Coated fibre composites using rubbery and ductile fibre/matrix interlayers

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COATED FIBRE COMPOSITES USING RUBBERY AND DUCTILE FIBRE/MATRIX INTERLAYERS

by

JAGMINDER DHILLON

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of the Loughborough University of Technology

1991

Supervisors: Mr J F Harper Dr L M Mascia

Institute of Polymer Technology and Materials Engineering

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Advanced composite materials possessing high specific stiffness and strength have been successfully employed as structural materials in the aerospace, military and automotive industries. Despite the advantages that composites have over other materials, further expansion has been restricted by their brittleness. The aim of this research project was to improve the energy absorbing capabilities of unidirectional glass fibre epoxy resin composites by coating the fibres with an interlayer. UHMWPE was used as the interlayer because of its outstanding toughness while EPDM of low modulus was used to assess the difference between energy absorption through plastic deformations (UHMWPE) and highly elastic deformations (EPDM).

A preliminary investigation was carried out on the coating of glass fibres with polymer solutions. A bonding mechanism to couple the interlayers to the glass fibres and epoxy matrix was developed using organofunctional silanes. Interlayered composites were then manufactured at three coating levels and their performance evaluated using a variety of mechanical tests. The behaviour of composites with interlayers was also modelled using a finite element analysis approach. A mesh consisting of a two fibre system was considered.

Non-continuous coatings of irregular thickness were obtained using a solution coating process. Significant improvements in adhesion to glass were obtained by grafting a mercaptosilane onto EPDM and a methacrylate silane onto UHMWPE. Improvements in the adhesion of UHMWPE to the epoxy matrix were demonstrated by a maleic anhydride treatment and also by the methacrylate silane.
Stiffness and strength properties of UHMWPE interlayered composites increased consistently with the methacrylate silane treatment, confirming the ability of the silane to improve interfacial bonding. Decreases in stiffness and strength properties as a function of interlayer thickness were attributed to the excessive thickness and poor quality of the coatings, with EPDM interlayered composites sustaining the greatest losses. Appreciable increases in the damping capacity and the observed ductile deformation of UHMWPE from short beam shear tests emphasised the potential ability of UHMWPE interlayers to improve the toughness of composites through a yielding mechanism. The finite element analysis provided confirmation of this by revealing the capability of thin UHMWPE interlayers to reduce stress concentration effects and provide a local deformation facility. This theoretical study also showed that UHMWPE interlayers are most effective at higher volume fractions.
The author wishes to express his thanks to Mr J F Harper and Dr L M Mascia (Project Supervisors) for their invaluable guidance and understanding throughout the project. The assistance provided by Dr V Nassehi during the theoretical part of this study also proved invaluable. The author is most grateful to all the academic and technical staff at the IPTME for their assistance and advice during the research programme.

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ABBREVIATIONS

σ  stress
ε  strain
E  elastic modulus
σ_m  stress in matrix at failure strain of fibres
σ_f  compressive strength
G  shear modulus
V  volume fraction

Subscripts
f  fibre
m  matrix
c  composite
L  longitudinal direction
T  transverse direction
CHAPTER 1

INTRODUCTION

1.1 FIBRE REINFORCED POLYMER COMPOSITES

Composite materials may be defined as substances consisting of two or more distinct parts, with an interface or interphase region separating them. This definition encompasses many different types of composites, including microscopically dispersed materials such as metallic alloys, and those which contain distinguishable constituents on a macroscale.

Fibre-reinforced plastics can be regarded therefore as macrocomposites. The matrix of lower stiffness and strength transfers external loads to the stiff and strong fibres. The matrix also binds the fibres together in the required configuration and protects them from surface damage and the environment. Historically, one of the first naturally occurring fibre composites is wood, which is composed primarily of cellulose chains embedded in lignin matrix. One of the earliest man-made fibre composites may have been building blocks made with straw (reinforcing fibre) dispersed in mud (matrix).

The rapid growth of fibre reinforced plastics in engineering applications has been achieved mainly by the replacement of traditional metallic materials. The higher specific modulus and specific strength which can be achieved in the composites, compared to other engineering materials, make them very favourable in applications such as transport, where a weight reduction results in greater efficiency and energy savings. Another factor that makes composite materials attractive is that they can be tailor-made to meet specific
design requirements. The performance of the final product can thus be optimised more efficiently.

Composite properties are determined by a number of factors including: stiffness and strength of the fibres, fibre diameter, fibre length and fibre length distribution, fibre uniformity, fibre volume fraction, fibre orientation, the properties of the resin matrix, the fibre-matrix interface and void content.

The importance of the fibre-matrix interface should be emphasised since it plays a vital role in determining composite performance. The interface transfers applied stresses from the matrix to the fibres. Good interfacial bonding is essential for high stiffness and strength, good shear and off-axis strengths and is very important for environmental resistance (see Section 2.2.1).

In terms of volume consumption, glass fibres are the most popular among the three common types of reinforcing fibres glass, carbon and aramid. This is due to their low cost and respectable performances. The form of the reinforcement is also important. Fibres may exist as continuous fibres (e.g. unidirectional fibres, bidirectional woven fabrics) or as discontinuous fibres (e.g. short chopped fibres, chopped strand mat). The continuous form imparts the greatest reinforcement into the composite.

Carbon fibres are usually prepared from polyacrylonitrile, rayon or pitch fibres. The precursor fibres are heated at temperatures up to 400°C in the presence of oxygen and then carbonised at high temperature (~1500°C) in the presence of an inert gas. After manufacture the fibres are usually oxidised and surface treated to
increase the adhesion of the matrix to the fibre. Type I fibres are carbonised to give maximum stiffness but relatively low strength, while type II offer maximum strength.

Aramid fibres, developed by Du Pont and known by the tradename Kevlar, are composed of aromatic polyamide polymer units (poly(paraphenylene terephalamide)). High modulus and strength fibres are produced by extrusion and spinning processes. Kevlar fibres, in contrast to brittle carbon and glass fibres can fail in a ductile manner exhibiting considerable necking.

Glass fibres are manufactured from various compositions based on silica (SiO₂) and oxides of calcium, boron, sodium, iron and aluminium. Continuous glass fibre filaments are produced by melting the blend of inorganic oxides and then passing the molten glass through a series of platinum bushings, each of which has several hundred holes in its base. The glass filaments are drawn mechanically downwards and a size is usually applied before the bundles of filaments are wound onto drums. The size is usually applied as a very thin coating to the fibres by spraying them with a water solution containing an emulsified polymer and a coupling agent. The size has the following functions:

a) to protect the fibres from damage
b) to bind the individual fibres together for ease of processing
c) to impart antistatic properties
d) to bond the glass surface to the matrix through a coupling agent.

The most important factor that determines the strength of glass fibres is the damage which the fibres sustain during processing operations. Fine surface cracks may form resulting in variable tensile strengths.
The most commonly used glass is E glass (electrical), since it has good strength, stiffness, electrical and weathering properties. C glass (corrosion) has a higher resistance to chemical corrosion than E glass, but is more expensive and possesses lower strength properties. S glass is also more expensive than E glass but has higher strength and is more temperature resistant.

A summary of the mechanical properties and other features of the main types of reinforcing fibres is shown in Figure 1.1, in the form of a stress-strain curve. It should also be noted that a number of other high modulus and strength fibres are used in high performance composites. These include boron, silicon carbide, metallic and inorganic whiskers and high modulus polyolefins.

The polymers used as matrix materials in fibre composites can be classified as thermosetting or thermoplastic. Thermosetting resins are usually isotropic and are regarded as brittle solids. The most common resin used in composites is unsaturated polyester due to its low cost and adaptability to fabrication of large structures. However, epoxy resins have superior strength and stiffness with a lower shrinkage on curing and a lower coefficient of thermal expansion. They also adhere well to reinforcing fibres and fillers and find applications in high performance composites due to their high cost.

A wide variety of epoxy resins and curing agents are available to give a broad range of properties after cure. The most common epoxy resin is made by reacting Bisphenol A with epichlorohydrin to give a low molecular weight (oligomer) uncured diglycidyl ether of Bisphenol A (DGEBA). An excess of epichlorohydrin is generally used to ensure the
ends of the polymer chains are terminated with epoxide groups (to facilitate further chain extension and crosslinking). The number of repeating units within the polymer is dependent on the quantities of the reactants. Curing agents used to produce three dimensional networks include aliphatic, cycloaliphatic or aromatic amines and acids or acid anhydrides. The crosslinking reaction usually occurs through the opening of the strained epoxide ring and can involve the secondary hydroxyl groups.

Nylon and polypropylene are the most commonly used thermoplastic polymers. Thermoplastic matrices are normally used with short fibre reinforcement.

Since the Second World War, the production of reinforced plastics has increased constantly. Today reinforced plastics have found markets in land transportation, construction and corrosion-resistant equipment due to their advantageous properties. Due to their high costs, advanced composites (high performance) are mainly used in the aerospace and military industries (aircraft and missile applications). Other markets include recreational uses, industrial products and automotive parts. The market for advanced polymer composites is projected to grow throughout this decade. This predicted growth is due mainly to accelerated demands by civilian aircraft and helicopter industries. Commercial aircraft such as the Boeing 757 and 767 currently contain about 4 per cent by weight of advanced composites. Within the next ten years this may rise to as much as 65 per cent.

High volume composites (large volume markets) have mainly found applications in the automotive industry. The continual search for less weight with greater strength, corrosion resistance and lower
production costs have made high volume composites desirable to automotive manufacturers. Future growth may include increased applications in large structural parts and exterior panels. However, the rate of growth is forecasted to be slower than that of advanced composites.

1.2 AIMS OF THE INVESTIGATION

Although reinforced plastics appear to be very appealing as engineering materials, many challenging problems have to be overcome to allow for their future continual expansion. Due to the high stiffness and strength of reinforcing fibres and the low failure strain of many preferred matrices such as thermosetting resins, one of the main weaknesses of composites is their brittleness. Even low energy (velocity) impacts can cause localised damage which can lead to catastrophic failure. Localised damage in composite aircraft panels for example can arise during maintenance or service use, leading to eventual failure with possible disastrous consequences. Unfortunately, it is difficult to detect internal damage using non-destructive inspection in such critical applications.

Interfacial modifications and the use of modified thermosetting resins or thermoplastics (e.g. polyamides, polysulphones) in composites improves their energy absorbing capabilities and damage tolerance, although a significant reduction in desirable properties such as stiffness and strength may inevitably occur. Thus, there is a perpetual need for further development to improve the toughness of fibre reinforced plastics whilst retaining adequate mechanical stiffness and strength.
The principal aim of this research project is to improve the energy absorbing capabilities of fibre reinforced plastics by introducing polymer interlayers onto the fibres. The use of an intermediate layer at the fibre-matrix interface can reduce the detrimental stress concentrating effects of the fibres, particularly under transverse loading. Previous workers have mainly concentrated on rubbery interlayers. In this work, ultra-high molecular weight polyethylene was chosen as the interlayer because of its exceptionally high ductility and relatively high strength and modulus. For comparative purposes, ethylene-propylene-diene monomer (EPDM) which has a similar chemical structure to UHMWPE, was chosen to represent a rubbery interlayer material possessing high energy absorption properties. Hence, the more specific aims of this project were:

a) to coat E glass fibres with the interlayer polymer, and

b) to manufacture composites with these coated fibres and to appropriately test the mechanical properties of the resultant unidirectional composites.

A further objective was to model the behaviour of such composites with interlayers using the finite element analysis approach.
2.1 FUNDAMENTAL UNIDIRECTIONAL COMPOSITE PROPERTIES

An introductory description is given of the elementary properties of unidirectional composites. A universal theoretical model relating to the design of unidirectional composites is outlined (rule-of-mixtures). This section thus provides the necessary background needed to understand the complex behaviour of composites.

2.1.1 Longitudinal Tensile Stiffness and Strength
The "rule of mixtures" is widely used to predict the modulus and strength of unidirectional composites in the longitudinal direction, due to its simplicity. If the fibres and matrix are considered to be loaded in parallel then the total stress applied to the composite is the sum of the stresses in the fibre and matrix. Thus:

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

This general equation defines the stresses before failure. If the strain in the matrix is the same as the strain in the fibre,

\[ \varepsilon_C = \varepsilon_f = \varepsilon_m \]

Then, it follows that

\[ E_L = E_f V_f + E_m V_m \] (2.1)
Equation 2.1 reveals that each component of the composite will contribute to the composite property in proportion to their volume fraction - the rule of mixtures.

Predictions from the rule of mixtures are quite accurate when tensile loads are applied and agree well with experimental results [1]. Useful approximate values are given when it is used for composites that do not behave elastically (i.e., at high strains).

To increase the fraction of total load carried by the fibres (hence to use them more efficiently) it is necessary to maximise the ratio of the fibre matrix moduli and to maximise the volume fraction of fibres. Since usually $E_f / E_m \approx 20$ and high fibre volume fractions are utilised, the longitudinal tensile modulus is dominated by fibre properties. As well as providing fibre property information, the longitudinal tensile modulus gives an indication of the fibre-matrix bond strength.

Composite strength predictions are also derived from the rule of mixtures. The failure strain of most thermosetting resins is greater than that of the reinforcing fibres ($\varepsilon_m > \varepsilon_f$). Hence, initiation of failure in continuous fibre composites occurs when the fibres reach their fracture strain. This assumes that all the fibres fail at the same strain. At high volume fractions, once the fibres break, the extra load cannot be supported by the matrix, and composite failure occurs. The ultimate tensile strength of the composite under these conditions is described by the equation:

$$\sigma_c = \sigma_f V_f + \sigma_m (1-V_f)$$
Deviations from the rule of mixtures for the stiffness and strength may occur in practice. These are due to the following factors which are neglected by this simple model:

a) misorientation of fibres  
b) non-uniform strength of fibres due to flaws etc  
c) interfacial bonding variations  
d) residual stresses.

2.1.2 Transverse Stiffness and Strength
A similar approach can be adopted to predict the transverse modulus of unidirectional composites. When a transverse stress is applied to the composite, the composite strain is the sum of the matrix strain and fibre strain. Thus,

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

The stress in the matrix is assumed to be the same as the stress in the fibres. This leads to the equation:

\[ \frac{1}{E_T} = \frac{V_f}{E_f} + \frac{V_m}{E_m} \]  

(2.2)

It can be concluded from equation 2.2 that the fibres have little effect on increasing the transverse composite modulus unless high volume fractions are used, therefore this is a matrix dominated property. Predictions from equation 2.2 are only approximate when compared with practical results, since the assumption that the stresses in the fibres and matrix are equal is inaccurate.
Under longitudinal loading the fibres support a large proportion of the load. However, this does not occur under transverse loading. The high modulus fibres restrict matrix deformation and cause strain and stress concentrations in the matrix close to the fibres giving rise to a non-uniform stress distribution. Consequently, composite failure occurs at a much lower strain than the failure strain of the unrestrained matrix. Hence, a reduction in transverse strength occurs in the presence of fibres (unlike transverse modulus).

Transverse tensile strength predictions are based on the strength of the matrix. The transverse tensile strength can be expressed as:

\[ \sigma_T = \frac{\sigma_m}{S} \]

where \( S \) is the strength-reduction factor. This factor may be calculated from strength of materials methods or by numerical solution techniques such as finite element methods [2].

2.1.3 Compressive Properties

The longitudinal compressive modulus predicted by the rule of mixtures (equation 2.2) may differ from experimental findings. This may be explained by the fact that composite behaviour under compressive loads is dominated by matrix properties (e.g. shear modulus), unlike the longitudinal tensile modulus which is fibre property dominated. Buckling of fibres under longitudinal compressive loads is restricted by the surrounding matrix, and thus the longitudinal compressive strength is also dependent on matrix properties. Rosen [3] developed equations to predict the longitudinal compressive strength. For extensional or out of phase mode of buckling, at low volume fractions, the compressive strength is given by
\[ \hat{\sigma}_1 = 2 V_f \left[ V_f E_m E_f / 3(1-V_f) \right]^{1/2} \]

and for shear or in plane mode of buckling, at high volume fractions

\[ \hat{\sigma}_1 = G_m / (1-V_f) \]

Extension of the matrix occurs at low volume fractions, while at high volume fractions the matrix is subjected to shear deformations.

However, the predicted strengths calculated according to these models are much greater than experimental results. In practice there are several factors that can reduce the support given by the matrix and surrounding fibres to prevent buckling which will reduce the compressive strengths. These include:

a) fibre bunching, which results in resin rich areas
b) presence of voids
c) poor fibre alignment which results in some fibres being preferentially orientated for buckling
d) differences in Poisson ratios between fibres and matrix, which can result in fibres debonding
e) visco-elastic deformation of the matrix
f) non-isotropic behaviour of fibres e.g. Carbon and Kevlar 49 fibres which have low transverse and shear moduli [4].

Also a number of other modes of failure exist under compressive loading which were not considered by Rosen. These include the following. Transverse splitting may initiate compressive failure. Transverse tensile strains arise from the Poisson ratio effect and can result in cracking between fibres. Ewins and Ham [5] investigated the
nature of compressive failure in unidirectional carbon fibre composites. They concluded that longitudinal compressive failure may occur by shear failure mode on a plane of maximum shear stress. The experimental results of Hancox [6] suggested that carbon fibre composites fail in a shear mode at approximately 45° to the fibre axis. Argon [7] suggested that regions of misaligned fibres form a failure nucleus by undergoing a "kinking" process. Although this resembled the in-phase buckling of the Rosen model, it operated at a stress level below the ideal buckling strength. In regions of misalignment the applied compressive stress produces an interlaminar shear component. When the shear stress becomes equal to the interlaminar shear strength of the composite, then the lamellae (or fibres) in the region slide and rotate. This movement further increases the shear stress and the shear collapse band propagates outwards by means of stress concentrations at the top of the band. Similarly Chaplin [8] also considered that the lower compressive strengths were due to the composites sensitivity to defects. Such defects could initiate failure and then be able to propagate through the material. Failed glass fibre composites revealed a band of sheared material in which extreme debonding had taken place.

Failure under compressive transverse loads generally occurs by shear failure of the matrix with possible fibre crushing or debonding.

2.2 THE FIBRE-MATRIX INTERFACE

2.2.1 The Importance of the Interface to Mechanical Properties
Although the reinforcement and matrix are important factors in determining tensile and compressive properties, the overall performance of a composite also depends on the nature of the bond
between matrix and fibre. High stress concentrations develop at the interface because of large differences between fibre and matrix moduli, cure shrinkage of thermosetting resins and because of loads applied to the structure.

The fibre-matrix interface transfers externally applied loads from the matrix to the reinforcing fibres. The mechanism of stress transfer and the variation of stresses along the fibre length was studied by Cox [9]. This led to the very well known theory of stress transfer - the shear lag analysis, which has been quoted in numerous textbooks [2,4].

Energy absorption is limited in brittle matrix fibre composites (low \( \varepsilon_m \)) with strong interfacial bonding since cracks propagate through the matrix and fibres, causing catastrophic failure. Weak interfacial bonding leads to greater damage zone areas and thus an increase in energy absorption is observed (energy absorbing mechanisms discussed in Section 2.3). These contradictory requirements for good tensile properties and good fracture toughness imply that an optimum fibre matrix bond strength is required for satisfactory all round composite performance.

A strong interfacial bond is also essential for higher transverse strengths and for good environmental performance. A good bond usually enhances water resistance of polymer matrix composites. Water can diffuse through the polymer and damage the interface through debonding and weaken the fibres. In the case of glass fibres, attack by water can cause leaching of ions from the glass with consequent cracking and spalling. The harmful effects of water absorption on composite properties becomes even worse when poor interfacial bonding exists.
When composites with poor bond strengths are subjected to thermal stresses, premature failure can occur at the weak interface because of differential thermal expansions of fibres and matrix. A weak interface can reduce the compressive strength by facilitating fibre buckling. The interface can also serve as a nucleation site, a preferential adsorption site and a site for chemical reactions.

2.2.2 General Adhesion Theories with Respect to the Glass Fibre-Matrix Interface

As discussed, the adhesion between fibre and matrix is a major factor in determining composite performance. The adhesion of the fibre to the matrix at the interface may be attributed to the following mechanisms, according to Hull [4]:

a) Adsorption and Wetting

The surface energy of the fibre should be greater than that of the resin for easy wetting to occur. Thus, glass and carbon fibres (surface energies 560 and 70 mJ m\(^{-2}\) respectively) should be easily wetted by polyester and epoxy resins (surface energies 35 and 43 mJ m\(^{-2}\) respectively). Although the surface energy is important in the initial wetting of the fibre by the resin, if a chemical reaction occurs between the fibre and matrix, the initial surface energies may not be important in the final bond between fibre and resin.

b) Electrostatic Attraction

A difference in electrostatic charge between the fibre and the resin at the interface may contribute to forces of attraction bonding the fibre to the resin. Electrostatic attractions are unlikely to strongly influence the final bond strength but may have an important role in the orientation of any chemical added to aid bonding (coupling agent) on the surface of glass fibres.
c) **Interdiffusion**
Bonding between two surfaces may occur by diffusion of the molecules of one surface into that of the other, resulting in molecular entanglement.

d) **Chemical Bonding**
The presence of chemical bonds at the interface are of great importance to the bond strength. Bonding between glass fibres and thermosetting resins may be increased by the presence of a chemical coating on the glass fibres. Chemical bonds may be formed between the glass and coating and between the coating and resin. In the case of composites based on carbon fibres and thermosetting resins, the improved bonding obtained by surface oxidation of carbon fibres can also be explained by chemical bonding.

e) **Mechanical Adhesion**
The mechanical interlocking of two surfaces can result in some bonding between fibre and matrix. Good initial wetting of the fibres is critical in allowing intimate contact between the two materials.

Van der Waals and other low energy forces may be involved in adhesion as well. The shrinkage of the resin during cure and the differential thermal expansions of matrix and fibres may also affect the bonding of the fibre to the resin.

The application of silane coupling agents to glass fibres greatly enhances fibre-matrix bonding. Coupling agents form only a fraction of the coating applied on commercial glass fibres. The majority of the
Coating (size) consists of a film forming polymer such as polyvinyl acetate (for general purpose applications), epoxy or polyester resins (for high performance thermosetting resins) and a lubricant (usually a fatty acid ester).

The silica rich surface of E glass is able to adsorb water readily (hydrophobic) to produce a well bonded hydrated surface layer. Nishioka and Schranke [13] studied the thermal desorption of water from E glass. They concluded that water existed on glass fibres either as physically adsorbed water, chemisorbed molecular water (strongly bound surface water), surface hydroxyl groups or bulk water. The presence of water cannot be avoided in commercial processing and its existence leads to a large reduction in glass fibre surface energy. Hence, part of the function of the silane coupling agent is to provide a strong water resistant bond.

Silane coupling agents are organic-inorganic compounds with a general formula \( R-(\text{CH}_2)_n\text{Si(OR')}_3 \), where \( R' = \text{CH}_3 \) or \( \text{CH}_3\text{CH}_2 \). The \( R \) group is the resin reacting or compatible group such as vinyl, methacrylate or epoxy. The chemical structures of some common commercial coupling agents are given in Table 2.1. Plueddemann [14] considered a very simple model to account for the bonding mechanism of silanes to glass fibres and to the matrix - see Figure 2.1. The \( \text{Si(OR')}_3 \) groups are hydrolysed to \( \text{Si(OH)}_3 \) in the aqueous size solution. The trihydroxy silanols are able to compete with water at the glass surface and hydrogen bonding with surface hydroxyl groups takes place. On drying the fibres, a reversible condensation reaction occurs producing a polysiloxane bonded to the glass surface. The silane coated fibre presents a surface of compatible \( R \) groups to the resin, which can form chemical or physical bonds with the thermosetting resin during the
cure process. Plueddemann suggested that the silane glass bond at the interface is capable of reversible hydrolysis to relieve local shear stresses at the interface—see Figure 2.2. The reversible mechanism allows the covalent bond to reform.

With the advent of modern spectroscopic/analytical techniques for surface characterisation it became possible to study the structure of the interface in greater detail. These characterisation techniques include Fourier-Transform Infra-Red (FT-IR), Nuclear Magnetic Resonance (NMR), Electron Spectroscopy for Chemical Analysis (ESCA), Secondary Ion Mass Spectroscopy (SIMS), Electron Spin Resonance (ESR) and others. Hence, recently an understanding of the interfacial structure has been significantly broadened from the simple models and adhesion theories. It is now known that the glass matrix region is not a simple layer but consists of complex structures. Silane coupling agents form multi-layered structures on glass fibres with chemically bonded polymerised silane, with chemisorbed and physisorbed oligomeric silane layers present [15]. The first monolayer consists of an extensively crosslinked silane network strongly bonded covalently to the glass surface. Above this first layer (but near to the glass surface) there are lightly bound chemically adsorbed oligomeric silane layers. Also, a second chemisorbed silane layer exists further out as a loosely bound structure. The outermost layer consists of physisorbed silane oligomers that can be washed away with organic solvents.

Ishida [10], in a recent review, concluded that the silane coupling agent matrix interface was a diffuse boundary where resin penetration into the chemisorbed layers occurred and migration of physisorbed silane oligomers into the matrix phase took place. The chemically bonded monolayer and the interpenetrating chemisorbed silane matrix
network (IPN) are thought to be mainly responsible for the adhesion mechanism. Other possible bonding mechanisms between the silane on the glass and the matrix, involving the physisorbed layers were mentioned [15]. The physisorbed oligomeric silane may be compatible in a liquid matrix and form a copolymer, between the physisorbed silane and matrix layers, during resin cure. The thickness of the resulting interphase may be substantial due to the distance that the physisorbed silanes are capable of migrating. The role of the physisorbed silane on composite mechanical properties was suggested to be dependent on the mechanical properties of the copolymer between the physisorbed silane and matrix.

Pawson and Jones [16] showed that the removal of the outer physisorbed layer from amino propyl triethoxysilane coated glass fibres significantly improved the interfacial shear strength (determined from the fragmentation of a single filament embedded in a vinyl ester resin).

Glass manufacturers are often not willing to disclose the exact nature of their coatings on glass fibres. This is because manufacturers have developed surface coatings to meet specific requirements of various matrix systems, in a competitive market. Drumm and Ullicny [11] analysed the nature of the coating mixtures found on commercial glass fibres using spectroscopic techniques such as FT-IR and NMR. The amounts of coatings varied from 0.54 to 4.22 weight percent with the heaviest amount on random mats and the least on rovings. A mixture of bisphenol A epoxy as the unreacted resin and polyether as the lubricant were identified on epoxy resin compatible glass fibres.
Thomason [12] conducted a similar but more comprehensive investigation into the nature of coatings on glass fibres. Using XPS, SIMS and contact angle measurements he was able to provide qualitative information about the distribution of the coating on the fibre surface and was also able to identify well and poorly coated fibres. Thomason interpreted the increase in C/Si ratio (from XPS) and the drop in hysteresis (from contact angle results) as to suggest the surface was becoming more chemically homogeneous and better coated. Thomason's results showed that the distribution of the coating was good on some epoxy compatible fibres while on others from different manufacturers the distribution was poor (i.e. coatings concentrated in small islands on the surface). This variation in distribution of surface coatings will inevitably lead to variations in the properties/structure of the interface and thus of the composite. The main components of the coatings, extracted using acetone, were identified as 65-75% epoxy resin with 25-35% of an ethoxylated compound. The remaining 10-20% of the coating was presumed to contain the silane coupling agent. Further suggestions were made (from XPS and SIMS results) that some reactions may have occurred between the silane and another component of the mixture. Thomason thus questioned current theories and remarked that further investigations were necessary to elucidate the silane coupling mechanism. Hence, the structure of the interface (or more precisely the interphase region) between glass fibres, silane coupling agents and the matrix is very complex. At present, it is generally accepted that chemical and physical bonds are important to the adhesion mechanism.
2.3 TOUGHNESS IMPROVEMENT OF COMPOSITE MATERIALS

As already mentioned, the usual high stiffness and strength of reinforcing fibres and the low failure strain of thermosetting matrix resins are detrimental to composite toughness. Also as the degree of adhesion of the fibre-matrix interface increases, the stiffness and strength properties of the composite increase, whilst sacrificing toughness. Conversely, a weak interfacial bond improves the toughness at the expense of the stiffness and strength. Hence, a prime objective of material scientists is to maximise the specific stiffness and strength of composites whilst retaining the composites ability to tolerate impact loads. In engineering applications a composite must be able to sustain some damage without undergoing immediate catastrophic failure.

When a load is applied to a material, it can absorb energy by two basic mechanisms: (a) plastic deformation (yielding), (b) creation of new surfaces. Several mechanisms have been presented to account for the toughness of composites. These are reviewed in the following section.

2.3.1 Toughness Mechanisms of Composites

The fibre pull-out theory of Cottrell and Kelly [17,18] considers the frictional work during fibre pull out to account for the toughness of composites. During fibre fracture of a composite with a tough matrix, failure may proceed by broken fibres being pulled out of the matrix rather than fibres fracturing again - see Figure 2.3a. The crack initiated at a fibre break may be unable to propagate through the tough matrix. The work done during fibre pull out is considered to be a major contribution to the fracture energy of a composite. The pull
out energy per unit area for a continuous fibre composite, according to Kelly, can be expressed as:

\[ R_{\text{pull-out}} = \frac{V_f \sigma_f l_c}{12} \]

where \( l_c = \frac{\sigma_f d}{2\tau} \) critical transfer length.

