell (9). An amplifier (13) supplies a proportional tension to the deformation of the specimen.

The suspension system, comprising wire (6) pulley and counter weights (1), eliminates all axial loading on the specimen. A shock absorber (7) attenuates external vibrations. The copper oven (4) is long in comparison to the length of the specimen, allows the temperature of the specimens to be varied from 100 to 679 K, with a minimum temperature gradient.

FIGURE 4.21: Torsion pendulum
The unidirectionally reinforced composite samples were produced with the fibres parallel to the z axis of the specimen.

The lower part of the specimen was fixed, whereas the upper part was tested in torsion.

b. Experimental conditions

Curves of tanδ were determined, with increasing temperature, at three frequencies (1, 0.1 and 0.01Hz). The temperature increased linearly as a function of time, at 15K/hour, but the temperature was maintained at a constant value during each measurement period (of 1 - 7 minutes).

The specimen was enclosed in a bell under a vacuum of 0.5 bar with the bell immersed in a container of liquid nitrogen. This technique was used not only to cool the specimen in the early stages of the experiment, but also to trap water molecules against the walls of the bell, which limited problems due to humidity. Such a procedure is particularly important for the PA66 samples which have a hydrophilic matrix.

Polypropylene

The polypropylene based samples were tested in a temperature range from 100K to 400K (-173 to 127°C), in order to study their viscoelastic behaviour from the beginning of the secondary transition, β, in the glassy region, to the end of the glass transition and the beginning of the rubbery plateau (Section 2.5.2.4). Above 400K the specimens rigidity was insufficient to remain within the measuring limits of the apparatus.
Polyamide 6.6.

PA66 based specimens were tested using a temperature range of 100K to 425K (-173 to 152°C), in order to examine their behaviour in the glassy, the glass transition and the rubbery regions (described in Section 2.5.3.4).
REFERENCES

CHAPTER V
RESULTS
5.1 INTRODUCTION

A large range of experimental techniques were employed to analyse the structure and mechanical behaviour of the size-modified and the matrix-modified systems. Each technique provided unique information about the fibre, the size and the matrix, both individually and when combined in the composite, which lead to a better understanding of the behaviour of the bulk material.

V.2 STRUCTURAL CHARACTERIZATION

The structure of the specimens was studied with two series of experiments, one giving overall structural information (Section 5.2.1) and the second giving a more localized structural characterization (Section 5.2.2).

5.2.1 STRUCTURAL CHARACTERIZATION

5.2.1.1 Transmission Optical Microscopy

Bulk, macrostructural characterization of the polymer and composite was achieved with polarized light microscopy. Both matrix polymers are semi-crystalline and exhibit an array of spherulitic structures in an amorphous background.

a. Size Modification

i. Polymer

The PA66 matrix was examined after heat treatment (160°C for 15 mins per 0.32 cm thickness), as shown in Figure 5.1. A spherulitic structure was observed, however, the relatively thick specimen (approximately 0.05mm) rendered detailed observations and spherulite diameter measurement difficult. Thinner specimens could not be obtained by microtoming as the polymer was relatively difficult to cut.
FIGURE 5.1: Transmission optical micrographs of the PA66 polymer, after heat treatment, showing a spherulitic structure.
FIGURE 5.2: Transmission optical micrograph of the PA66 matrix composite
ii. Composite

The matrix of the composite samples was spherulitic, as shown in Figure 5.2. Observation of the specimens did not reveal a zone of transcrystallinity (the growth of columnar crystals) around the fibre. However, the preparation of these samples was difficult, due to the different intrinsic properties of the fibre and the matrix, and the necessity of a very thin film sample for this particular technique.

b. Matrix Modification

i. Polymer

*Effect of processing conditions*

A comparison of the optical microscope plates of Figure 5.3 shows the effect of the various preparation techniques on the structure of the unmodified matrix polymer. The compression moulded, unprocessed polypropylene has a granular crystalline structure with dark and bright areas of positive and negative birefringence. Examination of the same polymer, after processing in an internal mixer, reveals the formation of a spherulitic structure, typical of that observed for isotatic polypropylene (1). The dark and bright spherulites are of type I and III respectively (as described in Section 2.5.2.2), both of which are characterized by a Maltese Cross extinction pattern. Type III spherulites have a strong negative birefringence, which is characterized by a highly luminous appearance. The larger size (approximately 0.04mm in diameter) and concave edges of the Type III spherulites are indicative of a faster growth rate than that of the type I spherulites, as is predicted by Padden and Keith, and Norton and Keller (1, 2).

Observation of the injection moulded samples revealed similar structures with large spherulites of a fibrous appearance or of the mixed type described in Section 2.5.2.2. The spherulites are space-filling and, where they impinge, form straight or near-straight boundaries. Polyhedral spherulites were hence observed for the thin film specimens. An average spherulite diameter of 0.05mm was measured for the unprocessed polypropylene.
FIGURE 5.3: Effect of processing conditions on polypropylene
FIGURE 5.4: Effect of the addition of a free radical initiator
FIGURE 5.5: Effect of chemical modification - the MA system
FIGURE 5.6: An example of a polypropylene matrix composite
Effect of the addition of a free radical initiator

A discernable effect of the addition of a peroxide, for processed compression moulded samples, was an apparent break down of the spherulitic structure and a reduction in crystallite size (from 0.042mm to 0.034mm). Only a few relatively large, bright spherulites remain, as seen in Figure 5.4. A similar alteration of the structure was observed for the injection-moulded samples in the presence of a peroxide.

Effect of chemical modification - the MA system

The chemically modified polymer samples examined were produced in the same manner, by mixing in a Buss Ko kneader, followed by injection moulding. Only the unmodified polypropylene specimen exhibited the fibrous spherulitic structure, shown in Figure 5.3, with the spherulites truncated by impingment. The chemically-modified polypropylene samples all had a structure comprising of both positively and negatively birefringent crystals, as shown in Figure 5.5. MA01 (polypropylene + MA) consisted of Type I and Type III spherulites, with additional bright points dispersed throughout the structure. These precipitates, of approximately 100nm in diameter, were also observed in the MA101 polymer (polypropylene + MA + I). Further examination of the MA101 spherulites revealed that their diameters were similar to those measured for the MA02 specimen (polypropylene + I), with the dark, Type I spherulites of approximately 0.025mm in diameter and bright, Type III spherulites of 0.037mm. MA103 had a granular structure, with the occasional Maltese cross extinction pattern, of a Type III spherulite. These structures typically had a diameter of 0.012mm.

ii. Composite

In similar manner to the PA66 composites, the preparation of the polypropylene composites was difficult. However, transmission optical microscopy revealed the spherulitic nature of the polypropylene matrix, as shown in Figure 5.6.

5.2.1.2 Percentage Weight of Fibres

The percentage weight of fibres and the calculated fibre volume fraction, for the size-modified (PA66 matrix) and matrix-modified composites (polypropylene matrix), are
given in Table 5.1. Additionally, the results for the matrix-modified granules, produced by the reactive processing techniques (Buss-Ko kneader for Series 1 and 2 and twin screw extruder for Series 3), are tabulated.

<table>
<thead>
<tr>
<th>CODE</th>
<th>% WEIGHT OF FIBRES Wf</th>
<th>FIBRE VOLUME FRACTION Vf</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GRANULES</td>
<td>I.M. COMPOSITE</td>
</tr>
<tr>
<td>SIZE 1</td>
<td>-----</td>
<td>49.3</td>
</tr>
<tr>
<td>SIZE 2</td>
<td>-----</td>
<td>47.7</td>
</tr>
<tr>
<td>SIZE 3</td>
<td>-----</td>
<td>47.7</td>
</tr>
<tr>
<td>SIZE 4</td>
<td>-----</td>
<td>51.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SIZE MODIFICATION (Vetrotex - PA66 matrix)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SERIES 1</td>
</tr>
<tr>
<td>ICIHW60F</td>
</tr>
<tr>
<td>MA00F</td>
</tr>
<tr>
<td>MA101F</td>
</tr>
<tr>
<td>MA103F</td>
</tr>
<tr>
<td>PM103F</td>
</tr>
<tr>
<td>PA103F</td>
</tr>
</tbody>
</table>

| SERIES 2 |
| ICIHW60F | ----- | 28.4 | ----- | 0.12 |
| MA103BF  | 28.9  | 29.1 | 0.13 | 0.13 |
| PM203F   | 28.5  | 29.3 (29) | 0.12 | 0.13 |
| PM303F   | 30.9  | 31.2 (33) | 0.14 | 0.14 |

| SERIES 3 |
| BT03F    | ----- | 21.1 | ----- | 0.09 |
| BT05F    | 26.83 | 27.9 | 0.115 | 0.12 |

**TABLE 5.1:** Percentage weight and volume fraction of fibres in the composite samples

I.M. COMPOSITE = final sample produced by injection moulding

( ) Value measured with a DSC apparatus at the Institut Français de Petrole
From the results in the above table it can be seen that the fibre volume fraction is relatively constant for the size-modified samples, averaging 0.3 (standard deviation, std =0.01). The matrix-modified systems show a much greater variation in fibre volume fraction, which for Series 1 can be attributed to non-optimized processing parameters. Series 2, fabricated using a similar methodology to Series 1, but at a later date, shows a more constant fibre volume fraction (average of 0.13 std=0.01), due to better processing control.

Series 3 again shows a considerable variation in fibre content (0.10 std 0.02), which arose from problems with glass-fibre feed controls.

A similar "burn-off" technique (heating for two hours at 105°C to remove all the water followed by 15 minutes at 600°C to burn-off the size) was employed to assess the quantity of size coating the fibres. Table 5.2 summarizes the percentage weight results.

<table>
<thead>
<tr>
<th>CODE</th>
<th>% WEIGHT OF SIZE</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIZE MODIFICATION (Vetrotex)</td>
<td></td>
</tr>
<tr>
<td>SIZE 1</td>
<td>0.7</td>
</tr>
<tr>
<td>SIZE 2</td>
<td>0.7</td>
</tr>
<tr>
<td>SIZE 3</td>
<td>0.7</td>
</tr>
<tr>
<td>SIZE 4</td>
<td>0.9</td>
</tr>
<tr>
<td>MATRIX MODIFICATION (Union Carbide)</td>
<td></td>
</tr>
<tr>
<td>Commercial size, A1100</td>
<td>1.0</td>
</tr>
</tbody>
</table>

**TABLE 5.2:** Percentage weight of size on the E-glass fibres

It can be seen that all the sizes were present in approximately the same percentage weights.

**5.2.1.3 Fibre Length Distribution**

Histograms of fibre length as a function of frequency, for the injection moulded composites, are given in Figure 5.7. An average of 5000 fibres was measured for each specimen. This number of fibres gives a good statistical evaluation of the fibre length distribution, as shown by the histograms of Figure 5.8. Table 5.3 gives the average fibre length and the standard distribution for each of the composite samples.
FIGURE 5.7: Fibre length as a function of frequency for the injection moulded composites.
<table>
<thead>
<tr>
<th>CODE</th>
<th>TRUE FIBRE LENGTH ($\mu$m)</th>
<th>END-POINT LENGTH ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AVERAGE LENGTH</td>
<td>STANDARD DEVIATION</td>
</tr>
<tr>
<td>SIZE MODIFICATION (Vetrotex - PA66 matrix)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SIZE 1</td>
<td>185</td>
<td>120</td>
</tr>
<tr>
<td>SIZE 2</td>
<td>161</td>
<td>111</td>
</tr>
<tr>
<td>SIZE 3</td>
<td>124</td>
<td>79</td>
</tr>
<tr>
<td>SIZE 4</td>
<td>160</td>
<td>112</td>
</tr>
<tr>
<td>MATRIX MODIFICATION (Aston University - polypropylene matrix)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SERIES 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ICIHW60F</td>
<td>193</td>
<td>148</td>
</tr>
<tr>
<td>MA00F</td>
<td>330</td>
<td>242</td>
</tr>
<tr>
<td>MA101F</td>
<td>169</td>
<td>97</td>
</tr>
<tr>
<td>MA103F</td>
<td>255</td>
<td>130</td>
</tr>
<tr>
<td>PM103F</td>
<td>157</td>
<td>96</td>
</tr>
<tr>
<td>PA103F</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>SERIES 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ICIHW60F</td>
<td>184</td>
<td>149</td>
</tr>
<tr>
<td>MA103BF</td>
<td>267</td>
<td>214</td>
</tr>
<tr>
<td>PM203F</td>
<td>249</td>
<td>207</td>
</tr>
<tr>
<td>PM303F</td>
<td>259</td>
<td>220</td>
</tr>
<tr>
<td>SERIES 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BT03F</td>
<td>306</td>
<td>307</td>
</tr>
<tr>
<td>BT05F</td>
<td>307</td>
<td>333</td>
</tr>
</tbody>
</table>

**TABLE 5.3: Average fibre lengths**

where True length is the distance, along the skeleton, between the extremities of the fibre.

End-point length is measured between the end-points of the fibre.

Skeletization of the digital images of the fibres during image analysis reduced the width of the fibres to one pixel. During this operation the length of the fibre is also reduced. The "true" length measured corresponds to the length of the fibre skeleton and is therefore less than the real length. The resulting fibre length distribution is
FIGURE 5.8: Histogram of fibre length as a function of frequency, with different total numbers of fibres measured.
FIGURE 5.9: Effect of the inclusion of the partial fibre lengths on the histogram of fibre length as a function of frequency, for the injection moulded composites.
**FIBRE LENGTH DISTRIBUTION**

![Graph of fibre length distribution](image)

**FIGURE 5.10:** Typical histogram of fibre length as a function of frequency, which includes all fibre lengths.

![Graph of fibre breakdown](image)

**FIGURE 5.11:** Fibre break down during the various stages of composite manufacture, for the matrix-modified samples.
artificially skewed towards the short fibre lengths. An internal correction for fibre length loss during image analysis was added to the "FIBRES" program, which gives the "end-point" length. This represents the length between the extremities of the fibre, rather than the skeleton. A variation of approximately 3% was observed between these measured lengths.

The fibre length measurement program employed excluded all the partial fibres, i.e. all the particles touching the edge of the screen. As the image acquisition was achieved by incrementally moving the microscope stage, these fibres, therefore, were not included in the fibre-length distribution. Figure 5.9 compares the histograms produced for the same data acquisition, both with and without the inclusion of the fibres touching the edge of the screen. It can be seen that by including the partial fibres the proportion of short fibres (of less than 200µm) was increased. The average fibre length was consequently reduced from 337µm to 329µm.

A polynomial equation has been used to fit each of the histograms. This method was appropriate as the data obtained for the very short fibre lengths was not accurate. External artefacts such as dust and marks on the microscope lense, and on the glass slide support, as well as artificially created short fibres (during preparation of the sample for pyrolysis and during handling of the resulting fibres) were found to dramatically increase the number of short fibre measured. Figure 5.10 shows a typical histogram of a fibre length distribution which includes all the fibres. It can be seen that the fibres of less than 50µm dominated the distribution. As the longer fibres play an important role in the mechanical behaviour of the composite, all the fibres of less than 50µm in length were excluded from the fibre length distribution.

By tailoring the parameters as described an accurate fibre distribution was obtained.

Fibre breakdown during the various stages of composite manufacture, for the matrix modified system, was established by comparing the results for the granules and the injection-moulded samples with the original fibre length of 4.5mm. These results are shown schematically in Figure 5.11. Reactive processing in a Buss-Ko kneader produced severe fibre degradation, giving fibres between 5 and 10% of their initial length. The method adopted during twin-screw extrusion resulted in less fibre failure than in the Buss-Ko kneader. Less significant fibre degradation was observed following injection moulding.
Comparison of the average fibre length, for a given manufacturing process and for various volume fractions, has shown that generally an increasing quantity of fibres results in a shorter average fibre length. Only Series 1 of the matrix-modified composites does not follow this trend. This phenomenon was also observed by Hill (3), who also showed that the fibre length distribution skews towards the shorter fibre lengths with an increasing fibre volume fraction.

### 5.2.1.4 Fibre Diameter Distribution

Figure 5.12 presents a cross-section of a mesh of fibres coated with Size 3. A considerable variation in diameter was observed. The range of values is extensive, the smallest and the largest fibre diameters being of 15.7μm and 21.9μm, respectively. An average diameter of 17.6μm (std 1.6μm) and 15.2μm (std 1.1) were measured for the fibres coated by the model sizes, and the commercial sized fibres, respectively.

### 5.2.1.5 Fibre Orientation Distribution

Fibre orientation was established for three injection moulded samples with short random fibre distributions. The fibre-volume fractions were 0.12, 0.14 and 0.3 respectively. Histograms of fibre orientation as a function of frequency of fibres of a given orientation and a photograph of the cross-section, for the specimens with fibre-volume fractions of 0.12 and 0.3, are shown in Figure 5.13. Three distinct zones were observed from the surface to the core of the specimen: for the sample with a fibre-volume fraction of 0.12 from the surface to a depth of approximately 0.4mm the fibres were randomly oriented, a band of parallel fibres, of approximately 3mm formed the second zone, and finally the central section consisted of randomly oriented fibres. The width of this final zone, measured from the centre of the specimen, was of about 2.6mm. Karger-Kocsis et al. (4) observed a similar structure in injection moulded poly(phenylene-sulphide) reinforced with either 30wt% glass fibres or 30wt% carbon fibres. He described the composite in terms of a natural laminate, consisting of two skin and one core layers of different thickness, and of different average fibre orientations.

From these results the Krenchel or orientation factor was calculated using the following equation:-
FIGURE 5.12: Cross section of a mesh of fibres
FIGURE 5.13: Histogram of fibre orientation as a function of frequency of fibres of a given orientation and the corresponding photograph of the cross-section.
where $\eta_0 = \text{Krenchel orientation factor}$

$\alpha_k = \text{fibre fraction oriented in angular increments away from the applied load}$

$\Theta_k$

The calculated Krenchel factor for the composites are given in Table 5.4.

<table>
<thead>
<tr>
<th>FIBRE VOLUME FRACTION</th>
<th>ORIENTATION FACTOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>0.64</td>
</tr>
<tr>
<td>0.14</td>
<td>0.64</td>
</tr>
<tr>
<td>0.30</td>
<td>0.80</td>
</tr>
</tbody>
</table>

TABLE 5.4: Orientation factor

5.2.1.6 X-Ray Diffraction

Typical graphs of intensity verses 20 for the PA66 and polypropylene samples are shown in Figures 5.14 and 5.15 respectively. A straight line was drawn, from A to B, to separate the intensity components above the line, which are proportional to the crystalline and amorphous scattering masses, from the intensity components below the line, which are background noise of incoherent, thermal and some amorphous scattering (5). The background noise, for the composite, includes both the non-proportional intensity components and the X-ray diffraction pattern of the glass fibres. A straight line cut-off remains appropriate as the X-ray diffraction pattern of E-glass fibres is linear, as shown in Figure 5.16. Hence the crystallinity values given for the composite are for the matrix material only.

a. Size Modification

Polymer/size alloys

The effect of the addition of a commercial size (Size B) or a matrix reactive polymer (Size A) to the structure of the PA66 matrix was assessed with X-ray diffraction. The peak positions and the crystallinities of the size alloys are tabulated in Table 5.5.
X-RAY DIFFRACTION

FIGURE 5.14: Typical X-ray diffraction pattern of PA66

FIGURE 5.15: Typical X-ray diffraction pattern of polypropylene

FIGURE 5.16: X-ray diffraction pattern of random glass fibres
TABLE 5.5.: Crystalline structure and crystallinity of the PA66 polymer alloys

(1) DSC measurement of the crystallinity of injection-moulded samples (measured at Vetrotex)
(2) DSC measurement of the crystallinity of the granules employed in the production of the injection-moulded samples (measured at Vetrotex)

The addition of the Size B in increasing quantities resulted in two distinct phenomena:

1) A peak observed at d=0.414nm or 2\(\theta\)=25.0°, the amplitude of which increased incrementally between B3% and B12%, as shown in Figure 5.17. As this peak was of a relatively low intensity for Size A (pure polyurethane), it can be concluded that the other constituents present in Size B play an important role in the formation of this particular reflection. The nature of these elements has not been disclosed by the size and glass manufacturer, Vetrotex.

2) The crystallinity of the polymer varied with the percentage addition of the size. The percentage variation of the crystallinity (with respect to the value measured for pure PA66) is presented as a function of the percentage addition of size in Figure 5.18. The polymer was analysed with a DSC apparatus before injection moulding and by DSC and X-ray diffraction after injection moulding. Although the values of crystallinity measured by X-ray diffraction were considerably greater than those evaluated with the DSC, the normalized variations were similar. Measurement of the crystallinity of the samples by X-ray diffraction hence can be effectively used as a crystallinity index, although this technique does not give a true value of the crystallinity due to the hypothetical nature of the parabola employed to define the form of the amorphous halo. A general increase in crystallinity was observed at low percentage additions of size. B12%, however, showed a marked decrease in crystallinity for both the X-ray diffraction analysis of the injection moulded samples and the DSC analysis of the polymer granules.
X-RAY DIFFRACTION

FIGURE 5.17: Comparison of the X-ray diffraction patterns of the matrix/size alloys

FIGURE 5.18: Percentage variation of the crystallinity of the matrix/size alloys as a function of the percentage addition of size.
Size-modified composites

The crystallinity of the polymer and composite are given in Table 5.6. All the values for the composite correspond to the matrix material only.

<table>
<thead>
<tr>
<th>CODE</th>
<th>FIBRE DISTRIBUTION</th>
<th>CRystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>AS-RECEIVED</td>
</tr>
<tr>
<td>POLYMER</td>
<td></td>
<td></td>
</tr>
<tr>
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<tr>
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<tr>
<td>SIZE 1</td>
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</tr>
<tr>
<td>SIZE 1</td>
<td>S.R.</td>
<td>68</td>
</tr>
<tr>
<td>SIZE 2</td>
<td>L.P.</td>
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<tr>
<td>SIZE 2</td>
<td>S.O.</td>
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<tr>
<td>SIZE 2</td>
<td>S.R.</td>
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<tr>
<td>SIZE 3</td>
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<tr>
<td>SIZE 3</td>
<td>S.O.</td>
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<td>SIZE 4</td>
<td>S.R.</td>
<td>73</td>
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**TABLE 5.6:** Crystallinity of the size-modified composites

Fibre distribution L.P. = long parallel fibres
S.O. = short oriented fibres
S.R. = short random fibre distribution

AS-RECEIVED = analysis of the sample before heat treatment, and after milling to produce a torsion pendulum test piece.

AFTER H.T. = analysis of the sample after heat treatment at 160°C for 9 minutes (this treatment was used to stabilize the crystallinity of the specimens)

These results show that the heat treatment generally produced an increase in the crystallinity of the samples. Before the heat treatment, and for a particular fibre distribution, the crystallinity of the matrix was approximately constant. The structure of the PA66 remained the same for a given fibre distribution, as indicated by the X-ray patterns of Figure 5.19. The PA66 polymer and all the composites with a unidirectional (L.P.) reinforcement exhibited strong peaks at \(2\theta = 24^\circ\) and \(28^\circ\).
FIGURE 5.19: Typical X-ray diffraction patterns for the PA66 matrix composites, of a given fibre distribution.
Both Kohan (6) and Cinquin (7) measured similar two peak structures, the position of the peaks, however, were at $2\theta=20^\circ$ and $24^\circ$. This displacement is related to the X-ray radiation source: cobalt, CoK$_{\alpha}$ ($\lambda=0.179$nm) was employed for the analysis of the size-modified composites, whereas copper CuK$_{\alpha}$ ($\lambda=0.154$nm) was used by Cinquin. The measured peak positions were recalculated for a Cu K$_{\alpha}$ source with:

$$\sin \theta_{\text{copper}} = \lambda_{\text{copper}} \sin \theta_{\text{cobalt}} / \lambda_{\text{cobalt}} \ [5.2]$$

where $n \lambda = 2d \sin \theta \ [5.3]$

and $n = \text{integer}$

- $\lambda = \text{X-ray wavelength}$
- $d = \text{interplanar spacing}$
- $\theta = \text{half angle of deviation of the diffracted rays from the incident X-rays}$

When changing the X-ray source and hence $\lambda$, only $\theta$ is a variable, therefore equation 5.3 can be simplified to equation 5.2. The recalculated values corresponded to those measured by Cinquin and were produced by the $\{100\}$ and $\{110\}$ reflections of the triclinic structure of PA66.

The structure of the short-oriented fibre and short random fibre reinforced composites were similar, but their diffraction patterns were not the same as those of the unidirectionally reinforced composites. A major difference between these systems is the method of fabrication: the long fibre composites were produced by compression moulding, whereas the short fibre composites were injection moulded. Processing therefore appears to have an effect on the structure.

b. Matrix Modification

X-ray diffraction analysis has shown the mixed nature of the structure of the polypropylene, i.e. monoclinic, $\alpha$ and hexagonal, $\beta$. A typical indexed pattern for the injection moulded polypropylene is shown in Figure 5.20. The prominent reflection at $d=0.55$nm is that of the $\{300\}$ plane of the hexagonal phase. The relative proportions of the monoclinic and hexagonal polymorphs are given by the $K'$-values in Table 5.7. As the $K'$-value tends to 0 the crystalline phase is of the $\alpha$, monoclinic form. A $K'$-value of 1 results from a purely hexagonal or $\beta$ crystalline structure. The X-ray diffraction results of crystallinity, for the polypropylene matrix samples, are also summarized in Table 5.7.
FIGURE 5.20: Typical indexed X-ray diffraction pattern for the injection moulded polypropylene.
The crystallinity values given for the composite refer to the matrix only, as for the PA66 composites.

<table>
<thead>
<tr>
<th>CODE</th>
<th>CRystallinity (%)</th>
<th>k'-Value</th>
<th>Melt Flow INDEX (g/10min) die=0.1181cm (3)</th>
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<tr>
<td><strong>SERIES 1</strong></td>
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<tr>
<td>POLYMER</td>
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</tr>
<tr>
<td>MA000</td>
<td>67 (44.8)</td>
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<td>62 (48.5)</td>
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</tr>
<tr>
<td>MA01</td>
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</tr>
<tr>
<td>MA02</td>
<td>59 (51)</td>
<td>5.80</td>
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</tr>
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<td>MA101</td>
<td>56 (42.9)</td>
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<td>60 (34.2)</td>
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<td>BT05F</td>
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TABLE 5.7: X-ray diffraction results for the matrix-modified system
( ) Crystallinity measured with a DSC apparatus (temperature range from 30 to 300°C with a heating rate of 10°C/min) -
1. Measured at Ecole des Mines
2. Measured at Institut Français de Petrole
3. Measured at Aston University
----- Peak at d=0.55nm not observed, therefore the sample is assumed to be of the monoclinic crystalline form only.

To facilitate analysis, the results have been grouped under appropriate headings and are presented in the form of histograms.

i. Polymer

**Effect of processing conditions**

Processing appeared to increase the relative quantity of the monoclinic phase (indicated by a decrease in the K'-value), although this phenomenon was limited after injection moulding, as shown in Figure 5.21. A hexagonal to monoclinic phase transformation therefore occurred during the manufacture of these specimens. The crystallinity varied between these samples with the minimum value of 63% evaluated for a processed (Buss-Ko kneader) injection moulded sample and the maximum of 71% for an unprocessed injection moulded specimen.