The above equation assumes that:

i) fibres break randomly at weak points
ii) the original shear strength of the filament/matrix bond is maintained during fibre pull out.

To achieve the greatest toughness (high \( R_{\text{pull out}} \)) the length \( l \) of the fibres should be slightly smaller than \( l_c \) and \( l_c \) should be as large as possible. Fibres will only pull out if \( l < l_c \). If \( l > l_c \) then the fibres are stressed to their limit, over most of their length and are able to fracture, instead of pulling out. \( l_c \) can be maximised by making the interfacial shear strength very small but this clearly will reduce stiffness and strength properties. The work of fracture may also be increased by increasing the diameter of the fibres. However, common reinforcing fibres have small fixed diameters to maximise stiffness and strength and contribute little to the work of fracture.

Outwater and Murphy [19] attributed the fracture energy (toughness) to the energy required to debond the fibre from the matrix. During the fracture process the fibres may become separated from the matrix. These types of debonding cracks break chemical or physical bonds at the fibre-matrix interface and occur when the fibres are strong and
the interface is weak. A debonding crack may also run in the adjacent matrix. Outwater and Murphy reported that debonding only takes place when the crack tip passes the filaments - see Figure 2.3b.

Their theory assumes that the failure strain of the fibre is greater than that of the matrix, thus allowing the crack tip in the matrix to go around the fibre. Debonding progresses until the fracture stress of the stretched filaments is attained. The excess strain energy of the stretched filaments, it is suggested, is the source of the debonding work. They also mention that an improvement in fracture energy can be obtained by reducing the fibre matrix bond and by increasing the fibre diameter.

Cook and Gordon [20] envisaged the debonding process differently. They proposed that interfacial failure can occur ahead of the crack tip due to the tensile component of the stress fields perpendicular to the fibre direction - see Figure 2.3c. This mechanism may occur if the interface is sufficiently weak and the resultant secondary crack may have the ability to arrest the primary crack (potential crack stopping mechanism). If a strong interfacial bond exists, the primary crack will propagate across the interface and fibre and proceed in a brittle manner. In either of the above cases, the larger the debonding area the larger the fracture toughness.

Matrix deformation and cracking may contribute to the total fracture energy of a composite. Although cracking and deformation of the matrix both absorb energy, the energy absorbed by plastic deformation can be considerably higher than the surface energy contribution. Piggott [21] suggested that when a fibre breaks, the strain energy of the fibre is redistributed to the matrix and this energy is dissipated
through plastic deformation of the matrix. Epoxy resins and other thermosetting resins are usually brittle and undergo limited amounts of deformation before fracture unlike some thermoplastics and metal matrices. Hence, the contribution of thermosetting resins to the total fracture energy through plastic deformation is relatively small.

Marston et al [22] concluded that the main toughness theories (pull-out, debonding and stress distribution) only successfully predict the toughness when the mechanism upon which they are based is the principal method of energy dissipation. A combination of the above mentioned mechanisms usually accounts for the total energy absorbed in the fracture process of a composite. A single mechanism cannot account for the observed toughness of a composite. They also pointed out that errors may arise in the toughness predictions when the assumptions made in the various theories are not observed. The assumption of Cottrell and Kelly that the shear strength of the interface is maintained during fibre pull-out may not always occur. Also, the fracture strain of polymeric matrices is usually greater than that of most common reinforcing fibres which contradicts Outwater and Murphy's assumption.

This led Marston et al to propose a general theory of composite fracture toughness which considered all the different modes of energy absorption. More importantly, they also incorporated the energy absorbed in creating new surfaces which had been neglected in the earlier theories. The work done in generating fibre fractured surfaces, matrix fractured surfaces and fibre matrix interfacial surfaces (debonding) were all taken into account. Hence, they suggested that the total fracture toughness of a composite can be obtained by summing up the separate contributions made by each toughening mechanism, that is:
\[ R_{\text{total}} = R_{\text{pull-out}} + R_{\text{redist}} + R_{\text{surfaces}} \]

The debonding energy contribution of Outwater/Murphy or Cook/Gordon is included in the \( R_{\text{surfaces}} \) term - the energy absorbed in creating new surfaces.

Finally, it should be noted that fractures of brittle reinforcing fibres account for a very small fraction of the total energy absorbed due to their low fracture strain.

2.3.2 Modifications of Composites to Improve Toughness

In the preceding section the different toughening mechanisms possible in fibre reinforced plastics were discussed. As well as the utilisation of these mechanisms by controlling fibre matrix interfacial adhesion, further modifications can be made to composites to enhance toughness. To date, several methods have been employed to provide energy absorption paths in composites. These include:

1. matrix toughening
2. hybridisation
3. duplex fibres
4. intermittent coating of fibres
5. delamination promoters ) controlled interlaminar
6. intermittent interlaminar layers ) bonding of laminates
7. complete fibre coating (innerlayers)

Techniques 4-7 rely upon modifying the interface between fibre and matrix or between two laminae. In this section these different methods are discussed and particular attention is given to a review of the use of fibre coatings in composites.
Increased energy dissipation may be attained by matrix modifications. The toughness gain of a composite through plastic deformations of a modified matrix is usually limited as compared to the actual matrix toughness improvement. This is due to fibre matrix interactions. The presence of stiff fibres limits the deformation potential of the modified matrix. Also fibre failure and debonding may occur before the full energy absorbing capability of the matrix is attained [23]. In extreme cases, the presence of a soft and weak modified matrix may drastically reduce the stiffness and strength of the composite resulting in a negligible improvement in toughness. Toughness improvement of brittle thermosets is usually achieved by the incorporation of small elastomeric inclusions. These discrete particles can act as energy absorbers. Rubber modified thermosets are prepared from a homogeneous solution of a rubber in the resin, which precipitates the discrete elastomeric phase during the curing reactions. Currently, one of the widely used toughening rubbers in epoxy resins is a carboxy-terminated butadiene-acrylonitrile random copolymer (CTBN) [34,24]. Other systems which rely on the precipitation of a glassy polymer such as polysulphone and polyetherimide have also been considered [35]. These high softening temperature plastics have the advantage of minimising the reduction in the glass transition temperature of the epoxy resin.

The impact properties of high modulus carbon fibre composites are relatively low compared to glass fibre composites ($E_{\text{carbon fibres}} < E_{\text{glass fibres}}$). In recent years, an effective method to enhance the impact properties of carbon fibre composites has been achieved by the addition of small amounts of lower modulus, high strength and higher strain fibres. The incorporation of two or more fibres in a single matrix is known as hybridisation. Glass fibres are frequently used to
improve the impact performance of carbon fibre composites. The addition of the relatively cheap glass fibres also reduces costs which is a limitation on the application of carbon fibre composites. The improved impact resistance is attributed to the increase in area of fracture surfaces created by the increased number of fracture modes available and the relative increased capability to store strain energy in the glass fibres [25]. Jang et al [26] also commented that the poor impact performance of composites was associated with the low failure strains of the reinforcing fibres. As a possible solution to this problem, they investigated the effect of utilising high strain, high ductility fibres in carbon fibre composites. They showed that the use of fabrics such as polyethylene, nylon and polyester, having low modulus but capable of large strains to failure, improved the impact resistance of carbon fibre laminates. The increase in the energy absorbing capabilities of the hybrid structures was explained by the observed large flexural plastic deformations of the ductile fibres and some delamination.

The "duplex fibre" concept of improving the pull out toughness of composites was suggested by Morley and Milliman [27]. The duplex reinforcing fibre consisted of a sheath and core. The sheath was strongly bonded to the matrix to provide good strength and the core element was frictionally bonded to the sheath to allow progressive decoupling on the application of a load. The core element never fractured and it bridged crack faces as the matrix failed. Work on two part steel reinforcing elements (steel wire encapsulated in a tube) in an epoxy resin showed that toughness could be improved by the core elements pulling out and by the resistance of further matrix crack propagation. However, in practice it was seen as difficult to prepare such duplex fibres and use them in real composite materials.
Atkins [28] intermittently coated fibres with a polyurethane varnish (a viscous fluid). The coated regions where interfacial bonding was weak, served both to blunt propagating cracks by the Cook Gordon debonding mechanism [20] and to produce larger fibre pull-out lengths. The strongly bonded uncoated regions ensured that the full strength of the composite was retained - see Figure 2.4. These energy absorbing mechanisms improved the fracture toughness of an 80% coated unidirectional boron fibre epoxy resin composite by 400% without any loss in strength. For a fully coated composite the toughness was increased further to over 500% at the expense of a 25% loss in tensile strength. Similarly, Mai and Castino [29] intermittently coated Kevlar fibres with a silicone fluid and a polyurethane varnish. The toughness was shown to increase by 300% at low strain rates and at high temperatures. Silicone fluid coated Kevlar fibre epoxy resin composites exhibited no toughness degradation after hydrothermal ageing unlike the untreated control composite.

The energy absorption of composite laminates can also be increased by promoting interlaminar delamination or splitting. This is usually achieved by controlling (weakening) the bonding between prepreg layers. Such "controlled interlaminar bonding" may be achieved by the use of delamination promoters and intermittent interlaminar layers. Favre [30] used either metallic or organic films (e.g. aluminium, nylon) as delamination promoters in composite laminates. These films were stacked between prepreg layers to induce extensive delamination which absorbs a great amount of energy. The main crack was found to propagate in a plane perpendicular to these films. The multiple splitting between layers imparted additional toughness to the laminate by blunting and diverting the main crack. A 170% increase in Charpy fracture energy was observed with no significant reduction in strength for carbon fibre epoxy laminates with nylon films.
In Jea and Felbeck's [31] work both full and perforated plastic films were used to promote delamination. Intermittent bonding between laminae was achieved by inserting layers of 7 μm thick Mylar films (polyester) between adjacent prepreg layers. Each Mylar film contained a matrix of holes to allow epoxy resin to flow between laminae. Strong bonding between laminae was achieved after curing and assisted to maintain strength and stiffness properties of the composite and to prevent premature complete delamination. The remaining film areas acted as weakly bonded regions capable of interlaminar cracking. Hence, both strength and toughness were achieved simultaneously. The enhanced fracture toughness (250% increase) was explained by the blunting and diverting of internal cracks. Similar investigations on full and perforated films was also undertaken by Mai et al [32].

A more generalised concept of controlled interlaminar bonding (CIB) was proposed by Jang et al [33]. The use of other perforated films, some of which were of lower cost and easier to fabricate, was explored. These films included paper, aluminium, polyester, polyamide and textile fabrics. They also reported that the incorporation of these perforated interlayers increased the fracture toughness without significantly reducing composite strength. Again, the interlayers appeared to promote delamination which aided the dissipation of strain energy and diverted and blunted propagating cracks through the Cook/Gordon mechanism [20].

Stress and strain concentrations in the vicinity of the interface result from a combination of:

a) the large difference between the fibre and matrix moduli, and
b) shrinkage and thermal stresses.
Hence, composite fracture is frequently initiated in the proximity of the interface where these stress concentrations exist. The concept of applying an interlayer around the fibres involves lowering these detrimental stress concentrations. One of the earliest attempts to improve the toughness of a composite by applying a rubbery interlayer to the fibres was described by Enever [36]. Carbon fibres were coated with a polyurethane rubber applied from solutions. The incorporation of coated fibres (from a 4% solution) in an epoxy matrix resulted in an improvement in toughness demonstrated by falling weight impact tests, without a reduction in flexural modulus. Damage was localised to the region of impact unlike the uncoated samples which sustained vast amounts of damage and delamination. However, the Charpy impact test showed little difference between the coated and uncoated composites. The polyurethane rubber was believed to bond well to the carbon fibres through the polyurethane amine curing agent and the isocyanate groups in the coating. Adhesion between interlayer and matrix was thought to occur by the epoxy resin intermingling with the interlayer to form a graded interface.

Further work in this area was limited until after the publication of a theoretical paper by Broutman and Agarwal [37] in 1974. The influence of an interlayer at the interface on mechanical properties was predicted using the finite element method. This approach is discussed further in Section 2.4. The application of a "rubber bumper" interlayer to large diameter glass filaments was described by Lavengood and Michino [38] and later amplified by Tryson and Kardos [116]. A plasticised epoxy resin interlayer was applied uniformly to 5 mm diameter glass filaments from solution in thicknesses ranging from 1 to 4 percent of the fibre diameter (thick coating). A 67% increase in transverse tensile strength, a 1000% increase in torsional fatigue...
life and a lower reduction in transverse strength after water exposure was observed with unidirectional coated glass filament epoxy resin composites. As well as providing a local deformation mechanism to reduce interfacial stress concentrations the interlayer was thought to heal flaws on the glass filaments and increase the intrinsic fibre strength.

Hancox and Wells [39] claimed that they were able to improve the work of fracture of carbon fibre epoxy resin composites by 100% without a decrease in flexural strength, by coating the fibres with 1% silicone rubber. Significant drops in flexural strength and no further increases in toughness were observed with greater amounts of coating. In this case, the coating was deliberately used to weaken the interfacial bond to maximise energy absorption by debonding and fibre pull out. Sung et al [40,41] applied a viscous silicone fluid to glass fibres and improved the fracture toughness of polyester composites by 150%. The toughening mechanism was established as the energy absorbed by the viscous shear work of the silicone fluid during extensive fibre pull-out. The energy absorbed was maximised by changing the fluid viscosity and thickness of the coating. However, the inevitable reduction in composite strength was only mentioned but not determined. Such a weak interface will lead to poor stress transfer resulting in a drastic reduction in stiffness and strength.

Electrostatic forces were used by Peiffer [42,43] to encapsulate glass fibres with a controlled, uniform layer of rubbery acrylic polymer from aqueous solutions. An improvement in the Izod impact strength of randomly oriented glass fibre epoxy composites containing these very thin interlayers was observed. It was also confirmed that the composite impact strength was a function of both interlayer thickness
and glass transition temperature (Tg). For maximum toughness and strength an optimum interlayer thickness (~0.2 µm) and a low interlayer glass transition temperature was required – see Figure 2.5. The interpenetrating polymer networks formed between the crosslinked acrylic system and the crosslinked epoxy system was believed to provide good adhesion between the interlayer and epoxy resin.

Using a single step on-line industrial process, Schlund and Lambla [44] manufactured 15 µm diameter glass fibres and coated them with various reactive lattices (acrylates) containing an amino silane. Although toughness properties of the resultant epoxy resin composites were not determined, dynamic mechanical analysis and short beam flexural tests were used to assess the effect of the acrylate interlayers. A latex coating with a Tg = -20°C improved the low temperature mechanical properties, increased the value of tan delta (improved damping capacity) and allowed plastic deformation without delamination during flexural tests. It was also shown that the uniformity of the coating as well as the nature of the latex governed composite mechanical behaviour.

Shelton and Marks [45] used high resolution X-radiography to study the effects of the incorporation of a ductile interlayer on the failure properties of composites. Glass fibre epoxy resin composites with and without a ductile interlayer were stressed to failure in three-point bending. Simple qualitative observations from this sub-surface analysis showed that the mode of failure and crack propagation were greatly influenced by the presence of an interlayer. They suggested that this would effectively raise the energy required for composite fracture and composites with interlayers would be beneficial to the leakage failure properties of composites utilised in pressure vessels and piping.
In Schwartz and Hartness's [46] work carbon fibres were solution coated with a nylon modified epoxy and a two phase elastomer modified epoxy resin and used to fabricate epoxy resin prepreg composites. The use of a modified, toughened matrix as the interlayer facilitated coating matrix compatibility and ensured bonding between interlayer and matrix. Inconclusive fracture toughness results were obtained from the double cantilever beam method. However, the concept of coating fibres improving the intrinsic composite toughness was borne out by scanning electron microscopy studies of the fractured surfaces. Deformation of the coating and large amounts of fracture surface within the matrix were apparent, suggesting that there was much greater energy dissipation in fracturing the coated fibre components. No significant differences in compressive and transverse tensile strengths were observed between coated and uncoated fibre composites.

McGarry et al [47] also solution coated carbon fibres with a mixture of CBTN rubber and epoxy resin. Prior to applying the interlayers the fibres were sized with an epoxy resin to improve adhesion between the rubbery coating and the carbon fibres. The impact resistance of unidirectional and cross plied epoxy resin laminates was evaluated using a Gardner impact tester. The presence of the rubbery coating decreased the amount and the extent of impact damage, with coatings containing higher proportions of rubber being more effective. Also, a reduction in interlaminar shear strength was mentioned with coated fibre composites. No other toughness or strength properties were given.

Gerard [48] similarly applied an elastomeric interlayer (CBTN - epoxy adduct) to oxidised carbon fibres, using an on-line filament winding process. Improvements in Charpy impact properties were observed with
no loss in flexural modulus at low levels of coatings. More recently, Gerard [49] introduced the same elastomeric interphase to glass bead and unidirectional glass fibre epoxy composites. The reported improvements were parallel with his previous work on carbon fibre composites. Also, a 25% improvement in fracture toughness was obtained with rubber coated glass bead, epoxy resin model composites. Both sets of his work confirmed again that an optimum interlayer thickness existed which resulted in an improvement in impact properties without any degradation in the elastic behaviour of the composite.

Electrodeposition has been used to obtain uniform interlayers of controlled thickness on conductive carbon fibres. Crasto and Subramaniam [50,51,52] used carbon fibres as electrodes in an electrolytic cell, to coat carbon fibres with various interlayers including butadiene-maleic anhydride (BMA) and ethylene-acrylic acid (EAA) copolymers. A reduction in interlaminar shear strength and improved impact properties were obtained with BMA coated epoxy resin composites. The weak interlayer matrix bond was responsible for multiple debonding and fibre pull-out and the consequent improvement in impact properties. Simultaneous improvements in impact strength (21%) and interfacial bonding (strong bond between interlayer and matrix) were reported with EAA fibre coated epoxy composites. In this case, the improved impact properties was attributed to the ability of the copolymer to deform and deflect/blunt propagating cracks.

Preliminary tests conducted by Bell et al [53] exhibited the same trend of lower interlaminar shear strength and higher Izod impact strength for coated carbon fibre epoxy resin composites. Their work also involved electropolymerising a random copolymer (methyl acrylate and acrylonitrile) in various thicknesses and ratios, onto commercial
carbon fibre bundles. Further investigations [54] revealed significant improvements in mode I fracture energy ($G_{Ic}$ improved by 50%) and a large reduction in mode II crack initiation energy ($G_{IIc}$). This loss was related to the poor adhesion between the interlayer and epoxy resin. The use of other electrocopolymerised interlayers based on acrylonitrile and various other monomers as a possible means of improving composite toughness was also further examined by Winolklasak and Bell [55].

Interlayers have mainly been incorporated into composites containing brittle thermosetting resins since significant toughness gains are expected compared to using ductile thermoplastic matrices. However, some work has been published on the use of interlayers in thermoplastic matrices. Pleudemann [56] investigated the use of thermoplastic rubber interlayers on the properties of glass filled polypropylene composites. Extensive preliminary tests were performed to evaluate the adhesion of a range of thermoplastic matrices to thermoplastic interlayer rubbers, using silane coupling agents. This was achieved by fusing thermoplastic resins against rubber coated glass microscope slides. No toughness gains were observed with injection moulded samples containing thermoplastic rubber coated chopped fibres. However, compression moulded polypropylene glass cloth laminates with a styrene-butadiene-styrene (SBS) rubber interlayer improved the impact strength by 150%, at the cost of a 10% reduction in flexural strength. Again increasing the thickness of the rubber interlayer significantly reduced the strength of the laminates without improving the toughness.

An extrusion coating process was used by Piret [57] to apply thermoplastic rubbery interlayers to glass fibres, for use in
polyamide 6/66 composites. The thermoplastic rubber was extruded through a T-shaped die while the glass fibre rovings were drawn through the die. Ethylene propylene rubber coated glass fibres improved the Gardner impact strength of polyamide 6,6 composites by 60% with no resultant reduction in tensile strength or other mechanical properties.

2.4 **FINITE ELEMENT ANALYSIS OF COMPOSITE MATERIALS**

Cox [9] was the first to investigate the stress distribution around a fibre in short fibre composites, using the now well known shear lag analysis. Nowadays, finite element analysis has enabled the internal stresses of a composite to be calculated and equally importantly allowed predictions of strength and stiffness. A simple model was used to simulate the structure and behaviour of spherical particle composites using the finite element analysis approach [91,92]. The internal stresses and predicted composite moduli of rubber filled polymers [91] and ceramic filled glass systems [92] were analysed. In both these cases of soft and rigid particulate composites good agreement of predicted moduli with experimental data was found. Broutman and Agarwal [37] extended their theoretical study further by investigating the influence of introducing an interlayer of finite thickness to spherical particle and aligned discontinuous fibre composites. They showed that the toughness, determined by the amount of strain energy absorbed could be maximised by controlling the interlayer modulus, whilst retaining adequate tensile properties. This revelation provided the impetus for experimental research into the use of interlayers in polymer composites. Subsequently, several workers provided experimental evidence confirming Broutman and Agarwal's findings (see Section 2.3.2).
Using results from a numerical analysis, Arridge [93] suggested that stress concentrations in the matrix of a fibre composite under transverse loading could be considerably reduced by incorporating an interlayer of low shear modulus and small Poisson's ratio. Experimental work on model composites consisting of up to three steel inclusions in an epoxy matrix exhibited an improvement (10% relative to specimens with holes) in the transverse tensile strengths of model composites, containing a flexibilised epoxy resin or silicone rubber interlayer [94]. However, when Broutman and Agarwal loaded a short fibre composite model in the fibre direction, varying the Poisson's ratio of the interlayer had an insignificant effect on the stress distributions.

The finite element analysis method has also been applied to many other related micromechanical aspects of composites. Sun and Wu [95] examined the effect of fibre end geometry on the normal and interfacial shear stress distribution of short fibre composites. These distributions were in good agreement with existing results obtained experimentally by using the photoelasticity method. It was also observed that the shear stress concentration occurred very near the fibre tip, particularly for V-shaped fibre ends. Similarly, Soh [96] analysed the interfacial shear stresses of a single short fibre model and compared the solution with photoelastic test results. A finite element analysis package was recently applied by Guild and Young to model the behaviour of glass sphere filled [97] and rubber sphere toughened [98] epoxy resin composites. A statistical model was developed to take into account the real random distribution of spheres. Good agreements were found between predicted values of stiffness and experimental measurements. However, their work was not extended further to examine the effect of introducing interlayers on composite properties.
2.5 ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE

2.5.1 General Properties and Thermoreversible Gels

In this section some of the outstanding properties of ultra high molecular weight polyethylene (UHMWPE) are described. Also since UHMWPE is able to form thermoreversible gels, and these were subsequently used in this project, the gelation process is also discussed.

UHMWPE is a high density polyethylene with a weight average molecular weight in the range 3-6 x 10^6 g/mole. Most commercial high density polyethylene (HDPE) grades have a weight average molecular weight range 100,000-200,000. There is no chemical difference between HDPE and UHMWPE since both are straight-chain linear polymers. UHMWPE is produced using a Ziegler-Natta catalyst similar to that used for conventional HDPE. It is produced by a batch or continuous slurry process and is supplied as a fine powder.

The high molecular weight (long molecular chains) provide UHMWPE with several unique properties. The outstanding high impact resistance of UHMWPE exceeds that of all other plastics, even at cryogenic temperatures. At temperatures of liquid helium (-269°C) this tough polymer can still withstand certain levels of impact without shattering. The wear resistance is greater than most other thermoplastics and in some cases superior even to high quality steel alloys. UHMWPE can be employed at temperatures up to 80°C under moderate loads. At temperatures above the crystalline melting temperature (135°C), some dimensional stability is still maintained, because of the high viscosity which resists gravitational forces. Under special conditions when not all of the UHMWPE product is exposed
to in service stresses, much higher temperatures can be tolerated. Other attractive properties include good chemical resistance, excellent environmental stress crack resistance and resistance to radiation. Also UHMWPE possesses low water absorption properties in common with all polyolefins.

Most thermoplastics like HDPE are usually melt processed using techniques such as extrusion, injection moulding or blow moulding. However, UHMWPE cannot readily be processed by conventional melt processing techniques, because of its high molecular weight and associated high melt viscosity. The polymer can although be processed by compression moulding at temperatures over 200°C. Twin screw extrusion is possible only with the aid of special additives (low molecular waxes/oils) and an appropriate die of special design must also be used.

Applications of UHMWPE are based on its remarkable properties. It is used in a variety of areas where high impact and wear resistance is required, including in the paper and chemical industries, in chutes and liners of bulk materials handling systems, and also in sporting equipment. A recent application is in very strong, light fibres produced by gel spinning [58,59].

An important feature of UHMWPE is that it is capable of forming thermoreversible gels. A polymer gel is a three-dimensional network of polymeric chains with chemical or physical associations (linkages) between different polymer chains, imbibed in a solvent [60]. Conventional gels consist of disordered chains covalently linked together in a swollen network, and are thermally stable. Thermoreversible gels however involve the formation of physical
crystallite links between associated chains. A very fluid dilute solution is converted into a rigid medium of high viscosity. Gelation occurs when dilute solutions are cooled, to form small crystallites, which can disappear on reheating to produce a solution again. Hence, "thermoreversible" gels can repeatedly alternate between the gel and solution state unlike more conventional type gels.

\[
\text{gel} \xrightarrow{\text{heat}} \text{solution} \xrightarrow{\text{cool}}
\]

Initially, thermoreversible gels were categorised into two general groups. The first group of gels formed under quiescent conditions with very high supercoolings. Isotactic polystyrene was observed to form gels under these conditions, amongst other vinyl polymers and copolymers. The form of crystallisation providing the connectedness was first postulated to be of fringed micellar type [61]. This was later, however, dismissed as a misconception since polymorphic crystalline structures were later observed. Micellar type structures were not considered necessary for gelation of vinyl polymers and other copolymers since lamellar crystallites were later found to be associated with such gels [62,63]. Although these types of gels have been extensively studied, they are not directly relevant to this research programme.

The second group required the polymer solution to be prestirred before cooling, to allow gel formation. Homopolymers including UHMWPE were considered to be within this class [60,64]. Three distinct stages were observed during the formation of these gels [65]:
a) Agitation or stirring of the solution above the crystalline temperature of the (semi-) crystalline polymer.

b) On cooling in a quiescent state the solution sets into a transparent gel.

c) Further cooling produces an opaque gel due to the onset of lamellar crystallisation.

The entire process may be reversed on reheating. The stirring stage was thought to produce some mode of molecular association even before the cooling and crystallisation stages. However, authors such as Edwards et al [66] later emphasised that gel formation in homopolymers did not necessarily require any type of prestirring of the solution, as had been previously insinuated [60,64,65]. It was shown that linear polyethylenes including UHMWPE can form gels from solvents such as toluene, p-xylene and decalin over the complete molecular weight range under quiescent conditions [66,67]. A critical polymer concentration is however an important requirement for the gelation process. Below this concentration, the well known isolated platelet like (lamella) crystallites precipitate. Mechanical agitation is probably only absolutely necessary to generate gels when an inadequate polymer concentration is used (less than critical concentration) [64]. Gels produced from the lower molecular polyethylenes are mechanically weak and can be broken up early by vigorous shaking, whereas at higher molecular weights they become much more rigid.

UHMWPE gels have been used to produce fibres of high modulus. Smith and Lemstra [68,69] described a gel spinning/drawing process in which a gel fibre was first obtained by spinning a solution of UHMWPE in
decalin into cold water. The gel fibre was then dried and hot drawn to very high draw ratios. Polyethylene filaments with a modulus of 90 GPa (comparable to the modulus of glass fibres) and tensile strength of 3 GPa were obtained.

Gel crystallised UHMWPE has been extruded in the solid state at temperatures around 140°C [70]. The gelation process enabled melt processing of unfilled and filled UHMWPE by reducing the chain entanglement concentration (chain alignment) and by plasticising the material.

As well as linear polyethylenes, the gelation behaviour of other homopolymers, such as polypropylene has been studied [60,69,71].

2.5.2 Adhesion and Grafting Functionalised Groups onto Polyethylene and Other Polyolefins

A strong bond between fibre and matrix is essential for good overall performance of polymer composites, as discussed in Section 2.2.1. Silane coupling agents have been extensively used to improve the strength of the interface between glass fibres and the matrix, through various adhesion mechanisms which have been already mentioned (Section 2.2.2.). Plueddemann [56] recognised the importance of also having strong interactions between the different interfaces in composites with interlayers. He used glass microscope slides as a rapid qualitative measure of the degree of adhesion between the various interfaces of composites with and without interlayers, using silane coupling agents [72,73]. He found that there was a very good correlation between the adhesion observed in microscope slide tests and the performance a silane provided in mineral filled resins and elastomers.
Enever [36] indicated that a polyurethane interlayer bonded well to carbon fibres (through chemical bonding) and formed an intermingling graded interface with the epoxy resin matrix. Peiffer [42] suggested that interpenetrating polymer networks provided good adhesion between acrylic interlayers and the epoxy matrix. Also, Piret [57] briefly mentioned that thermoplastic rubber interlayers could be grafted with an unsaturated silane or maleic anhydride to improve adhesion. Hence, establishing adequate bonding between the glass fibres, the UHMWPE interlayer and epoxy matrix was of importance in this project.