**Effect of the addition of a free radical initiator**

Figure 5.22 is a histogram showing the effect of the addition of a free radical initiator (I) on the crystallinity and K'-value of processed polypropylene. The crystallinity remained relatively constant, varying from 59% to 64%. Examination of the K'-value revealed a decrease in the proportion of the hexagonal phase on the addition of the peroxide, for both the compression moulded and injection moulded (Buss-Ko kneader) samples. Twin-screw extruder processed specimens only exhibited the monoclinic
CRYSTALLINITY (%)

X-RAY DIFFRACTION

COMPRESSION MOULDED SAMPLES
1. Unprocessed PP
2. Processed PP - internal mixer

INJECTION MOULDED SAMPLES
3. Unprocessed PP
4. Processed PP - Buss-Ko Kneader (MA00)
5. Processed PP - Twin Screw Extruder (BT00)

FIGURE 5.21: Effect of processing conditions on the crystallinity and the $K'$-value of polypropylene.
FIGURE 5.22: Effect of the addition of a free radical initiator on the crystallinity and the K'-value of polypropylene.
FIGURE 5.23: Effect of chemical modification on the crystallinity and the K'-value of polypropylene.
crystalline phase. A peroxide addition also resulted in an increase in the melt flow index (MFI), which indicates a decrease in molecular weight, Mw, as:

\[ M_w = MFI^{-1/\alpha} \cdot K \]  [5.4]

where \( \alpha \) and \( K \) = Mark-Houwink constants (which are characteristic for a given polymer system) (8)

Effect of chemical modification - the MA system

The addition of the maleic anhydride modifying agent (MA) to polypropylene provoked an increase in crystallinity and a decrease in \( K' \)-value (Figure 5.23). As described in the previous section, a peroxide addition (I) induced significant decreases in both the crystallinity and the proportion of the hexagonal phase. The combination of these chemical modifiers in the MA101 specimen (PP + MA + I) produced a behaviour similar to that of the peroxide modified sample (MA02). The \( K' \)-value remained low when the additional functional monomer was added to the system (MA103), but the crystallinity increased with respect to the other polypropylene samples modified in the presence of a peroxide.

ii. Composite

A comparison of the crystallinities of the polymer and the matrix of the composites revealed that the presence of the reinforcement generally produced an increase in crystallinity.

5.2.2 MICROSTRUCTURAL CHARACTERIZATION

Microstructural characterization of E-glass fibre reinforced thermoplastics has proved to be complicated, due to the insulating nature of the material, the very different intrinsic properties of the glass and the polymer, and the small diameter of the fibres. However, by employing the combination of techniques described in Section 4.2.2, a complete microstructural analysis of the specimen was possible. Emphasis was placed on the fibre/matrix interface, as this zone has been successfully examined. Fibre/matrix interphase analysis remains very difficult.
Surface Characterization

The physical aspect of the size coating the fibres was established with two methods: field emission gun scanning electron microscopy (FEGSEM) and X-ray photoelectron spectroscopy (XPS).

5.2.2.1 Field Emission Gun Scanning Electron Microscopy

FEGSEM and SEM micrographs of Size 3 (polyurethane + A1100 + Ti marker) are shown in Figure 5.24. The comparison of these photographs highlights the utility of the FEGSEM technique in surface coating studies, the size being highly contrasted on the glass fibre, due to the relatively low penetration depth of the electron beam (as described in Section 4.2.2.1). The fibres examined were coated with approximately 0.7 wt% for the model sizes and 1 wt% for the commercial size (Table 5.2). Hence the variations described in the following section are related to the nature rather than the quantity of size.

a. Size Modification

i. Size 1 (A1100 + Epoxy + Ti marker)

Micrographs of Size 1 are shown in Figure 5.25. The size layer appears to form a continuous coating on the fibres, punctuated by a random distribution of deposits, below the surface of the size. Interfibre adhesion is observed in Figure 5.25b.

ii. Size 2 (A1100 + Polypropylene)

The FEGSEM micrographs in Figure 5.26 show the uneven, but apparently continuous coating produced by Size 2.

iii. Size 3 (A1100 + Polyurethane)

The FEGSEM photographs in Figure 5.27 show that the size can be characterized by two types of size deposit. The first is an even distribution of quasi-circular islands of size, which vary between 350 nm and 1740 nm in diameter. The second is a random distribution of larger (up to 0.11 mm in length) polymer plaques. The area between these features is apparently size-free.
FIELD EMISSION GUN SCANNING ELECTRON MICROSCOPY

FIGURE 5.24: Comparison of the FEGSEM and SEM micrographs of Size 3.

FEGSEM micrograph of Size 3 (polyurethane + A1100)

Scanning electron microscopy micrograph of Size 3 (polyurethane + A1100)

FIGURE 5.24: Comparison of the FEGSEM and SEM micrographs of Size 3.
FIGURE 5.25: FEGSEM micrographs of Size 1 (epoxy + A1100 + Ti) showing a continuous layer of size on the fibres and precipitates below the surface of the polymer.
FIGURE 5.26: FEGSEM micrographs of Size 2 (polypropylene + A1100) showing a continuous layer of size, of a non-uniform depth.
FIGURE 5.27: FEGSEM micrographs of Size 3 (polyurethane + Al 100) showing two types of size deposit: circular islands of size and larger polymer plaques.
Islands of size

**FIGURE 5.28:** FEGSEM micrographs of Size 4 (polyurethane) showing a random distribution of size deposits
Extensive interfibre adhesion

FIGURE 5.29: FEGSEM micrographs of the commercial size, A1100, showing a continuous size layer.
iv. Size 4 (Polyurethane+Ti marker)

Both the shape and the distribution of the zones of this size were random (Figure 5.28). However, limited regions exhibited the island structure previously observed for Size 3.

b. Matrix Modification

i. Commercial size (Union Carbide)

Figure 5.29 exhibits the FEGSEM micrographs of the commercially sized glass fibres, employed to reinforce the matrix-modified composites. The fibres appeared to be coated with a relatively even, continuous layer of size. Extensive interfibre adhesion was observed, with zones of size of up to 10 μm thick measured between adjacent fibres.

5.2.2.2 X-Ray Photoelectron Spectroscopy

Survey spectra, for the size coated fibres and the corresponding size films (the latter for the size modified systems only) are presented in Figures 5.31 to 5.41. High resolution spectra were used to give the peak positions for each element. Errors in the peak positions may result from the spectrometer calibration and electrostatic charging of the specimen. The former is overcome by calibration of the spectrometer against standard values for copper and gold. The latter is resolved by making use of the chemical shift on both the Auger and photoelectron peak in the XPS spectrum. The separation of the peaks or the Auger parameter, \( \alpha \), gives a value independent of electrostatic charging (9). The silicon Auger parameter was calculated for all the specimens with:

\[
\alpha = E_B + E_K - h\nu \quad [5.5]
\]

where

- \( E_B \) = binding energy of the photoelectron peak
- \( E_K \) = kinetic energy of the Auger transition
- \( h = \) Planck's constant
- \( \nu = \) frequency
- \( h\nu = \) photon energy = 1486.6eV
Briggs and Seah (10) evaluated a modified Auger parameter with:

\[ \alpha^* = E_B + E_K \] {5.6}

as the photon energy is a constant. Equation 5.6 was therefore employed to facilitate comparison of the measured values with those published. The uncorrected binding energies are given for the positions of the peaks, which were subject to electrostatic charging. This phenomenon results in a shift of the peaks to higher eV values.

A further spectrum of a clean glass slide has been obtained to facilitate the analysis of these results. This spectrum is given in Figure 5.30.

**Glass slide**

E-glass was characterized by Si2p (108.20eV), Si2s (at approximately 149eV), Ca2p (at approximately 350eV), O1s (537.60eV) and Na 1s (1077.00eV), as shown in Figure 5.30. Additionally low intensity Cl2p and N1s peaks were detected. The former can be assumed to be due to the water layer which forms readily at the glass surface as described in Section 2.2.3. The latter peak may be due to the presence of air, perhaps dissolved in the water layer on the fibre surface. The silicon Auger peak was measured at 1603.15eV, giving a silicon Auger parameter of 1711.35eV. Soda glass and SiO2 have silicon Auger parameters of 1711.67eV and 1712.0eV respectively.

A carbon/oxygen ratio (C/O) of 0.43 was evaluated for the slide.

**a. Size Modification**

i. Size 1 (A1100 + Epoxy + Ti marker)

**Fibres**

A carbon 1s peak (C1s) of high intensity dominates the XPS survey spectrum of this particular size (Figure 5.31). Carbon is present in both elements of the coating, i.e. the epoxy and the A1100 silane coupling agent, but is not found in the glass. Hence the intensities of the high resolution oxygen and carbon peaks can be used to quantify the proportions of the glass and the size, assuming that carbon contamination is minimal.
FIGURE 5.30: Survey spectrum of a clean glass slide
X-RAY PHOTOELECTRON SPECTROSCOPY

UNIV OF SURREY SURFACE ANALYSIS LAB XPS - Spectrum V.G.Scientific
SBON003.XPS Region 1 / 7 Level 1 / 1 Point 1 / 1

**Survey spectrum**

---

**UNIV OF SURREY SURFACE ANALYSIS LAB Peak Synthesis V.G.Scientific**
SBON003.XPS Region 2 / 7 Level 1 / 1 Point 1 / 1

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<th>G/L %</th>
<th>Area %</th>
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<td></td>
<td>287.0</td>
<td>1.85</td>
<td>94</td>
<td>30</td>
<td>65</td>
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<tr>
<td></td>
<td>288.6</td>
<td>1.85</td>
<td>42</td>
<td>30</td>
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<tr>
<td></td>
<td>290.0</td>
<td>1.85</td>
<td>8</td>
<td>30</td>
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</table>

100% Height (Counts) : 20503
100% Area (keV/sec) : 57.01
Reduced Chi Squared : 65.29

---

Peak fitting of the C1s peak

**FIGURE 5.31:** Size 1 (epoxy + A1100 + Ti) coating on E-glass fibres
This hypothesis is reasonable as the sized-fibres present low energy surfaces which are not conducive to this artefact, and is confirmed by the relatively low value of the C/O ratio of the glass slide, compared to that measured for the sized fibres. The C/O ratio of Size 1 was 3.86. Low intensity peaks were observed for silicon (Si2p and Si2s), calcium (Ca2p), nitrogen (N1s) and sodium (Na Auger). Comparison of the Si2p peak position (105.0eV) with that of the clean glass slide (108.20eV) shows a shift to lower energy values. However, the silicon Auger parameter was evaluated as 1711.54eV which is similar to that of the glass slide. Examination of the published values (11) shows very small variations in the silicon Auger parameter between different types of bonding, hence although it was difficult to assign a particular bond type to Size 1, it was assumed that the parameter was due to Si bonding within the size rather than the glass. This assumption was supported by the FEGSEM micrographs of the Size 1 coated fibres, as an apparently continuous layer of polymer was observed on the surface of the glass (Figure 5.25). Therefore, from this result and the low intensities of the Ca 2p and Na Auger peaks (which are characteristic of the glass), it can be concluded that the glass of the fibre is almost completely covered by the size. In a similar manner the low intensity of the N1s peak is indicative of a silane layer buried beneath the epoxy, as nitrogen is only found in the A1100 coupling agent.

Peak fitting of the C 1s peak was used to ascertain the bonding within the sample. Three peaks noted at 287.0, 288.6 and 290.0 eV were attributed to C-H, C-O and C=O bonding respectively. Beamson and Briggs (11) measured primary C1s chemical shifts (eV) relative to a saturated hydrocarbon which is generally considered to have a binding energy of 285eV. They assigned a mean chemical shift of 1.5eV for C-O bonding and 2.90eV for C=O bonding which corroborates the measured results. The energy shift of 2eV, with respect to the published values, can be attributed to electrostatic charging.

Film

Epoxy

Intense C1s and O1s peaks were detected at 287.5eV and 535.6eV respectively, for the pure epoxy film, the C/O ratio of which is 4.22 (Figure 5.32). Peak fitting of the C1s revealed two peaks with their centres at 287.3 and 289.2 eV respectively. The former peak indicates C-H or C-C bonding and the latter the epoxy group, both of which are characteristic of an epoxy.
X-RAY PHOTOELECTRON SPECTROSCOPY

Univ of Surrey Surface Analysis Lab XPS - Spectrum V.G. Scientific
SBON100.XPS Region 1 / 7 Level 1 / 1 Point 1 / 1

Survey spectrum

Survey spectrum

Peak fitting of the C1s peak

FIGURE 5.32: Size 1 - Epoxy model film.
The high intensity C1s and O1s peaks observed for this film gave a C/O ratio of 3.91 (Figure 5.33). This value was intermediate between the C/O values measured for the Size 1 coated fibres and the pure epoxy film. In a similar manner to the epoxy film the deconvolution of the high resolution C1s peak gave rise to two peaks at 287.6 and 289.5 eV. Silicon from the silane coupling agent was not observed, which was a surprising result, as the A1100 was added in a high proportion (50%) to the epoxy. The relative proportions of the A1100 and epoxy on the E-glass fibres were 0.3% and 4.8% respectively.

ii. Size 2 (A1100 + Polypropylene)

Fibres

The XPS spectra for the polypropylene-based size are shown in Figure 5.34. The prominent C1s peak at 287.6 eV is attributed to the diphatic C-C/C-H bonding of the hydrocarbon thermoplastic. Satisfactory peak fitting of the C1s peak was not achieved, perhaps due to differential charging of the specimen. As for the Size 1 coated glass fibres, the C1s peak was of a great intensity, with a C/O ratio of 4.65. This result, in conjunction with the low intensities of the calcium and sodium peaks, again indicates that little or no glass was exposed. As the N 1s peak was absent, the silane was also considered as a buried layer, beneath a polypropylene overlayer. The hypothesis that the polypropylene completely covers the other elements (A1100 and glass) is supported by the positive slope of the background after the O 1s peak. This result is indicative of the inelastic scattering of buried near-surface oxygen, which is present in the glass, and, at a lower concentration, in the silane. The silicon Auger peak was 1711.83 eV, which is similar to the value given for a poly-dimethyl-silicone (1711.78).

Film

Polypropylene

The C/O ratio was very high (5.92) for the pure polypropylene film, exceeding that measured for the size coated fibres. Additional peaks were detected (Figure 5.35),
X-RAY PHOTOELECTRON SPECTROSCOPY

SURVEY spectrum

Peak fitting of the C1s peak

**FIGURE 5.33:** Size 1 - Epoxy + 50%A1100 model film.
FIGURE 5.34: Survey spectrum of Size 2 (polypropylene + A1100) coating on E-glass fibres
X-RAY PHOTOELECTRON SPECTROSCOPY

UNIV OF SURREY SURFACE ANALYSIS LAB XPS - Spectrum V.G.Scientific
SBON102.XPS Region 1 / 7 Level 1 / 1 Point 1 / 1

Radiation
Mg Kalpha
Max Count Rate 143596 CPS
Analyser 50 eV
Step Size 1.00 eV
Dwell Time 200 ms
No of Channels 1201
No of Scans 2
Time for Region 480 Sec
Acquired 17:48 24-Jun-92
Plotted 23:19 23-Jun-92

Survey spectrum

UNIV OF SURREY SURFACE ANALYSIS LAB Peak Synthesis V.G.Scientific
SBON102.XPS Region 2 / 7 Level 1 / 1 Point 1 / 1

Peak Centre F W H M Hght G/L Area
(eV) (eV) % % %
288.4 1.85 102 30 79
290.4 1.85 26 30 21

100% Height (Counts) : 47930
100% Area (kceV/sec) : 84.45
Reduced Chi Squared : 183.30

Peak fitting of the C1s peak

FIGURE 5.35: Size 2 - Polypropylene model film
including potassium K2p and K2s, as well as fluorine peaks (F Auger and F1s). These peaks are considered to result from the contamination of the polypropylene by the Teflon sheets used during fabrication. The oxygen present in the polypropylene was also due to PTFE contamination. C-H/C-C and C-O bonding in the film were ascertained by peak fitting.

Polypropylene + 50%A1100 (Figure 5.36)

The C/O ratio of 4.36 evaluated for the polypropylene/A1100 film was less than the values measured for the pure polypropylene film and the Size 2 coated fibres. Peaks for this size, Si 2p, Si 2s and N1s at 106.11, approximately 149eV and 403.00 eV respectively, were due to the A1100 coupling agent. Flourine contamination was greater than for the pure polypropylene film, as indicated by the intensity of the F1s and F Auger peaks, and by the peak fitting of the C1s peak, where fluorinated carbon peaks were measured. Four singlets were detected with their centres at 288.6, 290.3, 296.5 and 299.3eV. The latter two positions were attributed to C-F2 and C-F3 bonding.

iii. Size 3 (A1100 + Polyurethane)

Fibres

The XPS spectrum for Size 3 on E-glass fibres is shown in Figure 5.37. The C1s and the N1s peaks, at the uncorrected binding energies of 288.7eV and 403.8eV respectively, are due to the presence of the polyurethane/A1100 mixture on the surface of the fibres. The Si2p, Ca2p and sodium Auger peaks are characteristic of the E-glass (which contains approximately 52 - 56% SiO2, 16 - 25% CaO and 0 - 1% NaO, as well as other trace elements as described in Section 2.2.1). Unlike the previous two cases, it is the O1s peak which dominates this spectrum, as indicated by the relatively low C/O ratio of 1.25. The high intensity of this peak and the background slope, being negative, indicate that a considerable quantity of surface oxygen was present. The silicon Auger parameter measured was 1711.82, which is analogue to that of Size 2 on the E-glass fibres.

Four singlets were required for peak fitting, from which C-H, C-C, C=O and C=O bonding were established, although peak fitting proved difficult.
Peak fitting of the C1s peak

**FIGURE 5.36:** Size 2 - Polypropylene + 50% A1100 model film.
X-RAY PHOTOELECTRON SPECTROSCOPY

UNIV OF SURREY SURFACE ANALYSIS LAB XPS - Spectrum V.G.Scientific
SBON005.XPS Region 1 / 7 Level 1 / 1 Point 1 / 1

Survey spectrum

UNIV OF SURREY SURFACE ANALYSIS LAB Peak Synthesis V.G.Scientific
SBON005.XPS Region 2 / 7 Level 1 / 1 Point 1 / 1

Peak fitting of the C1s peak

FIGURE 5.37: Size 3 (polyurethane + A1100 + Ti) coating on E-glass fibres
Film

Polyurethane + 10% A1100

Figure 5.38 presents the XPS spectrum of the polyurethane/A1100 size film. A C/O ratio of 2.92 was evaluated for this specimen. Si 2p (105.95 eV), Si 2s and N 1s (403.97 eV) peaks, characteristic of the A1100/polyurethane mixture, were measured. Considerable fluorine contamination was observed with a relatively high intensity F1s peak at 692.85 eV, as for the polypropylene/A1100 mixture. Peak fitting revealed CF$_2$ and CF$_3$ as well as C-H and C-O bonds.

iv. Size 4 (Polyurethane + Ti marker)

Fibres

The urethane group [-HN-C=O-] can be characterized by carbon, oxygen and nitrogen. Peaks due to these elements were observed for the polyurethane coated glass fibres, as shown in Figure 5.39. Additionally Si2p and Si2s peaks were measured, which can be attributed to the glass as this was the only constituent of the specimen containing silicon atoms. A silicon Auger parameter of 1711.62 was evaluated, which approaches the published value for soda glass (1711.67). The C/O ratio for the Size 4 coated fibres was 1.23.

As for Size 1, the bonding in the polymer size layer was not established by peak fitting the C1s peak due to differential charging of the specimen.

Film

Figure 5.40 presents the XPS spectrum of the pure polyurethane film. Peaks characteristic of the polyurethane (C1s, N1s and O1s) as well as Teflon contamination (F Auger and F1s) were observed. The presence of low intensity Si2p (106.5 eV) and Si2s peaks indicated possible contamination of the polyurethane by the A1100 coupling agent. A C/O ratio of 3.70 was evaluated which is much higher than the value measured for the size coated fibres.
**X-RAY PHOTOELECTRON SPECTROSCOPY**

UNIV OF SURREY SURFACE ANALYSIS LAB XPS - Spectrum V.G.Scientific

SBON105.XPS Region 1 / 7 Level 1 / 1 Point 1 / 1

---

**Survey spectrum**

**Peak fitting of the C1s peak**

FIGURE 5.38: Size 3 - Polyurethane + 10%A1100 model film
FIGURE 5.39: Survey spectrum of Size 4 (polyurethane + Ti) coating on E-glass fibres
Peak fitting of the C1s peak

FIGURE 5.40: Size 4 - Polyurethane model film.
**X-RAY PHOTOELECTRON SPECTROSCOPY**

UNIV OF SURREY SURFACE ANALYSIS LAB  
XPS - Spectrum  
V.G. Scientific

SBON404.XPS  
Region 1 / 6  
Level 1 / 1  
Point 1 / 1

---

Survey spectrum

---

Radiation  
Al Kalpha  
Max Count Rate  
35135 CPS  
Analyser  
50 eV  
Step Size  
1.00 eV  
Dwell Time  
200 ms  
No of Channels  
1101  
No of Scans  
1  
Time for Region  
220 Sec  
Acquired  
09: 49 23-Dec-92  
Plotted  
09: 57 23-Dec-92

---

Peak fitting of the C1s peak

**FIGURE 5.41:** Commercial size, A1100, coating on E-glass fibres
Three singlets were necessary to achieve a satisfactory peak fit of the C1s peak. The centre of the peaks were at 288.6, 290.1 and 292.8 eV, as shown in Figure 5.40. C-H, C-O and C=O bonding were attributed to this size.

b. Matrix Modification

i. Commercial size (Union Carbide)

The XPS survey spectrum of the commercial size showed intense C1s and O1s peaks with additional low intensity Si2p, Si2s and N1s peaks (Figure 5.41). The elemental peaks characteristic of the A1100 employed in the model sizes were all detected for the commercial size. The C/O ratio was 4.61, which is relatively high, as was the case for Sizes 1 and 2, with which almost complete coverage of the glass fibres was achieved. This hypothesis was confirmed by the lack of the calcium and sodium peaks, which are characteristic of the E-glass. The silicon Auger parameter was 1711.7. The C1s peak comprises three singlets at 288.0, 289.5 and 291.1 eV, although the latter was of a very low intensity, indicating C-H, C-O and C=O bonding.

Bulk Characterization

In order to better understand the bulk structure of the size on the fibres glancing X-ray diffraction analysis has been employed.

5.2.2.3 Glancing X-ray Diffraction

Figure 5.42 compares X-ray diffraction patterns of Size 2 coated glass fibres, measured with the classic and glancing X-ray diffraction techniques. Additional peaks were observed for the latter spectrum which can be attributed to the size itself. An incident X-ray angle of 10° was employed as a further reduction of this angle to 5° produced no significant additional information on the structure of the size. A peak shift to lower "d" values and a peak broadening however, was obtained, as shown in Figure 5.43. A disadvantage of very small incident angles was that not only the specimen was analysed, but also the surrounding support.
FIGURE 5.42: X-ray diffraction patterns of Size 2, measured with the classic and glancing X-ray diffraction techniques.

FIGURE 5.43: Comparison of glancing X-ray diffraction patterns with an incident X-ray angle of 10° and 5°.
a. Size Modification

i. Size 1 (A1100 + Epoxy + Ti marker)

Fibres

Figure 5.44 presents the X-ray diffraction pattern of the epoxy/A1100 coated fibres. A broad peak was observed at $2\theta=25.65^\circ$, or $d=0.403\text{nm}$. From this result it can be seen that Size 1 has an amorphous structure.

Film

Epoxy

Pure epoxy, in film form, has an amorphous structure as shown in Figure 5.45. A broad peak was observed at $d=0.447\text{nm}$, with a very small inflection of the diffraction pattern at $d=0.217\text{nm}$. The breadth of the peak prevented its attribution to a particular reflection, however, the strongest reflections of organic materials tend to be situated in a similar $2\theta$ range.

Epoxy + 50%A1100

A similar diffraction pattern to that of the unmodified epoxy was detected for this film. Nevertheless the A1100 addition produced a reduction in the intensity of the peaks (Figure 5.46).

A comparison of the Size 1 X-ray diffraction patterns in Figure 5.47 shows that the structure of the polymer films is similar to that of the size coating on the E-glass fibres.

ii. Size 2 (A1100 + Polypropylene)

Fibres

The X-ray diffraction pattern of Figure 5.48 presents several crystalline peaks superimposed on the amorphous diffraction pattern of the glass. The
FIGURE 5.44: Size 1 (epoxy + A1100 + Ti) coating on E-glass fibres

FIGURE 5.45: Size 1 - Epoxy model film
FIGURE 5.46: Size 1 - Epoxy + 50%A1100 model film

FIGURE 5.47: Comparison of the Size 1 diffraction patterns for the fibre coating and the model films.
polypropylene/A1100 size coating on the fibres therefore has a semicrystalline structure.

Film

Polypropylene

The polypropylene film has a semi-crystalline structure, as shown in Figure 5.49, with high intensity peaks at the same peak positions as those measured for the bulk injection moulded polypropylene (from the matrix modification system). A monoclinic structure was hence deduced for the size film.

Polypropylene + 50%A1100

The addition of the silane coupling agent to the polypropylene reduces the intensity and the number of peaks observed. The peak positions were shifted to lower "d" values. However, this film remains highly crystalline, as shown in Figure 5.50.

Figure 5.51 compares the X-ray diffraction patterns of Size 2 both as a coating on the glass fibres and in film form, neither of which contain the titanium marker. The position and the intensities of the peaks of the size films were not the same as those of the size on the fibres, which leads to the conclusion that the size films are not truly representative of the sized fibres.

iii. Size 3 (A1100 + Polyurethane)

Fibres

The polyurethane/A1100 size coating on the E-glass fibres has an amorphous structure and exhibits a diffraction pattern similar to that of the glass (Figure 5.52).

Film

Polyurethane + 10% A1100

Figure 5.53 shows that the polyurethane/A1100 mixture, as a film, has a semi-crystalline structure with high intensity peaks at $\theta = 25.04$, 25.77 and 27.74°
GLANCING X-RAY DIFFRACTION

FIGURE 5.48: Size 2 (polypropylene + A1100) coating on E-glass fibres

FIGURE 5.49: Size 2 - Polypropylene model film
GLANCING X-RAY DIFFRACTION

FIGURE 5.50: Size 2 - Polypropylene + 50%A1100 model film.

FIGURE 5.51: Comparison of the Size 2 diffraction patterns for the fibre coating and the model films.
FIGURE 5.52: Size 3 (polyurethane + A1100 + Ti) coating on E-glass fibres

FIGURE 5.53: Size 3 - Polyurethane + 10% A1100 model film
FIGURE 5.54: Size 4 (polyurethane + Ti) coating on E-glass fibres

FIGURE 5.55: Size 4 - Polyurethane model film
GLANCING X-RAY DIFFRACTION

FIGURE 5.56: Comparison of the X-ray diffraction patterns of Sizes 3 and 4, both as a fibre coating and in film form.

FIGURE 5.57: Commercial size, A1100, coating on E-glass fibres.
iv. Size 4 (Polyurethane + Ti marker)

**Fibres**

The polyurethane size coating exhibited two crystalline peaks on an amorphous background, as shown in Figure 5.54. The position of the first of these peaks corresponds to the high intensity reflection detected at $\theta = 25.04^\circ$ for the Size 3 polymer film. The second peak also corresponds to a reflection, of low intensity, previously measured for the Size 3 film.

**Film**

Polyurethane

Polyurethane, in film form, is partially crystalline as indicated by the peaks of its diffraction pattern (Figure 5.55). Comparison of Size 3 and Size 4 shows that the addition of A1100 to the matrix reactive polymer results in a baseline shift and a decrease of peak intensity. In a similar manner to the polypropylene based films the A1100 also produced a shift of the peaks to lower "d" values.