Most commercial fibres are applied with silane coupling agents suitable for the more common thermosetting resins and not thermoplastic matrices. Thermoplastics can be divided into two broad classifications of reactive and non-reactive polymers [73]. Reactive polymers contain functional groups such as amide, ester, carboxyl, hydroxyl or halide that can react readily with other organofunctional groups at moulding temperatures. However, polyolefins are relatively non-reactive and thus more difficult to bond to other substrates. Most applications of silanes in reinforced thermoplastics involve systems where there is no hard evidence of chemical reaction between silane and polymer. Coupling non-reactive polyolefins to fillers through silanes has been described by Gahde [74] and Plueddemann [72] by the formation of an interpenetrating network (IPN) between the silane and matrix.

Polyolefins are not however completely inert since chemical bonding to other substrates can take place by grafting organofunctional groups onto the hydrocarbon chain. Unsaturated vinyl silanes have been grafted to polyethylene at 140°C in the presence of an organic peroxide (free-radical initiator) [75]. Crosslinking of the grafted
polyethylene can be subsequently induced by exposure to trace amounts of water at elevated temperatures in the presence of a condensation catalyst. This causes hydrolysis and condensation of the silane alkoxy groups to form siloxane crosslinks. This technology of silane grafting polyethylene has been successfully exploited on a large commercial scale to produce crosslinked low density and high density polyethylene for electrical cable insulation and water heating pipes. More recently, a vinyl silane was similarly grafted onto UHMWPE by melt extrusion [76]. As previously mentioned the inherent high melt viscosity of this high molecular weight polymer necessitated the use of a low molecular weight paraffin wax as a processing aid. Drawn UHMWPE filaments were subsequently crosslinked in order to improve their heat resistance. Adhesion of these reinforcing fibres to polar matrices (epoxy resin and nylon) was improved by plasma/corona surface treatments. Also, crosslinking of polymers through silane grafting has been extended to other polymers including ethylene-propylene elastomers [77].

Vinyl silanes coated on fillers have also been reported to graft onto polyethylene during injection moulding [74]. The use of azido functional silanes in glass sphere filled HDPE composites has been shown to markedly improve interfacial adhesion through direct chemical bonding [78]. These silanes react with polyolefins through insertion into the C-H bonds of the polymer.

Similarly, Stori and Dahl [79] studied the free-radical induced grafting reaction of HDPE to methacrylate silane treated glass surfaces and its effects on the mechanical properties of short glass fibre HDPE composites. Retention of mechanical properties after water exposure and the Charpy impact strength test were improved when the polyethylene was grafted to the glass surface.
Apart from the use of silanes, the adhesion of polyolefins to other polymers/substrates can also be promoted by the introduction of other reactive functionalities onto their backbone. Maleic anhydride has been grafted onto polyolefins including low density polyethylene [80] and polypropylene [81,82,83] also using a free radical initiator, in the melt state. Crosslinking of low density polyethylene and degradation of polypropylene was also suggested to accompany the grafting reaction when high levels of maleic anhydride or peroxide and higher temperatures were utilised. Peel tests on modified polypropylene films sandwiched between aluminium sheets (0.1 mm thickness) exhibited improvements in adhesion and identified an optimum level of grafting to achieve maximum adhesion [83].

UHMWPE has been grafted with maleic anhydride by melt processing at temperatures of about 250°C, again with the aid of a low molecular weight paraffin wax [84]. Significant improvements in the adhesion of stretched UHMWPE filaments to an epoxy resin were obtained. Shyu et al [85] were able to graft maleic anhydride onto polyolefins such as polypropylene using milder reaction conditions. This was achieved with the assistance of an amine catalyst, in both the molten and particulate state, although an explanation of how the catalyst accomplished this was not given. Adhesive polyolefin blends containing maleic anhydride grafted polypropylene have been used to bond polypropylene to polar materials such as nylon and ethylene-vinyl alcohol copolymers [86]. Maleic anhydride grafted polypropylene was prepared by the conventional method of reacting together polypropylene and maleic anhydride in the presence of peroxide, in the melt state. Satisfactory bonds were obtained when the adhesive blend was used to produce multilayered films which were then subsequently thermoformed into containers.
The earlier reported degradation of polypropylene [81] was reduced to some extent by conducting the maleic anhydride grafting reaction in a xylene solution at 120°C [87]. Another solution grafting reaction of maleic anhydride was later studied by Cimmino et al [88]. In this case the anhydride was similarly grafted onto an ethylene-propylene rubber copolymer in a xylene solution at 135°C. The low temperature impact resistance of polyamides was improved by incorporating the modified elastomer, to form a blend. The toughness enhancement was related to the observed strong adhesion between the rubber domains and the polyamide matrix, which was thought to occur through the formation of amidic linkages. Maleic anhydride was found to possess the highest reactivity towards the ethylene-propylene macroradicals compared to other unsaturated functionalities including dibutyl maleate [89]. This higher reactivity was suggested to be connected with the enhanced activation of the double bond due to a stronger electron attracting property of the anhydride group relative to the ester group.

The free radical grafting reaction of maleic anhydride onto polyolefins can also occur in suspension, as well as being carried out in the melt and solution state. Using liquid ketones as the dispersing medium, Banzi et al [90] reported improvements in the adhesion of maleic anhydride grafted ethylene-propylene copolymer to aluminium.
An initial objective of this study was to develop a coating procedure to apply two interlayer polymers, UHMWPE and EPDM uniformly and continuously onto glass fibres. UHMWPE was the main interlayer because of its outstanding toughness while EPDM was used as a soft rubbery interlayer for comparison. Since polyolefins have a low chemical reactivity and low affinity to other materials, it was also necessary to develop and analyse a coupling mechanism for bonding UHMWPE and EPDM to both the glass fibres and the epoxy matrix. The first two sections of this Chapter (3.1 and 3.2) describe the preliminary work conducted in an attempt to achieve these two aims.

3.1 EVALUATION OF COATINGS ON GLASS FIBRES

3.1.1 UHMWPE Solution/Gel Preparation and the Coating Process

The first part of the preliminary work involved experimenting with different techniques to develop a suitable coating procedure that would enable thin, continuous coatings to be applied. Several methods have been employed in the past for coating interlayers onto fibres, which have been reviewed in Section 2.3.2. However, since UHMWPE is not readily melt processable, solution coating was considered to be the most practicable route to obtain thin coatings.

Solutions of UHMWPE were prepared by refluxing a mechanically stirred solution of 1.2% w/w (4g) of UHMWPE (Hostalen GUR 412, Hoechst MW = 3.5-4 million) in p-xylene (400 ml) containing 0.1% w/w (0.2g) DTBPC (antioxidant 2,6-di-tert-butyl-p-cresol) at 135°C for 4 hours. UHMWPE
is difficult to dissolve because of its very high molecular weight and high crystallinity. Thus it was added to the xylene in small portions over a period of two hours. When UHMWPE powder is added all at once, a large clear lump of polymer is formed at the bottom of the reaction vessel, which will not dissolve even over many hours of refluxing.

The apparatus shown in Figure 3.1 was set up to allow E glass fibres (Equerove 23/24 CRC Fibreglas Ltd 600 tex, 13 µm diameter with epoxy compatible size) to be coated with a UHMWPE solution. The fibres were first passed through a hot xylene bath (70°C) to remove the existing size binding the individual filaments together, thus allowing the filaments to separate. To assist further in separating out the fibres, the roving was passed through a cylindrical compressed air jet. The separated fibres were then fed into a flask containing the UHMWPE solution, and then immediately passed through a hot air jet. The purpose of blowing hot compressed air through the fibres was to dry off the solvent rapidly while the filaments were still separated. The two flasks (containing the xylene and coating solution) were specially modified to allow the fibre to be fed into the flask through a side inlet and be passed under a metal bar to keep the fibre immersed in the solvent/solution. Glass fibres were coated at different temperatures in the UHMWPE solution and also in a 80:20 blend of ethylene acrylic acid copolymer (A3710M, BASF) UHMWPE solution. The effect of varying the compressed air pressure on fibre separation was also investigated. The coatings were examined under an optical microscope.
3.1.2 Further Studies on Fibre Coating

Since the quality of the coatings on the fibres appeared to be unsatisfactory (see Sections 4.1.1 and 5.1) further studies of the coating of glass fibres were carried out. A small number of xylene washed filaments were placed on microscope slides after being dip coated in the UHMWPE solution. The effect of removing the size and silane from the glass fibres was also examined by placing the fibres in a furnace at 600°C for 6 hours. The ability of UHMWPE solutions to form films on glass microscope slides and polyethylene substrates was also determined.

To investigate the effect of different polymer systems and the effect of concentration on the quality of the coatings, xylene washed glass fibres were dipped into various solutions of silane grafted EPDM, a low molecular weight polybutadiene (Ricon 150, Colorado Chemicals) A189 silane system and a phenoxy resin (Ucar, Union Carbide). The preparation of the polymer silane systems is detailed in Section 3.1.2. Epoxy sized glass fibres of 300 tex (Turner and Newall Ltd, 12 µm diameter) were used since it was thought that a roving with a fewer number of filaments would be easier to coat uniformly.

The effect of coating fibres with silane grafted UHMWPE solutions was also investigated (Section 3.2.4). The coatings were examined using optical and scanning electron microscopy. Coating thicknesses expressed as weights of coatings were also determined.
3.2 DEVELOPMENT OF BONDING METHODS FOR INTERLAYER POLYMERS BETWEEN GLASS AND EPOXY MATRIX

3.2.1 Grafting Organosilanes onto EPDM Polymer Chains

Thin amorphous EPDM films cast onto glass microscope slides from dilute xylene solutions (1%) are readily peelable due to lack of adhesion. Thus, to improve the bond between glass and EPDM, grafting of organosilanes onto EPDM chains in the melt state was first attempted. Four different types of EPDM, silane and peroxide systems were melt mixed in a Brabender mixer at 60 rpm. Detailed experimental conditions are given in Table 3.1.

A sulphonated EPDM was used because of its polarity which was expected to provide better wettability on glass and offered the possibility of bonding to the epoxy resin through SO\text{3}H reactions. Silanes A174 and Z6032 were chosen because they both contained double bonds which was thought could add to the EPDM in the presence of a free-radical initiator. Also both possessed other reactive functionalities useful for bonding to the epoxy resin. The mercapto silane (A189) had the advantage of being able to react with double bonds on the EPDM. The alkoxy groups of these silanes are readily hydrolysable in the presence of moisture/water and can then form a chemical bond with a mineral surface such as glass.

Samples from mixes 1-4 (see Table 3.1) were bonded to washed glass microscope slides in the molten state by placing the slides in an oven at 150°C for 30 mins. Using a razor blade a qualitative assessment of the improvement in bonding was made by attempting to peel the films off the slides.
Since solutions were used to coat the glass fibres and were planned to be used to prepare interlayer composites, further investigations into the most promising rubber silane systems (see Section 5.2.1) were carried out. The reactants used are given in Table 3.2. Each rubber was dissolved in xylene and heated to $100^\circ C$ when an excess (with respect to the rubber) of the silane system was then added. The solution was continually stirred for 20 mins at $100^\circ C$ to promote silane grafting onto the elastomer. On cooling, degreased glass slides were dip coated in these four solutions and allowed to dry. These coated glass slides were finally placed in an oven at $150^\circ C$ for 30 mins to promote bonding to the glass. Adhesion to glass was determined by the previously mentioned qualitative assessment.

3.2.2 Determination of Bond Strength of Treated EPDM Films

Single lap shear tests were used to provide a quantitative measure of the improvement in bonding between the modified EPDM and glass surface. This widely used test was chosen because samples are simple to construct and can provide a rapid comparative measure of bond strengths.

One millimetre thick glass microscope slides were degreased and partly coated with a freshly made 5% solution of EPDM in xylene with the A189 silane system (solution 1). These films were allowed to dry and several coats were applied to increase the thickness to a satisfactory level. Single lap shear specimens were produced by overlapping two coated glass slides and then placing them in an oven at $180^\circ C$ for 30 mins, under constant pressure (2 kg). Thin metal spacers coated with petroleum jelly were used to control the thickness of the resulting joints. The interfacial shear strength was determined by loading five test pieces in tension at a loading rate of 5 mm/min (see Figure 3.2).
Although cohesive failure of the modified elastomer was observed in most of the test pieces, the shear strength values were very low due to the low shear strength of the elastomer in its uncrosslinked state (see Figure 4.3). To overcome this problem dicumyl peroxide (2% by wt based on EPDM) was added to the cooled silane grafted EPDM solutions in order to crosslink the elastomer. Sandwich type lap shear specimens were constructed using compression moulded UHMWPE sheets to reinforce the joints and to minimise bulk failure, hence emphasising true interfacial failure, see Figure 3.3. Three millimetre thick glass slides were used to prevent glass failure during the test. The effect of the thickness of EPDM A189 layers was also determined by coating the glass slides with solutions of concentrations varying from 5 to 1% and a set of lap shear specimens were also constructed using 5% A189 (based on EPDM) to investigate the effect of reducing the amount of silane.

3.2.3 Infra-Red Analysis of Silane Grafted EPDM Films

The grafting reaction between EPDM and the A189 silane was examined using Transmission Infra-red Spectroscopy. A Pye Unicam Infra-red Spectrometer was used with a resolution of 4 cm\(^{-1}\) and a scanning time of 7 mins. Reference spectra were obtained for unmodified EPDM using a cast film and for the silane using two KBr discs. A control film (i.e. a mixture of unreacted EPDM and silane) was cast from a 5% EPDM A189 solution (solution 1). Another film was cast from a solution that had been stirred at 100°C for 15 mins. The unreacted silane was extracted from the thin films by immersion in propan-2-ol over a period of five days.

After drying the two transparent films were analysed at intervals and a quantitative evaluation was attempted.
3.2.4 Solution Grafting of Silanes on UHMWPE Chains

With a view to improving the adhesion between UHMWPE and glass, a similar study was conducted into the grafting of silanes onto UHMWPE chains. The addition of 10% Z6032 silane (based on UHMWPE) to a 2% UHMWPE solution at 120°C did not allow conventional gel formation on cooling. Instead, most of the UHMWPE adhered to the bottom of the flask.

This was an interesting observation of this study as it provided the first evidence that adhesion between glass and UHMWPE was being achieved. On cooling after grafting onto the UHMWPE, the silane chemisorbed on the surface of the glass vessel causing the UHMWPE to precipitate, thereby preventing gel formation. Adding a lower amount of Z6032 to the solution at 100°C, however, allowed gel formation to occur on cooling. Hence, to a 2% UHMWPE solution (3.44g in 200 ml xylene), 2% Z6032 (0.069g) and 0.5% (0.017g) benzoyl peroxide was added at 100°C, and the solution was refluxed for 24 hours with continual stirring. Samples of the gel were taken out after 4 and 24 hours and dried to a film at room temperature. Similar grafting reactions were carried out using a different silane, silane A174 (see Table 3.1 for structure).

The adhesion to glass was assessed by the single lap shear test. Higher shear strength values necessitated the use of 5 mm thick glass slides to prevent glass failure. Specimens were prepared by bonding the various UHMWPE films to the degreased glass slides at 280°C for 2 hours under constant load (5 kg). Also some washed glass slides were primed with a 0.5% Z6032 solution in propan-2-ol containing 0.005% dicumyl peroxide and 1% distilled water, and then used to prepare the lap shear specimens. All lap shear specimens were loaded in tension using an Instron testing machine at a rate of 5 mm/min.
3.2.5 Fourier-Transform Infra-Red (FTIR) Analysis of Silane Grafted UHMWPE Films

Modified UHMWPE thin films were cast onto glass slides from the gel and peeled off when dry for infra-red analysis. Using a Pye Unicam dispersive spectrometer, the silane peaks were very difficult to detect, so a Nicolet 20 DXC FTIR spectrometer was used instead. This type of spectrometer is a very powerful tool for observing chemical structures since many scans are added and averaged to improve sensitivity [99].

Silane grafted UHMWPE films were analysed in transmission before and after propan-2-ol extraction (to remove unreacted silane) using a resolution of 1 cm\(^{-1}\) and 20 scans.

3.2.6 Grafting Maleic Anhydride Onto UHMWPE Chains

To improve the bonding between UHMWPE and the epoxy resin matrix, grafting maleic anhydride onto UHMWPE was carried out using 2, 6 and 10% maleic anhydride (based on UHMWPE) and 0.5% benzoyl peroxide. These were added to a 1% UHMWPE solution (3.44g in 200 ml xylene) at 100\(^\circ\)C and refluxed for 3 hours (98% peroxide decomposition), with continual stirring. The gels were allowed to dry to films and subsequently bonded to aluminium epoxy single lap shear specimens to evaluate the change in adhesion - see Figure 3.4.

The UHMWPE films were sandwiched between two thin epoxy layers and the test pieces were placed in an oven at 80\(^\circ\)C for 3 hours, under constant load (2 kg) to bond the films to the resin. Five test pieces for each modified UHMWPE film were constructed and loaded in tension at a loading rate of 5 mm/min. As a comparison aluminium epoxy lap shear specimens were made using A174 silane grafted UHMWPE.
A qualitative and quantitative FTIR analysis was similarly attempted on the maleic anhydride grafted films, using methanol to remove the excess maleic anhydride (5 day immersion). A control film for FTIR analysis was cast from a gel prepared by adding 10% maleic anhydride to a 2% UHMWPE solution and refluxing for 3 hours at 100°C with continual stirring. All spectra were obtained using 20 scans and a resolution of 1 cm\(^{-1}\).

3.3 PRODUCTION OF COMPOSITES

3.3.1 Material Considerations

The materials shown below were used to manufacture unidirectional glass fibre composites.

a) The glass fibre used in this work was an untwisted reinforcement roving wound on a large cheese (ex-Turner and Newall Ltd). It consisted of 13 \(\mu\)m diameter filaments with a tex of 300 (g/kilometre) coated with an epoxy compatible size containing silane Al100*.

b) The epoxy resin used was Epikote 828 (ex-Shell). It is an unmodified liquid bisphenol A - epichlorohydrin epoxide resin of medium viscosity, with many applications including casting, impregnating and potting systems for the electrical industry, adhesives and mortars for the building industry and room temperature and elevated temperature curing laminating systems [100].

* (gamma-aminopropytriethoxysilane \(H_2N(CH_2)\_3 Si(OCH_2CH_3)\_3\))
c) Hexahydrophthalic anhydride, hardener HT907 (Ciba Geigy) was used as the curing agent. It is a white crystalline solid with a melting point of 35°C. A liquid tertiary amine accelerator, N,N-dimethylbenzylamine (Aldrich Chemicals) was used to shorten the curing time.

The low viscosity of the resin-hardener mixture made the system particularly suited for use as an impregnant [101]. The quantities of each component used and the curing schedule are given below:

<table>
<thead>
<tr>
<th>Parts by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>i) Diglycidyl ether of Bisphenol A (Epikote 828)</td>
</tr>
<tr>
<td>ii) Hexahydrophthalic anhydride (hardener HT907)</td>
</tr>
<tr>
<td>iii) N,N-dimethylbenzylamine (amine accelerator)</td>
</tr>
</tbody>
</table>

Cure conditions:  
100°C, 1 hr  
150°C, 1.5 hrs

3.3.2 Development of a Suitable Composite Manufacturing Method  
The objective of this part of the work was to develop a method to produce unidirectional glass fibre epoxy resin composites with interlayers using hand lay up techniques. A large metal leaky mould (180 mm wide x 200 mm long) was initially used to produce trial composites. Only four layers (2 passes) of glass fibres were manually wound onto a steel frame because it was thought that the use of a low volume fraction of fibres would make the preparation of coated fibre composites less time consuming. The solid white hardener was melted at 40°C and added to the warmed epoxy resin (40°C). On adding the accelerator the resin mixture was stirred to yield a clear low viscosity resin, and degassed by placing in a vacuum for 5 mins.
After applying a thin layer of silicone release agent to the leaky mould surfaces, the fibre-wound frame was placed in the mould and the resin was worked into the fibres using a laminating roller. The required composite thickness was obtained by placing 2 mm thick spacers in the edges of the mould. The mould was closed using two large G-clamps. After allowing the excess resin to 'leak' out from the sides the composite was step cured at 100°C for 1 hr and then at 150°C for 1.5 hours.

As the resultant composites possessed many voids, several different methods had to be used to obtain laminates of acceptable quality, including placing the mould before curing under vacuum for various times ranging from 5 to 30 mins, under different vacuum pressures and with and without the top half. The mould was also placed in a compression moulding press at 55°C, and the press "pumped" in an attempt to remove the entrapped air. Even after some considerable effort, it was not possible however to eliminate all the voids in composites containing very low quantities of fibres.

The use of high fibre volume fractions was thus unavoidable. To reduce the amount of fibres required, small composite samples were manufactured using a leaky mould and a frame of smaller dimensions (see Figure 3.5). A filament winding machine was used to ensure that, a uniform fibre distribution was obtained throughout each composite, that there was good alignment of fibres within each composite and equal volumes of fibres in each laminate. The rig simultaneously rotated the frame along its longitudinal axis while moving a feeder arm in the lateral direction. Ten passes (20 layers) were applied to the frame, each pass consisting of 15 windings. The degassed epoxy resin mixture was worked into the fibres over a period of 10 mins. The
bottom half of the mould containing the fibre wound frame was placed under vacuum for 5 mins at 50°C to remove the entrapped air and aid complete wetting of the fibres by the resin. The resin was further worked into the fibres, and the mould placed under vacuum for a final 5 mins to remove any remaining entrapped air from the resin. The top half of the mould was closed down to the 2 mm thick spacers using two small G-clamps and the composite cured using the same cure schedule. A composite that appeared to be void free was produced using this procedure.

3.3.3 Manufacture of Control and Interlayered Composites
Using the small leaky mould (Figure 3.5) and the exact method detailed in the last paragraph of Section 3.2.2, two slabs of dimensions 26 mm wide x 100 mm long x 2 mm thick were produced for each type of composite. PTFE coated polyester (Melinex) sheets were placed on both mould faces to obtain a smooth surface. Control samples of composites (i.e. without interlayers) were prepared by first passing the fibres through a hot xylene bath (70°C) and then winding onto a frame using the filament winding machine. The fibres were subsequently dried in an oven at 60°C for 6 hours, before the composites were prepared.

Both UHMWPE and EPDM interlayer composites were prepared using three thicknesses of coatings. This was achieved by using various solution concentrations and different number of passes through the coating solution. The UHMWPE and EPDM solutions were initially grafted with the silanes A174 and A189, respectively, developed in the preceding section. Since the highest shear strength in the aluminium epoxy lap shear tests was observed with the silane A174 it was not considered necessary to treat UHMWPE with maleic anhydride in the composite development work (see Figure 4.12). The types of solutions used and the number of coatings applied to the fibres are shown in Tables 3.3 and 3.4.
The fibres were slowly pulled through the coating apparatus (Section 3.1.1, Figure 3.1) and carefully wound onto a large drum. Approximately 100 metres of coated fibre was required to fabricate two composite samples. The amount of coating on the fibres was determined by weighing eight small lengths of fibre taken from different regions of the total fibre length. After winding the fibres onto a frame (15 windings, 10 passes), the fibres were dried at 60°C for 6 hours to remove any residual solvent. During the manufacture of composite samples a metal rod was used to work the resin into the coated fibres instead of a conventional roller, in order to prevent disturbing the coatings on the fibres. When using fibres with high coating thickness the process of working the resin into the fibres and placing under vacuum had to be repeated several times to allow complete wetting.

To ensure that the epoxy resin was being fully cured, samples were post-cured at 150°C for 3 hours, 6 hours and 20 hours and monitored by measuring the glass transition temperature by Differential Scanning Calorimetry.

During the manufacture of the first set of interlayer composites, a considerable amount of force was required to tighten the G-clamps to close the mould. A similar leaky mould was thus designed and made with high tensile steel bolts to provide the required clamping force (see Figure 3.6). Also the mould was designed such that only one slab (56 mm wide x 100 mm long x 2 mm thick) instead of two was produced. The six bolts allowed the mould to be closed down to the 2 mm spacers with much more ease since a greater force could be exerted by tightening the bolts.
3.4 EVALUATION OF MICROSTRUCTURE AND MECHANICAL PROPERTIES OF COMPOSITES

3.4.1 Microscopic Analysis

The distribution of UHMWPE and EPDM coatings around the glass fibres in the composites was determined using reflective optical microscopy. Microscope samples were prepared by mounting a section of the composites in an epoxy resin (Araldite MY750, 100 pbw, Hardener HY951, 10 pbw, Ciba-Geigy). The uneven surface of the samples was smoothed on a linisher and the resultant scratches removed by wet grinding on consecutively finer silicon carbide paper up to 1200 grit. Control samples of glass fibre composites were further polished on 6 \( \mu \text{m} \) and 1 \( \mu \text{m} \) diamond wheels to remove the fine scratches from the silicon carbide paper. Polishing the interlayered composites did not yield clear images on microscope examination even after periods of time longer than 5 mins. Well polished and highly reflective surfaces were obtained however using the following procedure. The samples were initially polished using alumina powder (5 \( \mu \text{m} \)) on a Selvyt cloth for 5 mins, with water as the lubricant. A 1 \( \mu \text{m} \) diamond wheel was then used to polish the sample for a final 4 mins. Using a micrometer eyepiece fitted to an Olympus microscope, the distribution of coatings was observed and thicknesses measured for each interlayer composite.

3.4.2 Fatigue Damage Assessment by Water Absorption

Since the process of composite manufacture was lengthy and relatively small sized slabs were produced, non-destructive techniques that involved small samples were favoured in determining the properties of composites. The suitability of a damage tolerance test using water absorption involving small samples was investigated. Samples were pre-fatigued using a three point bending rig (span/depth ratio = 5/1).
Samples of dimensions 10 mm wide x 12 mm long x 2 mm thick were carefully cut on a circular diamond cutting wheel and the cut edges smoothed with 600 grit silicon carbide paper. All the specimens used in the various tests (Sections 3.4.3-3.4.9) were also similarly smoothed. The samples under examination were loaded to 70% of the deflection at failure and fatigued to 10 cycles, at a loading rate of 1 mm/min. The amount of damage was then assessed by immersing undamaged, fatigued and fractured samples in a water bath at 60°C and monitoring the water uptake over a period of 17 days.

3.4.3 Dynamic Mechanical Thermal Analysis

Dynamic Mechanical Thermal Analysis (DMTA) is a powerful technique that allows the study of structure-property relationships in polymers. There are many types of instruments available which essentially differ from one another in the type of sample clamping arrangement used, giving rise to different modes of deformations and types of stresses. The dynamic mechanical properties of a material are determined as a function of temperature and frequency, by measuring the response to an oscillating force. These properties include the two components of the dynamic modulus (E', E'', see equation 3.1) and the mechanical loss tangent or damping factor, tan delta (see equation 3.2).

\[ E^* = E' + iE'' \tag{3.1} \]

where \( E^* \) = dynamic modulus

- \( E' \) = in phase component (or real, elastic or storage part of dynamic modulus)
- \( E'' \) = out of phase component (imaginary or loss part of dynamic modulus)
\[
\tan \delta = \frac{E'}{E''} \tag{3.2}
\]

The damping factor, tan delta corresponds to the ratio of lost energy (dissipated as heat) to energy stored under small strain oscillations, and gives an indication of the toughness or energy dissipating capabilities of a material. Apart from providing valuable information on the mechanical behaviour of the material, this method will also determine the main transition temperatures of samples (Tg), as the temperature at which tan delta goes through a maximum while the modulus E' undergoes a rapid decrease. For the case of composites additional energy losses can occur through dynamic interface frictions and interfacial molecular relaxations. Hence, DMTA was considered to be an ideal technique to assess the potential energy absorption properties of interlayered composites. A Polymer Laboratories DMTA instrument was chosen for this purpose, using the double cantilever mode.

A sample (40 mm long, 10 mm wide and 2 mm thick) was clamped at both ends and its central point vibrated sinusoidally by the drive shaft, at a frequency oscillation of 1 Hz. The strain is proportional to the linear displacement of the drive shaft which was set to 64 μm (x4) [102].

3.4.4 Interlaminar Shear Test

The interlaminar shear test is a three point bending test with a shorter span/depth ratio to maximise the level of the shear stress relative to the principal stress in the test piece. This simple test method was used to determine the effect of introducing interlayers on the interfacial strength of the composites.
The method used for obtaining interlaminar shear strength was the British Standards three point bend test method [103], using loading members of 3 mm diameter. The specimens (3 for each composite) were cut from the slab (12 mm long, 10 mm wide, 2 mm thickness), with the fibres parallel to the length. The specimens were tested at a loading rate of 1 mm/min with a span of 10 mm using an Instron test machine. After testing, a check was made that failure had occurred by interlaminar shear. Failed specimens were mounted in an epoxy resin and prepared for microscope examination using the procedure detailed in Section 3.3.1.

3.4.5 Determination of Flexural Properties

Flexural properties of the composites (i.e. modulus and strength) were evaluated using a three point bending test. Although non-standard test specimens were used, the span to thickness ratio and the length to thickness ratio were in accordance with the British Standards flexural test method [104]. Three samples were cut from each composite (40 mm long, 10 mm wide, 2 mm thick) with the fibres parallel to the length. The samples were loaded at a rate of 5 mm/min on a three point bending rig with a span of 30 mm, using an Instron test machine. The mode of failure was also observed.