Further comparison of the X-ray diffraction patterns for Size 3 and Size 4 (Figure 5.56), as both a fibre coating and in film form, revealed a considerable difference in the structure between the specimen types.

**b. Matrix modification**

i. Commercial size (Union Carbide)

**Fibres**

Figure 5.57 shows the amorphous nature of this size. A broad peak was measured at $\theta =29.72^\circ$ or $d=0.349\text{nm}$.

**Localized Structural Characterization**

Having established the macroscopic characteristics of the polymer coating on the fibres a finer analysis produced information on the localized structure of the size.
5.2.2.4 Transmission Electron Microscopy

Observation of the size/fibre interface, and the size itself, has been particularly successful. Samples fabricated with the technique described in Section 4.2.2.4 had areas of suitably thinned interfacial material without any apparent size polymer degradation. The protection of the size coating, by shading with the adjacent fibres hence allowed the depth of the size, and the uniformity of the layer to be established with considerable accuracy.

Controlled degradation created with the focussed electron beam during observation with the TEM, can also be employed to highlight the fibre/size interface, as shown in Figure 5.58. Oxygen, liberated by the radiolisation of the dangling Si-O bonds, which are present in the interfacial zone, form bubbles, which appear in a line at the edge of the size at the interface.

a. Size Modification

i. Size 1 (A1100 + Epoxy +Ti marker)

Figure 5.59 shows Size 1 on an E-glass fibre. The layers of differing contrast observed correspond to the fibre and the size as indicated by the diffraction patterns of these areas. The diffraction pattern of the glass was characteristic of all the fibres, regardless of the type of polymer coating. The halo observed at 0.31nm is characteristic of the distance between the closest silicon atoms of the SiO₄ tetrahedron, which can be considered as the unit cell of glass. It can be seen that this layer is amorphous and is of a non-uniform depth. A maximum thickness of 900nm was measured. Precipitates of approximately 25nm in diameter were present within the size. Twinning of the precipitates occurred under the effect of the electron beam, as shown in Figure 5.60. The indexed diffraction pattern (Figure 5.61) shows diffraction spots at 0.34nm. This distance is characteristic of the numerous derivatives of TiO₂, with the formula TiₙO₂ₙ₋₁, which are obtained by the periodic shearing of the octahedral structure. These precipitates were titanium oxide which was added as a marker to the model sizes. Additional halos were observed at 0.201nm {1 1 1} and 0.181nm {2 0 0} which correspond to the copper of the ring support. When ion milling a low ion beam angle was employed to prevent the damage of the size, but which also eroded the copper support. Copper from the ring was redeposited on the specimen as microcrystals. Figure 5.61 shows the diffraction pattern of the microcrystalline copper.
FIGURE 5.58: The size/fibre interface highlighted by bubbles, produced by the controlled degradation of the polymer of the size with the focussed electron beam.
Size 1 coating of an amorphous nature and a non uniform depth.

FIGURE 5.59: Size 1 (epoxy + A1100 + Ti) coating on an E-glass fibre.
FIGURE 5.60: Twinning of the titanium oxide precipitates under the effect of the electron beam.

Diffraction pattern of the titanium precipitates

Diffraction pattern of the microcrystalline copper.

FIGURE 5.61: Diffraction patterns of the titanium oxide precipitates and of the microcrystalline copper.
ii. Size 2 (Al100 + Polypropylene)

The polypropylene size has a semi-crystalline structure, as seen in Figure 5.62. The thickness of the size varied, with a minimum depth of 150nm. A few large crystallites were observed, surrounded by an array of smaller crystals. The diffraction pattern of this zone indicated that two crystalline materials were present, the copper from the ring support and two additional rings due to the semicrystalline structure of the polypropylene.

iii. Size 3 (Al100 + Polyurethane)

The fibre/size interface is clearly distinguished in Figure 5.63. The size layer is of a uniform thickness, but the thickness varies from one fibre to another as observed in Figure 5.63b. A maximum thickness of 300nm was measured in the observed zones. Examination of the size in greater detail revealed a stratum structure with two superimposed layers of differing contrast, as shown in Figure 5.64. The Al100/polyurethane mixture formed an amorphous coating on the E-glass fibres.

iv. Size 4 (Polyurethane + Ti marker)

Size 4 formed an amorphous layer on the glass fibres with clusters of precipitates creating variation in the thickness of the coating (Figure 5.64). The observed variation may be attributed to differences in the thinning rate of the polymer and the precipitates, the latter being more resistant to the ion milling process. The maximum depth measured was 500nm. In a similar manner to Size 1, the precipitates were identified as titanium oxide by employing the diffraction pattern of this zone. Copper was also detected from the diffraction pattern and was observed as fine microcrystals in the size, as shown in Figure 5.64b.

b. Matrix Modification

i. Commercial size (Union Carbide)

The commercial size has an amorphous structure, as shown in Figure 5.66. A uniform layer of a thickness of 395nm was observed.
FIGURE 5.62: Size 2 (polypropylene + A1100) coating on an E-glass fibre. The size has a semi-crystalline structure.
FIGURE 5.63: Size 3 (polyurethane + A1100) coating on an E-glass fibre. T.E.M. micrographs of the fibre/size interface, showing the amorphous nature of this size and its uniform thickness on a given fibre.

FIGURE 5.64: Size 3 (polyurethane + A1100) coating on an E-glass fibre. T.E.M. micrograph showing the stratum structure of the size.
FIGURE 5.65 Size 4 (polyurethane) coating on an E-glass fibre, with clusters of precipitates creating variations in the thickness of the polymer layer.

FIGURE 5.65b: Size 4 (polyurethane) coating on an E-glass fibre, showing fine microcrystals of copper.
FIGURE 5.66: Commercial size, A1100, coating on an E-glass fibre. The size has an amorphous structure.
Composite thin foil fabrication is difficult due to the different thinning rates of the matrix and the reinforcement. Various techniques were examined, as follows:

Ion milling of a bulk, thermoplastic composite resulted in the rapid pulverisation of the polymer, leaving the glass fibres unaffected. The glass/size/matrix interphase was destroyed. In order to reduce the ion milling period and hence overcome the differences in erosion rates, the composite was prethinned by mechanical polishing. Concave milling was employed to form a disc specimen with its centre and edges of 10 and 100μm respectively, the latter facilitating handling of the specimen. Preparation by mechanical polishing was found to damage the interfacial region, as the diamond paste became clogged in this zone. Thinning was completed by ion milling at cryogenic temperatures, as described in Section 4.2.2.4. Observation of the samples produced in this manner, with a SEM, reveals the topological artefacts created by the abrasion of the polymer by the ion beam. (Figure 5.67). The polymer surface is no longer flat, but is in the form of waves. Microprobe analysis of this region showed that prolonged ion milling was not only responsible for the non-uniformity of the polymers surface, but also produced chemical effects. Silicon from the fibre was redeposited on the areas in relief as shown by the comparison of the SEM photograph and the X-ray map of Figure 5.68.

Further reduction of the ion milling time was hence necessary to produce composite thin foils, without polymer degradation. Hydrofluoric acid was employed to partially dissolve the glass fibres. However this technique proved unsuccessful, as the glass fibres were reduced to a powdery consistancy, rendering the sample unsuitable for ion milling.

A polypropylene composite sample was fabricated from a "flashing", a very thin section (of less than 100μm) of composite squeezed from the mould during injection moulding. This sample was directly ion milled, producing fibre/size/matrix zones suitable for observation. The BT03F composite of Series 3 was examined. Three zones representing the fibre, the size and the polymer are indicated in the Figure 5.69. The polymer has failed, the failure path is highlighted with a series of large holes. From the micrograph, it can be seen that failure occurred in the matrix and hence this element constituted the weakest link of the composite interface. Fibre/size bonding was therefore relatively strong, as would be expected with the commercial size employed.
FIGURE 5.67: S.E.M. micrograph of a thin foil sample, after ion milling. The topological artefacts were created by the abrasion of the polymer by the ion beam.
FIGURE 5.68: S.E.M. micrograph and X-ray map of the redeposition of silicon from the fibre on to the areas of polymer in relief.
FIGURE 5.69: The fibre/matrix interphase of the BT03F composite (glass fibre reinforced polypropylene, with the commercial size, A1100).
5.2.2.5 Electron Energy Loss Spectroscopy (EELS)

The sized fibres were analysed by electron energy loss spectroscopy.

Figure 5.70 is a typical spectrum for the glass of the fibres, which was characterized by distinct calcium (Ca L\text{2,3} or 2p\text{1/2}, 2p\text{2/3}) and oxygen (O K or 1s\text{1/2}) edges at 346 and 532 eV respectively. Small silicon (Si L\text{2,3}) and aluminium (Al L\text{2,3}) edges were observed, which are characteristic of silica (SiO\text{2}) and oxidized aluminium, as shown in Figure 5.71 (12).

A very low intensity carbon edge was also detected for the glass which results from the metallization of the thin foil.

The polymer size suffered degradation under the focussed electron beam, as shown in Figure 5.72, rendering the analysis of this zone particularly difficult. To minimize this phenomenon, the electron beam was focussed to a spot size with an area of approximately 1\text{\mu m}^2, rather than to a point. The more diffuse probe had the advantage of limiting the deterioration of the polymer, but lead to a global analysis of the size rather than an analysis profile from the fibre/size interface to the edge of the size layer. Sizes 1, 3 and 4 were successfully analysed with this technique. For all these sizes a high intensity carbon edge at 283 eV was detected, indicative of the polymer of the coating. Ion milling resulted in the implantation of argon in the polymer, producing a low intensity argon edge at 245.2 eV. The marker, which was added to these sizes, was only detected for Size 1 and Size 4 (Figure 5.73) and only when the probe was positioned on the titanium oxide precipitates described in Section 5.2.2.4. An oxygen edge was not apparent as the ratio of the intensities of the titanium and oxygen edges, for TiO\text{2}, is of approximately 1:6, as shown in Figure 5.74. The low intensity of the oxygen edge therefore prevented its detection. In this zone, the carbon edge was not apparent. Therefore it can be concluded that the titanium forms localized precipitates with little or no polymer separating the individual grains and that the thickness of the precipitates was equal to that of the thin foil sample. The surrounding polymer was free of titanium contamination, as shown by the EELS spectrum of Figure 5.75 .

A calcium edge was observed for Size 3 (Figure 5.76), indicating that diffusion of this element, from the glass into the size, had occurred.
FIGURE 5.70: Typical EELS spectra for the glass of the fibres
FIGURE 5.71: Typical EELS spectra measured for silicon and silica samples and for aluminium and Al$_2$O$_3$ samples (12)
FIGURE 5.72: Degradation of the polymer of the size under the focused electron beam.
ELECTRON ENERGY LOSS SPECTROSCOPY

**FIGURE 5.73** : EELS spectrum of a cluster of titanium oxide precipitates.

**FIGURE 5.74** : Typical EELS spectrum of TiO$_2$. 
ELECTRON ENERGY LOSS SPECTROSCOPY

FIGURE 5.75: EELS spectrum of Size 1 (epoxy + A1100), away from the marker precipitates.

FIGURE 5.76: EELS spectrum of Size 3 (polyurethane + A1100) with an additional calcium edge.
The analysis of the samples confirmed that the layers observed by TEM were effectively the fibre and the size, but a more detailed analysis of the size was not possible with this technique.

5.2.2.6 Microprobe Analysis

Employing the thin foil samples produced for observation by transmission electron microscopy sufficiently improved the resolution of this technique to render it viable in the examination of the size coating on the E-glass fibres. The results are presented in the form of an X-ray map, with a geographical colour scale: from dark blue which represents the lowest concentrations to brown and then white for the highest concentrations.

a. Size Modification

i. Size 1 (A1100 + Epoxy +Ti marker)

Four elements were detected, silicon, Si, calcium, Ca, aluminium, Al, and titanium, Ti. The former three elements were found in relatively low concentrations in the area of size between two glass fibres, as shown in Figure 5.77. The titanium concentration was high locally, which corresponds to the titanium oxide precipitates randomly dispersed throughout the size, previously observed with the transmission electron microscope.

ii. Size 2 (A1100 + Polypropylene)

The size was highlighted by a low concentration of calcium, aluminium and silicon as for the previous case. However only a background noise reading for titanium was measured as this particular size does not contain the marker, as seen in Figure 5.78.
MICROPROBE ANALYSIS

FIGURE 5.77: X-ray map of Size 1 (epoxy + A1100 + Ti marker)
MICROBROBE ANALYSIS

FIGURE 5.78: X-ray map of Size 2
(polypropylene + A1100)
MICROPROBE ANALYSIS

FIGURE 5.79: X-ray map of Size 3 (polyurethane + Al100 + Ti marker)
FIGURE 5.80: X-ray map of Size 4 (polyurethane + Ti marker)
iii. Size 3 (A1100 + Polyurethane+ Ti)

An interfacial zone, between two fibres, which was poor in calcium, aluminium and silicon is shown in Figure 5.79. The size in this area apparently did not contain the titanium marker.

iv. Size 4 (Polyurethane +Ti marker)

Size 4 showed evidence of the Ti marker precipitates, as seen in Figure 5.80. The fibre appeared as a zone rich in calcium, aluminium and silicon, whereas the interfacial zones were poor in all these elements.

5.2.2.7 Fourier Transform Infrared Spectroscopy (FTIR) and FT-RAMAN Spectroscopy

As glass is a very strong infrared absorber with a very strong infrared signal, it overlaps valuable bands which characterize the size. The qualitative analysis of the polyurethane sizes was possible with FTIR spectroscopy as these polymers contain functional groups such as C-H, N-H and C=O which reside in specific spectral regions.

FT-Raman spectroscopy proved interesting for the study of the polymer coating on the fibres, as the spectra obtained differed considerably between the sizes, allowing specific functional groups to be assigned to each coating. These results, which support the results obtained from FTIR spectroscopy, are tabulated in Table 5.8.
<table>
<thead>
<tr>
<th>cm$^{-1}$</th>
<th>PEAK ASSIGNMENT</th>
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</thead>
<tbody>
<tr>
<td>3315</td>
<td>N-H</td>
</tr>
<tr>
<td>3064</td>
<td>N-H in NH$_2$</td>
</tr>
<tr>
<td>2987</td>
<td>C-H in CH$_3$CH</td>
</tr>
<tr>
<td>2964</td>
<td>C-H in CH$_2$</td>
</tr>
<tr>
<td>2924</td>
<td>C-H in CH$_3$CH</td>
</tr>
<tr>
<td>2905</td>
<td>C-H in CH$_3$CH</td>
</tr>
<tr>
<td>1913</td>
<td>CARBONYL GROUP</td>
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<tr>
<td>1727</td>
<td>PEAK ASSIGNMENT</td>
</tr>
<tr>
<td>1650</td>
<td>URETHANE GROUP</td>
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<tr>
<td>1603</td>
<td></td>
</tr>
<tr>
<td>1577</td>
<td>C-H in CH$_2$</td>
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<td>C-H in CH$_2$</td>
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<tr>
<td>1434</td>
<td>C-H in CH$_2$</td>
</tr>
<tr>
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<td>C-H in CH$_2$</td>
</tr>
<tr>
<td>1224</td>
<td>N-H</td>
</tr>
<tr>
<td>1181</td>
<td>EPOXY GROUP</td>
</tr>
<tr>
<td>1117</td>
<td>C-O-C (ether linkage)</td>
</tr>
<tr>
<td>1108</td>
<td>C-O-C (ether linkage)</td>
</tr>
<tr>
<td>930</td>
<td>C-H (Aromatic)</td>
</tr>
<tr>
<td>906</td>
<td>C-H (Aromatic)</td>
</tr>
<tr>
<td>803</td>
<td>Si-C</td>
</tr>
</tbody>
</table>

**TABLE 5.8:** Peak assignment for FTIR and FT-Raman spectra (13 - 26)

Figure 5.81 is of Size 1 (epoxy + A1100). Functional groups characteristic of both elements were detected, the NH$_2$ end group of the A1100, and the epoxy group. There was also evidence of the interaction of these molecules, resulting in the opening of the epoxy group to form the ether linkage (C-O-C) at 1108 cm$^{-1}$. From these results it can be concluded that the A1100/epoxy mixture was partially crosslinked.
FIGURE 5.81: FT-Raman spectrum of Size 1 (epoxy + A1100)
FIGURE 5.82: FT-Raman spectra of Sizes 3 and 4.
The FTIR spectra of Sizes 3 (polyurethane + A1100) and 4 (polyurethane) were identical, with bands of the same position and intensity. As the matrix reactive polymer was common to both sizes this characteristic finger print was considered to be due to the polyurethane. The presence of the polyurethane on the glass fibres was confirmed by the N-H band at 3315 cm\(^{-1}\), the carbonyl group at 1725 cm\(^{-1}\) and the urethane group at 1650 cm\(^{-1}\). The C-H band of the CH\(_2\) group appeared at several positions and was due to the presence of different CH\(_2\) groups in the polymer chain. Figure 5.82 presents the FT Raman spectrum of Size 3 and Size 4. An additional high intensity band was detected for Size 3 at 1925 cm\(^{-1}\). A similar band was observed for Size 1. Hence as the common element between these sizes was the A1100 coupling agent this peak can be attributed to bonding within the silane. In a similar manner it was deduced that the N-H band at 1301 cm\(^{-1}\) was due to a functional group of the A1100.

The ether linkage, C-O-C, was detected for all the samples in the 1040 to 1120 cm\(^{-1}\) wavenumber range. There is some discrepancy as to the nature of the functional groups characteristic of this band, and that of the C-H (aromatic) bonding, as these wavenumbers were assigned to the Si-O-Si (siloxane) linkage and the Si-O stretching mode of the SiOH groups of a silane coupling agent, respectively, by Chiang et al. (27).

V.3 PHYSICAL CHARACTERIZATION

5.3.1 Macromechanical Characterization

5.3.1.1 Tensile Testing

Injection moulded samples, with short random fibre distributions, were tensile tested to failure at a constant strain rate of 0.0002 s\(^{-1}\) at room temperature. The polymer samples were tested at a constant strain rate of 0.001 s\(^{-1}\). The tensile test results of yield stress, \(\sigma_y\), yield strain, \(\varepsilon_y\), failure stress, \(\sigma_f\), failure strain, \(\varepsilon_f\), and 0.5% secant modulus were measured for both modification systems. These parameters are defined in Figure 5.83. A secant modulus was evaluated to overcome the difficulties in measuring the Young's modulus, as the materials studied exhibited a non-linear behaviour almost from the beginning of the tensile test.

Each result is an average from tests on four specimens.
FIGURE 5.83: Definition of tensile test parameters.
a. Size Modification

Table 5.9 summarizes the mechanical properties of the size-modified samples.

<table>
<thead>
<tr>
<th>CODE</th>
<th>$\sigma_y$ (MPa)</th>
<th>$\varepsilon_y$</th>
<th>$\sigma_f$ (MPa)</th>
<th>$\varepsilon_f$</th>
<th>0.5% SECANT MODULUS (GPa)</th>
</tr>
</thead>
<tbody>
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<td>POLYMER</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>PA66</td>
<td>70.8 (0.1)</td>
<td>0.23 (0.01)</td>
<td>50.3 (0.0)</td>
<td>0.44 (0.03)</td>
<td>1.6 (0.3)</td>
</tr>
<tr>
<td>COMPOSITE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SIZE 1</td>
<td>-----</td>
<td>-----</td>
<td>123.7 (3.6)</td>
<td>0.01 (0.00)</td>
<td>13.0 (0.5)</td>
</tr>
<tr>
<td>SIZE 2</td>
<td>-----</td>
<td>-----</td>
<td>91.1 (0.5)</td>
<td>0.01 (0.00)</td>
<td>12.3 (0.9)</td>
</tr>
<tr>
<td>SIZE 3</td>
<td>-----</td>
<td>-----</td>
<td>109.3 (4.1)</td>
<td>0.02 (0.00)</td>
<td>12.8 (0.1)</td>
</tr>
<tr>
<td>SIZE 4</td>
<td>-----</td>
<td>-----</td>
<td>67.7 (4.5)</td>
<td>0.01 (0.00)</td>
<td>11.1 (0.1)</td>
</tr>
</tbody>
</table>

**TABLE 5.9**: Mechanical properties of the PA66 matrix materials (standard deviation)

From these results it can be seen that the failure stress and the 0.5% secant modulus vary with the size applied to the fibres. Strong interfacial bonding produces good mechanical properties hence Size 1 provides the best fibre/matrix adhesion whereas Size 4 shows the weakest interfacial interaction.

Failure surface micrographs are displayed in Figures 5.84 and 5.85.

i. Polymer

The polymer showed limited necking behaviour before failure.

ii Composite

The composite failure was characterized by two distinct fracture types. The first showed fibres coated with a layer of the matrix polymer, as seen in Figure 5.84. This failure was observed for Sizes 1 and 3, and is indicative of good fibre/matrix adhesion. The second failure type showed little or no evidence of interfacial bonding, as the fibres were apparently matrix-free. Considerable fibre pull-out was also observed in this case. Both Sizes 2 and 4 showed poor fibre/matrix adhesion and an example of a failure surface is given in Figure 5.85.
FIGURE 5.84: Good interfacial bonding observed for the Size 1 and Size 3-modified composites (PA66 matrix).
FIGURE 5.85: Poor fibre/matrix adhesion observed for the Size 2 and Size 4-modified composites (PA66 matrix).
b. Matrix Modification

Tensile test results for the matrix-modified system are given in Table 5.10.

<table>
<thead>
<tr>
<th>CODE</th>
<th>$\sigma_y$ (MPa)</th>
<th>$\varepsilon_y$</th>
<th>$\sigma_f$ (MPa)</th>
<th>$\varepsilon_f$</th>
<th>0.5% SECANT MODULUS (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SERIES 1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>POLYMER</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MA00</td>
<td>36.2 (4.3)</td>
<td>0.06 (0.02)</td>
<td>31.9 (2.4)</td>
<td>0.14 (0.50)</td>
<td>1.1 (0.1)</td>
</tr>
<tr>
<td>MA01</td>
<td>29.9 (5.2)</td>
<td>0.09 (0.01)</td>
<td>-----</td>
<td>-----</td>
<td>2.18 (0.1)</td>
</tr>
<tr>
<td>MA02</td>
<td>29.5 (3.1)</td>
<td>0.09 (0.01)</td>
<td>-----</td>
<td>-----</td>
<td>0.38 (0.04)</td>
</tr>
<tr>
<td>MA101</td>
<td>37.0 (9.6)</td>
<td>0.09 (0.00)</td>
<td>30.1 (0.3)</td>
<td>0.12 (0.10)</td>
<td>1.0 (0.1)</td>
</tr>
<tr>
<td>MA103</td>
<td>32.4 (0.2)</td>
<td>0.09 (0.00)</td>
<td>32.0 (0.3)</td>
<td>0.13 (0.25)</td>
<td>1.0 (0.1)</td>
</tr>
<tr>
<td>PM103</td>
<td>31.0 (2.9)</td>
<td>0.10 (0.02)</td>
<td>-----</td>
<td>-----</td>
<td>0.21 (0.1)</td>
</tr>
<tr>
<td>PA103</td>
<td>32.0 (2.1)</td>
<td>0.08 (0.01)</td>
<td>-----</td>
<td>-----</td>
<td>0.29 (0.1)</td>
</tr>
<tr>
<td><strong>COMPOSITE</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MA101F</td>
<td>-----</td>
<td>-----</td>
<td>66.3 (0.9)</td>
<td>0.06 (0.01)</td>
<td>1.6 (0.1)</td>
</tr>
<tr>
<td>MA103F</td>
<td>-----</td>
<td>-----</td>
<td>66.9 (1.6)</td>
<td>0.06 (0.01)</td>
<td>3.6 (0.3)</td>
</tr>
<tr>
<td>PM103F</td>
<td>-----</td>
<td>-----</td>
<td>74.3 (4.1)</td>
<td>0.04 (0.04)</td>
<td>2.3 (0.2)</td>
</tr>
<tr>
<td>PA103F</td>
<td>-----</td>
<td>-----</td>
<td>42.4 (2.1)</td>
<td>0.03 (0.03)</td>
<td>1.5 (0.1)</td>
</tr>
<tr>
<td><strong>SERIES 2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ICIHW60F</td>
<td>-----</td>
<td>-----</td>
<td>65.6 (0.5)</td>
<td>0.03 (0.00)</td>
<td>5.1 (0.4)</td>
</tr>
<tr>
<td>MA103BF</td>
<td>-----</td>
<td>-----</td>
<td>82.0 (0.9)</td>
<td>0.02 (0.00)</td>
<td>6.2 (0.6)</td>
</tr>
<tr>
<td>PM203F</td>
<td>-----</td>
<td>-----</td>
<td>76.0 (1.5)</td>
<td>0.01 (0.00)</td>
<td>6.7 (0.6)</td>
</tr>
<tr>
<td>PM303F</td>
<td>-----</td>
<td>-----</td>
<td>82.4 (2.3)</td>
<td>0.02 (0.00)</td>
<td>7.1 (0.5)</td>
</tr>
<tr>
<td><strong>SERIES 3</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>POLYMER</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BT000</td>
<td>30.3 (0.9)</td>
<td>0.09 (0.01)</td>
<td>-----</td>
<td>-----</td>
<td>0.4 (0.1)</td>
</tr>
<tr>
<td>BT00</td>
<td>30.8 (0.2)</td>
<td>0.08 (0.01)</td>
<td>29.0 (0.2)</td>
<td>0.15 (0.01)</td>
<td>0.6 (0.1)</td>
</tr>
<tr>
<td>BT01</td>
<td>-----</td>
<td>-----</td>
<td>15.9 (0.9)</td>
<td>0.02 (0.00)</td>
<td>1.0 (0.03)</td>
</tr>
<tr>
<td><strong>COMPOSITE</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BT03F</td>
<td>-----</td>
<td>-----</td>
<td>46.8 (1.2)</td>
<td>0.02 (0.00)</td>
<td>3.9 (0.1)</td>
</tr>
<tr>
<td>BT05F</td>
<td>-----</td>
<td>-----</td>
<td>68.7 (1.0)</td>
<td>0.02 (0.00)</td>
<td>6.5 (0.3)</td>
</tr>
</tbody>
</table>

**TABLE 5.10**: Mechanical properties of the polypropylene matrix materials (std)
i. Polymer

Polypropylene is a highly ductile polymer. Failure was not achieved for all the polymer modifications as the failure strain exceeded the displacement capacity of the tensile test machine (i.e. greater than 800%).

ii. Composite

Series 1

The non-optimization of the processing parameters of these specimens resulted in relatively poor mechanical characteristics. However the MA103F and PM103F modifications showed a greater potential for interfacial adhesion enhancement than the other samples. Areas of good and poor interfacial bonding were observed for these samples as well as the ICIHW60F and MA101F composites, as shown in Figure 5.86. The pull-out length was relatively long for all the specimens, reaching values of 0.6mm.

Series 2

An optimized manufacturing system produced much improved composite characteristics. Figure 5.87 displays examples of the scanning electron micrographs of the failure surfaces of the composites of Series 2. In general two types of matrix failure were observed: ductile and brittle. The physical aspect of the fibres in these zones also varied. In the former case the fibres tended to be misaligned and apparently matrix-free. This is indicative of poor interfacial bonding. In the latter case the fibres were coated by a layer of the matrix material. Strong fibre/matrix bonding can hence be deduced from this cohesive failure. The presence of these zones in polypropylene matrix composites was also described by Yue et al. (28)

Series 3

Poor fibre/matrix adhesion was observed for the BT03F sample (PP + I + G.F.), with the majority of the fibres being apparently matrix-free. Long fibres protruded from the failure surface, as shown in Figure 5.88. The considerable pull-out length was also indicative of the weak interfacial bonding. The BT05F sample, which contained the PM modifying agent, again exhibited a long pull-out length at the failure surface.
FIGURE 5.86: Typical fracture surface micrographs of the polypropylene matrix composites of Series 1.
MACROMECHANICAL CHARACTERIZATION

FIGURE 5.87: Scanning electron micrographs of the failure surfaces of the polypropylene matrix composites of Series 2.

Poor fibre/matrix adhesion

Good fibre/matrix bonding
MACROMECHANICAL CHARACTERIZATION

Poor fibre/matrix adhesion

FIGURE 5.88: Failure surfaces of the BT03F (PP + I + GF) sample of Series 3.

Good fibre/matrix bonding

FIGURE 5.89: Failure surface micrographs of the BT05F (PP + I + MA + GF) sample of Series 3.
However, some regions showed good bonding as clumps of polymer coated the fibres, as shown in Figure 5.89. Full modification produced in the twin screw extruder will be the subject of further study at the University of Aston.

5.3.2 Micromechanical Characterization

5.3.2.1 Microdrop Test

The microdrop-test proved a successful method for the measurement of interfacial shear stress for the polypropylene matrix samples. PA66, however, suffered severe degradation on heating in air and so could not be employed to form the polymer droplets required. An unmodified and a modified polypropylene were used to test the fibres coated with the model sizes. The results are tabulated in Table 5.11. Each result is the average from the measurement of twenty specimens.

<table>
<thead>
<tr>
<th>FIBRE COATING</th>
<th>MATRIX</th>
<th>AVERAGE DROPLET LENGTH (μm)</th>
<th>INTERFACIAL SHEAR STRENGTH-MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIZE MODIFICATION (Vetrotex)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SIZE 1</td>
<td>Unmodified PP</td>
<td>366 (43.4)</td>
<td>9.4 (2.3)</td>
</tr>
<tr>
<td>SIZE 2</td>
<td></td>
<td>344 (19.0)</td>
<td>11.8 (1.4)</td>
</tr>
<tr>
<td>SIZE 3</td>
<td></td>
<td>363 (23.5)</td>
<td>9.8 (2.0)</td>
</tr>
<tr>
<td>SIZE 4</td>
<td></td>
<td>331 (17.4)</td>
<td>8.2 (1.6)</td>
</tr>
<tr>
<td>SIZE 1</td>
<td>Modified PP</td>
<td>339 (17.8)</td>
<td>15.6 (1.6)</td>
</tr>
<tr>
<td>SIZE 2</td>
<td></td>
<td>350 (23.1)</td>
<td>&gt;17.7</td>
</tr>
<tr>
<td>SIZE 3</td>
<td></td>
<td>338 (25.1)</td>
<td>14.0 (1.6)</td>
</tr>
<tr>
<td>SIZE 4</td>
<td></td>
<td>337 (18.7)</td>
<td>12.0 (0.8)</td>
</tr>
<tr>
<td>MATRIX MODIFICATION</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COMMERCIAL SIZE</td>
<td>Unmodified PP</td>
<td>345 (18.2)</td>
<td>10.1 (2.9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>440 (20.8)</td>
<td>8.0 (0.8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>590 (23.1)</td>
<td>6.5 (0.2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>658 (26.7)</td>
<td>6.0 (0.9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>747 (39.8)</td>
<td>6.9 (0.8)</td>
</tr>
<tr>
<td>MA101</td>
<td></td>
<td>352 (24.8)</td>
<td>13.2 (3.1)</td>
</tr>
<tr>
<td>MA103</td>
<td></td>
<td>413 (30.8)</td>
<td>&gt;18</td>
</tr>
</tbody>
</table>

**TABLE 5.11: Microdrop test results (standard deviation, std)**
From Table 5.11 it can be seen that a modified polypropylene produced an improvement in the measured interfacial shear stress for all the sized fibres studied.

a. Size Modification

It can be seen for the size modified samples that the interfacial shear stress is dependent on the type of size employed, with the matrix reactive polymer playing an important role in the fibre/matrix bond strength. Thomason (29) showed similar results in glass fibre/polypropylene systems. He concluded that the silane coupling agent alone has little effect on the interfacial strength, but in combination with some other component of the coating, significant effects were found. For the specimens examined the polypropylene/A1100 mixture, of Size 2, gave the strongest interfacial shear strength. For the Size 2/modified polypropylene system all the specimens tested broke within the gauge length of the fibre. The force to produce the failure of these fibres was employed to calculate a lower limit of the interfacial shear stress, with an average droplet length of 350μm. Although this size produces poor interfacial adhesion in PA66 composites, it can produce an interpenetrating network at the size/matrix interface of a non polar matrix composite, resulting in a high interfacial shear stress value. This value is not valid for the polar PA66 matrix. Ranking the remaining model sizes from the weakest to the strongest interfacial bonding gave: Size 4 (polyurethane), Size 3 (polyurethane + A1100) and Size 1 (epoxy + A1100).

b. Matrix Modification

The effect of the modification of the polypropylene to enhance fibre/matrix adhesion and that of the size of the droplet employed on the interfacial shear stress, were studied for the matrix-modified system.

i. Effect of matrix modification

The modified polypropylene matrices, MA101 and MA103, produced stronger interfacial adhesion than an unmodified polypropylene, with the commercial A1100 size. Interfacial adhesion was further improved with the addition of the functional monomer proposed by Al Malika et al. (30) A value for the interfacial shear stress was not measured for the MA103 sample, as fibre failure preceeded fibre/matrix failure. A lower limit was calculated for this system, in a similar manner to that measured for the Size2/modified polypropylene composite.
ii. Effect of the length of the droplet on the interfacial shear stress

![Graph showing interfacial shear stress vs. droplet length]

**FIGURE 5.90:** Effect of the length of the polymer droplet on the interfacial shear stress

Figure 5.90 represents interfacial shear strength as a function of the length of the microdrop, for the commercial size and an unmodified polypropylene matrix. It can be seen that the shorter the droplet length the higher the value of \( \tau \). This is in good agreement with the results of Soulier (31).

iii. Load/ displacement graphs

For both the size modified and matrix modified systems the tests were classed by the form of the load/ displacement graphs into three categories. Examples of each graph type are given in Figure 5.91.
Type 1 was characterized by a linear increase in the load to a maximum value which corresponded to fibre/droplet interfacial failure. The load dropped to zero and remained at this value during the extraction of the drop from the end of the fibre. For Type 2 the first section of the graph was similar to that of Type 1, however, a second increase of the load was observed after its initial decrease to zero following interfacial failure. The load varied until the complete removal of the polymer droplet from the fibre. The final form, Type 3, differed from the previous cases in that a zero load was only achieved on the complete extraction of the drop.

The percentage number of each type of graph, for a given system, is tabulated in Table 5.12.
<table>
<thead>
<tr>
<th>SIZE</th>
<th>MATRIX</th>
<th>TYPE 1</th>
<th>TYPE 2</th>
<th>TYPE 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIZE 1</td>
<td>Unmodified PP</td>
<td>17</td>
<td>66</td>
<td>17</td>
</tr>
<tr>
<td>SIZE 2</td>
<td></td>
<td>38</td>
<td>62</td>
<td>------</td>
</tr>
<tr>
<td>SIZE 3</td>
<td></td>
<td>22</td>
<td>78</td>
<td>------</td>
</tr>
<tr>
<td>SIZE 4</td>
<td></td>
<td>------</td>
<td>100</td>
<td>------</td>
</tr>
<tr>
<td>SIZE 1</td>
<td>Modified PP</td>
<td>90</td>
<td>10</td>
<td>------</td>
</tr>
<tr>
<td>SIZE 2</td>
<td></td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>SIZE 3</td>
<td></td>
<td>75</td>
<td>25</td>
<td>------</td>
</tr>
<tr>
<td>SIZE 4</td>
<td></td>
<td>50</td>
<td>50</td>
<td>------</td>
</tr>
</tbody>
</table>

**TABLE 5.12**: Distribution of the form of the load/displacement graphs for the different fibre/matrix systems

From these results it can be seen that the proportion of Type 1 graphs increases with the modified polypropylene matrix. By comparing this result with those of Table 5.11, it can be concluded that a Type 1 graph arose from strong interfacial bonding. The variations in the percentage number of Type 1 graphs and the measured interfacial shear strength, of the different size/matrix systems, showed the same trend and hence confirm this hypothesis.

The graph type for the Size2/modified polypropylene and the commercial size /MA103 systems were not ascertained, as fibre failure preceded that of the interface.

iv. Failure Surfaces

The fibre/drop failure surface was examined with a scanning electron microscope after the microdrop test. Generally the location of the drop was easily repairable as shown in Figure 5.92. The fibre surfaces were relatively smooth for all the sizes, except for Size 1, where numerous asperities were observed before the extraction of the droplet. After testing, the fibres typically presented a streaked surface, although some smooth areas were observed. Examples of the failure surfaces are given in Figure 5.93.
FIGURE 5.92: Location of the original matrix droplet, observed after the microdrop test.
FIGURE 5.93: Failure surfaces of the size coated fibres, after the microdrop test.
5.3.3 Viscoelastic Analysis

5.3.3.1 Dynamic Mechanical Thermal Analysis

The results given in this section are an average from tests on a minimum of two specimens.

a. Size Modification

i. PA66/size alloys

A typical spectrum of tan\(\delta\) as a function of temperature for the PA66 exhibited three peaks at 136 (-137°C), 224 (-49°C) and 360 (87°C) K respectively (Figure 5.94). These peaks correspond to the \(\gamma\), \(\beta\) and \(\alpha\) transitions described in Section 2.5.3.4. After drying, in an oven at 60°C in the presence of silica gel, the temperatures of the \(\gamma\), \(\beta\) and \(\alpha\) relaxations increased by 1.3, 10.7, and 0.5°C respectively. This temperature shift was accompanied by a decrease of the amplitude of the \(\beta\) peak. An increase in the Young's modulus was also measured, the initial value being 1.17 GPa (std=0.05) and the value after drying was 1.22 GPa (std=0.16).

The study of the PA66/polyurethane size mixtures showed a shift of the glass transition temperature towards lower temperatures as the quantity of added polyurethane increased. The variation of the difference in temperature, \(\Delta T\), as a function of the quantity of size, is represented graphically in Figure 5.95. \(\Delta T\) is given by:

\[
\Delta T = T_{\alpha \ peak(PA66)} - T_{\alpha \ peak(PA66+size)} [5, 7]
\]

where \(T_{\alpha \ peak(PA66)}\) = glass transition temperature of the PA66 polymer

\(T_{\alpha \ peak(PA66+size)}\) = glass transition temperature of the polymer alloy

As for the unmodified PA66, the polymer alloys were subjected to a drying cycle. Similarly to the pure matrix material, drying produces a shift of the \(\gamma\), \(\beta\) and \(\alpha\) relaxations to higher temperatures and a diminution of the \(\beta\) peak intensity.
FIGURE 5.94: Typical spectrum of tan.δ as a function of temperature for the PA66 matrix polymer.

FIGURE 5.95: Variation in the glass transition temperature as a function of the quantity of size added to the matrix/size alloys.
ii. Size films

Average DMTA spectra for the model size films are given in Figure 5.96. Each size presents unique characteristics which are summarized in the following table.

<table>
<thead>
<tr>
<th>CODE</th>
<th>SPECIMEN</th>
<th>TRANSITION TEMPERATURE (K)</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIZE 1</td>
<td>EPOXY</td>
<td>1</td>
<td>High amplitude, narrow tan δ peak</td>
</tr>
<tr>
<td></td>
<td>EPOXY + 50% A1100</td>
<td>2</td>
<td>Transition 2 - large, of low amplitude. Transition 1 commences at 261K</td>
</tr>
<tr>
<td>SIZE 2</td>
<td>PP</td>
<td></td>
<td>film very brittle - failure in grips</td>
</tr>
<tr>
<td></td>
<td>PP + 50% A1100</td>
<td></td>
<td>film very brittle - failure at the beginning of the test</td>
</tr>
<tr>
<td>SIZE 3</td>
<td>PU + 10% A1100</td>
<td>3</td>
<td>Transitions 1 and 2 of low intensity</td>
</tr>
<tr>
<td>SIZE 4</td>
<td>PU</td>
<td>3</td>
<td>Transitions 1 and 2 of low intensity</td>
</tr>
</tbody>
</table>

**TABLE 5.13:** Dynamic-mechanical characteristics of the size films

The transition temperature corresponds to that of the maximum amplitude of the peak except for Size 1 (epoxy+A1100) where the temperature given represents the beginning of the relaxation.

By comparing the spectra of Figure 5.96 the effect of the addition of the A1100 silane coupling agent was assessed.

The dynamic-mechanical behaviour of the A1100/epoxy mixture was very different to that of the pure epoxy film (Figure 5.96). The moduli of these films were similar at low temperatures (150K), but the unmodified epoxy had a lower modulus in the rubbery region. The drop in modulus between 150K (-123°C) and 300K (27°C) was of 4.6 GPa and 3.75 GPa for the unmodified and modified epoxies, respectively. A marked decrease of the amplitude of the glass transition peak, and an increase in the temperature of this relaxation also resulted from the silane coupling agent addition.
DYNAMIC MECHANICAL THERMAL ANALYSIS

Size 1 - Epoxy and epoxy + 50% A1100 model films.

Size 3 - Polyurethane + 10% A1100 and Size 4 - Polyurethane model films

FIGURE 5.96: DMTA spectra for the model size films.
A1100 was used as the hardener for the epoxy system, both in the fibre coating and in the size film. However, in the polymer film the silane was added in a much higher proportion (50% A1100 / 50% epoxy) than in the size coating on the fibres (0.3% A1100 / 4.8% epoxy).

Polyurethane, either with or without the silane addition, was characterized by three transitions. The A1100 in this case did not appear to greatly perturb the structure of the matrix reactive polymer, as was the case for the epoxy system. However, the addition of the silane produced a decrease in the storage or real modulus from 2.4 to 1.8 GPa at 120°C. This variation was particularly marked at low temperatures (i.e. below the glass transition temperature, 290K) and became negligible in the rubbery plateau region (above 290K). The silane also produced an increase in the amplitude of the tan.δ peak of the glass transition.

iii. Composite ribbons

Composite ribbons, produced by the hot melt process described in Section 3.2.4.1, were tested with the DMTA, at a frequency of 5Hz. The resulting spectra of tan.δ as a function of temperature were similar for all the size-modified composites and were characterized by three transitions at approximately -150, -60 and 85°C (123, 213 and 358K) (Figure 5.97). These peaks correspond to the α, β and γ relaxations measured for the PA66 polymer (described in Section 5.3.3.1 PA66/size alloys). The behaviour of the composite was therefore dominated by the behaviour of the matrix polymer. Small variations in the amplitude and form of the peaks were observed between successive tests on specimens cut from the same composite ribbon. Examination of the ribbon showed that the distribution of fibres varied across its width with areas containing fibre bundles and zones of unreinforced matrix polymer. The differences between the spectra therefore can be attributed to the density of fibres in the section of the specimen submitted to horizontal shear.

Although this technique was not sufficiently sensitive to study the effect of a size on the behaviour of the composite, it resulted in spectra with a better resolution than those produced by DMTA tests on bulk composite samples in the compression-compression mode. The horizontal shear of the unidirectionally reinforced composite ribbons therefore represents a relatively simple dynamic mechanical test which is suitable for the comparison of composites with different matrices.
FIGURE 5.97: Typical DMTA spectrum for a composite ribbon tested in the horizontal shear mode.
b. Matrix Modification

The effect of matrix modification was evaluated for the polypropylene based composites. An initial study with the DMTA (described in Section 4.3.3.1) assessed the behaviour of the modified polymer.

i. Polymer

**Effect of processing conditions**

The spectra measured for the pure polypropylene samples are compared in Figure 5.98. Three relaxations were observed at -80, 5 and 90°C (193, 278 and 363K) for the unprocessed polypropylene. The polymer is sensitive to processing conditions as shown by the displacement of the tan.δ peaks.

**Effect of the addition of a free radical initiator**

Examination of Figure 5.99 reveals considerable changes in the polypropylene spectra on the addition of a peroxide. For the compression moulded sample, the peroxide produced a shift of the glass transition (α) to lower temperatures (from 15°C (288K) to 0°C (273K)), indicating an increased mobility of the relaxing phase. The amplitude of the glass transition also increased, revealing an increased proportion of the relaxing phase.

**Effect of chemical modification - the MA system**

The glass transition temperature, T<sub>g</sub>, increased when the polypropylene is modified by the maleic anhydride modifying agent. The position of this relaxation varied little between the unmodified polypropylene and the modified polypropylene in the presence of a peroxide, as shown in Figure 5.100.

The background noise observed for the tan.δ spectra was relatively high with respect to the signals measured for the transitions which characterize the material, due to the limited viscoelastic behaviour of thermoplastic materials. Hence, the small changes in behaviour produced by chemical modification were difficult to measure with accuracy. The composite specimens were not tested with this technique, as the amplitude of the signal was further reduced by the presence of the fibres, rendering analysis of the resulting spectrum very difficult. This problem was overcome with the torsion
FIGURE 5.98: Effect of processing conditions on the dynamic mechanical properties of polypropylene.

FIGURE 5.99: Effect of the addition of a free radical initiator on the dynamic mechanical properties of polypropylene.
FIGURE 5.100: Effect of chemical modification on the dynamic mechanical properties of polypropylene.
pendulum, which provides a sensitive tool for dynamic-mechanical analysis and produces high resolution spectra.

5.3.3.2 Torsion Pendulum

Each of the torsion pendulum spectra presented in this section represents the average of two tests. Figures 5.101 and 5.102 superpose the results of two tests for a Size 1 modified composite. The results are very similar in both the peak positions and intensity of the tan.δ spectra (Figure 5.101), and the plateaus of the shear modulus spectra (Figure 5.102). The small differences measured can be attributed to variations in fibre alignment and fibre volume fraction. X-ray analysis has shown that the crystallinity of the samples, which also influences the behaviour of the composite, remained relatively constant. The modulus is also dependent on the "form factor", FF, which is calculated with the following equation:

\[
FF = \left( \frac{b^3}{t} \right) \left[ 0.3333 - (0.192 \frac{b}{a}) \right] \]  \[5.8\]

where

- \(b\) = breadth of the specimen
- \(t\) = thickness of the specimen
- \(h\) = height of the specimen between the grips

Errors in the measurement of the dimensions of the specimen have a direct effect on the value of the modulus. Variations in the thickness of the specimen along its length also induces errors as described by Cavaille (32). As the measurement of tan.δ is direct and independent of external factors such as the "form-factor", it was employed for the analysis of the dynamic mechanical properties of the specimens. Additionally tan.δ maintains the same value whether it is derived from the moduli or the compliances of the system, therefore there is no ambiguity when quoting the tan.δ position. Tan.δ responds in a systematic way to the relaxing phase (33).

a. Size Modification

The size modified composites and a PA66 polymer sample were examined with the torsion pendulum at 0.01, 0.1 and 1Hz. Figure 5.103 is a typical torsion pendulum spectrum for a PA66 sample showing log 1/Q (or tan.δ) and G/G₀ (shear modulus/reference modulus, G₀=1E10) versus temperature. The behaviour of this thermoplastic was characterized by three transitions at 133.3, 213.0 and 340 K (1Hz), for the intial temperature cycle.
FIGURE 5.101: Superposition of the spectra of tan $\delta$ versus temperature for the Size 1-modified, unidirectional composites.

FIGURE 5.102: Superposition of the spectra of shear modulus versus temperature for the Size 1-modified, unidirectional composites.
FIGURE 5.103: Typical torsion pendulum spectrum for a PA66 sample.
PA66 was shown, by DMTA analysis, to be particularly sensitive to the presence of water, which gave rise to a secondary transition, $\beta$ (Figure 5.94). The $\beta$ relaxation, commenced at approximately 175K and extended to 275K, with its maximum at 213K, at 1Hz. This temperature range corresponds to the glass transition temperature of Size 1 at 263K measured with the DMTA. To minimize masking of the peaks characteristic of the sizes, a method was developed to reduce the presence of water before testing and produce "in-situ" drying during the test itself.

**Before testing**

- The specimens were stored in a dessicator with a dry atmosphere created with silica gel.
- Immediately prior to testing the specimen was submitted to a heat treatment of 9 minutes at 160°C.

**During testing**

- The bell, enclosing the oven and the specimen, was immersed in liquid nitrogen, throughout the test period, to trap water molecules against the metal walls.
- The test was carried out under a vacuum of 0.5 bar.

However, these precautions to limit environmental water interaction with the specimen proved insufficient as indicated by the significant $\beta$ peak of Figure 5.103.

Successful in-situ drying was achieved by repeating the test (heating from 100 to 425K at a rate of 15K/hour), after cooling at approximately 157K/hour, without compromising the vacuum created at the beginning of the first test. This procedure was repeated for a second time. Figure 5.104 compares the spectra of the three repetitions, with the third and final temperature cycle resulting in an almost complete elimination of the $\beta$ peak.

A temperature shift, towards higher temperatures was also observed on drying. The $\gamma$ and $\alpha$ transitions were measured at 148.1 and 358.0K respectively during the third repetition.

Graphs of tan$\delta$ versus temperature are presented for each size-modified composites. For a given size, comparisons were made between the different fibre distributions (long parallel, short parallel and short random). Further analysis of the results
FIGURE 5.104: In-situ drying to eliminate the β peak.
involved the comparison of the spectra for the different sizes for a given fibre distribution.

i. Effect of fibre distribution

A glass fibre addition to the PA66 provokes a decrease in the amplitude of all the transitions. This is due to the superposition of the spectra of the matrix and the fibre, the latter being linear in the temperature range examined.

The superposition of the spectra for the unidirectional, short oriented and short random fibre reinforced composites, for each size modification, showed that the different fibre distributions produced the same variation in the dynamic mechanical properties. An example is given in Figure 5.105. From this result it can be seen that the better the alignment of the fibres in the composite, the greater the amplitude of the glass transition. The maxima of the $\alpha$ relaxation peaks were all at approximately the same temperature of 343K, for a given size. The mid-height width of the transition peaks remained constant for a given size, therefore this parameter is independent of the type of reinforcement employed.

As the long parallel fibre composites showed maximum damping characteristics these results were exploited for the comparison of the different sizes.

ii. Effect of size modification

Figure 5.106 compares the spectra (first repetition) for the PA66 polymer and the composites modified with the Sizes 1, 2, 3, and 4, at 1Hz. The low temperature behaviour for all the composites was similar, with the amplitude, position and mid-height width of the $\beta$ and $\gamma$ peaks being independent of the size modification. The amplitude of the glass transition and the height of the rubbery plateau were dependent on the type of size employed. As an increase in the $\tan\delta$ value corresponds to increased damping, the sizes were classed from the lowest to the highest damping characteristics, giving: Size 1 (epoxy +A1100+Ti), Size 3 (polyurethane + A1100 + Ti), Size 2 (polypropylene +A1100) and Size 4 (polyurethane +Ti). From these results it can be seen that the addition of the silane coupling agent to the polyurethane matrix reactive polymer resulted in a reduction of the amplitude of the glass transition peak (from 0.070 to 0.064). The temperature of the glass transition and the mid-height
FIGURE 5.105: Superposition of the spectra, of tan. $\delta$ versus temperature, for the unidirectional, short oriented and short random fibre reinforced composites (PA66 matrix).

FIGURE 5.106: Superposition of the spectra (first repetition) of the PA66 polymer and the long fibre composites modified with Sizes 1, 2, 3 and 4, at 1Hz.
width of the $\alpha$ peak also varied slightly between the sizes and the PA66 polymer, as shown in Table 5.14.

<table>
<thead>
<tr>
<th></th>
<th>1st REPETITION</th>
<th>3rd REPETITION</th>
</tr>
</thead>
<tbody>
<tr>
<td>CODE</td>
<td>T (K)</td>
<td>WIDTH</td>
</tr>
<tr>
<td>POLYMER</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA66</td>
<td>343</td>
<td>56.0</td>
</tr>
<tr>
<td>COMPOSITE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SIZE 1</td>
<td>343</td>
<td>64.0</td>
</tr>
<tr>
<td>SIZE 2</td>
<td>338</td>
<td>74.2</td>
</tr>
<tr>
<td>SIZE 3</td>
<td>340</td>
<td>66.1</td>
</tr>
<tr>
<td>SIZE 4</td>
<td>343</td>
<td>74.8</td>
</tr>
</tbody>
</table>

**TABLE 5.14:** Effect of size modification on the glass transition peak  

- $T$ = temperature of the transition taken at the maximum peak height  
- WIDTH = width of the glass transition peak measured at mid-peak height  
- TAN.δ = maximum tan.δ value, or amplitude of the glass transition peak  
- 1st REPETITION = first temperature cycle of the torsion pendulum test.  
- 3rd REPETITION = final temperature cycle of the torsion pendulum test. The specimen can be considered as dry.

Drying the specimens in-situ (3rd cycle) resulted in an increase in the glass transition temperature, a decrease in the mid-height width and a very slight increase in the amplitude of the relaxation peak. For both the first and third temperature cycles the glass transition of the Size 2 modified composite was lower than those of the other composites, this variation being more clearly defined for the dried sample. The width and the amplitude of the glass transition peaks varied in a similar manner, with a relatively low intensity, narrow peak resulting from low damping properties.

Further examination of the spectra of the third repetition revealed a variation in the form of the tan. δ versus temperature graph in the zone between the $\beta$ and $\alpha$ peaks (from 213K to 340K), for Sizes 2 and 4. A comparison of the spectra of Sizes 1, 2 and 4 in this temperature range, is shown in Figure 5.107. The position of the observed increase in the tan. δ value for Sizes 2 and 4 corresponds to the glass transition temperatures of the sizes. Although the Size 2 film proved too brittle to be tested viscoelastically, the glass transition temperature of bulk polypropylene was measured...
FIGURE 5.107: Superposition of the spectra (third repetition) of the long fibre reinforced composites modified with Sizes 2, 3 and 4.

FIGURE 5.108: Comparison of the DMTA and the torsion pendulum spectra of the Size 3 and 4 model films and the Size 3 and 4 long fibre reinforced composites.
at 285K for the matrix-modified system. It was assumed that an addition of A1100 to
the polypropylene would not produce a dramatic variation in the viscoelastic properties
of the matrix reactive polymer. The glass transition temperature of the polyurethane
size film was at 290K (5Hz). Figure 5.108 compares the DMTA spectrum for this size
film with the torsion pendulum spectrum for the corresponding composite.

iii. Activation Energy

From the torsion pendulum results the activation energy of each transition was
calculated assuming that the thermally activated relaxations followed the Arrhenius law:-

\[ f = f_0 \exp \left( \frac{H}{RT_0} \right) \] [5.9]

where \( f = \) frequency
\( H = \) activation energy or enthalpy for the relaxation
\( R = \) gas constant =8.314J mol\(^{-1}\)
\( T = \) absolute temperature

A graph of \( \log f \) as a function of \( 1/T \) gives a straight line if this simple activation
energy barrier theory holds, as shown in Figure 5.109. Values for the activation
energies of the \( \gamma, \beta, \) and \( \alpha \) transitions are tabulated in Table 5.14.