3.4.6 Assessment of Impact Properties

The impact properties of the composites were determined using an instrumented Charpy impact test since the energy absorption capabilities of the interlayer composites were of major interest in this work. The Charpy impact test is basically a high speed three point bending test. Four samples were cut from each composite (50 mm long, 10 mm wide, 2 mm thick) with the fibres parallel to the length. A Rosand instrumented falling weight machine was used. The scan
interval of the machine was set to 20 ms and the delay before commencing recording set to 10. A sample was placed on the rigid supports and a 25 kg weight was dropped on the sample from a height of 1285 mm (impact velocity = 5 m/s) and the load history curve recorded. All results were subsequently recorded on a floppy diskette and the mode of failure noted.

3.4.7 Evaluation of Longitudinal Compressive Properties

This type of test was conducted to determine the effect of introducing interlayers on the compressive behaviour of the composites. The main problem of this test is the necessity to prevent buckling of the specimens. Current common test methods which provide side support involve mounting the specimens in a Celanese jig [105], an IITRI fixture [105], or in other antibuckling guide arrangements [106]. These methods rely on the use of shear loaded coupon specimens.

Prior to compression testing a tensile test was attempted. Aluminium end tabs were cut on a guillotine (25 mm long, 10 mm wide, 1 mm thick) and the edges smoothed and rounded on a linisher. After roughening the surface of the end tabs and the composite samples (of dimensions 100 mm length, 10 mm width, 2 mm thickness) on coarse silicon carbide paper, the end tabs were bonded to the samples using Araldite MY750 epoxy containing a 1:10 ratio of HY951 hardener. However, for all samples with intermediate and high levels of coating the end tabs became detached from the test pieces during testing, with a layer of composite still adhering to the end tab (cohesive failure of composite under end tab). This was believed to be due to the low interlaminar shear strengths of these composites (see Figure 4.25).
It was noted that control and low level coated specimens failed in the conventional manner, with the end tabs remaining attached. It was therefore concluded that compression test methods relying on shear loaded coupon specimens could not be used in this work.

Hence, a free standing compression test was conducted on short column specimens (10 mm long, 10 mm wide, 2 mm thick) using a Mand testing machine. Although no stability problems were presented, premature failure occurred by localised "brooming" (splitting) at the ends of the specimens.

A compression testing jig was designed and made for this work to eliminate brooming, enabling small sized specimens to be successfully tested without the use of end tabs (see Figure 3.7). Six specimens were carefully cut (14 mm long, 10 mm wide, 2 mm thick), with the fibres parallel to the length. By placing each specimen in a specially designed jig (see Figure 3.8) the two ends were meticulously ground to give a specimen length of 12 mm using 1200 grit silicon carbide paper. The jig was used to ensure that these edges were parallel and perfectly flat as this is a vital requirement for this type of compression test. Following preparation the specimens were inserted into the grooves of the metal blocks to prevent brooming and a close fitting metal sleeve was placed over the top of this arrangement to align the two metal blocks and provide extra stability (see Figure 3.7). A compressive load was applied to the assembly using a Mand servo-screw testing machine at a loading rate of 1 mm/min and the mode of failure observed.
3.4.8 Volume Fraction Analysis

The volume fraction of fibres was determined using an ignition loss method. Small samples were placed in crucibles and heated to 600°C in a furnace for 4 hours, to burn off the resin. After cooling in a dessicator the remaining glass fibres were weighed. The fibre volume fraction was calculated from the following equation:

\[ V_f = \frac{1}{1 + \frac{\rho_g}{\rho_m} \frac{c-f}{f}} \]  

(3.3)

where 
- \( c \) = weight of composite sample before burn off 
- \( f \) = weight of remaining fibre after burn off 
- \( \rho_g \) = density of glass 
- \( \rho_m \) = density of resin

It should be noted that for the interlayered composites, the density of the interlayers was incorporated into the \( \rho_m \) term using the rule of mixtures.

3.4.9 Resin Density Measurement and Void Content Determination

The quality of the manufactured composites was assessed by microscopic examination and by calculating the void content of the composite samples. This was achieved by first measuring the density on both the cured resin and the composites, using a 10 cm\(^3\) density bottle. (Note also that the cured resin density is also required for the volume fraction calculation). The density of the specimens was obtained using the following equation:

\[ \text{Specimen density} = \frac{W_s \rho_w}{W_{WO} + W_s - W_{W+S}} \]

(3.4)
where \( W_{\text{wo}} \) = weight of density bottle containing water only

\( W_{\text{w+s}} \) = weight of density bottle containing specimen and water

\( W_s \) = weight of specimen

\( \rho_w \) = density of water (\( \approx 1.000 \text{g/cm}^3 \))

The theoretical density of the composites was calculated and the void content determined by calculating the difference between the theoretical and measured densities (see equations 3.5 and 3.6).

\[
T_d = 100 \left( \frac{T_m + T_g + T_i}{\rho_m + \rho_g + \rho_i} \right) 
\]

where \( T_d \) = theoretical density

\( \tau_m \) = weight % of resin in composite

\( \rho_m \) = density of resin

\( \tau_g \) = weight % of glass fibres in composite

\( \rho_g \) = density of glass

\( \tau_i \) = weight % of interlayer (when applicable)

\( \rho_i \) = density of interlayer (when applicable)

\[
V = \frac{100 (T_d - M_d)}{T_d} 
\]

where \( V \) = volume percent void content

\( M_d \) = measured composite density

3.5 MISCELLANEOUS SPECTROSCOPIC ANALYSIS

In the coating process, the glass fibres were washed in xylene in an attempt to remove the size and allow separation of the individual filaments. Using FTIR spectroscopy and X-ray Photoelectron Spectroscopy (XPS), the nature and amounts of substances being removed from the glass fibres by this washing process were evaluated.
3.5.1 Surface FTIR Spectroscopy

Transmission FTIR spectroscopy is not a surface IR method since there is no surface selectivity in this method. An IR incident beam passes through both the surface and the bulk. The spectrum contains a linearly proportional contribution of each part. Hence, the fraction of the surface species in the spectrum is generally very low.

The improved signal/noise ratio of FTIR spectroscopy and the highly quantitative nature of the transmission technique usually allows the bulk spectrum to be digitally subtracted from the spectrum of the sample with the surface species contribution included. A difference spectrum is obtained which corresponds to the surface species only [108].

Fibre surface analysis was carried out on a Nicolet 20DXC FTIR spectrometer using three different sampling techniques:

a) direct transmission of fibres
b) transmission using pressed KBr discs
c) diffuse reflectance spectroscopy (DRIFT).

Spectra were obtained for heat cleaned glass fibres (600°C, 6 hours), sized glass fibres (as supplied) and hot xylene (70°C) washed glass fibres using a resolution of 2 cm\(^{-1}\) and 500 scans. A software package available with the spectrometer was used to carry out the subtraction process.

Spectra for the surface species on the glass fibres were obtained by subtracting the heat cleaned fibre spectrum from the sized fibre spectrum. The materials removed on washing were evaluated by subtracting the heat cleaned spectrum from the washed fibre spectrum and the washed fibre spectrum from the sized fibre spectrum. A typical subtracted spectra from the DRIFTs analysis is shown in Figure 4.46.
CHAPTER 4
RESULTS

4.1 OBSERVATIONS ON THE FIBRE COATING STUDIES

4.1.1 Coating of Glass Fibres with UHMWPE Solutions
After preparing the UHMWPE solutions the three distinct stages reported by Narh et al [65] during gel formation were observed, that is from a clear solution at 130°C, the onset of gelation occurred at approximately 100°C, while the transition to a turbid viscous gelatinous mass took place at about 90°C.

During the coating process (Figure 3.1), the washing treatment and the passing of fibres through the compressed air jet had the desired effect of separating out the individual filaments, which were otherwise bound together with the size. The coatings obtained from the solution in the temperature range 90-120°C were all found to be non-uniform. As the temperature was reduced the amount deposited on the fibres increased, and at a coating temperature of 90°C (gel state) a large uptake of gel around the fibres was observed, making it impossible for the hot air jet to separate the fibres and prevent them from sticking together. Using a high compressed air pressure had the effect of blowing away only some of the gel. The coatings in all these cases consisted of short discontinuous lengths of UHMWPE of different thicknesses with lumps dispersed throughout the length of the fibres. At lower temperatures (100-90°C) the fibres tended to have a thicker coating around the exterior filaments with lumps on the inner filaments. A 80/20 blend of an ethylene acrylic acid copolymer (A3710M) UHMWPE solution gave coatings of similar quality. Examples of
the typical coatings are shown in Plates 4.2 and 4.3. Plate 4.1 shows an optical micrograph of three 12 µm diameter uncoated glass filaments. The characteristic smooth surface of the glass is evident. The typical irregularity of the coatings is shown in Plate 4.2. One filament is coated with a thick film, the other with no apparent coating. Plate 4.3 shows a short length of a single filament which has been continuously coated with a thin film. It should be noted that only small portions of the filaments were found to have this type of high quality coating.

4.1.2 Dip Coating of Glass Fibres with Different Polymer Solutions

Immersing a smaller number of filaments into untreated and silane grafted (A174) solutions of UHMWPE at different temperatures did not appear to improve the coatings. After removing the size and silane off the fibres by burning (0.9% weight loss) the filaments separated out with much more ease and subsequently were more difficult to handle. Coatings on these fibres were slightly improved but still patchy, and a few filaments with no coating were observed. Plates 4.4 and 4.5 show scanning electron micrographs of the types of coatings obtained. A few filaments have thick uneven coatings while others possess small regions of fibrilated UHMWPE. UHMWPE had a tendency to form such fibrils in regions where patchy films were not formed.

Dip coating of degreased microscope slides in a UHMWPE solution produced thin continuous films almost completely over the whole slide. The films varied in thickness in places. It was also observed that on dipping a large diameter filament (glass rod of 5 mm diameter) a thin continuous film formed around the surface. Similar thin films were obtained on a polyethylene substrate.
Similar trends were observed in the nature of the coatings with the other different polymer systems. The effect of varying the solution concentration on the amount of coating on the fibres (weight percent) for EPDM and the low molecular weight polybutadiene is shown in Figures 4.1 and 4.2. At low concentrations of 1-3% (Figure 4.1), a few filaments appeared to be coated with short lengths of polymer. At higher concentrations (above 5%) a much thicker continuous coating around the outer filaments was observed, binding all the filaments together (see Plate 4.6). Most inner filaments possessed patchy coatings, of which some were coated with good continuous uneven lengths.

Glass fibres dipped in phenoxy resin solutions (5% w/w) were difficult to separate for microscopic analysis because a tough rigid coating encapsulated the whole fibre.

4.2 SILANE GRAFTING ONTO EPDM CHAINS

4.2.1 The Bonding of Different EPDM Systems to Glass and Single Lap Shear Test Results

The qualitative results obtained from attempting to graft the various silanes onto EPDM chains in the melt and solution state are given in Tables 4.1 and 4.2 respectively.

In the lap shear tests the maximum load to failure was recorded and the mode of failure observed for each test piece. The shear strength was calculated using the simple equation:

\[
\text{Shear strength} = \frac{\text{Load to failure (N)}}{\text{Bond Area (mm}^2)}
\]  

(4.1)
Five samples were tested for each type of bond and the mean determined. The results are shown in the form of a bar chart in Figure 4.3 (and also in Table A1).

4.2.2 Infra-red Analysis of EPDM Silane Grafted Films

The reference spectra for EPDM and the A189 silane used for grafting are shown in Figures 4.4 and 4.5. The main peaks were assigned using a correlation chart. The EPDM spectrum showed the characteristic peaks of a hydrocarbon polymer, while the strongest peaks of the A189 silane spectrum were due to the methoxysilane group (SiOCH₃). The S-H stretching bond of the A189 silane is characteristically weak.

The Beer-Lambert law is commonly used for quantitative infra-red analysis - see equation 4.2:

\[ \text{Absorbance} = k \cdot c \cdot l \]  \hspace{1cm} (4.2)

where \( k \) = absorptivity constant
\( c \) = concentration
\( l \) = path length (thickness of film)

It states that the absorption of a species is proportional to its concentration. The analysis is usually carried out by measuring the absorbance at a particular wavelength for a set of standards of known concentration to generate a calibration curve.

The concentration of an unknown is determined by measuring the absorbance at a given wavelength and extrapolating from the calibration curve. Since a set of standards were not available an absorbance ratio was used to give an indication of the amount of
silane grafted to the EPDM. Figure 4.6 shows the spectrum of the silane grafted EPDM (1:1 ratio) heated film. The peaks due to the EPDM and silane were identified using the two reference spectra (Figures 4.4 and 4.5). The methoxysilane band at 1090 cm\(^{-1}\) was the strongest silane peak detected. The C-H vibration of UHMWPE at 720 cm\(^{-1}\) was used to eliminate the variations in film thickness (i.e. as an internal standard). Thus the absorbance ratio of the methoxysilane band (1090 cm\(^{-1}\)) and the C-H rocking vibration (720 cm\(^{-1}\)) was chosen to give an indication of the amount of silane in the EPDM - see below.

If \(A = k \cdot c \cdot l\).

\[
\frac{A_x}{A_y} = \frac{k_x \cdot c_x \cdot l_x}{k_y \cdot c_y \cdot l_y} \cdot \frac{A_x}{A_y} = a \cdot c_x
\]

where \(x = SiOCH_3\)

\(y = C-H\)

The absorbance ratios for the control and grafted EPDM heat treated films were calculated over the propan-2-ol extraction period and are presented in Table 4.3. The typical reduction in the methoxysilane peak observed using the extraction for the heat treated film is shown in Figure 4.7.

4.3 S\textsc{ILANE} GRAFTING OF UHMWPE

4.3.1 Lap Shear Test Results

The shear strength was calculated using equation 4.1 and the mean determined using five samples for each type of joint. The results are presented in bar chart form in Figure 4.8 (and also Table A2).
4.3.2 FTIR Analysis of Silane Grafted UHMWPE Films

The peaks due to the silane were detected by expanding portions of the spectra using the on-line computer. The relevant silane peaks were then assigned for the Z6032 grafted UHMWPE and A174 grafted UHMWPE films before and after immersion in propan-2-ol and are shown in Figures 4.10 and 4.11.

4.4 MALEIC ANHYDRIDE GRAFTING OF UHMWPE CHAINS

4.4.1 Lap Shear Test Results

The shear strength of these jointed specimens was also calculated using equation 4.1 and the mean determined using five samples. The results are presented in the form of a bar chart in Figure 4.12 (and also in Table A3).

4.4.2 FTIR Analysis

The spectra obtained from an UHMWPE film and a film produced from a solution of UHMWPE treated with 10% maleic anhydride (relative to UHMWPE) are shown in Figure 4.13. These solution grafted films from now on are referred to as maleic anhydride treated films. The peaks due to maleic anhydride were clearly distinguishable. The sharp intense peak between 1799-1623 cm\(^{-1}\) and the smaller peak at 1890 cm\(^{-1}\) were assigned to the symmetrical and asymmetrical C=O stretching modes. The bands at about 1220 cm\(^{-1}\) and 990 cm\(^{-1}\) were identified as the C-O stretching vibration of maleic anhydride. The absorbance ratio \(A_{C=O} (1708 \text{ cm}^{-1})/A_{C-H} (720 \text{ cm}^{-1})\) was used to give an indication of the amount of maleic anhydride present in the films. This approach was similar to the one adopted previously in Section 4.2.2. Absorbance ratios were calculated before and after the methanol wash for 2% and 10% maleic anhydride treated films and the results are presented in
Table 4.4. The typical reduction in the C=O peak after the removal of unreacted maleic anhydride is shown in Figure 4.14.

4.5 MECHANICAL PROPERTIES OF COMPOSITES

4.5.1 Observations from the Microscopic Examination of Polished Samples

The average coating coverage on the fibres for the two sets of composites interlayered with UHMWPE and EPDM are given in Table 4.5. A significant variation in the amount of coating along the lengths of the fibres was observed for each batch produced. Also, the difference between the various levels of UHMWPE coated fibres was not as distinctive as in the EPDM coated fibres.

The distribution of the coating for fibres containing 2.8% UHMWPE was very uneven, with many filaments appearing to have no coating at all. A typical coating on the fibres obtained is shown in Plate 4.7. A coating of about 10 \( \mu \text{m} \) thickness partially surrounded a fibre bundle. A few odd lumps ranging in size (15-30 \( \mu \text{m} \)) dispersed between the fibres were also observed. The intermediate level coated composites appeared to have more coatings around whole fibre bundles and have many more lumps. The thickness of the UHMWPE around each fibre bundle varied between 2 and 15 \( \mu \text{m} \), while larger lumps up to 60 \( \mu \text{m} \) were also observed (see Plate 4.8). Many more fibre bundles were encapsulated with thin (2 \( \mu \text{m} \)) to thick (up to 60 \( \mu \text{m} \)) coatings in the high level composites. A greater number of lumps (10-30 \( \mu \text{m} \)) within the fibre bundles were also observed (see Plates 4.9 and 4.10).

The composites interlayered with low level EPDM appeared to have a very sparse coating. Few areas appeared to have a thin coating (1-5
μm) around fibre bundles and odd small lumps (20 μm) were also observed. Coatings around the intermediate level EPDM interlayer composites tended to encapsulate fibre bundles. Instead of forming a distinct layer around the outer filaments as observed in the UHMWPE composites (Plate 4.9), the EPDM coatings appeared to penetrate a few of the outer filaments. Small (10 μm) to large (50 μm) lumps were also observed within the fibre bundles (see Plate 4.11). With the high level EPDM interlayer composites, the coatings were able to penetrate much further into the fibre bundles (see Plate 4.12). The penetration distance was about 70 μm (5-6 outer filaments). Some smaller lumps were also observed within the innermost filaments.

4.5.2 Damage Assessment Test
The amount of water absorption (% weight) was calculated for each sample and the average determined. The results for undamaged, fatigued and fractured specimens are shown in Table 4.6.

4.5.3 Dynamic Mechanical Thermal Analysis
The storage modulus (E') and tan delta as a function of temperature for the UHMWPE and EPDM interlayered composites is shown in Figures 4.15, 4.16 and 4.19 to 4.22. The modulus at 20°C was plotted against the amount of coating on the fibres and shown in Figures 4.17 and 4.18. The glass transition temperature (Tg) of the epoxy resin for the various composites is presented in Table 4.7. Tan delta values at the Tg were also determined and are presented in Table 4.8. A plot of tan delta for UHMWPE is shown in Figure 4.23 and part of the plot is compared with the high level UHMWPE and control composite in Figure 4.24.
4.5.4 Interlaminar Shear Test

The apparent interlaminar shear strength (ILSS) was calculated using the following equation [103]:

\[
\text{ILSS} = \frac{0.75F}{bd}
\]  

(4.3)

where 
- \( F \) = force at fracture
- \( b \) = width of test piece
- \( d \) = thickness of test piece

The results are presented graphically in Figure 4.25 (and also in Table A4). Typical load deflection curves for the UHMWPE and EPDM interlayered composites are shown in Figure 4.26.

The control composites were found to fail in shear with a single interlaminar shear crack running through the midplane of the sample (see Plate 4.13). All the interlayered composite samples, on the other hand, possessed several cracks meandering through the interlayer fibre coatings. Plate 4.14 shows typical interlaminar shear cracks running through the UHMWPE coatings around fibre bundles. A few voids can also be observed. These may have resulted during the manufacturing process or may have been caused by the removal of the coating during the polishing procedure. Similar modes of failure were observed with the EPDM composites. An optical micrograph of an interlaminar shear crack running through an EPDM coating around a fibre bundle is shown in Plate 4.15. The interlaminar shear cracks running through the high level UHMWPE interlayered composite were examined further at higher magnifications. Typical micrographs are shown in Plates 4.16-4.18. From these micrographs it is evident that the UHMWPE had undergone
ductile deformations as the interlaminar shear crack passed through the coating.

4.5.5 Flexural Properties

The flexural strength was calculated using the formula below [104]:

\[
\sigma_f = \frac{3FL}{2bh^2}
\]  

(4.4)

where:
- \( F \) = maximum applied load
- \( L \) = span
- \( b \) = width of test piece
- \( h \) = thickness of test piece

The secant flexural modulus at \( \varepsilon = 0.0075 \) (1 mm deflection) was calculated using equation 4.5 and the mean similarly determined for each composite.

\[
E_{\text{flex}} = \frac{L^3}{4bh^3} \frac{F}{\bar{Y}}
\]

(4.5)

where \( F \) is the load at \( Y = 1 \) mm.

Since there was slight variation in volume fraction, the strengths and moduli were normalised to a standard fibre volume fraction of 60% (Table A5). The results are presented graphically in Figures 4.27 to 4.30. The typical load deflection curves are shown in Figures 4.31 and 4.32.
The control composites failed by cracks initiated by tensile stresses with the formation of a kink zone on the compressive side. However, the interlayer composites failed by interlaminar cracking (delamination) due to shear stresses. As the interlayer content increased a greater number of delamination cracks occurred. The composite with 4.6% UHMWPE interlayer, not treated with silane, showed the greatest amount of delamination compared to the other UHMWPE interlayered composites. No tensile cracks were observed in the interlayered composites. A typical scanning electron micrograph of a fractured surface from a high level UHMWPE interlayered composite sample is shown in Plate 4.19.

4.5.6 Impact Properties

The instrumented Charpy impact tests recorded the load history during each impact event as shown in Figure 4.33. The load-time history can be divided into two distinct regions, a region of fracture initiation and a region of fracture propagation. The total impact energy \( E_I \) (proportional to area under force time curve) is the sum of the energy required to initiate failure \( E_I \) and the energy absorbed in damage propagation \( E_P \). The total Charpy impact energy alone may provide a confused picture about the fracture behaviour of a composite. The separated values of \( E_I \) and \( E_P \) are significant on the other hand, as a high strength brittle material with a large initiation energy but small propagation energy and a low strength ductile material with a small initiation energy but large propagation energy, may have the same total impact energy but behave quite differently. Beaumont et al [114] defined a dimensionless parameter called the ductility index (DI) to assess the impact performance of different materials.
For each sample the impact strength, secant modulus at $\varepsilon = 0.04$ (using equations 4.4 and 4.5), total impact energy, initiation energy and ductility index were determined, all results being the average of four tests. The results are presented graphically in Figures 4.34-4.40 (and also Table A6), while the typical load deflection curves are shown in Figure 4.41. The control samples failed by cracks propagating from the bottom (tensile) across the thickness of the samples. This had the effect of almost breaking the samples in half. A little delamination and fibre splitting on the tensile side was also observed. This mode of failure is similar to that observed for the control flexural test specimens. The low level UHMWPE and EPDM interlayered composites also exhibited fractures initiated on the tension side propagating through the thickness of the samples but to a lesser extent as they sustained a greater amount of delamination. Composite samples with higher levels of UHMWPE interlayers including those not treated with silane delaminated over the entire length of the specimen, with no tensile cracks being apparent. The intermediate level EPDM interlayered composite samples exhibited delamination cracks running approximately half way along the length of the specimens. The high level EPDM interlayered composite showed little sign of damage with only short delamination cracks being observed.

4.5.7 Compressive Properties

The compressive strength was calculated using the formulae:

$$\sigma_c = \frac{F}{bd}$$  \hspace{1cm} (4.6)

where $F =$ maximum load carried
\hspace{1cm} $b =$ width
\hspace{1cm} $d =$ thickness
The secant compressive modulus was determined at a strain of -1.0%. The mean strength and moduli results were normalised to a 60% fibre volume fraction and are presented graphically in Figures 4.42 to 4.45 (and also in Table A7). The compressive load deflection curves exhibited a sudden and catastrophic type failure for all the composites including the high level interlayer composites. This is in contrast to the ductile and progressive failure observed with the interlayer composites in the shear and flexural tests.

Two distinct types of compression failures could be identified for all specimens, i.e.

1. Longitudinal splitting along the gauge length with some lateral and out of plane deformation.

2. Formation of a kink band across the width of the specimens. Fibre failure did not appear to have occurred significantly in the samples.
5.1 COMMENTS ON FIBRE COATING STUDIES

The observations in Section 4.1 have revealed that continuous thin coatings of controlled thickness along the entire length of the fibres were difficult to obtain using a simple solution coating process or a simple dipping method. Coating the fibres in the viscous gel state of the UHMWPE solution clearly did not allow adequate impregnation, a thick coating was formed instead around the outer filaments. The solutions at temperatures of 110°C and above had a low viscosity (Brookfield viscosity = 28 mPas) and hence the solutions were able to impregnate the whole fibre bundle. During the coating operation the fibre bundle was seen to splay out in the UHMWPE solution appearing to allow wetting of the fibres. Using a Cahn Contact Angle Analyser the wettability of glass fibres was assessed. The contact angle of para-xylene and propan-2-ol on both heat cleaned and epoxy sized glass fibres was found to be zero, confirming that the solvent used was able to completely wet out the fibres. However, maximum adhesion between a solid surface and a liquid may not necessarily occur with the lowest contact angle [109]. In this work it was envisaged that grafting a silane onto the interlayers would also assist in obtaining uniform coatings through the formation of chemical bonds between the glass and interlayers as well as improving the adhesion to retain satisfactory composite mechanical properties.

One other advantage of using UHMWPE as an interlayer which has not been given much attention so far, is its ability to form films from
solutions through the gel state on cooling and evaporation of solvent. This was observed on dipping glass slides into the solution and has been reported by several authors including Barham [60] and Smith et al [67]. Thus, the gel state appears to be an essential precursor for film formation. Conventional crystalline polymers precipitate into grainy powders on cooling from solution. Using such polymers as an interlayer would not be satisfactory, because potential coatings from solution would be of a particulate nature. In the latter case a further heating stage would then be required to allow the particles to fuse together to form a film, but this would "fuse" the fibres together. An important point to reiterate here, which has become apparent in this study, is that although UHMWPE is able to readily form films on glass slides and large diameter single glass filaments, uniform films along the entire length of a glass fibre roving is not easily obtained. Patchy uneven films are formed instead. This may be due to the difference in geometry between the slides, large diameter filaments and glass fibres. The glass fibre bundle consists of many fine fibres, generally hexagonally packed with many interstitial spaces. Cercone [109] considered the dynamics of a liquid being forced through a pore to illustrate the problem of forcing a liquid resin through the interstitial spaces to allow complete impregnation of the roving. He stated that the pressure required to force the liquid past the fibre walls can be very great, forming a resistance to the flow of the liquid through the fibres (separate from air displacement). The diameter of the fibres is also an important factor. Fine glass fibres of 12 μm diameter possess a greater surface area to be wetted and coated, than a larger diameter fibre occupying the same volume. The flowing fronts of the coating solution going around the circumference of small diameter fibres may quickly meet between fibres and weld. Spreading along the fibre length would require a driving
force which can only be provided by a drag flow such as pulling the fibres through an orifice or between two rollers. Also, it may not be readily possible to separate each individual fine filament using the xylene wash, to allow thorough impregnation. Instead coatings may form around small groups of fibres especially at higher solution concentrations. It should be noted here that not only did the xylene wash serve to separate out the fibres but also allowed the fibres to be prewetted, increasing the rate of solution penetration by increasing the capillary action.

Observations on coatings obtained from the EPDM and other solutions revealed a similar type of behaviour. Polybutadiene (Ricon 150 CH₂-CH=CH-CH₂) was used to investigate the effect of using a very low molecular weight polymer on the quality of the coatings. It was thought that a low molecular weight polymer may form continuous coatings, however no improvements in the quality of the coatings were obtained, at low solution concentrations. From Figure 4.1 the transition between poor and relatively good coatings can be seen with changing concentration. The good coatings at the higher levels were considered to be much too thick. The amount of UHMWPE on the fibres was found to be approximately 3% (w/w) when using a 2% (w/w) solution at 110°C, which is lower than the corresponding amounts for EPDM (10%). It was not possible to prepare solutions at higher concentrations of UHMWPE because of the low solubility and the very high viscosity of the solutions produced.

Coatings on the fibres were examined using optical and scanning electron microscopy. The resolution of optical microscopy is limited by the wavelength of visible light to about 0.5 μm. It is possible to obtain a resolution down to about 0.01 μm using scanning electron
microscopy. Reflective optical microscopy enabled the overall quality of the coatings to be assessed rapidly over long lengths of fibre bundles. A more detailed analysis was achieved using scanning electron microscopy. The areas of very thin coatings could be observed more easily. Observations from optical microscopy were generally consistent with those from scanning electron microscopy.

Thomason's [12] study of coatings applied to commercial glass fibres showed that the thickness distribution of the coating was good in some fibres and poor in others. He stated that these poor coatings consisted of small concentrated islands on the surface. However, Schlund and Lambla [44] claimed that they were able to apply a reactive latex continuously to glass fibres by using an on-line industrial fibre manufacturing process.

5.2 BONDING OF EPDM TO GLASS USING SILANE COUPLING AGENTS

5.2.1 Grafting Silanes on EPDM Chains in the Melt and in Solution
A methacrylate silane with a double bond (A174) was attempted to be grafted onto the sulphonated rubber using benzoyl peroxide as a free radical initiator (Table 4.1, mix 1). However, the adhesion to glass of this modified rubber was poor. First the modified EPDM (removed from the glass slide) was not soluble in xylene and second it exhibited a lower extensibility indicating that some crosslinking of the rubber had taken place. The poor adhesion to glass may thus have been due to the predominance of the crosslinking reaction. A small improvement in bonding to glass was observed with the sulphonated EPDM grafted with silane Z6032 system after carrying out the reactions in both the melt and in solution. This may suggest that the reactive SO₃H groups were able to form physical or chemical bonds with the cationic
styryl silane (possible interactions between $\text{SO}_3\text{H}$ groups and amino groups of the silane to form a sulphonamide).