<table>
<thead>
<tr>
<th>CODE</th>
<th>ACTIVATION ENERGY kJmol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRANSITION</td>
<td>( \gamma )</td>
</tr>
<tr>
<td>CYCLE 1</td>
<td>47</td>
</tr>
</tbody>
</table>

| POLYMER |
| PA66 |
| SIZE 1 | 45 | 37 | 89 | ----- | 274 | 272 |
| SIZE 2 | 46 | 38 | 73 | ----- | 307 | 305 |
| SIZE 3 | 53 | 32 | 80 | ----- | 295 | 299 |
| SIZE 4 | 48 | 32 | 64 | ----- | 307 | 300 |

**TABLE 5.15:** Activation energies for the unidirectionally reinforced composites,
calculated with the Arrhenius law

1. First temperature cycle of the torsion pendulum test
3. Third temperature cycle, the specimen can be considered as dry.
FIGURE 5.109: Activation energy calculations for the PA66 matrix composites.
Leung (34) calculated the activation energy of the glass transition of dry PA6 as 280kJmol⁻¹. Similar values of 295 and 297kJmol⁻¹ were evaluated by Varlet (35) for PA12 in the wet and dry conditions. He also measured the activation energies of the γ and β transitions for PA12 as 51 and 80kJmol⁻¹ for the wet polymer, and 42 and 76kJmol⁻¹ for the dry polymer, respectively. These results support those tabulated in Table 5.15.

b. Matrix Modification

The torsion pendulum proved particularly successful in the characterization of the matrix modified systems, which employ very small quantities of modifier, due to its great sensitivity. Figure 5.110 is an example of a typical spectrum of log.1/Q (or tan.δ) and G/G₀ (shear modulus/refernece modulus, G₀=1E10) as a function of temperature. Three transitions β, α or glass transition and α⁰("crystalline") were observed at 250, 280 and 375K respectively. The transition temperature is defined by an upper limit for the β relaxation and by the maxima of the α and α⁰ peaks as shown in Figure 5.111.

i. Polymer

Comparison of the polymer samples of Series 3 at each frequency (0.01, 0.1 and 1 Hz) showed that the amplitude of the peaks varied little with the applied frequency, but there was a noticeable change in the form of the peaks, as shown in Figure 5.112. At 1Hz, the glass transition peak was better defined with a distinct trough on the high temperature side of the α relaxation. This good definition may be due to the relatively limited influence of molecular movements other than that of the main relaxation process, at this relatively high frequency. The spectra at 1Hz were therefore employed for the analysis of the viscoelastic behaviour of the polypropylene based specimens.

Effect of processing conditions

Figure 5.113 compares the polymer samples BT000, MA00 and BT00. The polymer, in both its unprocessed (BT000) and processed forms (MA00 in a Buss-Ko kneader and BT00 in a twin screw extruder), exhibited similar viscoelastic behaviour with their glass transition temperatures at 283.0K, 278.8K and 286.1K, respectively.
FIGURE 5.110: Typical torsion pendulum spectrum for a polypropylene sample.
FIGURE 5.111: Definition of the transition temperatures for a polypropylene-based specimen.
FIGURE 5.112: Comparison of the polymer samples of Series 3, at 0.01, 0.1 and 1Hz.
FIGURE 5.113: Effect of processing conditions on the viscoelastic properties of polypropylene.

FIGURE 5.114: Effect of the addition of a free radical initiator on the viscoelastic properties of polypropylene.
The amplitude of the glass transition peak, and the high temperature crystalline transition varied between the specimens of Series 1 (MA00) and Series 3 (BT000 and BT00). As the processing control was greatly improved for the latter series these differences may be attributed to the quality of the sample. However, from the results of Series 3, it can be seen that a decrease in the intensity of the \( \alpha \) transition results from processing in a twin screw extruder.

**Effect of the addition of a free radical initiator**

The presence a peroxide systematically produced a shift of the glass transition to a lower temperature (from 286.1K to 265.0K, for Series 3) and an increase of the amplitude of this peak (of 0.002, for Series 3). This phenomenon was observed for both the Series 1 and 3 samples, as shown in Figure 5.114. A similar result was obtained for the compression moulded samples tested with the DMTA (Section 5.3.3.1b), where a shift of 15°C was measured between the \( \alpha \) relaxations of the unmodified and peroxide modified polypropylene.

**Effect of chemical modification - the MA system**

Chemical modification of the polypropylene induced variations in the glass transition peak position and form, and affects the crystalline transition, as seen in Figure 5.115. As described in the previous section the addition of a peroxide (MA02) produced a decrease in the \( \alpha \) relaxation temperature and an increase in the amplitude of this peak. The polypropylene/MA sample (MA01) also showed a decrease in the glass transition temperature (from 278.8K to 271.5K), however, the amplitude of the peak was similar to that of the MA00 sample (unmodified polypropylene). The high temperature behaviour also differed with a higher \( \alpha^c \) transition temperature and a lower \( \alpha^c \) peak height, for this particular modification.

**ii. Composite**

**Series 1**

Figure 5.116 compares the viscoelastic spectra of the composite samples of Series 1. A glass transition temperature of 282K was representative of all the samples, but a considerable variation in the intensity of the \( \alpha \) peak was observed.
FIGURE 5.115: Effect of chemical modification on the viscoelastic properties of polypropylene.

FIGURE 5.116: Comparison of the polypropylene matrix composites of Series1.
Ranking the specimens from the highest to the lowest damping characteristics gave: PA103F, MA00F, MA000F, and MA103F.

Series 2 (Figure 5.117)

Variations were detected between the composites of Series 2. A glass transition temperature of 280.0K was measured for the PM203F, PM303F and the commercial ICIHW60 samples. The temperature of this relaxation was slightly higher, at 282.0K, for the MA103BF modification. In a similar manner to Series 1, the amplitude of the α peak varied with the composite modification employed. Tan. δ values of 0.028, 0.030, 0.030 and 0.043 were evaluated for the MA103BF, PM203F, PM303F and ICIHW60F composites respectively.

Series 3

A comparison of the composite samples of Series 3 is shown in Figure 5.118. The glass transition temperatures were measured at 271.3 and 274.5K for BT03F and BT05F respectively. A variation in the amplitude of these peaks was also observed, the BT03F composite exhibiting a higher intensity glass transition peak than the BT05F specimen.
FIGURE 5.117: Comparison of the polypropylene matrix composites of Series 2.

FIGURE 5.118: Comparison of the polypropylene matrix composites of Series 3.
REFERENCES

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31. J.P. SOULIER, private communication
CHAPTER VI
INTERFACIAL ADHESION
EFFICIENCY MODEL
VI INTERFACIAL ADHESION EFFICIENCY MODEL

NOMENCLATURE

\[ \eta_0 = \text{Krenchel orientation factor (Section 5.2.1.5)} \]
\[ E_f = \text{Young's modulus of E-glass fibres} = 73 \text{GPa} \]
\[ V_f = \text{Fibre volume fraction (Section 4.2.1.2)} \]
\[ L_{\text{min}} = \text{minimum fibre length of the fibre length distribution} \]
\[ L_c = \text{Critical fibre length} \]
\[ Q(L) = \text{Normalized fibre length distribution} \]
\[ L_{\text{max}} = \text{maximum fibre length of the fibre length distribution} \]
\[ \varepsilon_c = \text{Composite strain} = 0.005 \]
\[ G_m = \text{Shear modulus of the matrix} = \frac{E_m}{(2(1+\nu))} \]
\[ E_m = \text{Young's modulus of the matrix} \]
\[ \nu = \text{Poisson's ratio} \]
\[ V_m = \text{Matrix volume fraction (Section 4.2.1.2)} \]

6.1 INTRODUCTION

A rating of the adhesion-efficiency of each interfacial modification was evaluated by comparing the experimental 0.5% secant modulus with a theoretical value, at 0.5% strain, assuming perfect or 100% bonding, and 0% or no bonding. The maximum theoretical modulus (100% bonding) was calculated with the formula suggested by Berlin et al. (1):-

\[
E_{\text{th max}} = \eta_0 E_f V_f \left[ \int_{L_{\text{min}}}^{L_c} \frac{L}{2L_c} Q(L) \, dL + \int_{L_c}^{L_{\text{max}}} \left[ 1 - \frac{L_c}{2L} \right] Q(L) \, dL \right] + E_m V_m \quad [6.1]
\]
Equation 6.1 is considered to be a reasonable predictor of the properties of a short fibre reinforced composite and is of practical use (2). The minimum theoretical modulus, for 0% bonding, was calculated with:

$$E_{th\ min} = E_m V_m \ [6.2]$$

As all the composites were in an injection moulded form, numerous calculations were necessary as the real behaviour of the composite is partially dictated by the:

a) the complicated orientation distribution of the fibres

b) the fibre volume fraction

c) the broad fibre length distribution

Experimental data for all the above parameters was exploited allowing all the mechanical differences to be attributed to a particular modification of the fibre/matrix interface.

### 6.2 KRENCHEL ORIENTATION FACTOR, $\eta_0$

The orientation factor, $\eta_0$, was calculated for three different fibre volume fractions from the fibre orientation distributions measured by image analysis (Section 5.2.1.4). It was assumed that the value measured for the longitudinal cross-section was representative of the bulk composite. Orientation factors of 0.80 and 0.64 were measured for the PA66 and polypropylene composites respectively. The difference between these values can be attributed to many factors, such as the geometry and the thickness of the mould, the injection ram speed, the melt and the mould temperatures and the moulding material (both the type of polymer and the fibre volume fraction) (3,4). All of these parameters varied between the size-modified and matrix-modified systems. Bright and Darlington (4) studied the fibre orientation distribution in similar composites to those examined, but all the parameters were constant, except for the matrix polymer. They showed that the outer layer of fibres in the PA66 matrix composite remained parallel to the injection moulding direction, even when the flow geometry was strongly divergent, whereas the outer layers of fibres in a polypropylene matrix composite tended have a random-in-the-plane orientation, except when constrained by a unidirectional flow geometry. The resulting Krenchel factor for the polypropylene composite was less than that of the PA66 matrix composite.
The orientation factor was found to be insensitive to small increases in volume fraction (of 0.02), as shown by the comparison of the polypropylene composites in Section 5.2.1.4.

The Krenchel factor gives an underestimation of the reinforcing capacity of the fibres, as the fibres acting at 90° to the loading direction are ignored.

6.3 FIBRE VOLUME FRACTION, $V_f$

From the percentage weight of fibre results (Section 5.2.1.2) a fibre volume fraction was calculated for each composite type. As the injection moulded samples were produced in batches, this result was assumed to be valid for all the composites of a given modification. The composite was considered to consist of two elements; the reinforcement and the matrix. Hence the matrix volume fraction was evaluated with:-

$$V_m = 1 - V_f \quad [6.3]$$

This value is an overestimation of the matrix volume fraction as the size and the porosity of the sample are ignored.

6.4 FIBRE REINFORCEMENT EFFICIENCY - FIBRE LENGTH DISTRIBUTION

The reinforcing efficiency of the fibres is dependent on the fibre length distribution and on the diameter of the fibres. The fibre length distribution was separated into two parts, one consisting of the subcritical length fibres (shorter than $L_c$) and the other containing the supercritical length fibres (longer than $L_c$).

The contribution of the subcritical class of fibres is described by:-

$$\int_{L_{\min}}^{L_c} \frac{L}{2L_c} Q(L) \, dL \quad [6.4]$$

where $L_{\min} = \text{minimum fibre length} = 50\mu m$ for all of the fibre length distributions.
This lower bound was fixed by the limitations of the image analysis, as described in Section 5.2.1.3

The contribution of the supercritical fibre class is described by:

\[
\begin{align*}
L_{\text{max}} &= \int \left[1 - \frac{L_c}{2L}\right] Q(L) \, dL \quad [6.5] \\
L_c &
\end{align*}
\]

For these calculations the critical length, Lc, must be evaluated. The critical length was defined as the fibre length required to carry the maximum stress, s_Ef, where s is the strain applied to the composite.

6.5 Critical Length, Lc

A critical length for the fibres, at 0.5% strain, was established for each composite system. As the deformation considered is relatively low, the Cox model is appropriate for the critical length calculations as it considers that both the fibre and the matrix behave elastically and that interfacial bonding is perfect. Tensile testing was employed to mechanically characterize the matrices. The results are tabulated in Table 6.1.

<table>
<thead>
<tr>
<th>MATRIX</th>
<th>(\sigma_Y) (MPa)</th>
<th>(\varepsilon_Y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA66</td>
<td>70.8</td>
<td>0.23</td>
</tr>
<tr>
<td>PP</td>
<td>36.2</td>
<td>0.09</td>
</tr>
</tbody>
</table>

**TABLE 6.1:** Mechanical characteristics of polyamide 6.6 and polypropylene

It can be seen that the strain to provoke yield and hence plastic behaviour exceeds the value of 0.5%. The matrix behaviour is therefore effectively elastic for the considered strain.

The Cox model is given by:

\[
\sigma_f = E_f \varepsilon_c \left[1 - \cosh \beta \left(L/2-x\right)\right] \quad [6.6]
\]

\[
\cosh \beta \left(L/2\right)
\]
258

where

\[ \beta = \left( \frac{2G_m}{E_f r^2 \ln(V_f - 1/2)} \right)^{1/2} \] \[6.7\]

and \( L = \) fibre length
\( x = \) distance from the fibre end (see Section 2.6.2 b)

Bader (5) proposed an adaptation of the formula described by Cox, where he defines \( \beta \) as a function involving the volume fraction rather than the ratio of interfibre spacing/fibre radius, which is appropriate for injection moulded samples, with a random fibre orientation distribution.

The critical fibre length was evaluated at the composite strain of 0.5%. This length was defined by the point at which the stress of the fibre reaches 0.9\( \sigma_{f_{\text{maximum}}} \) or 0.9\( E_f \varepsilon_c \). This arbitrary value of 0.9\( \sigma_{f_{\text{maximum}}} \) was originally employed by Rosen (6). The term "x" of equation 6.6 in this case refers to the transfer length which is equal to \( L_c/2 \).

Hence the critical length can be calculated with:

\[ 0.9\sigma_{f_{\text{max}}} = E_f \varepsilon_c \left[ 1 - \frac{\cosh \beta (L/2-x)}{\cosh \beta (L/2)} \right] \] \[6.8\]

or

\[ 0.9 E_f \varepsilon_c = E_f \varepsilon_c \left[ 1 - \frac{\cosh \beta (L/2-x)}{\cosh \beta (L/2)} \right] \] \[6.9\]

\[ 0.9 = \left[ 1 - \frac{\cosh \beta (L/2-x)}{\cosh \beta (L/2)} \right] \] \[6.10\]

\[ 0.1 \cosh \beta (L/2) = \cosh \beta (L/2-x) \] \[6.11\]

consider that \( A = \beta (L/2) \)
and \( C = \beta x \)
then \( \cosh \beta (L/2) = \cosh A = (e^A + e^{-A})/2 \)
and \( \cosh \beta (L/2-x) = \cosh (A - C) = (e^{A-C} + e^{C-A})/2 \)
therefore

\[ 0.1 (e^A + e^{-A})/2 = (e^{A-C} + e^{C-A})/2 \quad [6.12] \]

\[ 0.1 (e^A - e^{-A}) = (e^{A-C} + e^{C-A}) \quad [6.13] \]

\[ 0.1 e^C(e^A + e^{-A}) = e^A + e^2C e^{-A} \quad [6.14] \]

\[ e^{2C} e^{-A} - 0.1 e^C(e^A + e^{-A}) + e^A = 0 \quad [6.15] \]

The polynomial equation in \( e^C \) has the solutions:

\[ e^C = 0.1 (e^A + e^{-A}) (+/-) \sqrt{0.1^2 (e^A + e^{-A})^2 - 4e^A e^{-A}}/2 = 0 \quad [6.16] \]

\[ \beta x = 0.1 (e^{2A+1}) (+/-) \sqrt{0.1^2 (e^{2A+1})^2 - 4}/2 \quad [6.17] \]

\[ x = \beta \ln \left[ 0.1 (e^{2A+1}) (+/-) \sqrt{0.1^2 (e^{2A+1})^2 - 4}/2 \right] \quad [6.18] \]

Equation 6.17 can be simplified by considering that

\[ \cosh \beta L/2 = e^{\beta L/2} \]

and that

\[ \cosh \beta (L/2 - x) = e^{\beta (L/2 - x)} \]

which holds for the large numerical values obtained for \( \beta L/2 \) and \( \beta (L/2 - x) \)

therefore equation 6.11 simplifies to give

\[ x = 1/\beta \ln(10) \quad [6.19] \]

and

\[ L_c = 2 \left(1/\beta \ln(10)\right) \quad [6.20] \]

The critical length is hence dependent on the shear modulus of the matrix, the Young's modulus of the fibres and the fibre volume fraction. This value is independent of the strain applied to the composite.
Employing values of 3.2GPa and 1.5GPa for the moduli of the PA66 and the polypropylene matrices respectively gave the critical length values tabulated in Table 6.2.

<table>
<thead>
<tr>
<th>MATRIX</th>
<th>MODULUS (GPa)</th>
<th>Lc (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA66</td>
<td>3.2</td>
<td>146</td>
</tr>
<tr>
<td>POLYPROPYLENE</td>
<td>1.5</td>
<td>251</td>
</tr>
</tbody>
</table>

**TABLE 6.2: Critical fibre length (Cox model)**

A Poisson's ratio of 0.3 was assumed for both matrices.

It can be seen that a stiffer matrix reduces the critical length.

The Cox model is deficient in that it does not take into account all relevant parameters and considers that the maximum shear stress is at the fibre ends. This model assumes that the interface is infinitesimally thin, but the size layer was measured to have depths of up to 900nm by TEM, as described in Section 5.2.2.5. Also the matrix in proximity to the fibre is considered by Cox to have the same properties as the matrix in bulk form. Again the experimental results have shown that the size and the matrix polymers have unique characteristics and that the behaviour of the PA66 matrix/size alloys is dependent on the quantity of size present (Sections 5.2.1.5 and 5.3.3.1). Galiotis (7), however, showed that the behaviour of a real composite can be approximated by this model.

### 6.6 NORMALIZED FUNCTION OF THE FIBRE LENGTH DISTRIBUTION Q(L)

The Q(L) was calculated from the fibre length distributions measured for the central section of the composite specimens. The distributions obtained were considered as representative of those of the composites at 0.5% strain. This assumption is valid as at this strain level the stress in the fibres is 0.37GPa. The probability of fibre failure is therefore minimal, as shown in Figure 6.1.
A polynomial equation was evaluated with the programme developed by Baxevanakis (9) for each histogram of fibre length as a function of frequency. An example of curve fitting is shown in Figure 6.2.
A complete fibre length distribution was not obtained as only insufficiently accurate data for the very short fibre lengths (less than 50µm) was available by image analysis (Section 5.2.1.3). A full fibre length distribution was expected to be Gaussian. Hill (10) showed that an increasing fibre volume fraction skews the distribution towards the shorter fibre lengths. This can be explained by increased fibre attrition with the denser packing of the fibres resulting from a larger proportion of reinforcement. He measured fibre length distributions for the fibre weight fractions of 0.1, 0.2 and 0.3, as shown in Figure 6.3. The studied composites contain relatively high fibre weight fractions of approximately 0.3 and 0.5 for the matrix-modified and the size-modified samples respectively.

**FIGURE 6.3:** Fibre length distributions measured by Hill (10)

Very short fibres represent a low reinforcing capacity in the composite. However, by excluding them, the normalized function of the fibre length distribution is an underestimation of the reinforcing capabilities of the fibres.

6.7 RESULTS

Table 6.3 summarizes the characteristics of the size-modified and matrix-modified samples, required for the theoretical calculation.
<table>
<thead>
<tr>
<th>CODE</th>
<th>$\eta_0$</th>
<th>$W_f$ (%)</th>
<th>$V_f$</th>
<th>$V_m$</th>
<th>$L$ (µm)</th>
<th>$L_{\text{max}}$ (µm)</th>
<th>$d$ (µm)</th>
<th>$E_m$ (GPa)</th>
<th>$L_c$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIZE 1</td>
<td>0.80</td>
<td>49.3</td>
<td>0.30</td>
<td>0.70</td>
<td>188 (118)</td>
<td>775</td>
<td>17.6</td>
<td>1.6</td>
<td>242</td>
</tr>
<tr>
<td>SIZE 2</td>
<td>0.80</td>
<td>47.7</td>
<td>0.29</td>
<td>0.70</td>
<td>167 (120)</td>
<td>675</td>
<td>17.6</td>
<td>1.6</td>
<td>246</td>
</tr>
<tr>
<td>SIZE 3</td>
<td>0.80</td>
<td>47.7</td>
<td>0.29</td>
<td>0.71</td>
<td>126 (78)</td>
<td>650</td>
<td>17.6</td>
<td>1.6</td>
<td>246</td>
</tr>
<tr>
<td>SIZE 4</td>
<td>0.80</td>
<td>51.3</td>
<td>0.32</td>
<td>0.68</td>
<td>158 (109)</td>
<td>475</td>
<td>17.6</td>
<td>1.6</td>
<td>236</td>
</tr>
</tbody>
</table>

**SIZE MODIFICATION (Vetrotex - PA66 matrix)**

**MATRIX MODIFICATION (Aston University - polypropylene matrix)**

**SERIES 1 COMPOSITE (F)**

<p>| | | | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>MA101</td>
<td>0.64</td>
<td>22.6</td>
<td>0.09</td>
<td>0.91</td>
<td>165 (93)</td>
<td>650</td>
<td>15.2</td>
<td>1.1</td>
<td>357</td>
</tr>
<tr>
<td>MA103</td>
<td>0.64</td>
<td>23.8</td>
<td>0.10</td>
<td>0.90</td>
<td>247 (125)</td>
<td>900</td>
<td>15.2</td>
<td>1.0</td>
<td>366</td>
</tr>
<tr>
<td>PM103</td>
<td>0.64</td>
<td>37.9</td>
<td>0.18</td>
<td>0.82</td>
<td>161 (95)</td>
<td>750</td>
<td>15.2</td>
<td>1.1</td>
<td>301</td>
</tr>
<tr>
<td>PA103</td>
<td>0.64</td>
<td>23.0</td>
<td>0.10</td>
<td>0.90</td>
<td>339 (192)</td>
<td>775</td>
<td>15.2</td>
<td>1.1</td>
<td>349</td>
</tr>
<tr>
<td>ICIHW 60</td>
<td>0.64</td>
<td>28.6</td>
<td>0.12</td>
<td>0.88</td>
<td>188 (154)</td>
<td>775</td>
<td>15.2</td>
<td>1.0</td>
<td>351</td>
</tr>
</tbody>
</table>

**SERIES 2 (1) COMPOSITE (F)**

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<table>
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<tr>
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<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>MA103B</td>
<td>0.64</td>
<td>29.1</td>
<td>0.13</td>
<td>0.87</td>
<td>274 (217)</td>
<td>1225</td>
<td>15.2</td>
<td>1.4</td>
<td>297</td>
</tr>
<tr>
<td>PM203</td>
<td>0.64</td>
<td>29.3</td>
<td>0.13</td>
<td>0.87</td>
<td>252 (207)</td>
<td>1050</td>
<td>15.2</td>
<td>1.4</td>
<td>291</td>
</tr>
<tr>
<td>PM303</td>
<td>0.64</td>
<td>31.2</td>
<td>0.14</td>
<td>0.86</td>
<td>260 (214)</td>
<td>1375</td>
<td>15.2</td>
<td>1.4</td>
<td>291</td>
</tr>
<tr>
<td>ICIHW 60</td>
<td>0.64</td>
<td>28.4</td>
<td>0.12</td>
<td>0.88</td>
<td>196 (162)</td>
<td>900</td>
<td>15.2</td>
<td>1.4</td>
<td>286</td>
</tr>
</tbody>
</table>

**SERIES 3 COMPOSITE (F)**

<p>| | | | | | | | | | |</p>
<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>BT03</td>
<td>0.64</td>
<td>21.1</td>
<td>0.09</td>
<td>0.91</td>
<td>330 (340)</td>
<td>1760</td>
<td>15.2</td>
<td>1.0</td>
<td>374</td>
</tr>
<tr>
<td>BT05</td>
<td>0.64</td>
<td>27.9</td>
<td>0.12</td>
<td>0.88</td>
<td>309 (343)</td>
<td>1600</td>
<td>15.2</td>
<td>1.0</td>
<td>351</td>
</tr>
</tbody>
</table>

**TABLE 6.3:** Structural and micromechanical characteristics (standard deviation)

Definitions of symbols are those given for equation 6.1

$L =$ average fibre length measured by image analysis.

(1) Modulus of polypropylene measured at the IFP for Series 2
In the injection moulded composites examined the average fibre length, and the majority of the fibres were shorter than the critical length. A similar result was obtained by Bader and Bowyer (11) for PA66 reinforced with 15 vol.% of glass fibres, who showed that 80% of the fibres were below the critical length. As the reinforcing efficiency of subcritical length fibres is low, strong fibre/matrix bonding is essential in these composites to ensure good mechanical properties.

The results of Table 6.3 were employed, in conjunction with the normalized fibre length distribution, to calculate the maximum theoretical modulus, $E_{th\ max}$, with equation 6.1 and the minimum theoretical modulus, $E_{th\ min}$, with equation 6.2. Table 6.4 compares the measured and the theoretical mechanical characteristics and gives an adhesion efficiency value for each composite.

<table>
<thead>
<tr>
<th>CODE</th>
<th>$\sigma_f$ (MPa)</th>
<th>$E$ (GPa)</th>
<th>$E_{th\ min}$</th>
<th>$E_{th\ max}$</th>
<th>ADHESION EFFICIENCY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIZE MODIFICATION</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SIZE 1</td>
<td>123.7</td>
<td>13.0</td>
<td>1.1</td>
<td>15.4</td>
<td>84</td>
</tr>
<tr>
<td>SIZE 2</td>
<td>91.1</td>
<td>12.3</td>
<td>1.1</td>
<td>16.8</td>
<td>73</td>
</tr>
<tr>
<td>SIZE 3</td>
<td>109.4</td>
<td>12.8</td>
<td>1.2</td>
<td>16.7</td>
<td>77</td>
</tr>
<tr>
<td>SIZE 4</td>
<td>67.7</td>
<td>11.1</td>
<td>1.1</td>
<td>17.0</td>
<td>65</td>
</tr>
<tr>
<td>MATRIX MODIFICATION</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SERIES 1 COMPOSITE (F)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MA101</td>
<td>66.3</td>
<td>1.6</td>
<td>1.0</td>
<td>4.0</td>
<td>40</td>
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<tr>
<td>MA103</td>
<td>66.9</td>
<td>3.6</td>
<td>0.9</td>
<td>4.8</td>
<td>75</td>
</tr>
<tr>
<td>PM103</td>
<td>74.3</td>
<td>2.3</td>
<td>0.9</td>
<td>7.1</td>
<td>32</td>
</tr>
<tr>
<td>PA103</td>
<td>42.4</td>
<td>1.5</td>
<td>1.0</td>
<td>4.3</td>
<td>35</td>
</tr>
<tr>
<td>SERIES 2 COMPOSITE (F)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MA103B</td>
<td>82.0</td>
<td>6.2</td>
<td>1.2</td>
<td>5.8</td>
<td>107</td>
</tr>
<tr>
<td>PM203</td>
<td>76.0</td>
<td>6.7</td>
<td>1.2</td>
<td>5.5</td>
<td>122</td>
</tr>
<tr>
<td>PM303</td>
<td>82.4</td>
<td>7.1</td>
<td>1.2</td>
<td>6.9</td>
<td>103</td>
</tr>
<tr>
<td>ICIHW60</td>
<td>65.6</td>
<td>5.1</td>
<td>0.9</td>
<td>5.8</td>
<td>89</td>
</tr>
<tr>
<td>SERIES 3 COMPOSITE (F)</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>BT03</td>
<td>46.8</td>
<td>3.9</td>
<td>0.9</td>
<td>7.0</td>
<td>56</td>
</tr>
<tr>
<td>BT05</td>
<td>68.7</td>
<td>6.5</td>
<td>0.9</td>
<td>7.6</td>
<td>86</td>
</tr>
</tbody>
</table>

**TABLE 6.4**: Adhesion efficiency calculation

$$E = 0.5\%\ secant\ modulus$$
As the minimum theoretical modulus was approximately constant for all the composites the adhesion-efficiency was calculated with respect to the perfect or 100% bonding theoretical modulus. From the results of Table 6.4, the specimens were ranked in order of the strength of the fibre/matrix adhesion.

The size-modified composites were classed as follows: Size 4 (polyurethane), Size 2 (polypropylene + A1100), Size 3 (polyurethane + A1100) and Size 1 (epoxy + A1100) from the weakest to the strongest interfacial bonding. The silane coupling agent is therefore an important element in adhesion promotion, however, its efficiency is conditioned by the choice of the matrix reactive polymer. The interaction of the matrix reactive polymer and the matrix and their compatibility are essential for effective interfacial bonding.

In a similar manner the matrix-modified composites were rated, with respect to the fibre/matrix bond strength. It can be seen from Table 6.4 that the samples of Series 2 showed the strongest interfacial adhesion. MA103BF, PM203F and PM303F were all produced under optimized processing conditions, and contained three chemical modifiers, a peroxide, a modifying agent (either maleic anhydride or PM, a derivative of this molecule) and an additional functional monomer. The adhesion efficiency measured for these composites was greater than that of the commercial material (ICIHW60F) which was manufactured under the same conditions. Therefore the in-situ reactive processing technique developed enhances interfacial adhesion, and consequently the performance of the composite.

Problems due to non-optimized processing parameters were responsible for the relatively low adhesion efficiencies evaluated for the samples of Series 1. Additionally the MA101F composite was not a fully modified system, as it only contained the peroxide and maleic anhydride modifying agent. By adding the additional functional monomer an improvement of 35% in the interfacial bonding was produced, as shown by the comparison of the results for the MA101F and MA103F composites. The maleic anhydride derivatives, PM and PA, did not appear as satisfactory modifying agent substitutes from this first series of tests. However, the analysis of these samples by infrared spectroscopy (by Aston University) indicated the good potential bonding capacity of the PM system.

The specimens of Series 3 were not fully modified, so their low adhesion efficiencies were as expected.
Results from the microdrop tests were used to recalculate the critical length with an extended version of the Kelly-Tyson model proposed by Mittal et al. (12). This equation defines the critical length at a particular applied strain and is given by:

\[ L_c = \frac{E_f \varepsilon_c d}{2\tau} \quad [6.21] \]

Hence, unlike the Cox model, the value of the critical length is dependent on the strain applied to the composite.

Table 6.5 compares the measured and calculated values of critical length at 0.5% strain.

<table>
<thead>
<tr>
<th>CODE</th>
<th>( L_c ) (1) (( \mu )m)</th>
<th>( \tau ) measured (MPa)</th>
<th>( L_c ) calculated (( \mu )m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PURE PP</td>
<td>MODIFIED PP</td>
<td>PURE PP</td>
</tr>
<tr>
<td>SIZE MODIFICATION</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SIZE 1</td>
<td>342</td>
<td>206</td>
<td>9.4 (2.3)</td>
</tr>
<tr>
<td>SIZE 2</td>
<td>272</td>
<td>181</td>
<td>11.8 (1.4)</td>
</tr>
<tr>
<td>SIZE 3</td>
<td>328</td>
<td>229</td>
<td>9.8 (2.0)</td>
</tr>
<tr>
<td>SIZE 4</td>
<td>392</td>
<td>268</td>
<td>8.2 (1.6)</td>
</tr>
<tr>
<td>MATRIX MODIFICATION</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COMMERCIAL SIZE/(MA00)</td>
<td>274</td>
<td>-----</td>
<td>10.1 (2.9)</td>
</tr>
<tr>
<td>COMMERCIAL SIZE/(MA101)</td>
<td>-----</td>
<td>210</td>
<td>-----</td>
</tr>
<tr>
<td>COMMERCIAL SIZE/(MA103)</td>
<td>-----</td>
<td>154</td>
<td>-----</td>
</tr>
</tbody>
</table>

**Table 6.5:** Measured and calculated values of the critical length at 0.5% strain, employing the extended Kelly-Tyson model and the Cox model.
From these results it can be seen that the values of $L_c$ calculated with the Kelly-Tyson model are size dependent, for the size modified composites. As strong interfacial bonding results in a reduction of the critical length, the specimens were ranked from the weakest to the strongest fibre/matrix adhesion as follows: Size 4 (polyurethane), Size 3 (polyurethane + A1100), Size 1 (epoxy + A1100) and Size 2 (polypropylene + A1100). This order was valid for both the unmodified and modified polypropylene matrices. Size 2, with an interfacial shear stress which exceeded 17.7MPa, exhibits greater adhesion enhancement than was predicted by the adhesion efficiency model. However, the model considers bonding in a PA66 matrix whereas the microdrop test employed a polypropylene matrix. The incompatibility of the PA66 and the polypropylene, which have polar and non polar natures respectively, explain the discrepancy between these results. A non polar size produces an interpenetrating network with a non polar matrix, and hence strengthens the size/matrix interface.

**CONCLUSION**

The adhesion efficiency model has proved an effect tool for ranking the mechanical properties of the composites, as a function of the adhesion efficiency at the interface. In a similar manner the microdrop test results were employed to class the composites with respect to the strength of the fibre/matrix adhesion. This again is an effective tool for interface studies, however, this technique treats model composites which were not submitted to the same processing conditions as the bulk material.
REFERENCES

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8. S. BONFIELD, Final Year Project, University of Surrey (1988)
9. C. BAXEVANAKIS, private communication
CHAPTER VII
DISCUSSION
VII DISCUSSION

7.1 INTRODUCTION

A large range of experimental techniques have proved necessary for this study of the influence of the fibre/matrix interface on the behaviour of E-glass reinforced thermoplastics, as each element of the composite namely fibre, interphase and matrix, presents both different intrinsic characteristics and handling properties.

VII.2 SIZE-MODIFIED COMPOSITES

7.2.1 INTRODUCTION

Interfacial adhesion was varied by applying four model sizes to the E-glass fibre reinforcement of the PA66 matrix composites. All the elements which make up the size-modified composites have been examined both individually and combined in the composite material. Figure 7.1 is a schematic representation of the fibre/matrix interphase, each section of which is described in the following chapter.

FIGURE 7.1: The fibre/matrix interphase

7.2.2 MATRIX

A Maranyl A100 PA66 polymer, supplied by ICI, was employed for the matrix of the size-modified composites. All the size-modified samples were produced by Vetrotex and their manufacture is the subject of another thesis (1).
Transmission optical microscopy has shown that the PA66 matrix polymer consisted of an array of spherulitic structures, as shown in Figure 5.1. The semi-crystalline nature was confirmed with DSC, as a first order transition, or the melting point was observed, and by X-ray analysis, where crystalline peaks were detected, superimposed on an amorphous halo. An average crystallinity of 36.6% and a crystallinity index of 71% were measured with these techniques. X-ray diffraction revealed that the crystalline structure was triclinic, which is the equilibrium crystal structure below the Brill transition temperature of 175°C, as described by Bunn and Gardner (2).

ICI recommended a heat treatment at 160°C for 15 minutes per 0.32 cm thickness of the specimen, to stabilize the crystallinity of the PA66. Examination after this heat treatment with X-ray analysis showed a small increase in the crystallinity (71% and 74% before and after the heat treatment, respectively) and no apparent effect on the crystal structure. Starkweather et al.(3) showed that the crystal structure is dependent on the processing temperature and the cooling rate, as given by Figure 7.2.

ICI recommended a heat treatment at 160°C for 15 minutes per 0.32 cm thickness of the specimen, to stabilize the crystallinity of the PA66. Examination after this heat treatment with X-ray analysis showed a small increase in the crystallinity (71% and 74% before and after the heat treatment, respectively) and no apparent effect on the crystal structure. Starkweather et al.(3) showed that the crystal structure is dependent on the processing temperature and the cooling rate, as given by Figure 7.2.

The injection moulded samples were produced at a temperature between 280 and 300°C followed by an air quench. From Figure 7.2 it can be seen that the centre of the diffraction peaks, on heating to 160°C, approach each other, to form a single peak at 175°C. However, as the specimens were tested at room temperature, both before and after the heat treatment, and were cooled at similar rates after manufacture and annealing, the measured X-ray diffraction peak positions were almost identical.

FIGURE 7.2 : Changes in the diffraction pattern of PA66 with temperature
The repeated heating (to a maximum temperature of 425K) and cooling cycles during a torsion pendulum test had no apparent effect on either the structure or the crystallinity of the samples. Morgan (4) studied the crystallisation of polymer fibres, and plotted the rate of crystallisation as a function of the temperature, as shown in Figure 7.3.

![Diagram showing crystallisation ranges of polymer fibres](image)

**FIGURE 7.3:** Crystallisation ranges of polymer fibres

----- = rate of crystallisation was too rapid to be measured

From this diagram it can be seen that the crystallisation range of PA66 is from -20°C to 240°C, with optimum crystallisation at approximately 150°C. As the torsion pendulum cycles did not affect the crystallinity of the PA66, even though the specimen was maintained within the crystallisation range for long periods, the heat treatment was considered to fully crystallize the polymer.

**b. Physical characterization**

The 0.5% secant modulus of 1.6 GPa and the failure stress, $\sigma_f$, of 50.3 MPa and failure strain, $\varepsilon_f$, of 44% measured by tensile testing were similar to the values given in Section 2.5.5.3 (5) for a PA66 in its non-dried state. Curtis et al. (6) reported that the failure behaviour of an unfilled PA66 is dependent on the manufacturing temperature. PA66 moulded at 265 to 270°C showed ductile behaviour (with a failure strain exceeding 100%) whereas a moulding temperature of 300°C produced relatively brittle failure, with a failure strain of 4.9%. Hence the intermediate value for the failure strain obtained, for the PA66 studied, may result from the injection moulding temperature range employed (between 280 and 300°C).
PA66 was particularly sensitive to water as shown by viscoelastic analysis. The presence of water affects both the dynamic mechanical and the mechanical properties of the polymer. Hygrothermal ageing of PA66 has been widely studied (7,8). Pufer and Sebenda (9) showed that the insertion of water molecules between two neighbouring amide groups produces a plastification of the polymer. Three configurations of the water addition exist as given in Figure 7.4.

![Figure 7.4: Insertion possibilities of water in PA66](image)

1. between two carbonyl groups
2. between CO and HN groups of neighbouring chains
3. condensation of a water molecule on an "inserted" H$_2$O group

The viscoelastic behaviour of PA66 (before drying) was characterized, with the torsion pendulum, by three peaks at -139.9, -60.2 and 66.9°C, as shown in Figure 5.103. The $\gamma$ transition is considered to be due to localized movement of the -CH- groups between the amide groups in the amorphous phase and the $\alpha$ transition as a pseudo glass transition resulting from the onset of rotational freedom of fifteen monomeric units, as described in Section 2.5.3.4. There is some discrepancy as to the origin of the $\beta$ transition. The form of this peak is dependent on the thermal history of the specimen. Two types of $\beta$ relaxation have been defined, one water related and the other linked to the structure of the polymer (10). This latter form is present in quenched samples, but not in those which have been slow-cooled or annealed. The heat treatment proposed by ICI, which has little apparent effect on the crystalline structure of the specimen, annealed the sample above its glass transition temperature, hence minimizing the
probability of the structure related $\beta$ transition. This was confirmed by the development of the successful in-situ drying technique, described in Section 5.3.3.2, which showed that this relaxation was effectively water dependent for this particular PA66 polymer, as the $\beta$ peak was eliminated after the third temperature cycle. Drying was also accompanied by an increase in the temperature of the $\gamma$, $\beta$ and $\alpha$ transitions. In the presence of water, the H-bonding between the PA66 macromolecules fails, promoting chain mobility and hence inducing a decrease in the transition temperature. Heuvel and Huisman (11) described a similar H-bond failure in polyamide 6 samples.

c. Conclusion

The Marany A100 PA66 matrix examined was semi-crystalline with a triclinic structure. Optimum crystallinity of the polymer was achieved by annealing at 160°C, and this heat treatment also rendered the $\beta$ transition independent of the structure of the polymer. The presence of this transition indicated the water sensitivity of the PA66.

7.2.3 POLYMER/SIZE ALLOYS

The study of polymer/polyurethane size alloys has permitted a greater understanding of the interphase region. The size/matrix interphase section (Figure 7.1) was considered as a gradation of combinations of the PA66 and Size B or Size A. Polymer/size alloys, which corresponded to specific points of this variation in concentration, were studied. Figure 7.5 shows the proposed interphase structure.

![Figure 7.5: The size/matrix interphase](image-url)
The polymer/size alloys were prepared in the form of injection moulded specimens, with size concentrations of 3, 5, 7 and 12%.

a. Structural characterization

X-ray and DSC analyses have shown a variation of the crystallinity and the structure of the polymer alloy specimens, as shown in Table 5.5. Generally an increasing crystallinity results from an increased proportion of added size, but when the addition exceeds a threshold value of 12%, this trend is no longer obtained. Two hypotheses may explain the observed behaviour:-

1) the size acts as an impurity and as a site of preferential nucleation

2) the size plastifies the PA66 matrix, with the increased mobility of the PA66 macromolecules facilitating crystallization.

b. Physical characterization

Dynamic mechanical analysis has shown that the viscoelastic behaviour of the size alloys is dominated by the properties of the PA66. Effectively both the pure PA66, and the PA66/size alloys were characterized by three characteristic viscoelastic transitions at -137, -49 and 86.9 °C (136, 224 and 360K). A peak specific to the size was not observed. DSC analysis measured the glass transition temperature of the polyurethane of the size at -38°C (235K), whereas, with the DMTA the temperature for this relaxation, for the polyurethane size film, was at 17°C (290K). The difference in temperature can be explained by the preparation of the samples and the nature of these techniques. Granules of polyurethane, used in the polymer/size alloys, were directly employed for the DSC analysis. The polyurethane film was produced from a solution, dried and then heated between Teflon sheets at 100°C, before testing with the DMTA. Additionally the DSC represents a purely thermal technique whereas, the DMTA is a dynamic method. Viscoelastic behaviour is frequency dependent, with an increasing frequency resulting in an increase in the glass transition temperature. This was clearly shown by the torsion pendulum results, where the transitions measured at 0.01, 0.1 and 1 Hz were respectively displaced towards higher temperatures. This phenomenon can be explained by considering the time of response related to each frequency. At high frequencies, there is less time for chain uncoiling to occur. Hence the material will appear to be relatively stiff compared to the same material tested at
lower frequencies. In the latter case the polymer chains have more time to move, and therefore the glass transition is attained at lower temperatures. An increase of approximately 6°K was measured for a tenfold increase in frequency, for the PA66 polymer.

The possibility of masking the size specific peak by the β peak was considered as the temperature range of this transition was measured from -98.2 to 1.9°C or 175 to 275K. Drying of the specimen revealed that masking does not occur. However, a shift of the glass transition temperature towards lower temperatures was measured, as the quantity of added polyurethane increased. This trend can be modelled with the Flory - Fox law (Figure 7.6):-

\[
T = T_1 V_1 + T_2 V_2 [7.1]
\]

where \( T = \alpha \) peak temperature of the polymer alloy
\( T_{1,2} = \alpha \) transition temperature of the constituents 1 and 2
\( V_{1,2} = \) volume fraction of constituents 1 and 2

![Graph](image)

**FIGURE 7.6:** Prediction of the glass transition temperature with the Flory-Fox law

Compatibility of the polymer of the size and the PA66 was hence established, as an intermediate single peak, whose location was composition dependent, was observed, rather than two individual peaks corresponding to the matrix and the size. This latter case is for non-compatible systems, where the components maintain their intrinsic characteristics. An example of an incompatible system was found to be ABS (acrylonitrile butadiene styrene), as shown in Figure 7.7. Separate damping peaks
FIGURE 7.7: DMTA spectrum of an incompatible system (ABS - acrylonitrile butadiene styrene).
were measured at -80°C and 115°C, which correspond to the polybutadiene (rubber component) and the styrene-acrylonitrile copolymer (matrix) respectively. The low temperature peak was produced by the glass transition in polybutadiene \([-\text{CH}_2-\text{CH}]=\text{CH}\text{-CH}_2\text{In}\] whereas the high temperature peak was due to the onset of rotational freedom of the polystyrene backbone. No interaction occurred and hence no peak shifts were measured. The glass transition process of the polystyrene matrix was not composition dependent. This result confirms the presence of separate peaks for a non compatible system, and hence ratifies the compatibility of the PA66/size alloys.

c. Conclusion

The study of the polymer/size alloys determined the behaviour of the matrix in the proximity of the sized fibres. Matrix polymer/size compatibility was also established for the polyurethane-based size. This compatibility is essential in the formation of strong interfacial bonding, and hence for good mechanical characteristics in the composite material.

Structural changes were induced by the modification of the PA66 with Size A and Size B. It seems likely that the measured increase in crystallinity results from the plastification of the PA66 polymer with the matrix-reactive polymer, as this hypothesis suggests a single phase and compatibility between the elements. This was confirmed by viscoelastic analysis. The impurity hypothesis considers the polyurethane as a non compatible element and is consequently improbable.

Significant quantities of the size were required to produce slight temperature shifts. Although high percentages of size may exist locally at the interface, within a composite, the size represents a volume fraction of approximately 0.03, assuming that the size forms a uniform layer, 300nm thick, on the fibre surface. Therefore, in the composite, if intermediate peaks form due to a compatible PA66/size system, the peak displacement will be difficult to measure. Additionally, if there is limited size/matrix interaction, detection of size specific peaks is unlikely. Varlet (12) showed the interaction of incompatible polypropylene/polyamide 12 polymer alloys. A shoulder due to the polypropylene was observed on the low temperature side of the \(\alpha\) peak of PA12, when the fraction of polypropylene was of 70%, for the alloy before drying. He also showed that the the individual peaks were more easily detected in a dry system than one in the non-dried state.
Dufresne et al. (13), however, measured a peak specific to an elastomeric interphase, which represented a volume fraction of 1% of the total composite (DGEBA-DDA matrix reinforced with glass beads). The technique employed was thermostimulated current/creep spectroscopy. The viscoelastic analysis of thermosetting polymers is facilitated by the relatively high damping characteristics of these materials, which may aid the detection of low volume fraction elements.

### 7.2.4 SIZE FILMS

#### 7.2.4.1 Structural characterization

The structure of the size films was composition dependent, the A1100 generally producing a decrease in the amplitude of the crystalline peaks of the sample, as shown by X-ray analysis (Section 5.2.2.3). XPS spectroscopy also revealed that the addition of the silane to a matrix reactive polymer systematically resulted in the reduction of the C/O ratio. The latter observation suggests that the quantity of oxygen in the coupling agent was relatively high in comparison to the other elements of the coating.

**a. Size 1 - Pure Epoxy and Epoxy + 50 % A1100 Films**

The Size 1 film samples had an amorphous structure, as shown by X-ray diffraction. XPS analysis of the films revealed a relatively high C/O ratio. Bonding, typical of the elements of the size, was shown by peak fitting the C1S peak of the XPS spectrum.

**b. Size 2 - Pure Polypropylene and Polypropylene +50% A1100 Films**

Compared with the other sizes, the polypropylene-based size films showed relatively high crystallinity, as revealed by the large number of crystalline peaks of their X-ray diffraction patterns (Figures 5.49 and 5.50). From these results the structure of the sizes was established as monoclinic, the stable, most widely occurring polymorph of polypropylene. The C/O ratio, measured by XPS, was high, as was expected from the chemical formula of the hydrocarbon matrix reactive polymer (-CH\_2-CH\_CH\_3-). Contamination of the size film by the Teflon sheets was responsible for the presence of the fluorine peaks, for both films, and perhaps for the oxygen peak of the pure polypropylene film. The fluorine contamination was greater for the polypropylene/A1100 size. If this contamination is considered to result from stripping
of Teflon from the mould surface, it can be deduced that the polypropylene/A1100 mixture produces stronger bonding than the pure polypropylene.

c. Size 3 - Polyurethane +10% A1100 Film and Size 4 - Pure Polyurethane Film

Both Sizes 3 and 4 had semi-crystalline structures in the film form, as shown in Figures 5.53 and 5.54. Fluorine contamination of both films and some silicon contamination of Size 4 were detected. The fluorine contamination was greater for Size 3, as indicated by the increased intensity of the F1s peak of Figure 5.38. This result supports the hypothesis that the addition of the A1100 coupling agent to a matrix reactive polymer, promotes improved bonding.

7.2.4.2 Physical characterization

The dynamic mechanical analysis of the size films has shown that each size has unique characteristics, which are affected by the presence of the A1100 coupling agent.

An epoxy system, with the A1100 acting as the hardener, constituted Size 1. The silane coupling agent dramatically altered the properties of the epoxy film, reducing the amplitude of the glass transition peak and increasing the modulus in the rubbery region (Figure 5.96). A proportionality can be assumed between the rubbery modulus and the number of crosslinked points in the three dimensional network created by the interaction of the silane and the epoxy, as:

\[ G = \frac{\rho RT}{M_c} \]  [7.2]

where \( G \) = shear modulus
\( \rho \) = density
\( R \) = gas constant
\( T \) = absolute temperature
\( M_c \) = mean molecular weight of the chain between successive crosslinks

An increase in \( G \), the modulus, at a given temperature, and assuming a given density, results from a decrease in \( M_c \), and therefore an increase in the number of crosslinks. Although the values given by equation 7.2 are rather approximate, they give a good indication of the density of crosslinking. Therefore, from the results of Section 5.3.3.1 a ii, it can be seen that the crosslink density increased by approximately five times in
the presence of the silane, which confirms that crosslinking of the epoxy was produced with the A1100. Chauchard et al. (14) observed a similar increase in the rubbery modulus and consequently in the crosslink density, for a composite, when A1100 was added to the epoxy size coating a R-glass fibre reinforcement.

A general increase in the modulus was expected at both low and high temperatures due to the crosslinking provoked by the A1100. Heinze et al. (15) showed that crosslinking produced relatively small increases in the modulus in the glassy region of natural rubber (i.e. below the glass transition temperature). For the samples examined the modulus of the modified epoxy at 150K was slightly less than that of the pure epoxy, and this difference increased as the glass transition temperature (at -10°C) was approached. This result may be explained by the high proportion of A1100 in the size film (50%), which may have formed an additional polysiloxane film, rather than just producing a cross linked network. The polysiloxane formation is shown schematically in Figure 7.8.

\[
\begin{align*}
\text{EPOXY} & \quad + \quad \text{SILOXANE} \\
\text{SILANE} & \quad \text{OPEN CYCLE}
\end{align*}
\]

\[\begin{array}{c}
\text{Si} - \text{O} - \text{Si} - \text{O} - \text{Si}
\end{array}\]

**FIGURE 7.8 : Polysiloxane formation**

As the A1100 in the fibre coating reacts readily with the glass surface, as described by Chiang et al. (16), the type of interaction with the matrix reactive polymer and the homopolymerisation of the silane are limited. Therefore the interaction of the elements of the epoxy/A1100 film appears not to be representative of the interaction occurring in the size on the E-glass fibres.

Although both the polyurethane and the polyurethane+10% A1100 mixture were characterized by three relaxations at -163, -67 and 18°C (136, 206 and 291K), the amplitude of the peaks increased with the silane addition, as shown in Figure 5.96. This effect was accompanied by a decrease in the modulus. An increase in modulus was expected as the silane coupling agent was assumed to react with the polyurethane, reducing the mobility of the matrix reactive polymer macromolecules, and hence increasing the stiffness of the mixture. This was not the case, as in a similar manner to
the epoxy-based size films, the behaviour of the A1100 was not restricted in the size films. The glass transition temperature of the size films was relatively high, as the $\alpha$ relaxation temperature of the polyurethane was evaluated at -38°C by DSC analysis. From these results it seems unlikely that the polyurethane-based sizes, in film form, are representative of the fibre coating.

7.2.4.3 Conclusion

The structure and the behaviour of the model sizes were dependent on the matrix reactive polymer added to the silane coupling agent. The latter element generally produced a decrease in the amplitude of the crystalline peaks measured by X-ray diffraction which indicates a decrease in the crystallinity of the polymer. The silane addition also influenced the viscoelastic properties of the film. From the structural and physical results obtained for the model films, it can be seen that the A1100 behaves in an unexpected manner. This is due to the relatively high proportion of the silane coupling agent and the absence of the glass surface. Therefore the fibre appears to play an important role in the formation of the structure of the size.

7.2.5 REINFORCEMENT

E-glass fibres of an average diameter of 17.6$\mu$m (std 1.6$\mu$m) were employed as the reinforcement for all the size-modified composites. The fibres have a circular cross-section, but significant variations in diameter were measured from 15.7$\mu$m to 21.9$\mu$m, which can be attributed to variations in the diameters of the bushings of the spinneret. The manufacturing process is described in Section 2.2.2.

Four model sizes were applied to the fibres to give composites with very different interfacial characteristics with a PA66 matrix, as described in Table 7.1.

<table>
<thead>
<tr>
<th>CODE</th>
<th>COMPOSITION</th>
<th>PREDICTED CHARACTERISTICS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIZE 1</td>
<td>Epoxy + A1100 + Ti</td>
<td>Good interface - localized</td>
</tr>
<tr>
<td>SIZE 2</td>
<td>Polypropylene + A1100</td>
<td>Poor size/matrix interface</td>
</tr>
<tr>
<td>SIZE 3</td>
<td>Polyurethane + A1100 + Ti</td>
<td>Good interface</td>
</tr>
<tr>
<td>SIZE 4</td>
<td>Polyurethane + Ti</td>
<td>Poor glass/size interface</td>
</tr>
</tbody>
</table>

**TABLE 7.1**: Predicted characteristics of the model interfaces
The characterization of the size coating on the fibres, and the size/glass interface was rendered particularly difficult by the small diameter of the fibres, the very thin layer of size (typically 300nm) and the insulating nature of the materials. An extensive range of experimental techniques have permitted the surface, the bulk, and the localized structure of the size to be established.

7.2.6.1 Size 1 - Epoxy + A1100 + Ti

Size 1 consisted of an A1100/epoxy mixture to which titanium oxide was added as a marker.

The fibres were tightly bound in the mesh. Interfibre adhesion was such that the fibres tended to break more readily than the interface when separating individual fibres from the mesh for the microdrop tests. Observation of the filaments with the scanning electron microscope revealed a number of bulky asperities on the glass surface, of up to 15μm in length. These features may be due to external artefacts deposited on the sticky surface of the fibre, or due to a local build-up of the size, or clusters of titanium oxide precipitates just below the surface of the size.

a. Structural characterization

This size forms a continuous, amorphous coating on the fibre, as shown by the FEGSEM and TEM micrographs of Figures 5.25 and 5.59. A depth of size of 900nm was measured with TEM. The average depth of the coating was calculated from the burn-off results for the size, which are given in Table 5.2, assuming that the polymer layer was uniform, and that the densities of the fibre and the polymer were 2600 and 1200 kg m\(^{-3}\) respectively. By employing equation 4.1 and a fibre diameter of 17.6μm, the thickness of the polymer was evaluated as 67nm. This is thinner than the depth of the size measured, however, this difference can be accounted for by considering the variation in the depth of the size along the fibre length, the assumed density value of the polymer and the experimental value of the weight fraction of size.