Mix 3 (sulphonated EPDM silane A174 system, Table 4.1), was used to investigate the effect of using a different peroxide. Dicumyl peroxide appeared to slightly improve the adhesion of the elastomer to glass, compared to mix 1 (sulphonated EPDM silane A174 system with benzoyl peroxide). This may possibly suggest that dicumyl peroxide is more efficient as a free radical initiator than benzoyl peroxide. A conventional EPDM with a 5% diene content and the cationic styryl silane (see Table 3.1 for chemical structure) were mixed together in the solution state (Table 3.2, solution 3) without a peroxide because it was thought that mixing at an elevated temperature would generate free radicals and allow the addition of the silane through its double bond to the polymer. However, since a poor bond to glass was obtained this phenomenon was believed not to occur to any great extent.

The best adhesion to glass was observed with an EPDM grafted with silane A189 (mix 4 and solution 1). After carrying out the grafting reaction in both the melt and solution state cohesive failure of the uncrosslinked rubber was observed with the bond to glass remaining intact. The use of mercaptosilanes (A189) in elastomers is not uncommon. It has been used to provide an elastomer filler bond in mineral filled EPDM compounds and as a result has improved the physical properties [110]. Mercaptofunctional silanes are able to add to non-activated double bonds (without peroxide) in the presence of a catalyst (CBS, see Table 3.1). The grafting reaction is discussed in Section 5.2. Polybutadiene (Table 3.2, solution 4) was thus used as a comparison since it has a greater diene content than EPDM. Both EPDM and polybutadiene exhibited the same type of cohesive failure
indicating that the mercaptosilane is an effective coupling agent for EPDM. Hence the EPDM grafted silane A189 system was chosen to be the only one to be studied further.

5.2.2 Single Lap Shear Tests

Single lap shear tests were performed on the EPDM grafted silane A189 system to give a better assessment of the bonding to glass. The low shear strength obtained from the first set of samples (Figure 4.3), was indicative of the low strength of uncrosslinked EPDM. The modification of the test pieces (see Section 3.2.2) had the desired effect of increasing the shear strength and allowed the EPDM glass bond to be tested, rather than the bulk.

Without the silane the glass EPDM interface cleanly failed at a low shear strength. The addition of the silane improved the shear strength by 150%. Failure had mainly occurred at the glass EPDM interface but there was some evidence of a small amount of EPDM adhering to the glass. Reducing the thickness of the EPDM progressively improved the shear strength of the bond to 1.75 MPa (≈400% increase). Since the EPDM layers had become very thin, the failed joints were examined under an optical microscope to assess whether failure was cohesive or interfacial. Patches of EPDM were observed on both the UHMWPE and on the glass surfaces suggesting a mixed mode of failure had occurred i.e. glass/EPDM and EPDM/UHMWPE interface failure. The highest shear strength (4 MPa) and hence best bond was obtained by lowering the silane content to 5% (based on EPDM) in the solution grafting process. A larger amount of silane appeared to be detrimental to the adhesion of EPDM to glass. This significant improvement is probably due to the reduction of this excess brittle polymerised silane on the glass surface. Failure in these samples
occurred cleanly at the EPDM/UHMWPE interface. Hence, an EPDM glass bond which was stronger than the bond between EPDM and UHMWPE had been obtained. In an attempt to improve this bond, the UHMWPE plaques were first primed with the EPDM solution. However, a similar mode of failure was observed with a reduction in the shear strength, possibly resulting from the increase in thickness of the weak EPDM layer. Also the diffusion of EPDM into UHMWPE may not readily occur.

These tests have revealed that a satisfactory bond had been developed that could be used for bonding EPDM interlayers to glass fibres in a composite, based on the assumption that the small single lap shear joints can reliably simulate the conditions experienced in the interfacial region of a composite.

5.2.3 Infra-red Analysis of EPDM Grafted A189 Films

An initial 88% reduction in the amount of silane was observed for the heat treated film after the first day of extraction, suggesting that a vast excess of silane was added (see Table 4.3). This was also concluded from the lap shear tests which showed a great improvement in shear strength with a reduction in the amount of silane added. Since the absorbance ratio of the heat treated film was always higher than the control even after five days of propanol extraction, it was evident that a small amount of silane had grafted onto the EPDM. The possible reaction occurring between EPDM and silane A189 is shown in Figure 5.1. The mercapto group is able to add to a double bond of EPDM to form a sulphur linkage in the presence of a catalyst.

The lap shear results suggested that this grafting reaction had occurred to a sufficient extent, by significantly improving the EPDM glass bond through the formation of siloxane bonds with the glass surface.
5.3 **SILANE GRAFTING OF UHMWPE**

5.3.1 **Lap Shear Tests**

The single lap shear test was used as before to provide a comparative measure of the adhesion of UHMWPE to glass. A 200% increase in shear strength was observed when 2% Z6032 was added and refluxed for 4 hours (Figure 4.8). A 24 hour reflux however slightly reduced the adhesion to glass (150% increase). This was probably due to the degradation of the UHMWPE resulting in crumbly silane grafted UHMWPE films. The UHMWPE glass bond always failed in a brittle manner in these tests.

The use of the Al74 silane proved to give a greater shear strength (6.96 MPa) than the corresponding Z6032 film (3.9 MPa). A different mode of failure was also observed with some of these joints and this was also evident from the load/deflection curves (see Figure 4.9). After a partial failure of the glass UHMWPE bond, the UHMWPE deformed as the test progressed, while the remaining UHMWPE adhered to the glass slides. This is a desirable mode of failure as it indicates that the glass UHMWPE bond is strong enough to allow the UHMWPE to yield during failure. These improvements in the adhesion to glass suggested that the UHMWPE and the silane are grafted to form chemical bonds during refluxing and the silane is able to form siloxane links to glass.

The effect of priming the glass slides with a silane was also investigated because most glass fibres have an existing silane coating. Further dramatic improvements in shear strength were obtained when Z6032 primed glass slides were bonded to the silane grafted UHMWPE films. The highest shear strength was observed when Z6032 was used as the primer for the Al74 grafted UHMWPE joints (11.5 MPa). A combination of two different silanes appeared to be favourable in
enhancing the bond strength of UHMWPE to glass. It is believed that cationic styryl silanes (Z6032) form interpenetrating networks with polyolefins [72]. Thus the additional improvement in shear strength with primed glass slides may have been due to the formation of such a network at the glass UHMWPE interface. The failure mechanisms of the samples also involved UHMWPE yielding. Note also that the comments made about the lap shear test in the last paragraph of Section 5.2.2 also apply here.

5.3.2 Qualitative FTIR Analysis
This analysis was carried out to determine whether grafting reactions were occurring from solution treatments. Apart from the advantages mentioned in Section 3.2.5 the computer software available with the FTIR spectrometer also allowed the spectra to be expanded, to make detection of the silane bands easier. This was not possible with the Pye Unicam dispersive spectrometer. The various spectra expanded between 1200-1000 cm\(^{-1}\) are shown in Figures 4.10 and 4.11. After the Z6032 and A174 silane grafting of the UHMWPE solution, a broad shallow peak between 1200-1000 cm\(^{-1}\) was observed which was not clearly present in the untreated film. This broad band was associated with the numerous overlapping Si-O-x vibrations of the silane which occur in this region. The many smaller peaks within the broader peak were distinguished by eliminating the UHMWPE peaks and then assigning the remaining ones to the different SiO-x vibrations. After removal of the unreacted silane by washing in propan-2-ol the broad shallow silane peak reduced to a much narrower and sharper band consisting of three peaks. Two of these peaks coincided with those of UHMWPE, the other being attributed to the methoxysilane (SiOCH\(_3\)) vibration at 1130 cm\(^{-1}\). The peaks due to the other SiOCH\(_3\) vibration at 1208 cm\(^{-1}\) and the multiple peaks between 1077 and 1010 cm\(^{-1}\) due to the SiOSi stretching
vibrations (and possibly augmented by SiOH vibrations) were all missing from the spectra of the washed film. The presence of the intense methoxysilane peak at 1130 cm\(^{-1}\), after removing the unreacted oligomeric silane confirmed that the grafting reaction of the silanes onto the UHMWPE had indeed occurred in solution. A quantitative analysis was not attempted because of the multiple nature of the silane peaks. It was difficult to precisely distinguish a particular SiO peak from the broad band which encapsulated all the different silane bands as well as the UHMWPE peaks.

The possible free radical initiated grafting reaction mechanisms that occurred between UHMWPE and Al74 is shown in Figure 5.2. A similar mechanism is envisaged for the UHMWPE Z6032 system. The thermal decomposition of the peroxide generates radicals which abstract a hydrogen atom from the polyethylene chain forming a macroradical and an alcohol. The vinyl silane is then able to attach itself onto this radical site. Note that this is only a simple reaction scheme and other reactions are possible. These may involve the solvent terminating reactive radical sites on the polyethylene chain and hence inhibiting the grafting reaction (solvent effects discussed further in Section 5.4.2).

The greater improvement in shear strength of the Al74-g-UHMWPE film compared to that the Z6032-g-UHMWPE film may suggest that this grafting reaction (formation of a covalent bond) occurred to a lesser extent in the Z6032 solution. A possible explanation for this is that the bulky phenyl group of Z6032 may restrict the interactions between the double of the silane and the long chain macroradical (steric hindrance effect).
The methacryloxypropyltrimethoxysilane (Al74) has been similarly grafted onto high density polyethylene (HDPE) to improve the adhesion to glass fibres in HDPE glass composites [79]. In this particular case, Stori and Dahl first applied the silane and peroxide to the glass fibres/spheres from solution. The grafting reaction took place when the glass fibres/spheres were melt mixed. Scanning Electron Microscopy of fractured surfaces showed good adhesion to glass. Much higher relative impact strengths were obtained for the Al74 grafted composites. This was explained by the observed ductile deformation of the polyethylene at the glass surface of a glass sphere HDPE composite. It was encouraging to observe similar deformations of UHMWPE during the lap shear tests in the early stages of this work.

The observed ductile deformation in Stori and Dahl's work also reinforces the idea of using UHMWPE as an interlayer. It should be noted that UHMWPE is tougher than a conventional HDPE grade and thus has a greater ability to undergo ductile deformations and absorb energy.

5.4 MALEIC ANHYDRIDE GRAFTING ONTO UHMWPE

5.4.1 The Lap Shear Test

A progressive increase in shear strength was observed on the addition of 2, 6 and 10% maleic anhydride to the UHMWPE solution (see Figure 4.12), the maximum increase being 100% with 10% maleic anhydride. The UHMWPE-epoxy bond always failed and the remaining UHMWPE on the aluminium strips was easily peeled off the epoxy layer when no maleic anhydride was used, but this became difficult with a 10% maleic anhydride treatment of the UHMWPE. The epoxy layer on the aluminium was very hard to scrape off even with a razor blade. These improvements in adhesion indicate that maleic anhydride was able to
graft onto the UHMWPE in solution and subsequently form chemical or physical bonds with the epoxy resin whilst curing.

Mootooka [84] grafted maleic anhydride onto UHMWPE by extrusion. The adhesion of stretched filaments to an epoxy resin was evaluated using a pull out test. The filaments were embedded in the resin and the force required to pull them out was measured. A 140% increase in pulling force was measured when the UHMWPE was melt mixed with 1 phr maleic anhydride and 0.01 dicumyl peroxide. Banzi et al [90] grafted maleic anhydride onto olefinic polymers using a suspension method. The adhesion to metals was determined by measuring the peel strength of a sandwich structure. The grafted polymer was pressed between two sheets of aluminium foil and the force required to peel away the foil measured. A 68% improvement in peel strength was observed when an ethylene propylene copolymer was grafted with 0.5% maleic anhydride using 0.02% benzoyl peroxide. These improvements in adhesion are comparable with those obtained in this work. In this work a 99% increase in shear strength was obtained with the use of 10% maleic anhydride, while Mootooka [84] was able to achieve a similar improvement in adhesion using only 1 phr maleic anhydride, by melt processing. This observation emphasises the importance of the physical state in which the reaction is carried out. The use of solutions of low concentration probably reduces the rate of reaction since the number of polymer maleic anhydride molecular collisions or interactions is reduced in the presence of a large amount of solvent. Also as briefly mentioned in Section 5.3.2, the solvent may also interfere with the grafting reaction and reduce the amount of grafting. This effect is discussed further in the following section. The probability of polymer maleic anhydride interactions may be increased by using higher concentrations. UHMWPE concentrations
above 2% (w/w) are difficult to obtain because of its high molecular weight, and in any case increasing the concentration of normal polymers would lead to viscosity problems. The use of Al74 silane treated UHMWPE films resulted in the highest shear strength. The 150% increase in shear strength was slightly better than the improvements obtained by Mootocka.

5.4.2 FTIR Analysis
The absorbance ratio after the methanol wash was used as a measure of the amount of grafted maleic anhydride (see Table 4.4). The amount of grafting in the 10% maleic anhydride film appeared to be greater than in the 2% film. Using a greater concentration of maleic anhydride increased the reaction efficiency of polymer maleic anhydride interactions. The presence of a small amount of maleic anhydride in the 10% maleic anhydride film without peroxide even after the methanol wash suggested that a minimal amount of grafting was occurring due to the free radicals generated by the use of high temperature. The large reduction in the absorbance ratios after the methanol wash (~70%) suggested that only a small portion of the maleic anhydride was grafting onto the UHMWPE. A low reaction rate in the dilute solution and solvent effects may have been responsible for the low efficiency of grafting (discussed later). However, as with the other grafted polymers, these small amounts of grafting gave a satisfactory improvement in adhesion to the epoxy resin. It was useful to note that on heat treating a UHMWPE film further grafting took place, possibly because there was a large amount of unreacted maleic anhydride in the film.

The possible reaction mechanism is shown in Figure 5.3. This scheme is analogous to the silane reaction mechanism and is similar to the
mechanism proposed by Cimmino et al. [88] for the grafting of maleic anhydride onto an ethylene propylene copolymer. The first stages of macroradical generation have already been shown in Figure 5.2. The activated double bond of maleic anhydride may then add to the UHMWPE macroradical to form a grafted macroradical which can lead to the formation of a grafted succinic anhydride group by further free radical transfer reactions. As mentioned before, other combinations and disproportionation reactions involving the macroradicals are possible. However, the formation of a poly maleic anhydride side chain on the polyethylene main chain is unlikely, due to steric hindrance [88].

The solvent para-xylene may also be involved in this reaction, as previously mentioned and provide an explanation for the low grafting efficiency (dilution effect). The importance of the solvent on the degree of grafting was also recognised by Devito [89]. Shechter and Barker [111] studied the reaction of arylalkanes including para-xylene with maleic anhydride and a peroxide. They reported that para-xylene underwent a rapid addition reaction with maleic anhydride in the presence of di-tert-butyl peroxide. Hence the formation of such an acyl anhydride and the ability of the solvent to form radicals may inhibit the grafting reaction. Some of the possible interfering secondary reactions involving solvent molecules and peroxide generated solvent radicals are shown in Figure 5.4. Solvent molecules may consume the necessary peroxy radicals and subsequently lower the number of macroradicals. Termination of the reactive radical sites on the macroradicals may also take place by transfer or combination reactions. It should also be noted that resonance stabilisation of the solvent radicals is likely, delocalising the odd electron about the ring. Secondary reactions described here may also occur in the silane grafting reactions.
The improvement in shear strength of the maleic anhydride UHMWPE lap shear joints was not only due to the formation of covalent bonds between UHMWPE and maleic anhydride but also attributable to the coupling of the maleic anhydride grafted UHMWPE to the epoxy resin. These linkages may take the form of ester bonds arising from reactions between hydroxyl and epoxide groups of the epoxy resin and the maleic anhydride. Similarly, the enhanced adhesion of the Al74 silane grafted UHMWPE film to epoxy can be explained by interactions between the silane and epoxy resin. It is possible that the unbound silane associated with the UHMWPE films is capable of migrating into the epoxy layer to form an interpenetrating network with the resin during the curing process. This type of mechanism has been used as a possible explanation for the adhesion of the matrix to the silane (see Section 2.2.2). Also hydrogen bonding between the carbonyl groups of the silane Al74 and the hydroxyl groups of the epoxy resin may contribute to achieve adhesion.

5.5 CONSTITUTION OF INTERLAYERED COMPOSITES

Using Differential Scanning Calorimetry the glass transition temperature ($T_g$) of the cured epoxy resin was determined to be 141°C (see Figure 5.5). No change in $T_g$ was observed with 3, 6 and 20 hr post-cured samples, confirming that the resin was being completely cured. It was decided from the preceding work that the Al74 silane would be used to couple the UHMWPE interlayer to the glass and epoxy resin in the composites. The best improvement in adhesion was found to be exhibited by grafting the interlayer UHMWPE polymer with silane Al74 (i.e. $\text{CH}_2=\text{CCH}_3\text{COO(CH}_2)_3\text{Si(OCH}_3)_3$). The possible mechanisms responsible for these improvements have been discussed in the preceding sections. The Al89 silane ($\text{HS(CH}_2)_3\text{Si(OCH}_3)_3$) was used to
provide a bonding mechanism for the EPDM interlayer to the glass fibres. It was envisaged that curing the epoxy resin and EPDM together during composite manufacture would allow the 'interlacing' of the epoxy resin with the EPDM to form an IPN structure at the interface hence providing better adhesion. A similar mechanism was believed to occur by Enever [36] and Peiffer [42] between their rubbery interlayers and an epoxy resin matrix.

5.6 MECHANICAL PROPERTIES OF COMPOSITES

5.6.1 Microscopic Analysis
The difficulties experienced in producing well polished surfaces were probably related to the soft nature of the interlayer materials, giving rise to smearing during polishing. Scanning electron microscopy was not able to clearly distinguish between the UHMWPE layer and the epoxy resin matrix especially at high magnifications, making the examination of the coating distribution very difficult. With optical microscopy on the other hand the colour contrast between the different phases enabled them be easily distinguished. Enever [36] also stated that it was not readily possible to identify the polyurethane interlayers and the epoxy matrix from scanning electron micrographs of fractured surfaces and even etching surfaces of coated samples failed to highlight the polyurethane interlayers.

The coatings in the composites were irregular and lumpy, consistent with the observations made from the preliminary work carried out on fibre coating. Instead of the formation of a thin uniform interlayer around each individual filament, the coatings appeared to be partly or wholly around fibre bundles with a certain amount near and in between filaments, surrounded by the epoxy matrix. Although the high level
EPDM coatings penetrated the inner filaments to a greater extent, the amount of EPDM on the fibres was too large to be considered as an effective interlayer. In Enever's [36] work, carbon fibres were coated with a polyurethane interlayer using solutions varying in concentration from 1 to 10% by weight. A 4-5% solution was established to provide an optimum coating level of 10% by weight on the fibres. A similar concentration (4%) was used to produce the high level EPDM interlayered composites, and a similar level of coating was also observed on the glass fibres. However, in Enever's work no direct mention was made of the quality or the nature of the coatings on the carbon fibres. With a similar amount on the glass fibres, the coatings were found to be non-uniform and irregular in this work.

Several authors calculated the thickness of the interlayers from the coating weight, assuming that all the fibres were evenly coated and these have been summarised in Table 5.1. These calculated interlayer thicknesses were always less than one micron, but as mentioned earlier, the thicknesses were based on the dubious assumption that the fibres are uniformly coated. Hancox and Wells [39] only briefly mentioned that silicone rubber coatings tended to bind groups of fibres together. No other detailed comments were made about the quality and uniformity of the actual coatings. The coating uniformity and continuity was assessed by Peiffer and Nielsen [42] on large diameter glass fibres (3 mm). Scanning electron micrographs at high and low magnifications revealed that the coating was uniform over the whole-fibre surface. The actual interlayer composites were prepared using 6 mm diameter short glass fibres. Gerard [49] stated that the coating thicknesses were very small and thus it was very difficult to see the coatings by scanning electron microscopy. Also filaments were only perfectly separated with the minimum amount of coating (0.66% wt,
0.024 μm). Bell et al [53] recognised that it was difficult obtain thin uniform coatings around individual fibres and to prevent coated fibres from sticking together using fibre coating processes such as solution dipping. Electropolymerisation was thus used to apply thin high molecular weight copolymers to commercial 8 μm diameter carbon fibres. An acrylonitrile coating on the carbon fibres appeared to be 'grainy' (from scanning electron microscopy) and was thought to be due to the crystallinity of the polymer. Very even and smooth coatings of about 2 μm thickness were claimed to be observed with the various methyl acrylate acrylonitrile copolymers. They were able to control the sticking of the fibres up to a coating thickness of 0.2 μm, but this was still a major problem at higher coating thicknesses.

The theoretical coating thicknesses calculated for the UHMWPE and EPDM interlayers assuming that all the fibres were uniformly coated (Figure 5.6) are of the same order of magnitude as those obtained by previous workers and are deemed to be very thin. However, the observed coatings of the intermediate and high level UHMWPE/EPDM interlayered composites were considered to be much too thick and irregular compared to the calculated thicknesses of this work and of previous workers. The low level UHMWPE and EPDM coated fibre composites appeared to have a few fibre bundles with incomplete coatings of thickness 1-10 μm. Using a more dilute UHMWPE solution (< 0.5%) with a view to obtaining thinner coatings did not give film formation because of the inability of UHMWPE to form a gel and thus the coatings were grainy (similar to Bell's polyacrylonitrile coatings). The main reason for obtaining uneven coatings, especially with UHMWPE on the other hand, was associated with its inability to uniformly coat each filament in a controlled manner. Peiffer and Nielson [42] were able to control the build up of their uniform rubbery interlayers on glass fibres by using
electrostatic forces. The surface charge of the glass was reversed using colloidal alumina so that oppositely charged latex particles would be attracted to the surface. After a monolayer was formed further deposition was inhibited by electrostatic repulsion. Similarly Bell et al [53] used electrocopolymerisation to obtain uniform continuous coatings on carbon fibres.

In this work a few filaments appeared to be coated when solutions of low concentration were used. This suggested that coatings around individual filaments may have been too thin in places to be identified even with scanning electron microscopy. During the coating process, the roving was observed to spread out in the solution, allowing the filaments to be impregnated. Since only a few fibre bundles were observed to have thick coatings (1-10 µm) the remaining filaments are expected to have coatings thinner than the calculated values, (< 0.2 µm), which cannot be revealed by using scanning electron microscopy, as it has also been mentioned by Gerard [49]. A possible future approach may involve analysing regions of fibres where there appears to be no such coating by surface sensitive techniques to ascertain whether such ultra thin coatings exist. X-ray photoelectron spectroscopy (XPS) measurements could be used to detect very thin coatings on the fibres [12], since this technique has a sampling depth of about 5 nm (very surface sensitive). Another possibility is to use a chemical tag or labellant so that the uptake of polymer onto the fibres can be monitored and assessed more easily using XPS and other surface spectroscopic techniques. Cazeneuve et al [112] used techniques such as XPS and Auger Electron Spectroscopy (AES) together with a labellant (silver nitrate) to confirm the presence of a thin polymer layer (0.6-2 nm) at the surface of pull out fibres in short fibre composites.
5.6.2 Damage Assessment Test

It was hypothesised that the amount of damage sustained by the composites could be determined by water absorption tests since the water would diffuse into the cracks caused by the fatigue cycle. The difference in the amount of water uptake between the undamaged, fatigued and fractured samples (Table 4.6), however, was found to be too small to provide an accurate measure of the amount of damage incurred by the different interlayer composites. The similar amounts of water uptake for the undamaged and fatigued samples suggests that the fatigued samples did not produce a sufficient amount of internal cracks. The fractured samples in fact failed in shear with the conventional interlaminar shear cracks being observed. Even these broken samples, although containing several cracks, did not absorb a significantly large amount of water (compared to the undamaged sample) suggesting that this type of damage tolerance test is not suitable for the intended purpose.

5.6.3 Dynamic Mechanical Thermal Analysis

The dynamic moduli of the UHMWPE and EPDM interlayered composites were lower than the control composite (see Figures 4.15 and 4.16). A certain reduction in modulus was expected because of the introduction of coatings of lower stiffness compared to the epoxy matrix (see theoretical model in Section 6.3.1). The moduli as a function of temperature of the various UHMWPE and EPDM interlayered composites were similar and overlapped in some cases. However, from Figures 4.17 and 4.18 a downward trend in dynamic modulus (at 20°C) with the increase in coating level was apparent. A 11% reduction in dynamic modulus was observed with the high level UHMWPE interlayered composite, whereas the high level EPDM interlayered composite suffered a 30% reduction in modulus. Above -30°C the modulus of this high level
EPDM interlayered composite decreased dramatically. The modulus values obtained from dynamic tests using cantilever bending modes have been reported by Mascia [113] to be inaccurate because of clamping arrangements. However, it was suggested that these errors are relatively unimportant when tests are carried out on a comparative basis.

The introduction of glass fibres into the epoxy resin increased the glass transition temperature (Tg) of the epoxy matrix from 142 to 147°C (see Table 4.7). A progressive decrease in Tg of the epoxy resin was observed, however, with increasing levels of UHMWPE coating; the lowest Tg being recorded for the 4.6% UHMWPE not treated with silane. A similar downward trend in Tg was also observed with the EPDM interlayered composites.

The above results point to the importance of the interlayer relaxations, not only in controlling the overall losses but also in determining the temperature of the maximum losses. Tg measurements at one frequency, however, are insufficient as they do not take into account kinetic effects hence an accurate assessment would require measurements at various frequencies and the determination of the activation energies involved. A secondary transition at about -40°C which is associated with cooperative motions of glycidoxy and diphenylpropane groups of the epoxy resin

\[
(-OCH_2-CH-CH_2-, \quad \text{CH}_3 \quad \text{C} \quad \text{O} \quad \text{CH}_3)
\]
was observed in the pure epoxy resin tan delta plot (see Figure 4.19). It is worth noting also that this transition was much weaker in the composites and is possibly due to dilution effects of glass which are elastic. The value of tan delta at the Tg of the epoxy resin for the UHMWPE and EPDM interlayered composites was generally higher than the corresponding value for the control composite (see Table 4.8). Tan delta was also much higher for the UHMWPE interlayered composites from -60 to 100°C (see Figures 4.19 and 4.20); became three times the values for the control specimen above 20°C for the high level coatings. No clear trend was apparent with increasing UHMWPE coating level, other than the observation that above 0°C tan delta generally increased with UHMWPE content. Similarly, tan delta values for the EPDM composites were higher than the control sample between -60 and 80°C and increased by a factor of 3 for high level coatings. Tan delta also increased with EPDM content. The large peak at about -40°C, which is clearly evident in the high level EPDM interlayered composite, results from the superposition of losses due to \( \beta \) relaxations in the epoxy resin matrix, as mentioned earlier, and those associated with the \( \alpha \)-relaxations of the EPDM. Accordingly the modulus of such EPDM interlayered composites reduced drastically, in accordance with the deductions made above and the predictions from the theoretical model (see Section 6.3.1).

Such large increases in mechanical losses are expected to increase the toughness of the composites. The glass transition temperature of UHMWPE was estimated to be about -100°C (see Figure 4.23), and is associated with motions of the amorphous regions. The much broader peak at about 100°C on the other hand results from the molecular motions associated with melting of the crystals. From Figure 4.23 and more clearly from Figure 4.24, it can be seen that tan delta for the
high level UHMWPE interlayered composite begins to increase in the same region as tan delta for pure UHMWPE. This supports the validity of the concept of toughness enhancement by means of UHMWPE interlayers. Schlund and Lambla [44] also found that a latex interlayer, exhibiting a Tg of -20°C increased the value of tan delta.

5.6.4 Interlaminar Shear Test

A progressive reduction in the interlaminar shear strength was observed with increasing the amount of coating on the fibres (see Figure 4.25). This indicates that increasing the amount of coating on the fibres tended to reduce the strength of the interlayer between the two phases in the composites (discussed later). From Figure 4.25 the interlaminar shear strength of a 4.6% A174 silane treated UHMWPE interlayered composite was read off to be 20 MPa. This compares with the value of 17.6 MPa for an interlayered composite not treated with silane, suggesting that the A174 silane was able to improve the interfacial bonding by 14%. At low levels of coating the interlaminar shear strengths of the UHMWPE and EPDM interlayered composites were similar probably because at these levels the coating appeared to be sparse and irregular, hence attributing the high interlaminar shear strengths primarily to the strong bonding between the glass fibres and epoxy resin.

Similar trends in the decrease of interlaminar shear strength as a function of amount of coating were observed by Enever [36] and Hancox [39]. On comparing the results obtained from the EPDM interlayered composites with those from Hancox and Wells (Figure 5.7), it can be seen that an almost parallel reduction in interlaminar shear strength is observed with increasing coating level. In both these cases the fall of interlaminar shear strength is more rapid at first, but then
becomes slower. A comparison of the percentage reduction of interlaminar shear strengths between this work and the work of other authors has been made and the results are presented in Table 5.2.

The reductions observed in this work are of the same magnitude as those obtained by other researchers, with similar decreases in shear strength being observed for EPDM interlayered composites of this work and those obtained for silicone coatings in composites by Hancock and Wells [39]. For thick interlayer coatings Bell et al [53] suggested that the reduction in shear strength may have been associated with a weaker interlayer epoxy bond and the sticking together of fibres in bundles.

As previously mentioned the interlaminar shear test is basically a three point bending test. This implies that the initial slope of the load deflection curves are indicative of the modulus of these materials. It can be seen from Figure 4.26 that a progressive decrease in the stiffness (slope) of the composites is observed with increasing interlayer content. This observation is consistent with the results obtained from the dynamic mechanical thermal analysis (Figures 4.17 and 4.18). The control composite exhibited a brittle type failure while the interlayer composites possessed ductile type load deflection curves. After attaining a maximum stress, the interlayer composites continued to deform at a constant stress level, unlike the control composite which broke in a brittle fashion.

Similar changes in load deflection curves were obtained by Lambla [44] and Gerard [48] who also noted a transition from brittle to ductile deformations, and reported that after the test the interlayer composite samples recovered their initial shape. In this work the high
level UHMWPE and EPDM interlayered composites also returned to their initial shape after large amounts of deformation but sustained several interlaminar shear cracks. Lambla [44] claimed that latex interlayered composites ($T_g\text{interlayer} = -20^\circ C$) displayed large amounts of recoverable deformation without delaminating, while Gerard [48] mentioned that this type of recoverable deformation is very important for the enhancement of fatigue properties.

The difference in load deflection curves was also reflected by the different modes of failure. Microscopic examination of polished composites revealed that while the control composites exhibited normal shear failure, the interlayer composites possessed many cracks meandering through the interlayers (Section 4.5.4). The weak thick interlayers appeared to provide a failure path for the cracks to follow. This was not considered to be advantageous insofar as the reduction of the interlaminar shear strength as a function of UHMWPE/EPDM coating weight is probably related to the ease of interlaminar crack propagation through the thick interlayers and not so much indicative of the interfacial bonding between the various phases. Thus, the interlaminar shear strength of the interlayer composites is not only reflective of the interfacial bonding but also of the cohesive property (strength) of the interlayers. In any case, two separate toughening mechanisms could be distinguished from the microscopic examination for the UHMWPE interlayered composites:

a) formation of new surfaces
b) the deformation of UHMWPE interlayers.

The latter mechanism was considered to be the most important and beneficial for toughness enhancement. As the cracks propagated through
the UHMWPE interlayers further energy absorption occurred through the ductile deformation of the UHMWPE layer. One of the main reasons for choosing UHMWPE as the interlayer is its large ductility, which seems to be a vital criterion for toughness improvement of the composites. The deformed UHMWPE could be seen on either side of the cracks (Plates 4.17 and 4.18) as drawn fibrils resembling stalactites and stalagmites in a cave, suggesting that good bonding between UHMWPE and glass was achieved.

5.6.5 Flexural Properties
A reduction in flexural strength of both the UHMWPE and EPDM interlayered composites was observed with increasing amounts of coating, giving a maximum reduction of 53 and 85% respectively (Figures 4.27 and 4.28). However, the scatter of results, especially for the UHMWPE interlayered composites made the establishment of an exact relationship between the flexural modulus and level of coating difficult (Figures 4.29 and 4.30). The reduction in flexural modulus for the high level UHMWPE and EPDM interlayered composites was considerably less, i.e. 9 and 43% respectively, but once more confirming the importance of having a reasonably high interlayer modulus. The flexural strength and modulus of the UHMWPE interlayered composites with no silane treatment was however, lower than the corresponding silane treated samples (Figure 4.29), showing also a much more severe level of delamination. This confirms that the A174 silane was effective in improving the interfacial bonding but may not have been sufficient to prevent delamination.

Flexural strength results by Hancox and Wells [39] were compared with those of the EPDM interlayered composites and are shown in Figure 5.8. The fall off in flexural strength as a function of percentage weight
coating of silicone and EPDM rubber coatings is similar. In fact at a 6% coating level both systems sustained about a 60% decrease in flexural strength. The maximum reduction in flexural modulus observed by Enever [36] was 76% for interlayer composites coated with a 10% polyurethane solution, compared with a 43% reduction with EPDM at a 8.2% level in this work.

In the present work all the interlayer composites failed by delamination. A plot of flexural strength versus interlaminar shear strength for both sets of interlayered composites is shown in Figure 5.9. It can be seen that a linear relationship between flexural strength and interlaminar shear strength can be established, arising from the similarity of the mode of failure in these two tests. Thus the values of flexural strength for the interlayered composites probably did not reflect the true flexural strength of the interlayered composites (i.e. tensile stress initiated fractures) but were more indicative of the interlaminar shear strength (i.e. interlaminar shear initiated fractures).

The load deflection curves for the flexural tests showed the same trends as those from the interlaminar shear test (see Figures 4.31 and 4.32). The control composite exhibited a brittle type curve while the curves from the interlayer composites were more ductile in nature. Although the first major failure occurred at a lower stress (compared to the control), the interlayer composites were still able to sustain further deformations, unlike the control composites which failed catastrophically. During the testing of interlayer composites loud cracks were heard and these were accompanied by small jumps in the load deflection curves. These cracks were due to the progressive delamination of the samples, which involved significant amounts of energy absorption.
Plate 4.19 shows a scanning electron micrograph of a delaminated fracture surface from a high level UHMWPE interlayered sample. X-ray photoelectron spectroscopy was used in an attempt to determine the nature of the fractured surface. However, the elemental ratios of the fractured surface obtained from the analysis did not allow clear identification of the surface composition. It is believed that because no bare glass was distinguishable from the scanning electron microscopy studies, the delaminated surface was most likely to be composed of a combination of UHMWPE and epoxy resin. Failure through the UHMWPE interlayers may occur (similar to the mode of failure observed in the interlaminar shear test) because of its lower stiffness and strength and its excessive thickness. Jang et al [33] also mentioned that the cohesive failure of relatively weak delamination promoters including polyester and nylon based fabrics, may be responsible for delamination.

The scatter of flexural modulus results may have been due to the following reasons:

a) coating non-uniformity
b) misorientation of fibres - all the fibres may not have been perfectly aligned
c) void content discussed in section 5.6.8
d) variation in fibre strength due to broken or damaged fibres

5.6.6 Impact Properties

Figures 4.34 and 4.35 show that the impact strength decreases as a function of level of coating for both the UHMWPE and EPDM interlayered composites. The impact strength for the UHMWPE interlayered composites is higher than that of the EPDM interlayered composites of corresponding coating levels with a maximum reduction of 28 and 65%
being observed, respectively. The strengths obtained from the impact tests were greater than those obtained from the flexural tests, indicating the effect of loading rate. The impact strength of the UHMWPE interlayered composite not treated with silane was lower than the corresponding A174 silane treated interlayered composite (Figure 4.34). This was consistent with results from the flexural tests and confirmed that the silane was able to improve the interfacial bonding. These reductions in impact strength are again probably related to the thickness and non-uniformity of the lower stiffness and strength coatings.

Although a reduction in the total energy absorbed in fracture by impact loading was observed with interlayer content, the proportion of propagation energy increased as a function of interlayer content (Figure 4.38). This was reinforced by the observed increase in ductility index as a function of percentage coating (Figures 4.39 and 4.40). The work of Gerard [49] also showed that the propagation energy as a fraction of the total energy increased with coating thickness. The ductility index for the control was low and approximately equal to the value quoted by Beaumont et al [114] on studying glass epoxy composites (0.4). These control samples failed in a brittle manner exhibiting a low propagation energy (Figure 4.41).

The increase in ductility index of the interlayered composites confirmed once again their ability to improve the energy absorbing capabilities of these composites. The increase in ductility resulted from the severe delamination induced by the low interfacial shear strength. From Figure 5.10 a linear relationship between impact strength and interlaminar shear strength can be approximated. A similar relationship also existed between the flexural strength and
interlaminar shear strength. The typical load deflection curves of
the interlayered composites demonstrate the propagation of these
delamination cracks (Figure 4.41) and were similar to the curves
obtained from the interlaminar shear and flexural tests. The reduction
in initiation energy with decreasing interlaminar shear strength is
shown in Figure 5.11. The highest ductility index within the UHMWPE
interlayered composites was observed for the composite with
interlayers not treated with silane. This was not unexpected because
it exhibited the lowest interfacial shear strength. The improved Izod
impact strength of electropolymerised interlayer composites was
related by Bell et al [53] to the lower interlaminar shear strength,
allowing debonding between the interlayers and matrix to occur. The
low amount of delamination in the intermediate and high level EPDM
composites highlighted their flexibility and damage tolerance.

Peiffer [43] and Gerard [49] found that an optimum coating thickness
(0.2 \( \mu \text{m} \) and 0.03 \( \mu \text{m} \) respectively) was required for maximum impact
properties. Peiffer [43] observed a progressive decrease in impact
energy/strength at interlayer thicknesses greater than 0.2 \( \mu \text{m} \). Hence,
this reinforces the suggestion that the observed reductions in impact
strength and total impact energy in this work were related to the very
thick irregular coatings. An optimum coating thickness had not been
established. The interlayers appeared to promote delamination through
the reduction of the interlaminar shear strengths. This was similar to
the effect of the delamination promoters described by Favre [30], Jea
[31] and Jang [33], consisting of full and perforated films stacked
between prepreg layers in order to induce extensive delamination on
impact, thereby absorbing a great amount of energy. Additional
toughness was imparted by blunting and diverting the main crack.
5.6.7 Compressive Properties

A progressive reduction in compressive strength and modulus was observed with increasing interlayer content (Figures 4.42-4.45). The compressive strength and modulus of the UHMWPE interlayer composites were also higher than the corresponding EPDM interlayered composites. 11% and 76% reductions in compressive strength were observed with the high level UHMWPE and EPDM composites, respectively. The reductions in modulus (3% and 26% respectively) were again lower than the observed reductions in strength. The strength and modulus of UHMWPE interlayered composites with no silane treatment was again lower than the corresponding silane A174 treated interlayered composite. In these compressive tests the ends of the fibres were loaded. Since the same type of fibres were always used, the compressive modulus did not show much variation as a function of interlayer content, unlike the strengths which are influenced by the failure mode.

The observed splitting in the samples was caused by transverse strains generated in the specimens. A kink band was also often seen in both control and interlayer failed samples. The formation of a kink band is similar to the in-plane buckling of the fibres that Rosen [3] considered but occurs at a lower stress level. A combination of both the transverse tensile splitting and kink band formation mechanisms appeared to contribute to the failure of all the composites. No trend in either mode of failure mechanism could be identified as a function of interlayer content. Chaplin [8] explained that defects within the samples act as stress concentrators and initiate the kink band. In the case of the interlayer composites, large irregular lumps of UHMWPE or EPDM may be considered as such defects, in addition to those due to misaligned fibres. The reduction in compressive strength as a function of interlayer content may be explained by the following two reasons:
1. The presence of the lower stiffness interlayers around the fibres provide less support compared to the brittle epoxy matrix and hence make it easier for the fibres to bend.

2. The reduced interlaminar shear strength of the interlayer composites may cause cohesive failure of the interlayer or debonding of the fibres in the initial stages of the test (as the interlaminar shear stress component increases), subsequently reducing the support and further facilitating fibre matrix bending to form a kink band.

Other possible factors that may have reduced the compressive strength of all the composites have been outlined in Section 2.1.3.

5.6.8 Void Content

The void content for the various composites are shown in Tables 4.9 and A8. Although a low void content was observed with the control composite, the void content was higher in the interlayer composites, increasing slightly with interlayer content. Voids in the composites may have arisen from two main causes. Firstly, incomplete wetting out of the fibres by the resin may have occurred, especially for the thick interlayer coated fibres even though great care and attention was taken during the manufacturing process. Secondly, volatiles may have been produced during the curing process of the resin. These volatiles may have been due to the presence of residual solvent in the interlayers or created by the decomposition products of the peroxide used to cure the EPDM. The void content of a composite may significantly affect the mechanical properties. Voids can reduce the magnitude of the interlaminar shear strength, longitudinal and transverse flexural strength and modulus and increase the scatter in
strength properties. Hence, the voids in the interlayer composites may have also contributed to the reduction in strength and modulus and also masked the toughening effect.

5.7 FTIR ANALYSIS OF GLASS FIBRES

The direct transmission and KBr pressed disc techniques were only able to clearly identify the C-H stretches from the subtracted spectra. It was difficult to resolve other peaks because of excessive noise, although the DRIFTS analysis was also able to resolve a broad band between 1612-1055 cm\(^{-1}\), consisting of two main peaks (see Figure 4.45). These peaks were assigned to a combination of groups including C-H and O-H bends (1450, 1375 cm\(^{-1}\)) and the symmetrical stretching vibration of the epoxy ring (1246 cm\(^{-1}\)) augmented by the C-O stretch (1260-1000 cm\(^{-1}\)) and the SiO stretching vibrations. These bands were attributed to the epoxy dressing and silane present on the fibres. The amount of surface material washed off the fibres was estimated by measuring the absorbance of the methylene asymmetric stretch before and after washing, suggesting that about 70% of the surface coating had been removed by the washing process. A 0.5% weight loss was also recorded. This surface material removed is most likely to be the epoxy size since fibre separation occurred after washing. X-ray photoelectron spectroscopy studies on the fibres revealed that a reduction in carbon content occurred on washing and that the carbon oxygen ratio was very similar to that of the epoxy resin (4:1), on subtracting out the oxygen contribution due to bare glass, reinforcing the above comments. Thomason [12] reported that approximately 80-90% of the coating from epoxy compatible glass fibres could be removed by extraction in acetone while Pawson and Jones [16] commented that the physically adsorbed aminosilane layer could be removed by immersing the glass fibres in water, consequently improving the interfacial shear strength.
CHAPTER 6

MODELLING THE BEHAVIOUR OF INTERLAYER COMPOSITES USING FINITE ELEMENT ANALYSIS

6.1 INTRODUCTION

The finite element method is a computer-aided mathematical technique for obtaining approximate numerical solutions to complex differential equations that predict the response of physical systems subjected to external influences. Many commercial programmes exist today that implement the finite element approach to solve civil, aerospace and structural engineering problems and are widely used in many industries. The finite element method also allows the micromechanical analysis of composite materials. A knowledge of the stress distributions can facilitate the understanding of composite behaviour under applied loads. The stresses can be used to calculate the composite modulus and regions of high stress concentrations can be identified which can reveal likely failure locations.

In this work a two dimensional finite element programme originally developed by Dr V Nassehi (Chemical Engineering Department, Loughborough University) was used. The finite element method was used as a powerful tool to study the micromechanical behaviour of unidirectional glass fibre composites with interlayers, without becoming directly involved with the underlying mathematics. The following section describes the stages involved in defining the problems used in this work and describes the nature of the output data produced. These stages have been summarised in the form of a block diagram in Figure 6.1.
6.2 THE FINITE ELEMENT ANALYSIS PROCEDURE

6.2.1 Mesh Generation
A basic mesh representing a cross-section of two fibres embedded in a matrix was initially constructed and coarsely split into eight noded quadrilateral elements (see Figure 6.2). This mesh was used to model the transverse properties of a unidirectional fibre composite with a 60% fibre volume fraction (square array) under plane strain conditions ($\varepsilon_Z = 0$). Transverse properties of composites are very critical since the properties in this direction are the lowest and determine mostly the lower limits of their performance. Thus it was considered important to study the effect of interlayers on transverse properties. Stress intensifications occur through the interaction of the stress fields of neighbouring fibres as well as arising from large differences in the elastic properties of the two materials. Previous workers [37,91,97] have only considered single sphere or fibre systems, thus neglecting the effect of sphere or fibre interactions. The 'parent mesh' was then refined using a pre-processor computer programme called MESHGEN. The programme automatically subdivides the mesh in a specified manner and generates the mesh data. As well as saving time the pre-processor reduces the occurrence of errors in the mesh data. The mesh was refined by varying amounts to determine the required refinement level to produce a solution of suitable accuracy. A refined mesh consisting of 230 elements and 977 nodes was subsequently used for this analysis. Similar refined meshes with interlayer thicknesses ranging from 0.2 µm to 0.65 µm were also constructed to model the behaviour of interlayer composites. Typical refined meshes are shown in Figure 6.3.
6.2.2 Creation of an Input Data File

The structure of the input data file is shown in Figure 6.4. The order and format in the file was very critical and important to allow the finite element programme to read the data correctly. The first \((5 + \text{NMAT})\) lines were entered manually to the data file. Throughout this work the Youngs modulus of the fibres was taken to be 78 GPa (typical of E-glass fibres) and that of the matrix to be 4500 MPa (typical of an epoxy resin). The Youngs modulus of the interlayer was varied between 1 and 1000 MPa. The shear and bulk moduli were subsequently calculated assuming that Poisson's ratio was 0.5 for each material. (The present finite element model presents excessive computational difficulties for lower Poisson ratio values). Mesh coordinates and element connectivity data were obtained from the pre-processor. The connectivity data indicated which nodes were in each element and which nodes were connected to their neighbours. The various boundary conditions used in this work (i.e. applied deformations) are discussed in a following section (6.2.4). The last line of the data file contained the word 'FALSE' to indicate that no temperature loading was applied. This programme had the facility to model the effect of uniform temperature loadings but at present this has not been perfected.

6.2.3 Process Output Data Files

After reading the input data file, the programme calculated the following:

i) Nodal displacements and new deformed mesh coordinates

ii) The tensile stresses in the x and y directions and the shear stress in the xy plane for each node

iii) The Von Mises stress at each node.
The Von Mises stress is defined as:

\[ q_{vm} = \left[ \frac{1}{2} (\sigma_x - \sigma_y)^2 + \frac{1}{2} (\sigma_y - \sigma_z)^2 + \frac{1}{2} (\sigma_z - \sigma_x)^2 + 3 \tau_{xy}^2 \right]^{1/2} \]

(6.1)

where \( \sigma_y \), \( \sigma_x \) and \( \sigma_z \) are the tensile stresses along the x, y and z axes and \( \tau_{xy} \) is the shear stress in the xy plane.

Under plane strain conditions \( \sigma_z = \nu(\sigma_y + \sigma_x) \), where \( \nu \) is the Poisson's ratio. For an incompressible material \( \nu = 1/2 \), hence substituting for \( \sigma_z \), the Von Mises equation under plane strain conditions becomes:

\[ q_{vm} = \left[ \frac{3}{4} (\sigma_x - \sigma_y)^2 + 3 \tau_{xy}^2 \right]^{1/2} \]

(6.2)

Equation 6.2 was used by the programme to calculate the Von Mises stress at each node. This failure criterion was used to predict where failure was most likely to initiate. As well as producing a main output file containing (i) and (ii) the programme also created four minor output files named 'sigma x', 'sigma y', 'tau xy' and 'vmstres1'. These minor files contained the data in a suitable format to be read by a post-processor programme called 'GRAPHICS'. The main purpose of this interactive graphics programme was to allow the numeric output of the finite element programme to be visualised and interpreted. It allowed plots such as scalar contour fields to be produced.
6.2.4 Boundary Conditions

Initially the sides AB and AD were fixed in the x and y directions respectively, and a 0.1% tensile strain (in the y direction) was applied to the top nodes along BC (see Figure 6.2). Solutions were produced for a model composite with 60% fibre volume fraction first without an interlayer, by varying the matrix modulus from 1 to 4500 MPa and then with interlayers ranging in thickness (0.2 μm to 0.65 μm) and with modulus varying from 1 MPa to 1000 MPa. The transverse modulus of the composites was calculated by determining the average stress along the top boundary BC resulting from the applied strain. The average stress along the boundary BC was calculated by taking into account the varying distance between the nodes. The results from the no interlayer composites were compared with those predicted from existing micromechanics theory. However, the stress distributions in the model were not symmetrical for the two fibres and thus the boundary conditions were considered to represent a hypothetical situation in which one fibre is allowed to move in relation to the other fibre - referred to as the separable fibre model (see Figures 6.5 and 6.6). Subsequently the boundary conditions were changed to describe a more realistic situation where both fibres are fixed and, therefore, are experiencing the same deformation (constrained fibre model). The nodes along AB and CD were fixed in the x direction and the nodes at B and D were fixed in the y direction. A 0.1% tensile strain was applied to the nodes at A and C (see Figure 6.2). This represented a symmetrical shear type deformation. Solutions were produced for a 0.2 μm interlayer varying in modulus from 1 MPa to 10 GPa with a fibre volume fraction of 60% and for interlayered composites with a volume fraction of 20%.
6.3 DISCUSSION

6.3.1 Transverse Tensile Loading of the Separable Fibre Model

The effect of varying the number of elements on the calculated transverse modulus is shown in Table 6.1 and are compared with the value obtained using the Tsai equation [115] shown below.

\[
E_2 = 2[1 - \nu_f + (\nu_f - \nu_m)]V_m [(1-C) \frac{K_f(2K_m+G_m) - G_m(K_f-K_m)V_m}{(2K_m+G_m) + 2(K_f-K_m)V_m} + C \frac{K_f(2K_m+G_f) + G_f(K_m-K_f)V_m}{(2K_m+G_f) - 2(K_m-K_f)V_m}]
\]

where \( K_f = \frac{E_f}{2(1-\nu_f)} \)

\( K_m = \frac{E_m}{2(1-\nu_m)} \)

\( G_f = \frac{E_f}{2(1+\nu_f)} \)

\( G_m = \frac{E_m}{2(1+\nu_m)} \)

\( C = 0 \)

\( E_2 = \) Transverse Composite Modulus

\( \nu = \) Poisson ratio

\( V = \) volume fraction

subscripts \( f = \) fibre; \( m = \) matrix
It can be seen from Table 6.1 that as the number of elements was increased, the solution became more accurate. Using a mesh consisting of 230 elements the model underestimates the modulus by 5%, while the 480 element mesh overestimates the modulus by 5% compared to the value obtained by the Tsai equation but took much longer to solve. Hence a 230 element mesh was used throughout the interlayer analysis. The predicted composite transverse modulus from the finite element method as a function of the matrix modulus was compared to the modulus values calculated from the Tsai equation (in Figure 6.7). A good agreement between the two methods is observed. Figure 6.7 also illustrates the strong influence of the matrix modulus on the transverse composite modulus. It is of interest to note here that according to the Tsai equation [115], the Poisson's ratio of the fibres and the matrix have little effect on the composite modulus. Guild and Young's [97] predictions of the modulus for epoxy resin filled with glass spheres were slightly higher than experimental values. In their work, they modified their results to account for a more realistic random filler distribution. Kinsella [117] previously obtained results from the finite element programme used in this work which were in general agreement with those obtained by Guild and Young [97] and also with experimental results obtained by Smith [118]. Hence, the good agreement with the Tsai equation in this work, together with the work of Kinsella gives sufficient confidence for the predictions made about the behaviour of interlayer composites. These results are shown in Figure 6.8 as a function of interlayer modulus for three different interlayer thicknesses. A similar type of trend for the predicted modulus was also observed by Broutman and Agarwal [37] (see Figure 6.9) in their work related to short fibre interlayer composites. It can be seen from Figure 6.8 that as the interlayer modulus was reduced from that of the epoxy matrix, the transverse composite modulus reduced considerably.
A similar type of behaviour is observed as the interlayer thickness is increased for a given interlayer modulus. In general the observed reduction in the modulus predicted by the finite element method follows the same trend as the values obtained experimentally. For example, Figure 6.10 compares the variation of dynamic modulus obtained from the Dynamic Mechanical Thermal Analysis work and the predicted modulus for $E_{\text{interlayer}} = 1000$ MPa as a function of UHMWPE interlayer thickness. This comparison is only qualitative because of the difference in the directions of the applied stresses in the two cases. It can be seen, however, that both exhibited very similar parallel trends and the percentage reduction in modulus for a 0.3 µm UHMWPE interlayer from the experimental work and the finite element method were 9.8 and 11.5% respectively, and are, therefore in close agreement. The variation of the dynamic modulus and the predicted modulus as a function of EPDM interlayer thickness ($E_{\text{interlayer}} = 1$ MPa) is shown in Figure 6.11. The finite element analysis predicted a much steeper initial decrease in transverse modulus compared to the experimental results obtained by the DMA measurements.

6.3.2 Tensile Loading of Constrained Fibre Composites

The effects of varying the interlayer modulus from 1 MPa (equivalent to the modulus of EPDM) to 500-1000 MPa (equivalent to the modulus of UHMWPE) and to 10 GPa (equivalent to a material with an intermediate modulus between the fibres and matrix) was studied for a fibre volume fraction of 60%. The effect of interlayer thickness and volumetric fraction was also investigated. The deformations illustrated in Figure 6.12 resulted from a 0.1% overall extension in the y direction. The two fibres experienced tensile deformations whereas the matrix underwent a shear deformation. Figures 6.13 to 6.15 show the stress variations within the composites resulting from the applied strains.
The diagrams show isobars (i.e. lines of constant stress) at the following levels: 4 MPa (approximately corresponding to the shear strength of EPDM), 10 MPa (approximately corresponding to the shear strength of UHMWPE) and 35 MPa (approximately corresponding to the shear strength of the epoxy matrix). These will provide an indication of likely failure locations in the interlayers or matrix within the composites, as well as the maximum Von Mises stress. The position and magnitude of the maximum stresses have been identified and are also shown in Figures 6.13 to 6.15.

a) **Effect of Interlayer Modulus**

Plot 6.13a represents the tensile stress distribution in the y direction for the no-interlayer composite. The most severe stress gradients occur chiefly at the fibre matrix interface and within the matrix between the fibres. This stress concentration effect is not unexpected because of the large difference in modulus between the contiguous phases and the high volume fraction of fibres. A 1 MPa interlayer drastically reduced the load carried by the composite (plot 6.13b). This was consistent with a 83% reduction in transverse modulus obtained from the separable fibre model (see Figure 6.8). The effect of introducing interlayers with modulus equal to 500 and 1000 MPa can be seen in plots 6.13c and 6.13d. Both interlayers reduced the stress gradients around the interface and localised the high stresses within the interlayer rather than in the matrix. Increasing the modulus of the interlayer to 10 GPa does not localise the stresses to the interlayer anymore, but brings the stress distributions to a situation very similar to the no-interlayer system i.e. the maximum stress also occurring in the matrix at 50° from the direction of the applied strain and increasing in magnitude. The maximum stresses for the 500 and 1000 MPa modulus interlayers occurred at the same angle but within
the interlayers, instead of the matrix. On the other hand, the maximum stress shifted into the matrix at a lower angle of 12° for the 1 MPa interlayer.

Plots 6.14a to 6.14e represent the tensile stress distributions in the x direction. The trends were similar to the stresses in the y direction. High stress gradients are observed at the fibre matrix interface and in the matrix for a composite without an interlayer, which for 500 and 1000 MPa modulus interlayer composites are reduced and localised to the interlayers. In fact these two stress distribution patterns (plots 6.14c and 6.14d) were very similar, while for the 10 GPa modulus interlayer the distribution was very similar to the no-interlayer composite.

The 500 and 1000 MPa modulus interlayers appeared to provide the most satisfactory results for toughness enhancement using ductile interlayers, insofar both transfer effectively the maximum stress from the matrix to the interlayer region. Hence a UHMWPE interlayer is an ideal system in terms of its modulus and high level of ductility. These results also substantiate the ability of UHMWPE interlayers at low thicknesses to improve the energy absorbing properties of glass fibre composites.

The shear stress distributions resulting from the 0.1% extension in the y direction are shown in Figure 6.15. Plot 6.15a shows the shear stress distribution in a composite without an interlayer. High shear stresses occur in both the matrix and in the fibre in the vicinity of the interface. This contour plot emphasises the importance of having good interfacial bonding. To achieve a high shear stress in the fibre the interfacial bond must be strong to prevent interfacial failure.
The 1 MPa interlayer (plot 6.15b) significantly reduced the stress levels, with the highest stress gradients occurring in the matrix, consistent with tensile stress observations. The introduction of 500 and 1000 MPa modulus interlayers reduced the level of shear stresses in the matrix and also reduced the detrimental high stress gradients at the fibre interface (plots 6.15c, 6.15d). The maximum shear stresses for the 500 and 1000 MPa modulus interlayers occurred in the fibres close to the interface and at the interlayer matrix interface, similarly highlighting the importance of attaining good interfacial bonding between the different phases. The shear stress distribution of the 10 GPa modulus interlayer (plot 6.15e) was similar to that of the no-interlayer composite, with the stress gradients occurring in the matrix and in the vicinity of the interlayer, while increasing in magnitude. The effect of interlayer modulus on the various maximum stresses is summarised in Figure 6.20. The 500 and 1000 MPa modulus interlayers reduce the stresses to an acceptable level, whereas the 1 MPa modulus interlayer reduces the stresses excessively and the 10 GPa modulus interlayer has an adverse effect increasing the maximum stresses.