Good coverage and hence wetting of the glass by this size was confirmed by XPS analysis, as the peaks characteristic of the glass, such as calcium and sodium, were not observed. XPS analysis has given some indication of the molecular build up of the
size layer on the fibres. The nitrogen of the A1100 was shown to be beneath the surface of the size, indicating a preferred orientation of the Si end-group of the A1100 molecules towards the glass surface. The formation of stable Si-O-Si siloxane bonds between the silane coupling agent and the glass was described by Jones (17).

XPS and X-ray analysis (glancing or traditional) were not sufficiently sensitive to detect the titanium, which was added in very small quantities (1.8%) as a marker to the size, as shown by the results in Section 5.2.2.2 and 5.2.2.3. TEM, EELS and microprobe analysis proved successful techniques for the marker observation. The titanium was in the form of titanium oxide precipitates (of the type TiO₂) of approximately 25nm in diameter. These were often observed in clusters of the thickness of the thin foil, with very little polymer between the particles. This structure as revealed by EELS, as the spectrum of the zone of precipitates showed a high intensity titanium peak, but a very low intensity carbon peak (Figure 5.73). This tendency was reversed for the size in the proximity of this area, as shown in Figure 5.75. The titanium therefore did not exhibit any tendency to diffuse through the polymer, but remained as a localized precipitate. Points were observed below the surface of the size with the FEGSEM which were significantly larger than the individual titanium oxide precipitates measured from the TEM micrographs. The thickness of the size was variable and the areas in relief can therefore be attributed to local build-up of the size polymer, and/or clusters of the marker precipitates, below the surface of the size.

The epoxy and A1100 are considered to form an intimate mixture. The epoxy was a DGEBA of a very short chain length, which reacts with the NH₂ group of the A1100, as shown in Figure 7.9.

![Figure 7.9: Reaction between the epoxy and the silane coupling agent](image-url)
FT-Raman spectroscopy detected functional groups characteristic of a partially cross-linked epoxy network, (NH, epoxy and C-O-C), which confirms that the interaction through an OH group (Figure 7.9) occurs in the size on the fibre surface. However, the ether linkage has the same wavenumber as the siloxane bond (Si-O-Si), as described in Section 5.2.2.7. Both types of bonding are present in this size, but it is probable that the band observed is the fingerprint of the ether linkage, as this group has a stronger signal than that of the siloxane bonding. Separation of the epoxy and silane was not revealed by TEM, which further confirms the mixture hypothesis. Therefore the probable structure of Size 1 on the glass fibres was as shown in Figure 7.10.

![Figure 7.10: Hypothetical structure of Size 1 on an E-glass fibre](image)

b. Conclusion

Size 1 forms an intimate mixture on the fibre, with an apparent orientation of the silicon of the A1100 towards the glass surface. Good wetting of the glass by this size was revealed by the continuous coating of polymer observed on the fibre surface. Size 1 has the capacity to form a good interface with a PA66 matrix polymer, but, the epoxy/A1100 tends to be relatively brittle and has poor fracture toughness.

7.2.6.2 SIZE 2 - Polypropylene + A1100

Polypropylene/A1100 mixture represents a poor potential size for PA66 matrix composites as the PA66/PP interaction is limited, due respectively to the polar and non-polar natures of these polymers. The fibres were not bound within the mesh
highlighting the poor interfibre adhesion characteristics, which, however, facilitated the fabrication of the specimens for the microdrop tests.

a. Structural characterization

FEGSEM micrographs show that the polypropylene/A1100 mixture forms a continuous, non-uniform layer of size on the fibre surface. The minimum thickness measured by TEM was 150nm. The glass was, however, completely buried by the size, as was clearly shown by the absence of the sodium peak from the XPS spectrum (Figure 5.34). A multilayer structure was indicated by XPS analysis, as the silicon and nitrogen from the A1100 appeared to be in a buried layer. Therefore it can be assumed that the silane coupling agent is found preferentially near the glass surface, and was coated with the polypropylene matrix-reactive polymer.

A schematic representation of Size 2 on the E-glass fibres is shown in Figure 7.11.

![Schematic representation](image)

**FIGURE 7.11:** Hypothetical structure of Size 2 on the E-glass fibres

The glass is coated by the silane coupling agent, which itself consists of three distinct layers, as described in Section 2.4.5 c. A silane treated glass surface does not have the surface tension that might be expected from the polar amine groups, but yields a value of 35mJ m\(^{-2}\) which is similar to a non-polar surface (18). Complete coverage of this surface by the non-polar polypropylene is therefore possible. The good wetting of the
glass by this coating can also be attributed to the manufacturing conditions of the sized fibres. A surfactant was added to the size mixture to produce an emulsion, which also aided wetting. Additionally the fibre underwent a heat treatment, after the application of the size, at temperatures in the melting temperature range of the polypropylene. The molten state of the polymer further enhanced the wetting properties of the size.

Evidence for the layer hypothesis, proposed in Figure 7.11, was not obtained with the transmission electron microscope, as the semi-crystalline structure of the size dominated the micrographs. The semi-crystalline nature of this mixture was also detected by glancing X-ray diffraction, which revealed the characteristic peaks of the crystalline, monoclinic phase of a polypropylene.

b. Conclusion

The A1100/polypropylene mixture possibly forms a multilayer structure on the E-glass fibres. Although this size better wets the reinforcement than Sizes 3 and 4, it is not a suitable size for the PA66 matrix, and therefore poor interfacial properties in the composite were expected. However, the polypropylene employed in Size 2 was chemically modified to produce some interaction with the A1100 coupling agent.

Generally non-polar sizes are employed with non-polar matrices. In this case the interphase is strengthened by the formation of an interpenetrating network. This was shown by the microdrop tests, where Size 2 gave the highest interfacial shear strength with the polypropylene matrix. Size 3 which represents a good potential size for polar matrices (the polyurethane having a polar nature) had an interfacial shear stress of 9.8MPa with the polypropylene matrix, i.e. 17% lower than Size 2. This phenomenon was even more marked for the modified polypropylene systems where the difference in the interfacial shear stresses between Sizes 2 and 3 exceeds 21%. Stamhuis (19) studied similar surface coatings in glass fibre reinforced polypropylene, one of which was designed for use in polypropylene and the other was designed for use in more polar polymers, such as PA66. He showed that an appropriate size significantly improves the impact strength of the composite, whereas the size for polar matrices, when employed with polypropylene, results in poor interfacial adhesion. These results are in good agreement with those obtained with the microdrop test.
Polyurethane/A1100 mixture, forms the basis of commercial sizes for PA66 matrix composites. As for Size 1 the fibres were tightly bound in the mesh, indicating good interfibre adhesion.

a. Structural characterization

Size 3 formed a non-continuous layer characterized by two deposit types: circular "islands" of size and large polymer plaques. The "island" structure is similar to that observed by Schrader et al. (20) for chemisorbed silane. It is therefore possible that the polyurethane is chemically bonded to the chemisorbed silane layer, as might be predicted from their molecular structures. The polarity of the various interfacial elements may also play a role in creating this characteristic structure. Glass is highly polar, as is the A1100/polyurethane mixture, which results in a mutual attraction. Extensive interfibre adhesion was observed with both the SEM and FEGSEM, as shown in Figure 7.12. The separation of the adhered fibres was responsible for the formation of the larger size deposits.

Although FEGSEM and XPS appear to show size-free areas between these deposits, TEM has shown that they are in fact covered with a very thin layer of size (approximately 10nm thick). The maximum thickness measured from the TEM micrographs was 300nm and represents the depth of a size deposit. The thicker areas of size show phase separation and a multilayer structure. Although the A1100 and the polyurethane have limited interaction when applied to as an aqueous solution to the fibre surface, the origin of the layers may not be the silane coated with the matrix reactive polymer. The analytical techniques employed, such as EELS, microprobe analysis and FTIR did not have a sufficiently good resolution to allow the characterisation of the observed strata. Chemical analysis of this zone by EELS (Energy Loss Spectroscopy) mounted on the TEM, gave a global spectrum for the size which was similar to that measured for the epoxy-A1100 size, with the exception of an additional calcium peak. Diffusion of such elements from the glass into a silane coupling agent was observed by Jones (21). Analysis of the size with this technique however was difficult as the focussed electron beam rapidly degraded the polymer size.
FIGURE 7.12: Interfibre adhesion observed for Size 3 (polyurethane + A1100)
A proposed build-up of the size layer is given in Figure 7.13.

Characteristic bands of the polyurethane and the A1100 coupling agent were detected by FTIR and FT-Raman. In a similar manner to Size 1 there was some discrepancy as to the origin of the bands at approximately 1500 and 930 cm\(^{-1}\). Both ether and siloxane linkages are present in this size coating, but as the C-O-C and C-H bonds have strong fingerprints, they overlap those of the Si-based groups.

Relatively poor wetting of the fibre with the size mixture was shown by the significant variations in the thickness of the polymer coating.

The size is amorphous, as was shown from X-ray analysis and the TEM micrographs. All the evidence indicates the lack of the titanium marker, which was not detected with either TEM, EELS or microprobe analysis. These techniques were shown to be sufficiently sensitive to ascertain the presence of the marker in Size 1. This result can be explained by the precipitating out of the titanium oxide in the size container, before the application of the coating to the fibres.

**FIGURE 7.13:** Hypothetical structure of the size on the surface of an E-glass fibre

1. Siloxane bond formation
2. Very thin layer of polymer observed between the deposits of size
b. Conclusion

Size 3 represents a good potential size for interfacial adhesion enhancement in PA66 matrix composites, due to the compatibility of these polymers, as was shown by the study of the PA66/size alloys. Both the polyurethane and the PA66 have polar natures, which aid the interaction at the matrix/size interface. The relatively poor wetting properties of the size should not inhibit the formation of strong bonding.

7.2.6.4 SIZE 4 - Polyurethane + Ti

Polyurethane without the presence of the silane coupling agent represents a poor potential size, as only limited bonding can occur between the glass fibre and this coating.

a. Structural characterization

A non-continous layer was observed with the FEGSEM (Figure 5.39), which demonstrates the relatively poor wetting of the fibre by the size. Affirmation of the poor wetting characteristics of the size was obtained with XPS analysis, as significant peaks, characteristic of the glass (calcium and sodium) were measured. Unlike Size 3, a very thin characteristic size layer was not observed with the TEM and all the areas of fibre/size interface examined displayed a relatively thick layer of size (500nm). These zones correspond to the irregular deposits of polyurethane observed with the FEGSEM. In this case the areas between the size deposits can be considered as size free.

The disposition of this size on the glass surface can be utilised to better understand the structure of Size 3 (polyurethane + A1100). It appears that the polyurethane matrix reactive polymer has poor wetting properties and that a continuous size layer is only formed on the fibre surface when the polyurethane is in the presence of the silane coupling agent.

X-ray analysis and TEM showed that the structure of the size was amorphous. Titanium oxide precipitates were observed with both the microprobe analysis and the TEM.
b. Conclusion

Size 4 is a poor potential size as the glass/size bonding is minimal and the polyurethane has poor wetting characteristics. Therefore the composite reinforced with the Size 4-coated fibres can be considered as a composite reinforced with uncoated fibres.

7.2.6.5 General Conclusion for the Size Coated Fibres

By employing a wide range of experimental techniques, the physical, structural and local nature of the size was established. Hypothetical bonding at the fibre/size interface has been proposed for the different sizes and their wetting capacities were assessed, allowing a greater understanding of the interphase in the composite material.

The physical aspect of the size on the glass fibre was shown to be greatly dependent on the nature of the matrix reactive polymer added to the A1100 coupling agent. Size 2, as for Size 1, better wets the fibre than Size 3 and Size 4. However, the compatibility of the matrix-reactive polymer and the matrix is also of great importance. As stated by Plueddemann (22), good coupling activity (as produced by Size 3), with poor wetting should give better final composite properties than a poor adhesion promoter (such as Size 2), which has superior wetting properties. The compatibility of PA66 and the polyurethane-based size was confirmed by the viscoelastic analysis of the polymer alloys. The microdrop test results have shown that a polypropylene-based size produces stronger bonding with a non-polar matrix than a polyurethane-based or polar size.

7.2.6.6 Comparison of Size Films and Size Coating on the Fibres

Comparison of the XPS results of the films and the coating on the glass fibres show considerable differences. The presence of the glass appears essential in producing certain structures, induced by a preferred orientation of the Si-O end groups of the A1100 molecule towards the glass surface, to form stable Si-O-Si bonds. Dirand (23) similarly found that a mould made of Teflon gave different properties at the surface of a vinylester polymer to those obtained with a glass mould.

Glancing X-ray diffraction also showed differences between the types of specimen, particularly in for Sizes 2, 3 and 4. Sizes 3 and 4, in film form, had a semi crystalline
structure, whereas these sizes, as a fibre coating, had an amorphous nature. It is probable that this difference is due to variations in the fabrication routes of these specimens. The size films underwent a relatively slow heating and cooling cycle conducive to the formation of crystallites, whereas the size coating was rapidly cooled.

b. Conclusion

Although the use of model composites in the form of superposed sheets is attractive, as the conformation facilitates characterization, it has been shown that the model is not always a good representation of the real material.

Having assessed the behaviour of the individual elements, and the validity of model specimens to characterize the elements when combined in the composite, the E-glass reinforced PA66 was analysed.

7.2.7 PA66 COMPOSITE

a. Structural characterization

Fibre orientation and fibre length distributions were established by image analysis for the injection moulded specimens, with a short random fibre reinforcement, produced by Vetrotex. A fibre orientation factor, $\eta_0$, of 0.80 was measured for the composites, which was independent of the nature of the size employed. Sanou et al. (24) showed that the shape of the flow front and hence the orientation of the fibres, are affected predominantly by the thickness of the mould cavity, and to a much lesser extent by the flow rate, the melt temperature, the matrix polymer and the fibre content. As all these parameters were constant in the size modified composites, the consistent value of 0.80, for the Krenchel factor, was as expected.

The PA66 matrix had a spherulitic structure, as shown in Figure 5.2. The crystalline phase for the unidirectional samples was triclinic as for the non reinforced matrix polymer. The crystal structure of the matrix was found to be independent of the size employed, but variations in the positions of the X-ray diffraction pattern peaks were observed between the different types of fibre reinforcement (Figure 5.19). The long,
Parallel fibre reinforced composites were characterized by two strong peaks at 2θ =23.6 and 27.7° (Co Kα radiation), or 20.2° and 23.6° (Cu Kα radiation).

For the short fibre composites (S.O and S.R of Table 5.6) only the 010, 110 reflection at 26.1 (Co Kα) or 22.2° (Cu Kα) maintains its relatively high intensity. Cinquin (25) showed that the {010} and {110} planes tend to be parallel to the surface of the specimen, and independent of the orientation of the fibres, with respect to the incoming X-ray, which supports these results. Although all the composites exhibit a triclinic structure, the second strong peak moves to a lower 2θ value (26.1° instead of 27.7°) for the short fibre composites. This difference between the X-ray diffraction patterns can be related to the manufacture of the composites.

b. Physical characterization

PA66 composites, with short randomly oriented fibres, were characterized by tensile testing. The mechanical properties of the different size modified samples, show a small variation in the 0.5% secant modulus, with a significant difference in failure stress. These results are in good agreement with the results obtained by Bader et al.(26).

The failure mechanisms were similar to those described by Karger-Kocsis et al. (27). Although their study considers the measurement of fracture toughness of glass fibre reinforced poly(phenyl sulphone), the failure mechanisms remain valid for other semicrystalline thermoplastic composites, such as those described in this manuscript. Three major mechanisms define the behaviour of these materials:-

1) ductile matrix yielding or brittle matrix fracture.

2) pull-out of the fibres which were perpendicularly oriented to the crack front

3) fibre/matrix separation in the central region of the specimen, where the fibres were aligned approximately parallel to the fracture plane.

This latter mechanism can also be employed to indicate the strength of the fibre/matrix bonding, as failure occurs at the weakest point of the interface. Fibre/matrix failure is hence produced in samples with limited reinforcement/matrix interaction, whereas coated fibres show strong fibre/matrix adhesion, the matrix representing the weakest link in the composite. A combination of the described failure mechanisms were
observed with the SEM. SEM micrographs of Sizes 2 and 4 showed fibre/matrix failure, while Sizes 1 and 3 presented matrix failure. Examples of these fracture surfaces are shown in Figures 5.84 and 5.85.

From the values calculated with the model described in Chapter 6, an adhesion efficiency rating was established for the size modified composites. Ranking from the lowest to the highest interfacial bonding enhancement gave: Size 4 (polyurethane), Size 2 (polypropylene + A1100), Size 3 (polyurethane + A1100) and Size 4 (epoxy + A1100).

Fibre/matrix adhesion was also assessed with model composites, which consisted of a drop of matrix polymer around a single fibre. The form of the graph of load versus displacement, the failure surface, and the calculated value of the interfacial shear stress, resulting from the microdrop tests on the model composites, were examined. Three typical load/displacement graphs were observed, as described in Section 5.3.2. The form of these graphs were employed as an initial indication of the strength of the interfacial bonding. Type I is indicative of good interfacial adhesion. In this case, the strain energy stored in the free length of the fibre is so high that immediate extraction of the drop follows interfacial failure. Poor interfacial bonding results in a load/displacement graph of Type III. Interfacial failure in this case was followed by the progressive extraction of the droplet resulting in considerable fibre/droplet friction (28). The second type of graph shows the intermediate case where the force applied was sufficient to extract the droplet along a certain length of the fibre, but insufficient to remove the drop completely. Some friction was therefore observed. Two phenomena were responsible for the friction: variations in the diameter of the fibre (of up to 0.2µm along a fibre length of 60mm), and local variations in the depth of the size on the fibres as observed by FEGSEM and TEM and described in Sections 5.2.2.1 and 5.2.2.4.

Experimental difficulties rendered the use of PA66 impossible for the microdrop test. An adaptation of the sample preparation, using an inert atmosphere, may overcome the problems encountered due to the degradation of the PA66. In this study a polypropylene matrix, in its unmodified and modified states, was employed to examine the promotion of interfacial adhesion enhancement by the model sizes. The modified polypropylene, activated to improve interfacial bonding systematically resulted in higher interfacial shear stress and a load/displacement graph of Type I. As a strong interfacial shear stress indicates strong fibre/matrix bonding, the adhesion efficiency of the sizes can be rated in a similar manner to that proposed by the adhesion efficiency
model of Chapter 6. Ranking from the lowest to the highest values of interfacial shear stress gave Size 4 (polyurethane + Ti), Size 3 (polyurethane + Al100 + Ti), Size 1 (epoxy + Al100 + Ti) and Size 2 (Polypropylene + Al100 + Ti). As described in Chapter 6 and in Section 7.2.3, the compatibility of the size and matrix polymers plays an important role in the enhancement of fibre/matrix bonding. The modulus of the size was also considered, the epoxy based size showing a higher dynamic modulus at room temperature than the polyurethane-based size.

The dynamic-mechanical behaviour of the size-modified composites was dominated by the properties of the PA66 matrix. Three peaks at approximately 133K, 213K and 340K were measured, which vary little from the peak positions of the pure matrix material. The viscoelastic properties of a fibre filled composite depend on the viscoelastic behaviour of the interphase and the constituent phases, and on their respective volume fractions. This result is therefore as expected, when considering the relative proportions of the elements which make up the composite. The volume fractions of the matrix, size and fibres were 0.67, 0.03 and 0.30 respectively. Behaviour changes due to the fibres in the 100 to 450K temperature range are minimal, as the glass is well below its glass transition temperature. Hence the glass contribution results in the diminution of the amplitude of the peaks, but does not influence the position of the relaxations. A similar observation was made by Cinquin et al. (29) for unidirectionally reinforced PA66. The size contribution is very small compared to that of the matrix.

The type of reinforcement, either unidirectional, short oriented or short random E-glass fibres, did not appear to play a role in determining the temperature of the glass transition. The temperature depends on the behaviour of the PA66 matrix and only varies by 2.8K between all the composite samples in their dried state (third repetition of the torsion pendulum test). The amplitude of this relaxation, however, varied with the type of reinforcement with a better fibre alignment resulting in an increase in the intensity of this peak. A similar result was observed by Akay et al. (30).

For a given reinforcement type, the amplitude of the glass transition varied with the size employed, but little variation was measured for the $\gamma$ and $\beta$ transitions as corroborated by the results of Cinquin et al. (29). Examination of the PA66 polymer showed that the latter relaxation was water dependent. Amplitude variations for the $\alpha$ relaxation depend on structural differences such as crystallinity and interfacial bonding. Other factors which play a role in the determination of the glass transition process are fibre orientation and fibre-volume fraction. An increase in fibre-volume
fraction produces an increase of the \( \alpha \) transition temperature due to the restriction of the mobility of the macromolecular chains at the fibre/matrix interface, assuming fibre/matrix adhesion. This phenomenon was studied in carbon reinforced epoxy systems by Gerard et al. (31). The fibre-volume fraction and orientation were shown to be relatively constant for all the composite samples, as shown in Table 5.1 and Table 5.4 respectively. As the \( \alpha \) relaxation involves motion within the amorphous phase, an increase in crystallinity produces a decrease in the amplitude of the glass transition peak, as predicted by Alfrey Jr. and Boyer (32). For polyamide 6, a shoulder is observed on the high temperature side of the \( \alpha \) peak, when the crystallinity exceeds a threshold value of 50% (33). All the PA66 samples examined had a similar fall-off on the high temperature side of the \( \alpha \) peak, suggesting a constant, low crystallinity. This proposition was confirmed by DSC and X-ray analysis. The observed variations in the amplitude of the glass transition can hence be attributed to the interfacial bonding mechanism.

The variations between the viscoelastic spectra were more clearly defined for the dried samples (after the third temperature cycle). It appears that the form of the tan. \( \delta \) versus temperature graph, between the \( \beta \) and \( \alpha \) transitions was also dependent on the type of size employed. For the Size2-modified composites, the increase in the tan. \( \delta \) value measured in this zone may be attributed to the presence of a peak specific to the polypropylene matrix reactive polymer. Therefore the in-situ drying technique developed improved the resolution of the torsion pendulum spectra, and enabled the origin of the \( \beta \) transition to be established.

Ranking the interfaces from the highest to the lowest damping characteristics gave: Size 4 (polyurethane), Size 2 (polypropylene + A1100), Size 3 (polyurethane + A1100) and Size 1 (epoxy + A1100). A decrease in damping is due to a reduction of the matrix chain mobility in the vicinity of the glass fibres, and corresponds to improved interfacial bonding (34, 35, 36). Size 4 therefore represents the weakest interface, whereas the epoxy/A1100 of Size 1 gives the best fibre/matrix bonding. This result reflects the rating calculated with adhesion efficiency model.

c. Conclusion

The mechanical and viscoelastic behaviour of the PA66 composites was shown to be dependent on the properties of the constituent elements and on the interface created between them. The enhancement of the interfacial bonding produced by each of the model sizes has been evaluated by three methods: the adhesion efficiency model, the
microdrop test and by viscoelastic analysis. The results obtained rank the sizes systematically in the same order, with the exception of Size 2 which shows excellent fibre/matrix bonding with a polypropylene matrix, due to the compatibility of the polypropylene-based size with this particular polymer. Table 7.2 summarizes the results.

<table>
<thead>
<tr>
<th>METHOD</th>
<th>WEAKEST TO STRONGEST INTERFACIAL BONDING</th>
</tr>
</thead>
<tbody>
<tr>
<td>MODEL</td>
<td>SIZE 4</td>
</tr>
<tr>
<td>MICRODROP TEST</td>
<td>SIZE 4</td>
</tr>
<tr>
<td>TORSION</td>
<td>SIZE 4</td>
</tr>
<tr>
<td>PENDULUM</td>
<td>SIZE 4</td>
</tr>
<tr>
<td></td>
<td>SIZE 2</td>
</tr>
<tr>
<td></td>
<td>SIZE 3</td>
</tr>
<tr>
<td></td>
<td>SIZE 1</td>
</tr>
</tbody>
</table>

**TABLE 7.2: Interfacial bond ranking**

**VII.3 MATRIX MODIFIED COMPOSITES**

**7.3.1 INTRODUCTION**

To enhance the interfacial adhesion in the polypropylene composites the matrix polymer was modified to produce a graft copolymer, which interacts readily with the sized-glass fibre. A graft copolymer comprises of molecules with one or more blocks connected as side chains to the backbone, having constitutional or configurational features different to those in the main chain (37). For this study, the backbone was the polypropylene macromolecule, and the maleic anhydride (MA) or synthesized compounds, PM and PA, were the side chain or graft.

**FIGURE 7.14: A simple graft copolymer**

where X is the unit in the backbone to which the graft is attached
The grafting of the modifying agent took place in the presence of a free radical initiator and a functional monomer. The latter element was added to increase the efficiency of the grafting reaction and hence enhance the properties of the composite through strong fibre/matrix bonding, as described in Section 2.5.2.6.

7.3.2 MATRIX

The polypropylene matrix had a relatively high crystallinity index, ranging from 55.6% to 70.5% (measured by X-ray diffraction) depending on the type of modification, either processing or chemical. The crystalline structure was also revealed by transmission optical microscopy. The crystallization of isotactic polypropylene generally occurs on the heterogeneities present in the bulk polymer and consists of an arrangement of macromolecules in the shape of lamellae growing radially from these nuclei, as described in Section 2.5.2.2 f. The resulting spherulitic structure is birefringent and hence can be detected with a polarizing microscope. Two crystalline polymorphs were widely observed in the isotactic polypropylene, namely the $\alpha$, monoclinic and the $\beta$, hexagonal phases, which are positively and negatively birefringent, respectively.

The behaviour of the matrix polymer and the synthesis of the graft copolymer, essential for adhesion improvement, were influenced by the processing conditions, the addition of the free radical initiator and chemical modification. The effects produced by each type of modification, on the structural and physical characteristics of the matrix polymer, are considered in the following sections.

7.3.2.1 Effect of processing conditions

Various manufacturing routes were employed for the production of the polymer and composite samples, which are given in Section 3.3.4. The polypropylene matrix was examined in its unprocessed state, both after compression and injection moulding (BT000), and as an injection moulded, processed polymer, with the reactive processing achieved either in a Buss Ko kneader (MA00) or in a twin screw extruder (BT00). An additional sample was processed in the Buss Ko kneader before compression moulding.
The structure and the crystallinity of the pure polypropylene samples were influenced by the fabrication technique employed, as shown by both transmission optical microscopy and by X-ray diffraction. The unprocessed, compression moulded polypropylene, which suffered no mechanical damage, had a fine granular crystalline structure, with a large proportion of the hexagonal phase. All the processed samples revealed spherulitic structures, and those which were injection moulded all exhibited a similar unique spherulitic type in the zones examined. This latter form was fibrous and resembled the spherulites described by Padden and Keith (38) as the "mixed-type". These crystallites have a monoclinic structure. The crystalline structure of the processed, compression moulded polymer consisted of two distinct types of spherulites, of type III (hexagonal) and of type I (monoclinic). Generally an increase in the severity of the manufacturing process resulted in an increase in the proportion of the α, monoclinic crystalline phase, and a resulting reduction in the quantity of the β, hexagonal phase. The latter crystalline polymorph is metastable. Therefore, for unmodified polypropylene, it can be concluded that mechanical and thermal degradation occurring during manufacture, induces the transformation from the metastable hexagonal phase to the stable monoclinic phase and that injection moulding aids the formation of the mixed spherulitic structure.

Some discrepancies between the observed microstructure, shown in Figure 5.3, and the K'-value (which is a measure of the relative proportions of the monoclinic and hexagonal phases), given in Table 5.7, were noticed. These differences can be explained by morphological heterogeneities within the injection moulded samples, both through the thickness of the specimen which gives rise to the skin-core structure (39) and along its length. X-ray diffraction patterns of the extremities of a tensile test dumbell specimen showed an absence of the β crystalline phase at the non-gate end of the sample. An example of typical diffraction patterns for the polymer are given in Figure 7.15. The assumption of an average morphology for the sample is therefore not valid. However, the X-ray results were consistently measured for the gate end of the tensile test specimen, and hence are comparative. Trotignon et al. (39) described similar structural variations and discussed their influence on the behaviour of injection moulded polypropylene composites. They showed that physical ageing is particularly affected by this phenomenon, but did not advance an explanation for this behaviour.

The degree of coarseness of the spherulites is dependent on the type of spherulite and on the manufacturing temperature. Although the compression moulded samples were
FIGURE 7.15: X-ray diffraction patterns of the extremities of a tensile test specimen.
produced at a lower temperature than those which were injection moulded, the fabrication temperatures can not be exploited to understand the measured variations in the diameter of the crystallites, as the different moulding processes resulted in the formation of different spherulitic types.

The MFI (melt flow index), which is inversely proportional to the molecular weight, varied between the samples which were produced by different fabrication routes. Jarrin et al. showed that the mean molecular weight lowered and the molecular weight distribution narrowed on processing, indicating mechanically-induced failure of the molecules. Mechanical degradation predominantly causes rupture in the middle of the polymeric chain, which affects the breadth of the molecular weight distribution. This narrowing is not observed for pure thermal degradation, which involves the failure of randomly positioned covalent bonds (40). Chain scission can be therefore assumed to have occurred, due to the mechanical and thermal degradation induced by processing.

The crystallinity was slightly reduced when the polymer was processed, either in a Buss Ko kneader or in a twin screw extruder.

b. Physical characterization

The variation in the structure, induced by the different processing routes, had a direct influence on the mechanical and viscoelastic performance of the polypropylene. From the tensile results in Table 5.10 it can be seen that the unprocessed polymer (BT000) was more ductile than the processed samples, MA00 and BT00. The higher molecular weight of the unprocessed polymer is responsible for the measured increase in the failure strain. Reis and Menges (40) showed that the Young's modulus and the tensile strength of the polymer are only significantly affected when the change in molecular weight is considerable. This supports the results obtained, as the failure stresses and the 0.5% secant moduli of the polypropylene samples were similar. Crystallinity also influences the mechanical response of the polymer, as the crystallites act as crosslinks in the matrix which inhibit the movement of the macromolecular chains. An increase in crystallinity therefore results in an improvement in the mechanical properties of the polymer. As the 0.5% secant moduli of the samples were constant, it can be concluded that the measured variations in crystallinity were not significant.

The viscoelastic properties of the polypropylene were determined with the DMTA and the torsion pendulum. This polymer was characterized by three transitions at -23, 7 and 102°C (250, 280 and 375K). Each relaxation has been attributed to particular
movements of the polymer chain, with the peak observed at 280K corresponding to the
glass transition. Details of the molecular movements are given in Section 2.5.2.4. The
low temperature viscoelastic behaviour was similar for all the polymer samples.
Although the viscoelastic properties of the samples of Series 1 and 3 can not be
directly compared, due to variations in the quality of the samples, from the BT000 and
BT00 results it can be seen that processing produces a decrease in the amplitude of the
glass transition peak (Figure 5.113). This phenomenon can be attributed to the shorter
molecular chain length of the processed polypropylene.

A slight increase in the temperature of the crystalline transition and its amplitude were
measured for the unprocessed sample (BT000) compared to that of the BT00 polymer.
The origin of this relaxation was established by Jourdan (41) as the diffusion of defects
through the thickness of the crystallites of the crystalline phase. The higher value of
crystallinity of the BT000 polymer, measured by X-ray diffraction, therefore appears
to be responsible for the observed variation. However, the relationship between the
crystallinity and the intensity of the αc peak is not simple as the number of defects
within the crystalline phase also influences this transition. This may explain the
relatively high amplitude measured for the MA00 sample, which has a similar
crystallinity index to that of the BT00 polymer, if the non optimized processing
parameters of Series 1 produced an increased quantity of defects in the crystalline
phase.

c. Conclusion

By varying the processing conditions the structure and hence the physical properties of
the polymer are modified. The fabrication route employed therefore influences the
final properties of the polymer.

Processing plays an important role in polymer modification as it can initiate the
grafting process by a free radical mechanism. Degradation of the matrix polymer is
responsible.

7.3.2.2 Effect of the addition of a free radical initiator

A peroxide free radical initiator was employed in the grafting reaction to initiate the
radical process. The desired interaction between the polypropylene and the peroxide is
given in Figure 7.16.
FIGURE 7.16: Free radical mechanism essential in the grafting process.

a. Structural characterization

A peroxide addition results in a series of dramatic structural changes, as shown by the comparison of the micrographs of the compression moulded samples, in Figures 5.3 and 5.4:

1) A reduction in the diameter of the Type III spherulites (of the hexagonal form) by up to 35%.

2) A reduction in the number of Type III spherulites

These observations were confirmed by the measured decrease in the K'-value. An increase in the proportion of the monoclinic phase therefore results from the addition of the free radical initiator. This transformation may be due to the chain scission produced by the addition of the peroxide (indicated by the relatively high MFI value).

3) The crystallinity remained relatively constant for all the samples, except for the peroxide modified polypropylene of Series 1 (MA02). Even though a smaller spherulite size was measured on the addition of a peroxide, the diameter of a spherulite does not reflect the crystallinity of the sample, but rather the conditions under which the polymer was crystallized (42).

The peroxide addition had a similar effect on the structure of the injection moulded polymers.
b. **Physical characterization**

Mechanical testing of the polymer has revealed that the peroxide renders the polypropylene brittle, with the failure strain for an unmodified polypropylene being over 800%, whereas that of the polypropylene/peroxide mixture was 2%, for Series 3. In a similar manner to the processed, unmodified samples, the measured decrease in the molecular weight was responsible for this decrease in the mechanical properties. Examination of the load/displacement curves for each of the tests of the Series 1 samples revealed a considerable variation in the failure behaviour of a polymer of a given modification. Therefore, the results for the MA02 specimen were not considered as representative of the behaviour of a peroxide-modified polypropylene.

Viscoelastic analysis revealed dramatic differences in the form of the tan δ versus temperature graphs on the addition of a peroxide. For Series 1, and Series 3 a shift of the glass transition temperature towards lower values, and an increase of the amplitude of this peak were observed, for the peroxide-modified polymer. A similar results was obtained for the compression moulded samples, tested with the DMTA, as shown in Figure 5.99. This viscoelastic behaviour was indicative of a shorter molecular chain length and an increased proportion of the relaxing phase, again affirming the MFI result of chain scission. The assumption that the relaxation strength is proportional to the number of chain atoms involved in a relaxation and also to the number of amorphous segments of that length, was confirmed by Alfrey Jr. and Boyer (32).

c. **Conclusion**

A peroxide free radical initiator is an essential element in the chemical grafting process, but it must be carefully controlled as an excess leads to undesirable side reactions, as given in Figure 7.17.

\[ \begin{align*}
\text{CH}_3 \\
\text{(CH}_2\text{C)} \\
\rightarrow \\
\text{CH}_3 + \text{CH}_2\equiv\text{CH}
\end{align*} \]

Chain scission occurs which results in a decrease in the molecular weight
Crosslinking produces a gel, and an increase in molecular weight.

**FIGURE 7.17:** Undesirable reactions between the free radical initiator and the polymer.

Both reactions are undesirable as the free radical is no longer available for grafting.

From the results obtained from both the structural and physical characterization of the polymer, it can be concluded that the effect of the addition of a free radical initiator to the polypropylene is a dramatic reduction of the molecular weight of the polymer.

7.3.2.3 **Effect of chemical modification - the MA system**

The synthesis of the graft copolymer was examined at each stage of the modification process. All the samples, from Series 1, were produced by premixing in a Buss-Ko Kneader before injection moulding. As the processing conditions were kept constant, the structural and physical variations observed were related to the chemical nature of the specimen.

a. **Structural characterization**

The chemically modified samples exhibited a bimodal spherulitic structure consisting of Type I and Type III spherulites. The diameter of the spherulites varied with the type of chemical modification. Similar spherulite diameters of 0.04 and 0.01mm (Type I and Type III respectively) were measured for MA02 (PP + peroxide, I) and MA101 (PP + MA + I). The peroxide addition to these samples appears to play an important role in determining the structure of the polymer.

The small precipitates, observed in the MA01 and the MA101 samples of Series 1, were the MA modifying agent, which has a low solubility in polypropylene. It can therefore be concluded that these polymer modifications were supersaturated in this additive. The precipitates were not observed for the MA103 modified polymer which
contained the same proportion of the modifying agent, but also contained the additional functional modifier developed by Al Malaika et al. (43).

The crystallinity varied slightly between the chemically modified samples. A small increase in the crystallinity was measured on the addition of the MA modifying agent to the polypropylene (MA01). The precipitates, observed by transmission optical microscopy, appear to act as nucleating agents in this particular modified polymer and hence promote crystallisation.

Chemical modification produced changes in the colour of the samples, both in the presence and absence of the fibre reinforcement. A qualitative colour coding (and an approximate description of the colour) was employed, based on the ICI paint colour coding (trade name DIMENSIONS).

<table>
<thead>
<tr>
<th>SAMPLE CODE</th>
<th>COLOUR</th>
<th>COLOUR CODE</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
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</tr>
<tr>
<td>MA00</td>
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</tr>
<tr>
<td>MA01</td>
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</tr>
<tr>
<td>MA02</td>
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<tr>
<td>MA101</td>
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</tr>
<tr>
<td>MA103</td>
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<tr>
<td>ICIHW60F</td>
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<td>0502-R</td>
</tr>
<tr>
<td>MA103F</td>
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<td>0.502-R</td>
</tr>
<tr>
<td>PM103F</td>
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<td>2010-Y40R</td>
</tr>
<tr>
<td>PA103F</td>
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<td>30320-Y20R</td>
</tr>
<tr>
<td>SERIES 2</td>
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<tr>
<td>MA103BF</td>
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<td>0605-Y26R</td>
</tr>
<tr>
<td>PM203F</td>
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<td>1040-Y10R</td>
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<tr>
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<tr>
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<td>1040-Y10R</td>
</tr>
<tr>
<td>BT05F</td>
<td>cornfield</td>
<td>1040-Y10R</td>
</tr>
</tbody>
</table>

TABLE 7.3: Colour changes observed on chemical modification
During chemical modification undesirable by-products can form, which discolour the polymer. However, the dark colour of the PM and PA samples is due to the benzene ring in these highly coloured modifying agents (PM is scarlet and PA is orange) rather than polymer degradation. This was confirmed by the relatively light colour of the MA composite samples.

b. Physical characterization

The mechanical behaviour of the chemically modified polymers was evaluated by tensile testing. From Table 5.10 it can be seen that the 0.5% secant modulus was relatively constant for all these samples. Variations in the failure properties were observed, but as described for the peroxide-modified polymers, there were considerable differences between the results of individual tests rendering these results invalid.

The viscoelastic properties were dependent on the type of modification, as shown in Figures 5.100 and 5.115. An increase in the amplitude of the glass transition peak was observed for the samples modified in the presence of a peroxide. This phenomenon can be attributed to the shorter molecular chain length of these samples.

c. Conclusion

By employing the functional monomer, the grafting of the modifying agent was enhanced, as was shown by the lack of maleic anhydride precipitates in the MA103 sample. Therefore the in-situ reactive processing technique is attractive as it minimizes losses of the modifying agent resulting in not only better potential adhesion in the composite, but also in a reduction in the cost and an increase in the safety of the process.

The results obtained also highlighted the necessity of optimized processing conditions to avoid inconsistent properties due to poor mixing. Uniform mixing of the polypropylene and the chemical modifiers can be achieved with the twin screw extruder, due to the high shear developed under such conditions. Therefore future processing should further improve the in-situ reactive processing technique.
7.3.3 REINFORCEMENT

E-glass fibres of an average diameter of 15.2μm (std 1.1μm) reinforced the matrix-modified composites. The fibres were in the form of meshes 4.5 mm long, with approximately 2000 fibres per mesh. These fibres were coated by an industrial size, commercialized as A1100 by Union Carbide, which has been developed to form covalent bonds with the glass surface, as discussed in Section 2.4.5. This particular size forms a continuous layer on the fibres, as shown by FEGSEM (Figure 5.29). XPS analysis also indicates the complete coverage of the fibre surface by the size, as the peaks characteristic of the glass (sodium and calcium) were absent from the spectrum, and the C/O ratio was relatively high. Similar results were obtained for Sizes 1 and 2 of the size-modified systems, which exhibited good wetting properties. The depth of the size was evaluated as 395nm with TEM. The TEM micrographs revealed the amorphous nature of the size, which was confirmed by the glancing X-ray diffraction pattern, shown in Figure 5.57.

7.3.4 MODIFIED POLYPROPYLENE COMPOSITE

Three series of matrix-modified composites were manufactured by Aston University. The first two series were produced by mixing in a Buss-Ko Kneader (single screw extruder), followed by injection moulding. The final series (Series 3) was prepared for injection moulding in a Betol BTS30 twin screw extruder. The latter technique is of particular interest, as it produces sufficient quantities of the modified material to render this process industrially viable.

a. Structural characterization

The fibre-volume fraction was measured with the method described in Section 4.2.1.2, and the fibre length and fibre orientation distributions were established by image analysis, for the matrix-modified composites. These parameters were employed to determine the effect of processing on the structure of the composite and the severity of the various fabrication routes. Optimization of the processing conditions for Series 2, was revealed by the relatively constant fibre volume fractions (Table 5.1), which approached the desired value of 0.13, and a longer average fibre length than Series 1. Comparison of these results with those of Series 3, however, showed that the use of the twin screw extruder produced a longer average fibre length, which should result in improved properties in the composite providing there is adequate fibre/matrix
adhesion. The variation in the average fibre lengths can be attributed to the severity of the process. The Buss-Ko kneader consists of a single screw, with reciprocating pins along the length of the barrel, which results in a harsh mixing environment. The fibres and the matrix granules were introduced simultaneously into the extruder and therefore both suffered similar degradation. In the twin screw extruder, the fibres were added at the end of the production line and hence fibre degradation was minimized. This difference was confirmed by the maximum fibre lengths measured for these systems, with the twin screw extruded samples containing fibres of twice the length of those in a specimen produced in a Buss Ko kneader. In a similar manner to the PA66 composite samples described in Section 7.2.7, the orientation of the fibres varied little between the different modifications. This was as expected as the injection moulding conditions and the geometry of the mould were constant. The effect of the fibre volume fraction on the Krenchel factor was shown to be negligible for the small variations measured. A value of 0.64 was evaluated for the Krenchel orientation factor.

The production of the thin films required for observation with the transmission optical microscope was difficult, as described for the PA66 composites. However, the structure of the matrix was spherulitic, with no observable modifications of the crystalline superstructure of the polypropylene adjacent to the glass fibres, as shown in Figure 5.6.

A general increase in the crystallinity of the matrix following the addition of the filler was measured by X-ray analysis. As the composite and the polymer samples were manufactured under the same conditions, this increase was attributed to the presence of the reinforcement. The glass fibre therefore acts as a site of preferential crystallite nucleation. Transcrystallinity, or the growth of columnar crystals formed at the fibre surface, has been studied by Folkes et al. (44). However, glass fibres are a particular case for which a transcrystallinity has not been observed. A preferential growth of spherulites occurs at the extremities and the intersections of glass fibres, but without a sufficient nucleation density to observe transcrystallinity (45).

Steidl et al (46) suggested that the hexagonal polymorph of polypropylene is more pronounced in composites with good interfacial bonding, due to the high shear stresses developed during injection moulding. This trend was not observed in the K'-values measured for the matrix-modified composites (Table 5.7).
b. Physical characterization

The mechanical characteristics of the injection moulded matrix-modified composites were evaluated by tensile testing. Variations in the properties of the composites were observed, as shown in Table 5.10. These differences were attributed to the strength of the fibre/matrix interface, on the quality of the specimen and the efficiency of the grafting process, as well as the reinforcement related parameters, such as fibre-volume fraction, fibre orientation and fibre length distributions.

Differences in the shape of the stress/strain graph and in the morphology of the fracture surfaces were employed to determine the fibre/matrix interaction. Good interfacial adhesion results in an increase in the Young's modulus and the failure stress (47). The effect of this parameter on the form of the stress/strain graph of glass fibre reinforced polypropylene was shown schematically by Sova et al.(48).

![Figure 7.18](image)

**FIGURE 7.18:** Form of the stress/strain graph as a function of the strength of the interfacial adhesion (48)

It can be seen that strong bonding results in brittle fracture just beyond the yield point, whereas a weak interface allows some drawing before ductile failure. This definition was employed to class the stress/strain graphs of the composites of Series 2 and 3. The BT03F, BT05F and ICIHW60F composites showed relatively weak interfacial bonding compared to that of the MA103BF, PM203F and PM303F specimens.
The mechanical characteristics of the composites were studied at room temperature, which is above the glass transition temperature of polypropylene, as was shown by viscoelastic analysis. Hence the amorphous zones of the polymer were in their "rubbery" state during tensile testing. The fracture morphology of the specimens was therefore complicated.

Failure in polypropylene composites produced zones of ductile and brittle matrix behaviour, as a result of differences in the speed of crack propagation. Ductile regions were produced by relatively slow speed debonding, whereas the brittle areas were created by fast crack propagation. Di Liello et al. (49) also observed that the overall deformation behaviour of glass fibre reinforced polypropylene was dominated by the elastic-plastic properties of the matrix.

In a similar manner to the PA66 matrix composites, the matrix-modified composites were analysed with the model proposed in Chapter 6. In this case the values calculated with the adhesion efficiency model have to be considered with respect not only to the fibre/matrix adhesion, but also to the processing route employed. However, by employing the moduli measured for the matrix polymer, produced under the same conditions as the composite, the effect of the quality of the specimen, and the processing conditions were minimized. Ranking the specimens from the weakest to the strongest interfacial bonding gives: PM103F, PA103F, MA101F, BT03F, MA103F, BT05F, ICIHW60F, PM303F, MA103BF and PM203F. The latter three specimens are from Series 2.

It can be seen that the Series 2 modification of the composite produced the most effective bonding, due to both efficient grafting and optimization of the processing conditions. The formation of strong size/matrix bonding results from a condensation reaction between the functionalities on the modifier adduct (the grafted modifying agent) and the amino groups of the silane coupling agent, which gives rise to amide linkages. This interaction was confirmed by Al Malaika et al. with IR spectroscopy. As described by several authors (17, 50) the A100 coupling agent readily forms stable siloxane bonds at the size/fibre interface. Therefore in the matrix-modified systems the bonding across the fibre/matrix interface consists of strong chemical bonds and as a consequence the interfacial adhesion is also strong. The interfacial bonding is shown schematically in Figure 7.19.
FIGURE 7.19: Bonding across the glass/polypropylene interface, produced by matrix modification.

The in-situ reactive processing technique proposed by Al Malaika et al (43), under the appropriate conditions, enhances the mechanical properties of the composite, with respect to a commercial sample, such as the ICIHW60F composite. The strong bonding produced in the samples of Series 2 was corroborated by the SEM micrographs of the failure surfaces of the tensile test specimens. Longer fibre pull-out lengths were observed for Series 1 and Series 3. The fibres tended to be matrix free for the weakest interfacial bonding, whereas the reinforcement was partially covered by the matrix for strong fibre/matrix adhesion. A similar result was described by Di Liello (49), who studied two systems, one with aluminium-coated fibres and the other with uncoated fibres, in a polypropylene matrix. The aluminium acted as a barrier to fibre/matrix interaction and the resulting failure surface consisted of matrix-free fibres and considerable pull-out. Al Malaika (51) showed an improvement in both the impact strength and the flexural strength of the composite on modification of the polypropylene matrix.

Again the microdrop test confirmed the adhesion efficiency ranking established with the model of Chapter 6. Three matrices of different modifications were studied with the fibre coated with the commercial A1100 size. A modified polymer produces
stronger bonding than the unmodified polymer, which suggests that the desired grafting reaction takes place and that this modification enhances the fibre/matrix adhesion. The efficiency of the grafting reaction depends on the type of chemical modification. Again the results of the microdrop test affirm that the addition of the functional monomer was important for effective adhesion promotion. Mader and Feitag (52) also showed a dramatic increase in the interfacial shear stress, from 4.91MPa for the homopolymer to 21.35MPa for a polypropylene modified with 5wt% acrylic acid (Polybond 1001). They concluded that differences in the composition of the sizes applied to the glass fibres had a lesser effect on the interfacial shear stress. This indicates that greater fibre/matrix bond enhancement can be achieved through matrix modification than through size modification.

From the observation of Size 2 and the hypothetical structure advanced for this mixture, it can be deduced that the fibres are probably completely wetted by the matrix polymer.

The effect of the droplet length on the interfacial shear stress was studied for the unmodified polypropylene/commercially sized fibre system. It was shown that the shorter the droplet length, the higher the interfacial shear stress. Soulier (53) studied similar model composite systems and observed a change in the shape of the drop, from a rounded to an elongated form, as the length of the droplet decreased. This variation in the form of the droplet may be responsible for the measured differences in interfacial shear stress. Stress concentrations occur at the point of fibre/drop contact. When the drop has an elongated form the contact angle is smaller than that of a round drop. As the surface tension is inversely proportional to the size of the contact angle the stress concentration increases with a decreasing drop size. Miller et al. (54) measured the contact angle as a function of the form of the drop, in an epoxy/Kevlar system. Their results are shown schematically in Figure 7.20.

FIGURE 7.20: Contact angle variation with the form of the droplet of matrix polymer
The viscoelastic analysis of the composite specimens was achieved with the torsion pendulum, which proved sufficiently sensitive for the detection of the variations in behaviour produced by the addition of small quantities of the modifiers. In a similar manner to the size-modified composites the amplitude of the glass transition peak was considered as representative of the strength of the fibre/matrix bond. For Series 1 the lowest damping was measured for the MA103F sample, indicating good interfacial bonding. This result was as expected, as this sample was fully modified and had a relatively high adhesion efficiency rating. A considerable difference was observed between the intensity of the \( \alpha \) relaxation peaks of the commercial sample and the other matrix-modified samples of Series 2, indicating the superior quality of the interface of the MA103BF, PM303F and PM203F specimens. The latter three samples all contained the additional functional monomer, which improves the grafting of the modifying agent to the polypropylene backbone and so enhances the strength of the fibre/matrix bond. Although the BT05F composite of Series 3 was not fully modified it showed better interfacial properties than those of the commercial sample (ICIHW60F). The interfacial adhesion efficiency model gave a similar rating for both these composites. Therefore, on the addition of the functional monomer, the modified polypropylene, processed in a twin-screw extruder, should have excellent mechanical properties.

c. Conclusion

The enhancement of the interfacial bonding by matrix modification was evaluated. It was shown that in situ reactive processing in the presence of a peroxide, a modifying agent and an additional functional monomer, and under optimized processing conditions, produced strong interfacial bonding and hence greatly improved the mechanical characteristics of the composite.
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VIII CONCLUSIONS

8.1 INTRODUCTION

The mechanical properties of glass fibre reinforced thermoplastics with matrices of Maranyl A100 (PA66) and ICI Propathane HF26 (polypropylene) can be greatly improved by the enhancement of the fibre/matrix adhesion, which ensures effective transfer of the stress from the matrix to the fibre. Strong interfacial bonding was achieved by two methods:

1. coating the fibres with a size specific to the matrix
2. using an in-situ reactive processing technique to graft functional groups to the polymer backbone in order to activate the macromolecular chains of the matrix.

8.2 EVALUATION OF THE STRENGTH OF THE FIBRE/MATRIX BONDING

Three methods for the evaluation of the strength of the fibre/matrix bond have been developed: the adhesion efficiency model, viscoelastic analysis and the microdrop test.

8.2.1 The adhesion efficiency model

The adhesion efficiency model is an effective method of comparing interfacial bonding in composites with not only different adhesion enhancement systems, but also different matrices, fibre-volume fractions, fibre length and orientation distribution. This technique has the advantage of considering the composite in its bulk form, but also has the disadvantage of requiring a large range of experimental values which take a long time to obtain.

8.2.2 Viscoelastic testing

The torsion pendulum has proved a successful tool for the characterization of the fibre/size interface, due to its great sensitivity. Other methods, such as the DMTA, were unable to detect the small changes in behaviour produced either by the size coatings, which represent only approximately 3 vol.% of the composite, or by the addition of very small quantities of the chemical modifiers. Again this method has the advantage of considering the composite in its bulk form, but is also sensitive to
variations in the properties of the composite, such as fibre-volume fraction and crystallinity.

8.2.3 Microdrop test

The production of the specimens required for the evaluation of the interfacial shear stress in model composites is particularly difficult with thermoplastic matrices. These difficulties have been overcome by employing the microdrop test. This method is an effective tool for interface studies, but it treats model composites which were not submitted to the same processing conditions as the bulk composite. The study of the effect of processing conditions on unmodified polypropylene has shown that the fabrication route plays an important role in the formation of a particular structure, which in turn influences the physical properties of the polymer.

Each of these methods has allowed the composites to be ranked in order of the strength of the interfacial bonding.

8.3 SIZE MODIFICATION

Four simplified sizes were rated, using the techniques described above, from the strongest to the weakest interface between the glass fibre and the PA66 matrix: Size 1 (epoxy + A1100), Size 3 (polyurethane + A1100), Size 2 (polypropylene + A1100) and Size 4 (polyurethane). The microdrop test employed a modified polypropylene matrix which lead to an inversion of the positions of Size 1 and Size 2.

From this rating the following conclusions can be made:-

a. Although there has been considerable research on the bonding between a silane coupling agent, such as γ-APS, and a glass, this study has shown that fibre/matrix interfacial bonding produced through the use of a size is dependent on the other elements which constitute the size. For strong adhesion the matrix reactive polymer chosen must be compatible with the matrix, such as a polyurethane-based size with a glass fibre reinforced PA66 (as shown by the model and viscoelastic analysis) or a polypropylene-based size with a polypropylene matrix (as shown by the microdrop test).
b. Good wetting of the fibre by the size is desirable, but it has been shown that poor wetting properties are not detrimental to interfacial bonding, if the size shows good coupling activity, as is the case of Size 3 (polyurethane + Al1100) with a PA66 matrix.

Additionally, the results from the size-modified systems showed that model size films, which are often studied due to their relatively easy handling properties, are not always representative of the size coating on the E-glass fibre. However the size coating on the fibres can be successfully examined by employing a wide range of experimental techniques, each of which provide essential information on different aspects of the polymer layer.

8.4 MATRIX MODIFICATION

In a similar manner to the size-modified samples the matrix-modified samples have been ranked in order of the adhesion efficiency. The following conclusions have been made from these results:

a. The study of matrix modification for interfacial adhesion promotion in glass fibre reinforced polypropylene has shown that the novel in-situ reactive processing technique proposed by Al Malaika et al. (1) is an effective method of bonding enhancement. Full modification of the polypropylene matrix, with a peroxide, a modifying agent and an additional functional monomer, produces very strong interfacial bonding and superior composite properties to either an unmodified or a commercially modified polypropylene composite.

b. The results have shown the processing conditions affect the efficiency of the bonding reaction and the structure of the polymer matrix itself. Effective mixing is essential for the production of composites with acceptable mechanical properties. Under the appropriate processing conditions, matrix modification provides a more effective method of adhesion improvement than the use of simplified sizes.

c. Additionally, this technique provides a relatively economical, simple method by which the properties of a thermoplastic matrix composite can be improved.
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