The Von Mises stress distributions were similar to those of the shear stress because of the dominance of the shear stress term in the Von Mises equation (see equation 6.2). Regions of maximum Von Mises stress were identified for the different interlayer moduli systems and are shown in plot 6.16a. These represent the most likely locations where failure may initiate. Plot 6.16a shows that failure in a composite without an interlayer and those with an interlayer modulus of 500 MPa and 10 GPa is likely to occur in the fibre close to the interface at 45°, assuming that a perfect bond exists between the different phases. Guild and Young [97] found that the maximum Von Mises stress occurred
at the glass sphere epoxy interface at 42° to the applied strain and
thus are in general agreement with the prediction of this work.
Failure may rather initiate at the interlayer epoxy interface for a
1000 MPa modulus interlayer while failure in the epoxy matrix is
predicted with the 1 MPa interlayer since the maximum Von Mises
stresses were identified in these regions. Failure in the epoxy resin
may involve the formation of cracks. Interfacial failure and
especially matrix cracking are not desirable for optimum toughness
enhancement, ideally the onset of failure should involve the yielding
of the ductile interlayer.

However, these may not be the only possible failure locations. Failure
may initiate before the maximum Von Mises stress is attained. Plot
6.15a reveals that failure may first occur in the matrix close to the
fibre (60° to applied strain) in the composite without an interlayer
where the shear strength of the matrix is exceeded. Plots 6.15c and
6.15d reveal that failure may first occur in the interlayer in the
region of the 10 MPa isobar. Also plots 6.13c and 6.13d show that the
stresses in the interlayers exceed the yield strength of UHMWPE (20
MPa). Thus the onset of failure may start by yielding of the
interlayer. The model's prediction of failure by yielding further
confirms the ability of UHMWPE interlayers to substantially improve
composite toughness whilst only suffering a 9% reduction in stiffness
(see Figure 6.8).

The shear strength of EPDM is not exceeded in the 1 MPa modulus
interlayer composite (plot 6.15b). Although a rubbery interlayer may
reduce the stress gradients in the matrix and interface and further
enhance the energy absorbing properties of the composite by deforming,
the onset of failure in this region was not predicted by this model
under a 0.1% strain applied in the y direction. Note, however, that a severe reduction in stiffness is also predicted with a thin 0.2 μm rubbery interlayer (see Figure 6.8).

b) Effect of Interlayer Thickness and Volume Fraction

Plots 6.17e and 6.18e show the tensile stress distributions for a thick (0.65 μm) 1000 MPa modulus interlayer. As with the 0.2 μm interlayer (plots 6.17d, and 6.18d) the high stresses were confined within the interlayer. In all these plots the maximum stress was reduced to a similar level and occurred in the interlayers between 40-50°. Although a similar type of shear stress distribution was observed to the 0.2 μm interlayer system, the maximum shear stress (30 MPa) in the 0.65 μm interlayer composite shifted to the matrix close to the interlayer epoxy interface (see plots 6.19d and 6.19e). The failure location predicted by the Von Mises criteria shifted from the interlayer epoxy interface to the middle portion of the matrix (plot 6.16b). However, as observed with the 0.2 μm interlayer, the shear stress in the interlayer and around its interface was similar to the shear strength of UHMWPE (plot 6.19e). The yield strength of UHMWPE was also exceeded in the interlayer (plot 6.17e). Thus a thicker interlayer of modulus equal to that of UHMWPE is still able to provide a deformation mechanism to relieve the high stresses, but would suffer from an unfavourable greater loss in transverse modulus (26% reduction compared to 9% for a 0.2 μm interlayer, see Figure 6.8).

Figures 6.17 to 6.19 show that ductile interlayers would provide the most benefit in enhancing toughness at higher rather than lower fibre volume fractions. On comparing the plots of the tensile stress distributions without an interlayer for composites with a fibre volume fraction of 20% with those with a fibre volume fraction of 60%, it is
evident that at low fibre volume fractions no harmful stress concentrations existed in the matrix or at the interface, so that the effect of the interlayers in relieving the high stresses was not so pronounced (see Figures 6.17 and 6.18). The absence of high stress gradients in the matrix at low fibre volume fractions can be explained by the greater interfibre distance limiting the interaction of stress fields resulting from each fibre (see plots 6.17a and 6.18a).

Other important observations to note include the following. The low level of stresses within the 20% fibre volume fraction composites (plot 6.17a for example), indicated the lower load bearing capability of this low volume fraction composite. The shear stress distribution at the low volume fraction revealed that no severe stress gradients existed, unlike the higher volume fraction composite which exhibited high shear stress gradients in the proximity of the interface (plots 6.19a and 6.19b). This reinforces the comment made earlier about the importance of achieving a good interfacial bond especially at high fibre volume fractions. The Von Mises stresses indicated that failure may also initiate at the fibre matrix interface for the 20% fibre volume fraction composite, like the composite with a fibre volume fraction of 60%, but at a greater angle of 80°. Note also that at this low volume fraction the shear strength of the epoxy matrix was not exceeded.

Broutman and Agarwal [37] evaluated the toughness of short glass fibre composites as a function of interlayer modulus by measuring the amount of strain energy absorbed in their analysis using the finite element method (see Figure 6.21). They suggested that the strain energy absorbed could be maximised by selecting an interlayer modulus of 70 MPa. The model presented in this work indicates that the UHMWPE interlayers reduce the stress gradients in the matrix and provide a local ductile deformation facility to also improve the toughness.
CHAPTER 7
CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The following conclusions can be drawn from the work conducted in this research programme:

1. Using a solution coating process it is not readily possible to obtain continuous thin polymer coatings along the entire length of glass fibres. Instead, non-continuous coatings of irregular thickness tend to form around individual and small groups of fibres, and as lumps between fibres. The coating solution used must be of a low viscosity in order to wet out the fibres. UHMWPE solutions above 110°C allow wetting of fibres, whereas the viscous gel state hinders coating impregnation. An important feature of UHMWPE solutions is its ability to form films on glass slides through the gel state, unlike other crystalline polymers which form grainy coatings. Since continuous films of UHMWPE are formed around large diameter glass filaments, a possible future approach to improve the UHMWPE coatings may involve utilising an industrial glass fibre manufacturing process. Individual glass filaments may be passed through a coating bath containing the silane grafted UHMWPE solution immediately after they have been drawn from the bushing.

2. The grafting of organofunctional silanes onto the EPDM and UHMWPE polymers in solution provides an effective means of coupling these interlayer polymers to glass. A mercaptosilane (silane A189) improves the bond between the EPDM and glass, as demonstrated by single lap shear tests. This part of the work
has also revealed that an excess amount of silane A189 is detrimental to the bond strength. Similarly, significant improvements in bonding to glass are obtained with silane A174 (methacrylate silane) grafted UHMWPE films.

3. Grafting maleic anhydride onto UHMWPE in solution is a useful method of improving the adhesion between the epoxy matrix and UHMWPE interlayer. Infra-red analysis on the various grafted films provides further evidence that the grafting reactions occur in solution and also infers that low levels of grafting (low reaction efficiency) are attained in solution. This suggests that interfering secondary reactions involving solvent molecules are also prominent, during the grafting reaction. Future work may involve the use of a maleic anhydride as well as a silane A174 treatment of UHMWPE prior to composite manufacture, to investigate the influence on composite performance.

4. Improvements in various UHMWPE interlayer composite strength and stiffness properties are consistently obtained using the silane A174 treatment. This strongly suggests that silane A174 is able to improve the interfacial bonding in the interlayered composites through the formation of chemical and physical bonds. Further evidence is provided by scanning electron micrographs of interlaminar shear cracks propagating through the UHMWPE. Hence, the lap shear tests are able to provide a rapid and reliable measure of the change in interfacial adhesion between the UHMWPE interlayers and glass.

Progressive reductions in strength and stiffness properties as a function of interlayer thickness are observed. Losses in the
different moduli and strengths are similar to each other, for a
given interlayered composite. EPDM interlayered composites
suffer the greatest losses in properties, highlighting the
advantage of using UHMWPE as an interlayer as opposed to a soft
rubber ($E_{\text{EPDM}}/E_{\text{UHMWPE}} = 0.001$). Reductions in interlaminar shear
strength and other mechanical properties of the interlayered
composites are most likely related to the excessive thickness and
poor quality of the coatings, and not so much the interfacial
bonding. The interlaminar shear strength of interlayered
composites is not only reflective of the interfacial bond
strength but also the cohesive strength of the interlayers. The
increase in ductility index is related to the observed severe
delamination induced by the low interlaminar shear strengths of
the interlayered composites.

However, the most promising results from a toughness enhancement
point of view are obtained from the DMTA work and short beam
three point bending tests. The increase in damping capacity (tan
delta) and the observed deformation of UHMWPE confirm the
potential of UHMWPE to improve the toughness of composites
through a yielding mechanism.

5. An important advantage of UHMWPE compared to EPDM and interlayer
materials used by previous workers is its exceptional toughness
and its ability to yield to large strains, whereas EPDM is much
weaker and softer and is only able to deform at lower stress
strain levels. To produce a beneficial improvement in toughness
without a significant loss in strength and stiffness properties,
this appealing ductile deformation mechanism has to be optimised.
This may be achieved if a very thin ($\approx 0.1 \mu m$) UHMWPE interlayer
is applied uniformly to each individual filament. As mentioned earlier, the use of a glass manufacturing process may allow such coatings to be obtained.

6. The principal conceptual behaviour of interlayers i.e. modifying the surrounding stress fields between fibres and subsequently reducing stress concentrations that exist between the fibres and matrix is borne out by the finite element analysis work. As well as substantiating the ability of thin UHMWPE interlayers to reduce stress concentrating effects, the constrained fibre model shows that the UHMWPE interlayers are able to localise the high stresses to the interlayer, enabling these harmful stresses to be relieved through the energy absorbing yielding mechanism with a minimal decrease in transverse modulus.

7. In general the reductions in transverse modulus predicted by the separable fibre model follow the same trends as the experimental results. Severe reductions in modulus are predicted for EPDM interlayered composites, in accordance with experimental findings. Also this study reveals that the use of ductile interlayers at higher rather than lower fibre volume fractions would be the most effective in enhancing toughness. Future work may involve modifying the finite element analysis programme to take into account the viscoelastic behaviour of polymers and to investigate the effect on interlayer composite performance. The behaviour of interlayered composites in the longitudinal direction may be modelled by constructing an appropriate mesh. The influence of temperature loadings may also be investigated.
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Figure 1.1 Typical Stress Strain Curves For The Three Common Types Of Reinforcing Fibres

Anistropic

poor compressive strength

Anistropic

Isotropic

<table>
<thead>
<tr>
<th>Tensile Stress (GPa)</th>
<th>Tensile Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>3.5</td>
</tr>
<tr>
<td>3.0</td>
<td>2.5</td>
</tr>
<tr>
<td>2.0</td>
<td>1.5</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

- Carbon Type I
- Carbon Type II
- Kelvar 49
- E Glass
\[
R-\text{SiX}_3 + H_2O \xrightarrow{\text{hydrolysis}} R-\text{Si(OH)}_3 + HX
\]

Silanol

\[
\begin{array}{c}
R \\
\text{HO-Si-OH}
\end{array}
\quad
\begin{array}{c}
R \\
\text{HO-Si-OH}
\end{array}
\quad
\begin{array}{c}
R \\
\text{HO-Si-OH}
\end{array}
\]

Hydrogen Bonding

Glass

\[
\begin{array}{c}
0 - \text{Si} - O - \text{Si} - O - \text{Si} - 0 \\
\text{M} \quad \text{M} \quad \text{M} \\
0 - \text{Si} - O - \text{Si} - O - \text{Si} - 0 \\
\text{M} \quad \text{M} \quad \text{M}
\end{array}
\]

Polysiloxane covalently bonded to glass surface

Organofunctional R groups react with matrix

FIGURE 2.1: A SIMPLE MODEL SHOWING THE ACTION OF SILANES FOR GLASS FIBRES IN A THERMOSETTING MATRIX
FIGURE 2.2: A REVERSIBLE HYDROLYTIC BOND MECHANISM TO RELIEVE STRESSES AT THE INTERFACE, PROPOSED BY PLEUDEMANN [14]
a) The fibre pull-out mechanism suggested by Cottrell and Kelly [17,18]

b) Debonding according to Outwater and Murphy [19]

c) Debonding according to Cook and Gordon [20] (crack stopping mechanism)

FIGURE 2.3: THE DIFFERENT FRACTURE MECHANISMS PROPOSED TO ACCOUNT FOR THE TOUGHNESS OF COMPOSITES
FIGURE 2.4: THE COOK/GORDON DEBONDING MECHANISM FOR AN INTERMITTENTLY BONDED COMPOSITE
Figure 2.5 Impact Strength Of Glass Fibre Composites With Interlayers Of Varying Thickness And Tg [43]

Interlayer Tg (°C)
- 80
- 10
- 14
- -56

Notched Izod Impact Strength (ft-lbs)

Rubber Interlayer Thickness (Å)
FIGURE 3.1: THE FIBRE COATING PROCESS
FIGURE 3.2: THE SINGLE LAP SHEAR TEST

FIGURE 3.3: SANDWICH TYPE LAP SHEAR TEST

FIGURE 3.4: ALUMINIUM EPOXY SINGLE LAP SHEAR TEST
FIGURE 3.5: THE LEAKY MOULD USED IN THE WET LAY-UP OF EPOXY COMPOSITES

FIGURE 3.6: MODIFIED NEW LEAKY MOULD USED IN THE WET LAY-UP OF EPOXY COMPOSITES
Metal block with 1 mm deep groove.

Square alignment sleeve

Assembly

FIGURE 3.7: THE COMPRESSION TEST FIXTURE

FIGURE 3.8: TOOL USED TO PRODUCE PERFECT PARALLEL SAMPLE EDGES FOR COMPRESSION TESTING
Figure 4.1 Graph Of % Weight Of EPDM Coatings On Glass Fibres Versus Solution Concentration

Figure 4.2 Graph Of % Weight Of Polybutadiene Coatings On Glass Fibres Versus Solution Concentration
Figure 4.3 Lap Shear Results For Glass–EPDM–UHMWPE–EPDM–Glass Systems

A = 5% silane*-grafted-uncrosslinked-EPDM solution (no UHMWPE)
B = 5% EPDM solution (no silane grafting)
C = 5% silane-grafted-EPDM solution
D = 2% silane-grafted-EPDM solution
E = 1% silane-grafted EPDM solution
F = As E but 5% silane, based on EPDM
G = As F with UHMWPE primed with 1% silane-grafted-EPDM solution

* Silane Al89
FIGURE 4.4: INFRA-RED SPECTRUM OF EPDM

FIGURE 4.5: INFRA-RED SPECTRUM OF SILANE A189

FIGURE 4.6: INFRA-RED SPECTRUM OF SILANE A189 GRAFTED EPDM
FIGURE 4.7: PORTIONS OF INFRA-RED SPECTRA FOR SILANE A189 GRAFTED EPDM AFTER PROPAN-2-OL EXTRACTION
Figure 4.8 Silane Grafted UHMWPE Lap Shear Results

A = No silane treatment
B = UHMWPE grafted with silane Z6032, 4 hr reflux
C = UHMWPE grafted with silane Z6032, 24 hr reflux
D = UHMWPE grafted with silane A174, 4 hr reflux
E = As B, with slides primed with 0.5% silane Z6032 solution
F = As D, with slides primed with 0.5% silane Z6032 solution
Figure 4.9 Typical Load Displacement Curves From UHMWPE Lap Shear Tests

(a) Deformation of UHMWPE

(b) Brittle bond failure

(a) eg. 2% silane A174 treatment

(b) eg. 2% silane Z6032 treatment
FIGURE 4.10: FTIR SPECTRA OF SILANE Z6032 GRAFTED UHMWPE

FIGURE 4.11: FTIR SPECTRA OF SILANE A174 GRAFTED UHMWPE
Figure 4.12 Epoxy/UHMWPE Lap Shear Results
FIGURE 4.13: FTIR SPECTRA OF MALEIC ANHYDRIDE GRAFTED UHMWPE

After methanol wash

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Figure 4.18 Plot Of Dynamic Modulus At 20°C As A Function Of % Weight Of EPDM Coating
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Figure 4.20 Tan Delta As A Function Of Temperature (60 to 180°C) For UHMWPE Interlayered Composites
Figure 4.21 Tan Delta As A Function Of Temperature (−60 to 60°C) For EPDM Interlayered Composites

Figure 4.22 Tan Delta As A Function Of Temperature (60 to 180°C) For EPDM Interlayered Composites
Figure 4.23 Tan Delta As A Function Of Temperature For UHMWPE And The Thick UHMWPE Interlayered Composite

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Figure 4.25  Plot Of Interlaminar Shear Strength As A Function Of % Weight Of UHMWPE And EPDM Coatings
Figure 4.26 Load Deflection Curves From The Interlaminar Shear Tests

1. Control
2. 2.8% UHMWPE
3. 3.7% UHMWPE
4. 4.2% UHMWPE
5. 4.6% UHMWPE no silane
6. 1.2% EPDM
7. 3.4% EPDM
8. 8.2% EPDM

Load

Deflection
Figure 4.27 Flexural Strength As A Function Of % Weight Of UHMWPE Coating

Figure 4.28 Flexural Strength As A Function Of % Weight Of EPDM Coating
Figure 4.29 Flexural Modulus As A Function Of % Weight Of UHMWPE Coating

Figure 4.30 Flexural Modulus As A Function Of % Weight Of EPDM Coating
Figure 4.31 Flexural Load Deflection Curves For UHMWPE Interlayered Composites

Figure 4.32 Flexural Load Deflection Curves For EPDM Interlayered Composites
Figure 4.33  Typical Load History During A Impact Test

\[ E_t = E_i + E_p \]

- Initiation phase
- Propagation phase

Load

Time
Figure 4.34 Impact Strength As A Function Of % Weight Of UHMWPE Coating

Figure 4.35 Impact Strength As A Function Of % Weight Of EPDM Coating
Figure 4.36 Impact Modulus As A Function Of % Weight Of UHMWPE Coating

Figure 4.37 Impact Modulus As A Function Of % Weight Of EPDM Coating
Figure 4.38  Impact Energies For UHMWPE And EPDM Interlayered Composites

- Intial Energy (Ei)
- Total Impact Energy (Et)

*no silane*
Figure 4.39  Ductility Index As A Function Of % Weight Of UHMWPE Coating

Figure 4.40  Ductility Index As A Function Of % Weight Of EPDM Coating
Figure 4.41  Typical Load Deflection Curves From The Impact Tests

- Control
- 4.8% UHMWPE
- 4.2% UHMWPE no silane
- 7.3% EPDM

Load

Deflection
Figure 4.42 Compressive Strength As A Function Of % Weight Of UHMWPE Coating

Figure 4.43 Compressive Strength As A Function Of % Weight Of EPDM Coating
Figure 4.44 Compressive Modulus As A Function Of % Weight Of UHMWPE Coating

Figure 4.45 Compressive Modulus As A Function Of % Weight Of EPDM Coating
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On hydrolysis able to form siloxane bond with glass.
FIGURE 5.2: THE POSSIBLE GRAFTING REACTION BETWEEN UHMWPE AND THE SILANE A174
FIGURE 5.3: THE POSSIBLE GRAFTING MECHANISM FOR MALEIC ANHYDRIDE ONTO UHMWPE
free-radical transfer reaction

free-radical transfer reaction

resonance stabilisation

combination reaction

FIGURE 5.4: SECONDARY FREE-RADICAL REACTIONS
Figure 5.5  DSC Thermogram Of The Cured Epoxy Resin

Figure 5.6  Calculated Coating Thickness As A Function Of % Weight Of UHMWPE And EPDM Coatings On Glass Fibres
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Figure 5.8 A Comparison Of Flexural Strength Results As A Function Of % Weight Of Coatings
Figure 5.9 Flexural Strength As A Function Of Interlaminar Shear Strength For UHMWPE And EPDM Composites

Figure 5.10 Impact Strength As A Function Of Interlaminar Shear Strength For UHMWPE And EPDM Composites
Figure 5.11 Initiation Energy As A Function Of Interlaminar Shear Strength
For UHMWPE And EPDM Composites

Correlation coefficient=0.907
FIGURE 6.1: THE DIFFERENT STAGES INVOLVED IN USING THE FINITE ELEMENT APPROACH

Parent mesh

MESHGEN preprocessor

Create input data file defining problem

Finite element programme

Numerical solution

Graphics post-processor

Solution displayed in graphical form
FIGURE 6.2: A 10 ELEMENT COARSE MESH REPRESENTING TWO FIBRES EMBEDDED IN A MATRIX ($V_f = 0.6$)

Figure 6.3a

Figure 6.3b

FIGURE 6.3: TYPICAL 230 ELEMENT REFINED MESSES FOR (a) A COMPOSITE WITHOUT AN INTERLAYER ($V_f = 0.6$) AND (b) A 0.2 $\mu$m INTERLAYERED COMPOSITE
FIGURE 6.4: STRUCTURE OF INPUT DATA FILE

**Format**

80A  Title of File
15   NITER
3I5 2F10 NCN NFP NRP SIF BIF
4I5  NNP NEL NBC NMAT
2F10 GRAVX GRAVY

3F10 2I5 SHM BLM EXP IFR ITO

I5 2F10 NN CORD1 CORD2

Mesh coordinates

10I5 Element connectivity data

2I5  F10 NN DOD MOD

Boundary conditions

FALSE (last line)

where:

NITER = 1, number of iterations
NCN = 9, number of nodes per element
NFP = 1, number of full integration points
NRP = 2, number of reduced integration points
SIF = 1, shear integration factor
BIF = 0, bulk integration factor
NNP = number of nodal points
NEL = number of elements
NBC = number of boundary conditions
NMAT = number of different materials
GRAVX = 0, gravity vector in x direction
GRAVY = 0, gravity vector in y direction
SHM = shear modulus
BLM = bulk modulus
EXP = thermal expansion coefficient
IFR-ITO = first and last element of each material
NN = node number
CORD1 = x coordinate
CORD2 = y coordinate
DOD = direction of displacement (x=1, y=2)
MOD = magnitude of displacement
FIGURE 6.5: SEPARABLE FIBRE MODEL: DISPLACEMENTS IN THE x AND y DIRECTIONS FOR A 0.1% EXTENSION IN THE y DIRECTION

FIGURE 6.6: PLOT TO SHOW THE TYPICAL UNSYMMETRICAL STRESS DISTRIBUTION OBTAINED WITH THE SEPARABLE FIBRE MODEL
Figure 6.7 Comparison Of Transverse Modulus As A Function Of Matrix Modulus Obtained By The Finite Element Method And Tsai Equation
Figure 6.8 Composite Transverse Modulus As A Function Of Interlayer Modulus For Different Interlayer Thicknesses

Figure 6.9 Composite Longitudinal Modulus As A Function Of Interlayer Modulus From Broutman And Agarwal's Work [37]
Figure 6.10 Comparison Of Dynamic Modulus And Predicated Transverse Modulus As A Function Of UHMWPE Interlayer Thickness

Figure 6.11 Comparison Of Dynamic Modulus And Predicated Transverse Modulus As A Function Of EPDM Interlayer Thickness
FIGURE 6.12: CONSTRAINED FIBRE MODEL
DISPLACEMENTS IN THE x AND y DIRECTIONS
FOR A 0.1% EXTENSION AT NODES A AND C
Plot 6.13a
No interlayer

Plot 6.13b
$E_{\text{int}} = 1 \text{ MPa}$

Plot 6.13c
$E_{\text{int}} = 500 \text{ MPa}$

Plot 6.13d
$E_{\text{int}} = 1000 \text{ MPa}$

Plot 6.13e
$E_{\text{int}} = 10 \text{ GPa}$

**FIGURE 6.13:** PLOTS OF TENSILE STRESS DISTRIBUTIONS (IN THE $y$ DIRECTION) FOR A 0.2 $\mu$m INTERLAYER VARYING IN MODULUS ($V_f = 0.6$)
FIGURE 6.14: PLOTS OF TENSILE STRESS DISTRIBUTIONS (IN THE x DIRECTION) FOR A 0.2 μm INTERLAYER VARYING IN MODULUS (V_f = 0.6)
FIGURE 6.15: PLOTS OF SHEAR STRESS DISTRIBUTIONS FOR A 0.2 µm INTERLAYER VARYING IN MODULUS ($V_f = 0.6$)

Plot 6.15a
No interlayer

Plot 6.15b
$E_{int} = 1$ MPa

Plot 6.15c
$E_{int} = 500$ MPa

Plot 6.15d
$E_{int} = 1000$ MPa

Plot 6.15e
$E_{int} = 10$ GPa
1. No interlayer ($V_f=0.6$)
2. 0.2 $\mu$m interlayer,
   $E_{int} = 1$ MPa
3. 0.2 $\mu$m interlayer,
   $E_{int} = 500$ MPa
4. 0.2 $\mu$m interlayer,
   $E_{int} = 1000$ MPa
5. 0.2 $\mu$m interlayer,
   $E_{int} = 1$ GPa

1. 0.65 $\mu$m interlayer, $E_{int} = 1000$ MPa ($V_f=0.6$)
2. No interlayer ($V_f=0.2$)
3. 0.2 $\mu$m interlayer,
   $E_{int} = 1000$ MPa ($V_f=0.2$)

FIGURE 6.16: PLOTS TO SHOW REGIONS OF MAXIMUM VON MISES STRESS
FIGURE 6.17: VARIATION OF SIGMA \( \gamma \) FOR COMPOSITES AT VOLUME FRACTIONS 0.2 AND 0.6 RESULTING FROM A 0.1% EXTENSION IN THE \( \gamma \) DIRECTION.

Plot 6.17a
\( V_f = 0.2 \)
No interlayer

Plot 6.17b
\( V_f = 0.6 \)

Plot 6.17c
\( V_f = 0.2 \)

Plot 6.17d
\( V_f = 0.6 \)
Interlayer Modulus = 1000 MPa
0.2 \( \mu \)m thick

Plot 6.17e
\( V_f = 0.6 \)
Interlayer Modulus = 1000 MPa
0.65 \( \mu \)m thick
Plot 6.18a
$V_f = 0.2$

Plot 6.18b
$V_f = 0.6$

No interlayer

Plot 6.18c
$V_f = 0.2$

Plot 6.18d
$V_f = 0.6$

Interlayer Modulus = 1000 MPa
0.2 \mu m thick

Plot 6.18e
$V_f = 0.6$

Interlayer Modulus = 1000 MPa
0.65 \mu m thick

FIGURE 6.18: VARIATION OF SIGMA $\sigma_x$ FOR COMPOSITES AT VOLUME FRACTIONS 0.2 AND 0.6 RESULTING FROM A 0.1% EXTENSION IN THE $y$ DIRECTION
FIGURE 6.19: VARIATION OF Tau xy FOR COMPOSITES AT VOLUME FRACTIONS 0.2 AND 0.6 RESULTING FROM A 0.1% EXTENSION IN THE y DIRECTION

Plot 6.19a
\( V_f = 0.2 \)

Plot 6.19b
\( V_f = 0.6 \)

No interlayer

Interlayer Modulus = 1000 MPa. 0.2 \( \mu \)m thick

Interlayer Modulus = 1000 MPa. 0.65 \( \mu \)m thick
Figure 6.20  Maximum Stresses As A Function Of Interlayer Modulus
As Predicated By The Constrained Fibre Model

Figure 6.21  Strain Energy Absorbed As A Function Of Interlayer Modulus
(Broutman And Agarwal,37)
TABLES
<table>
<thead>
<tr>
<th>Organofunctional R Group</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl</td>
<td>$\text{CH}_2 = \text{CHSi(OCH}_3)_3$</td>
</tr>
<tr>
<td>Chloropropyl</td>
<td>$\text{Cl CH}_2 \text{CH}_2 \text{CH}_2 \text{Si(OCH}_3)_3$</td>
</tr>
<tr>
<td>Epoxy</td>
<td>$\text{CH}_2 \text{CH CH}_2 \text{OCH}_2 \text{CH}_2 \text{CH}_2 \text{Si(OCH}_3)_3$</td>
</tr>
<tr>
<td>Methacrylate</td>
<td>$\text{CH}_2 = \text{C} - \text{COOCH}_2 \text{CH}_2 \text{CH}_2 \text{Si(OCH}_3)_3$</td>
</tr>
<tr>
<td>Primary Amine</td>
<td>$\text{H}_2 \text{N CH}_2 \text{CH}_2 \text{CH}_2 \text{Si(OCH}_2\text{H}_5)_3$</td>
</tr>
<tr>
<td>Diamine</td>
<td>$\text{H}_2 \text{N CH}_2 \text{CH}_2 \text{NH CH}_2 \text{CH}_2 \text{CH}_2 \text{Si(OCH}_3)_3$</td>
</tr>
<tr>
<td>Mercapto</td>
<td>$\text{HS CH}_2 \text{CH}_2 \text{CH}_2 \text{Si(OCH}_3)_3$</td>
</tr>
<tr>
<td>Cationic styryl</td>
<td>$\text{CH}_2 = \text{OC}	ext{H}_2\text{H}_4\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH(CH}_2)_3 \text{Si(OCH}_3)_3 \cdot \text{HCl}$</td>
</tr>
</tbody>
</table>

**TABLE 2.1:** TYPICAL COMMERCIAL SILANE COUPLING AGENTS
<table>
<thead>
<tr>
<th></th>
<th>Mix 1</th>
<th>Mix 2</th>
<th>Mix 3</th>
<th>Mix 4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(g)</td>
<td>(g)</td>
<td>(g)</td>
<td>(g)</td>
</tr>
<tr>
<td>Elastomer</td>
<td>Sulphonated EPDM (Uniroyal Il025)</td>
<td>Sulphonated EPDM (Uniroyal Il025)</td>
<td>Sulphonated EPDM II025</td>
<td>EPDM 25g 5% diene content</td>
</tr>
<tr>
<td></td>
<td>very low diene content</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silane</td>
<td>Union Carbide A174 0.75g Dow Corning Z6032 0.75g Union Carbide A174 0.75g Union Carbide A189 0.75g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic Peroxide</td>
<td>Benzoyl 0.05g Peroxide 0.2phr</td>
<td>Dicumyl Peroxide 0.05g CBS Accel-erator 0.25g 1 phr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixing Temp °C</td>
<td>140°C 140°C 180°C 140°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixing time</td>
<td>10 mins 10 mins 10 mins 10 mins</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Uniroyal II025 1.1% by wt of ionic groups

\[
A174 \text{ gamma-methacryloxypropyltrimethoxysilane } \ CH_2 = C \overset{\text{CH}_3}{\text{COO(CH}_2)_3\text{Si(OCH}_3)_3}
\]

\[
Z6032 \text{ cationic vinylbenzylsilane } (\text{CH}_3\text{O})_3\text{Si(CH}_2)_3\text{NHC}_2\text{H}_2\text{NHCH}_2\text{C}_6\text{H}_4 \text{CH=CH}_2 \text{ HCl}
\]

\[
A189 \text{ mercaptopropyltrimethoxysilane } \text{HS(CH}_2)_3\text{Si(OCH}_3)_3
\]

\[
\text{CBS } \text{N-cyclohexylbenzthiazylsulphenamide }
\]

\[
\text{Benzoyl peroxide } \overset{\text{CH}_3}{\text{C=O-O-C}}\text{O}
\]

\[
\text{Dicumyl peroxide } \overset{\text{CH}_3}{\text{C-O-O-C}}\text{CH}_3
\]

\[
\text{TABLE 3.1: EPDM FORMULATIONS USED FOR SILANE GRAFTING IN THE MELT STATE}
\]
<table>
<thead>
<tr>
<th>Solution 1 Wt(g)</th>
<th>Solution 2 Wt(g)</th>
<th>Solution 3 Wt(g)</th>
<th>Solution 4 Wt(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM 5% diene content</td>
<td>2.5g</td>
<td>Sulphonated EPDM I1025</td>
<td>1g</td>
</tr>
<tr>
<td>Silane A189</td>
<td>2.5g</td>
<td>Silane Z6032</td>
<td>1g</td>
</tr>
<tr>
<td>CBS Accele- rator</td>
<td>0.025g</td>
<td>Xylene</td>
<td>50g</td>
</tr>
<tr>
<td>Xylene</td>
<td>50g</td>
<td>Xylene</td>
<td>50g</td>
</tr>
</tbody>
</table>

**TABLE 3.2:** EPDM FORMULATIONS USED FOR SILANE GRAFTING IN THE SOLUTION STATE
<table>
<thead>
<tr>
<th>Solution Preparation</th>
<th>Number of Passes</th>
</tr>
</thead>
<tbody>
<tr>
<td>No silane treatment</td>
<td>2% UHMWPE solution (6.88g in 400 ml xylene)</td>
</tr>
<tr>
<td>Smallest thickness</td>
<td>0.5% UHMWPE solution (1.72g in 400 ml xylene) 2% Al74 (0.034g) 0.5% benzoyl peroxide (0.009g) UHMWPE Refluxed for 4 hrs at 100°C</td>
</tr>
<tr>
<td>Intermediate thickness</td>
<td>2% UHMWPE solution (6.88g in 400 ml xylene) 2% Al74 (0.138g) 0.5% benzoyl peroxide (0.034g) Refluxed for 4 hrs at 100°C</td>
</tr>
<tr>
<td>Largest thickness</td>
<td>As above 3 freshly prepared solutions used</td>
</tr>
</tbody>
</table>

**TABLE 3.3: EXPERIMENTAL CONDITIONS USED TO APPLY UHMWPE TO GLASS FIBRES**

<table>
<thead>
<tr>
<th>Solution Preparation</th>
<th>Number of Passes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest thickness</td>
<td>0.5% EPDM solution (1.72g in 400 ml xylene) 5% Al89 (0.086g) 0.5% CBS (0.009g) Stirred for 15 mins at 100°C 2% DCP (0.0344g) added on cooling</td>
</tr>
<tr>
<td>Intermediate thickness</td>
<td>2% EPDM solution (6.88g in 400 ml xylene) 5% Al89 (0.344g) 0.5% CBS (0.034g) Stirred for 15 mins at 100°C 2% DCP (0.138g) added on cooling</td>
</tr>
<tr>
<td>Largest thickness</td>
<td>4% EPDM solution (13.76g in 400 ml xylene) 5% Al89 (0.688g) 0.5% CBS (0.068g) Stirred for 15 mins at 100°C 2% DCP (0.275g) added on cooling</td>
</tr>
</tbody>
</table>

**TABLE 3.4: EXPERIMENTAL CONDITIONS USED TO APPLY EPDM TO GLASS FIBRES**
<table>
<thead>
<tr>
<th>EPDM Silane System</th>
<th>Sulphonated EPDM Al89</th>
<th>Sulphonated EPDM 26032</th>
<th>Sulphonated EPDM Al74 DCP</th>
<th>EPDM Al89 System</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Mix 1)</td>
<td>(Mix 2)</td>
<td>(Mix 3)</td>
<td>(Mix 4)</td>
</tr>
<tr>
<td>Extent of bonding to glass</td>
<td>Peeled easily off glass slide, rubber crosslinked</td>
<td>After persistent peeling bond failed</td>
<td>After persistent peeling bond failed rubber crosslinked</td>
<td>Cohesive failure of polymer. Good bonding to glass</td>
</tr>
</tbody>
</table>

**TABLE 4.1: QUALITATIVE RESULTS FROM GRAFTING SILANES ONTO EPDM IN THE MELT STATE**

<table>
<thead>
<tr>
<th>EPDM Silane System</th>
<th>EPDM Al89 (Solution 1)</th>
<th>Sulphonated EPDM 26032 (Solution 2)</th>
<th>EPDM Z6032 (Solution 3)</th>
<th>Polybutadiene Al89 (Solution 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extent of bonding to glass</td>
<td>Film not peelable off glass, cohesive failure of rubber</td>
<td>Bond failure after persistent peeling</td>
<td>Peeled easily off glass slide</td>
<td>Good bond to glass, cohesive failure of polymer</td>
</tr>
</tbody>
</table>

**TABLE 4.2: QUALITATIVE RESULTS FROM GRAFTING SILANES ONTO EPDM IN THE SOLUTION STATE**
<table>
<thead>
<tr>
<th>Absorbance SiOCH₃</th>
<th>Control film EPDM A189 (1:1) mixed at room temperature for 10 mins</th>
<th>Heat treated film EPDM A189 (1:1) mixed at 100°C for 10 mins</th>
</tr>
</thead>
<tbody>
<tr>
<td>No propan-2-ol extraction</td>
<td>0.30</td>
<td>0.32</td>
</tr>
<tr>
<td>After one day of propan-2-ol extraction</td>
<td>0.032</td>
<td>0.042</td>
</tr>
<tr>
<td>After five days of propan-2-ol extraction</td>
<td>0.020</td>
<td>0.034</td>
</tr>
</tbody>
</table>

**TABLE 4.3: ABSORBANCE RATIOS FOR EPDM A189 FILMS**

<table>
<thead>
<tr>
<th>Maleic Anhydride Treatment</th>
<th>Absorbance Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before methanol wash</td>
</tr>
<tr>
<td>2% maleic anhydride</td>
<td>0.03</td>
</tr>
<tr>
<td>10% maleic anhydride</td>
<td>0.475</td>
</tr>
<tr>
<td>10% maleic anhydride no peroxide</td>
<td>0.11</td>
</tr>
<tr>
<td>10% maleic anhydride film heated at 80°C, 3 hrs</td>
<td>0.62</td>
</tr>
</tbody>
</table>

**TABLE 4.4: FTIR ANALYSIS OF MALEIC ANHYDRIDE TREATED UHMWPE**
<table>
<thead>
<tr>
<th>Mean % weight of coating on fibres</th>
<th>UHMWPE</th>
<th>EPDM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lowest level</td>
<td>2.8</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>1.6</td>
</tr>
<tr>
<td>Intermediate level</td>
<td>3.7</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>3.5</td>
</tr>
<tr>
<td>Highest level</td>
<td>4.2</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>4.8</td>
<td>7.3</td>
</tr>
<tr>
<td>No silane treatment</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 4.5: AMOUNTS OF UHMWPE AND EPDM ON GLASS FIBRES IN THE INTERLAYERED COMPOSITES**

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Water absorption (mean % weight gain)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Undamaged</td>
</tr>
<tr>
<td>1</td>
<td>0.177</td>
</tr>
<tr>
<td>3</td>
<td>0.602</td>
</tr>
<tr>
<td>4</td>
<td>0.675</td>
</tr>
<tr>
<td>17</td>
<td>2.085</td>
</tr>
</tbody>
</table>

**TABLE 4.6: WATER ABSORPTION RESULTS FROM DAMAGE ASSESSMENT TEST**
<table>
<thead>
<tr>
<th>Sample</th>
<th>Glass transition temperature of epoxy resin (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy resin</td>
<td>142</td>
</tr>
<tr>
<td>Control composite</td>
<td>147</td>
</tr>
<tr>
<td>2.8% UHMWPE composite</td>
<td>143</td>
</tr>
<tr>
<td>3.7% UHMWPE composite</td>
<td>141</td>
</tr>
<tr>
<td>4.2% UHMWPE composite</td>
<td>139.5</td>
</tr>
<tr>
<td>4.6% UHMWPE composite (no silane)</td>
<td>139</td>
</tr>
<tr>
<td>1.2% EPDM composite</td>
<td>141.5</td>
</tr>
<tr>
<td>3.4% EPDM composite</td>
<td>138.5</td>
</tr>
<tr>
<td>8.2% EPDM composite</td>
<td>136.5</td>
</tr>
</tbody>
</table>

**TABLE 4.7: GLASS TRANSITION TEMPERATURES OF THE EPOXY RESIN IN VARIOUS INTERLAYERED COMPOSITES**

<table>
<thead>
<tr>
<th>Composite</th>
<th>Tanδ at Tg (x 10^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>2.92</td>
</tr>
<tr>
<td>2.8% UHMWPE</td>
<td>3.85</td>
</tr>
<tr>
<td>3.7% UHMWPE</td>
<td>4.05</td>
</tr>
<tr>
<td>4.2% UHMWPE</td>
<td>3.58</td>
</tr>
<tr>
<td>4.6% UHMWPE (no silane)</td>
<td>3.60</td>
</tr>
<tr>
<td>1.2% EPDM</td>
<td>2.75</td>
</tr>
<tr>
<td>3.4% EPDM</td>
<td>2.98</td>
</tr>
<tr>
<td>8.2% EPDM</td>
<td>3.16</td>
</tr>
</tbody>
</table>

**TABLE 4.8: VALUES OF TANδ AT THE GLASS TRANSITION TEMPERATURE OF THE EPOXY RESIN**
<table>
<thead>
<tr>
<th>Composite</th>
<th>Void Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.35</td>
</tr>
<tr>
<td>2.8% UHMWPE</td>
<td>1.5</td>
</tr>
<tr>
<td>3.7% UHMWPE</td>
<td>2.2</td>
</tr>
<tr>
<td>4.2% UHMWPE</td>
<td>2.0</td>
</tr>
<tr>
<td>4.6% UHMWPE (no silane)</td>
<td>2.4</td>
</tr>
<tr>
<td>1.2% EPDM</td>
<td>0.8</td>
</tr>
<tr>
<td>3.4% EPDM</td>
<td>1.9</td>
</tr>
<tr>
<td>8.2% EPDM</td>
<td>2.95</td>
</tr>
</tbody>
</table>

TABLE 4.9: VOID CONTENT RESULTS
<table>
<thead>
<tr>
<th>Authors</th>
<th>Interlayer</th>
<th>Interlayer thickness</th>
</tr>
</thead>
</table>
| Hancox and Wells [39]   | Carbon fibres coated with a silicone rubber from solution                  | Calculated maximum thickness = 0.2 μm  
Critical thickness = 0.03 μm  
(above which reduction in flexural strength observed) |
| Peiffer [42] and Nielsen [43] | Glass fibres encapsulated with a rubbery acrylic polymer | Calculated latex thickness = 0.1 μm |
| Gerard [49]             | Carbon fibres coated with a CBTN epoxy elastomer solution concentrations   | Calculated thickness of coatings =  
0.02 μm (min) − 0.4 μm (max) |
| Bell et al [53]         | Electropolymerised a methyl acrylate acrylonitrile copolymer onto carbon fibres | Coating thickness = 0.2 μm |
| McGarry [47] et al      | Carbon fibres coated with a CBTN rubber from solution concentrations       | Calculated coating thickness = 0.05-0.1 μm |

**TABLE 5.1: CALCULATED INTERLAYER THICKNESSES OF PREVIOUS WORKERS**
<table>
<thead>
<tr>
<th>Author</th>
<th>Reduction in interlaminar shear strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>40% (2.8% UHMWPE) - 67% (4.2% UHMWPE)</td>
</tr>
<tr>
<td></td>
<td>16% (1.2% EPDM) - 68% (8.2% EPDM)</td>
</tr>
<tr>
<td>Enever [36]</td>
<td>27% (1% solution concentration) -</td>
</tr>
<tr>
<td>Carbon fibres coated with a polyurethane</td>
<td>48% (6% solution concentration)</td>
</tr>
<tr>
<td>Hancox and Wells [39]</td>
<td>66% reduction with 6% coating</td>
</tr>
<tr>
<td>Carbon fibres coated with a silicone rubber</td>
<td></td>
</tr>
<tr>
<td>Bell et al [53]</td>
<td>23% reduction with 13% coating</td>
</tr>
<tr>
<td>Electropolymerisation of methyl acrylate acrylonitrile onto carbon fibres</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 5.2: A COMPARISON OF THE REDUCTIONS OBSERVED IN INTERLAMINAR SHEAR STRENGTH**
<table>
<thead>
<tr>
<th>Number of Elements</th>
<th>Transverse Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>6732</td>
</tr>
<tr>
<td>170</td>
<td>8495</td>
</tr>
<tr>
<td>230</td>
<td>10619 (-5%)</td>
</tr>
<tr>
<td>480</td>
<td>11733 (+5%)</td>
</tr>
<tr>
<td>Tsai equation</td>
<td>11155</td>
</tr>
</tbody>
</table>

**TABLE 6.1: EFFECT OF MESH REFINEMENT ON THE FINITE ELEMENT SOLUTION**
PLATES
PLATE 4.1: OPTICAL MICROGRAPH OF XYLENE WASHED GLASS FILAMENTS X140

PLATE 4.2: OPTICAL MICROGRAPH TO SHOW THE TYPICAL UHMWPE COATINGS ON GLASS FIBRES, X140
PLATE 4.6: OPTICAL MICROGRAPH OF A THICK COATING AROUND A FIBRE BUNDLE OBTAINED BY DIPPING INTO A 5% SILANE GRAFTED EPDM SOLUTION, X140

PLATE 4.7: OPTICAL MICROGRAPH OF THE TYPICAL COATING DISTRIBUTION IN THE 2.8% UHMWPE INTERLAYERED COMPOSITE, X200
PLATES 4.4 & 4.5: SCANNING ELECTRON MICROGRAPHS OF THE TYPICAL COATINGS OBTAINED BY DIPPING GLASS FIBRES INTO A SILANE GRAFTED UHMWPE SOLUTION AT 110°C

Plate 4.4: X400

Plate 4.5: X365
PLATE 4.6: OPTICAL MICROGRAPH OF A THICK COATING AROUND A FIBRE BUNDLE OBTAINED BY DIPPING INTO A 5% SILANE GRAFTED EPDM SOLUTION, X140

PLATE 4.7: OPTICAL MICROGRAPH OF THE TYPICAL COATING DISTRIBUTION IN THE 2.8% UHMWPE INTERLAYERED COMPOSITE, X200
Plate 4.8: Optical micrograph of the typical UHMWPE coating around a fibre bundle in the intermediate level (3.7%) interlayered composite, x100

Plate 4.9: Optical micrograph of the typical coating distribution in the high level (4.2%) UHMWPE interlayered composite, x100
PLATE 4.10: OPTICAL MICROGRAPH TO SHOW THE TYPICAL LUMPY COATING REGIONS IN THE HIGH LEVEL (4.2%) UHMWPE INTERLAYERED COMPOSITE, X100

PLATE 4.11: OPTICAL MICROGRAPH OF THE TYPICAL COATING OBSERVED IN THE INTERMEDIATE LEVEL (3.4%) EPDM INTERLAYERED COMPOSITE, X100
PLATE 4.12: OPTICAL MICROGRAPH OF THE TYPICAL HIGH LEVEL (8.0%) EPDM COATINGS - PENETRATE FURTHER INTO FIBRE BUNDLES, X100

PLATE 4.13: SCANNING ELECTRON MICROGRAPH OF A SINGLE INTERLAMINAR SHEAR CRACK IN A CONTROL COMPOSITE, X80
PLATE 4.14: SCANNING ELECTRON MICROGRAPH OF SEVERAL INTERLAMINAR SHEAR CRACKS PROPAGATING THROUGH UHMWPE COATINGS, X50

PLATE 4.15: OPTICAL MICROGRAPH OF AN INTERLAMINAR SHEAR CRACK PROPAGATING THROUGH AN EPDM COATING, X100
PLATES 4.16-4.18: SCANNING ELECTRON MICROGRAPHS TO SHOW THE DUCTILE DEFORMATION OF UHR-MPE INTERLAYERS

Plate 4.16: X10K

Plate 4.17: X2.8K
Plate 4.18: X9K

Plate 4.19: SCANNING ELECTRON MICROGRAPH OF A DELAMINATED FRACTURE SURFACE FOR A HIGH LEVEL (4.2%) UHMWPE INTERLAYERED COMPOSITE, X150
<table>
<thead>
<tr>
<th>EPDM Silane A189 Treatment</th>
<th>Shear Strength (MPa)</th>
<th>Mode of Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM Silane A189 (1:1)</td>
<td>0.22</td>
<td>Cohesive failure of polymer</td>
</tr>
<tr>
<td>0.2 mm EPDM thickness</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>Mean = 0.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sandwich sample (Figure 3.3)</td>
<td>0.31</td>
<td>EPDM glass bond failure</td>
</tr>
<tr>
<td>5% EPDM solution</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>No silane A189 or DCP</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>0.04 mm EPDM thickness</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>Mean = 0.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sandwich sample</td>
<td>0.97</td>
<td>EPDM glass bond failure (some EPDM on glass)</td>
</tr>
<tr>
<td>5% EPDM solution</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>EPDM A189 (1:1)</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>2% DCP</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td>0.04 mm EPDM thickness</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>Mean = 0.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As above but 2%</td>
<td>1.02</td>
<td>As above</td>
</tr>
<tr>
<td>EPDM solution</td>
<td>1.85</td>
<td></td>
</tr>
<tr>
<td>0.01 mm EPDM thickness</td>
<td>2.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.37</td>
<td></td>
</tr>
<tr>
<td>Mean = 1.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As above but 1%</td>
<td>1.60</td>
<td>Glass EPDM/UHMWPE interface failure</td>
</tr>
<tr>
<td>EPDM solution</td>
<td>2.04</td>
<td></td>
</tr>
<tr>
<td>0.005 mm EPDM thickness</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.73</td>
<td></td>
</tr>
<tr>
<td>Mean = 1.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As above but 5%</td>
<td>3.00</td>
<td>EPDM UHMWPE</td>
</tr>
<tr>
<td>A189 (based on EPDM)</td>
<td>4.5</td>
<td>interface failure</td>
</tr>
<tr>
<td></td>
<td>3.73</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>Mean = 4.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As above but UHMWPE plaques primed with EPDM solution</td>
<td>2.83</td>
<td>EPDM UHMWPE interface failure</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.78</td>
<td></td>
</tr>
<tr>
<td>Mean = 2.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silane Treatment (UHMWPE thickness = 0.2 mm)</td>
<td>Shear Strength (MPa)</td>
<td>Mode of Failure</td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>---------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>No silane treatment</td>
<td>0.98</td>
<td>Glass UHMWPE bond failure</td>
</tr>
<tr>
<td></td>
<td>1.42</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.72</td>
<td></td>
</tr>
<tr>
<td>Mean = 1.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2% silane Z6032 0.5% benzoyl peroxide 4 hr reflux</td>
<td>2.64</td>
<td>Glass UHMWPE bond failure</td>
</tr>
<tr>
<td></td>
<td>4.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.58</td>
<td></td>
</tr>
<tr>
<td>Mean = 3.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As above but 24 hr reflux</td>
<td>3.83</td>
<td>As above</td>
</tr>
<tr>
<td></td>
<td>3.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.47</td>
<td></td>
</tr>
<tr>
<td>Mean = 3.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2% silane Al74 0.5% benzoyl peroxide 4 hr reflux</td>
<td>7.44</td>
<td>Partial UHMWPE glass bond failure</td>
</tr>
<tr>
<td></td>
<td>7.00</td>
<td>Deformation of UHMWPE</td>
</tr>
<tr>
<td></td>
<td>8.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.81</td>
<td></td>
</tr>
<tr>
<td>Mean = 6.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2% silane Z6032 4 hr reflux Slides primed with 0.5% silane Z6032</td>
<td>6.58</td>
<td>As above</td>
</tr>
<tr>
<td></td>
<td>8.21</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.42</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.76</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.69</td>
<td></td>
</tr>
<tr>
<td>Mean = 7.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2% silane Al74 Slides primed with 0.5% silane Z6032</td>
<td>12.19</td>
<td>As above</td>
</tr>
<tr>
<td></td>
<td>10.74</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.89</td>
<td></td>
</tr>
<tr>
<td></td>
<td>11.63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>11.97</td>
<td></td>
</tr>
<tr>
<td>Mean = 11.48</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE A3: EPOXY LAP SHEAR TEST RESULTS

<table>
<thead>
<tr>
<th>Maleic Anhydride Treatment</th>
<th>Shear Strength (MPa)</th>
<th>Mode of Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>No treatment</td>
<td>1.76</td>
<td>Epoxy UHMWPE bond failure</td>
</tr>
<tr>
<td></td>
<td>1.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.42</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.68</td>
<td></td>
</tr>
<tr>
<td>Mean = 1.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.15</td>
<td>As above</td>
</tr>
<tr>
<td>2% maleic maleic anhydride</td>
<td>2.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.19</td>
<td></td>
</tr>
<tr>
<td>0.5% benzoyl peroxide</td>
<td>2.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.70</td>
<td></td>
</tr>
<tr>
<td>Mean = 2.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6% maleic maleic anhydride</td>
<td>2.75</td>
<td>As above</td>
</tr>
<tr>
<td></td>
<td>2.98</td>
<td></td>
</tr>
<tr>
<td>0.5% benzoyl peroxide</td>
<td>2.95</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.26</td>
<td></td>
</tr>
<tr>
<td>Mean = 2.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% maleic maleic anhydride</td>
<td>3.75</td>
<td>As above remaining UHMWPE difficult to peel off epoxy layer</td>
</tr>
<tr>
<td></td>
<td>3.02</td>
<td></td>
</tr>
<tr>
<td>0.5% benzoyl peroxide</td>
<td>3.48</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td>Mean = 3.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2% silane A174</td>
<td>5.10</td>
<td>As above</td>
</tr>
<tr>
<td>0.5% benzoyl peroxide</td>
<td>4.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.95</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.27</td>
<td></td>
</tr>
<tr>
<td>Mean = 4.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composite</td>
<td>Interlaminar Shear Strength (MPa)</td>
<td></td>
</tr>
<tr>
<td>-----------------</td>
<td>-----------------------------------</td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>66.69 65.58 65.33 Mean = 65.87</td>
<td></td>
</tr>
<tr>
<td>2.8% UHMWPE</td>
<td>41.37 38.31 38.07 Mean = 39.25</td>
<td></td>
</tr>
<tr>
<td>3.7% UHMWPE</td>
<td>29.28 30.36 29.53 Mean = 29.72</td>
<td></td>
</tr>
<tr>
<td>4.2% UHMWPE</td>
<td>22.43 21.68 20.54 Mean = 21.55</td>
<td></td>
</tr>
<tr>
<td>4.6% UHMWPE</td>
<td>18.46 16.30 18.15 Mean = 17.64</td>
<td></td>
</tr>
<tr>
<td>No silane</td>
<td>56.17 55.36 53.81 Mean = 55.11</td>
<td></td>
</tr>
<tr>
<td>1.2% EPDM</td>
<td>38.17 36.56 36.35 Mean = 37.03</td>
<td></td>
</tr>
<tr>
<td>8.2% EPDM</td>
<td>21.03 21.34 20.17 Mean = 20.85</td>
<td></td>
</tr>
<tr>
<td>Composite</td>
<td>Flexural Strength (MPa)</td>
<td>Secant Modulus at $\varepsilon = 0.0075$ (GPa)</td>
</tr>
<tr>
<td>---------------</td>
<td>-------------------------</td>
<td>-----------------------------------------------</td>
</tr>
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<td></td>
</tr>
<tr>
<td>4.2% UHMWPE</td>
<td>647.3</td>
<td>19.67</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>591.5</td>
<td>19.36</td>
<td></td>
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</tr>
<tr>
<td>No silane</td>
<td>648.9</td>
<td>18.75</td>
<td>63.3</td>
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<tr>
<td></td>
<td>589.8</td>
<td>19.84</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>571.9</td>
<td>19.39</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>604.7</td>
<td>20.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean = 609</td>
<td>Mean = 19.53</td>
<td>(577)</td>
<td>(18.51)</td>
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<td></td>
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</table>

\Continued
TABLE A7 (continued)

<table>
<thead>
<tr>
<th>Composite</th>
<th>Compressive Strength (MPa)</th>
<th>Compressive Modulus at $\varepsilon = -1%$ (GPa)</th>
<th>Fibre Volume Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6% EPDM</td>
<td>668.4</td>
<td>18.39</td>
<td></td>
</tr>
<tr>
<td></td>
<td>782.6</td>
<td>18.83</td>
<td></td>
</tr>
<tr>
<td></td>
<td>704.1</td>
<td>18.71</td>
<td>61.2</td>
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<td></td>
<td>616.9</td>
<td>18.79</td>
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<tr>
<td></td>
<td>624.3</td>
<td>17.17</td>
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</tr>
<tr>
<td></td>
<td>612.0</td>
<td>19.21</td>
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</tr>
<tr>
<td>Mean = 668</td>
<td>Mean = 18.52</td>
<td>(655)</td>
<td>(18.16)</td>
</tr>
<tr>
<td>3.5% EPDM</td>
<td>416.8</td>
<td>15.87</td>
<td></td>
</tr>
<tr>
<td></td>
<td>482.2</td>
<td>17.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>445.1</td>
<td>18.30</td>
<td>61.8</td>
</tr>
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<td></td>
<td>439.3</td>
<td>19.16</td>
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<tr>
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<td>474.9</td>
<td>15.60</td>
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<td>381.5</td>
<td>15.54</td>
<td></td>
</tr>
<tr>
<td>Mean = 440</td>
<td>Mean = 16.96</td>
<td>(427)</td>
<td>(16.47)</td>
</tr>
<tr>
<td>7.3% EPDM</td>
<td>208.3</td>
<td>14.98</td>
<td></td>
</tr>
<tr>
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<td>194.1</td>
<td>15.33</td>
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</tr>
<tr>
<td></td>
<td>186.6</td>
<td>16.60</td>
<td>63.3</td>
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<td>143.7</td>
<td>14.32</td>
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<td>169.8</td>
<td>14.67</td>
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<tr>
<td></td>
<td>153.2</td>
<td>17.47</td>
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</tr>
<tr>
<td>Mean = 176</td>
<td>Mean = 15.56</td>
<td>(166)</td>
<td>(14.75)</td>
</tr>
</tbody>
</table>

( ) Normalised to a 60% fibre volume fraction
### TABLE A8: VOID CONTENT RESULTS

<table>
<thead>
<tr>
<th>Composite</th>
<th>Measured Density (g/cm³)</th>
<th>Theoretical Density (g/cm³)</th>
<th>Void Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>2.0691 2.0703</td>
<td>2.0769</td>
<td>0.38 0.32</td>
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<td>Mean = 0.35</td>
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<tr>
<td>2.8% UHMWPE</td>
<td>2.0447 2.0329</td>
<td>2.0691</td>
<td>1.18 1.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mean = 1.5</td>
</tr>
<tr>
<td>3.7% UHMWPE</td>
<td>1.9934 2.0075</td>
<td>2.0458</td>
<td>2.56 1.87</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mean = 2.2</td>
</tr>
<tr>
<td>4.2% UHMWPE</td>
<td>2.0118 2.0017</td>
<td>2.0474</td>
<td>1.74 2.23</td>
</tr>
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<td></td>
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<td>Mean = 2.0</td>
</tr>
<tr>
<td>4.6% UHMWPE</td>
<td>2.0033 1.9907</td>
<td>2.0459</td>
<td>2.08 2.70</td>
</tr>
<tr>
<td>No silane</td>
<td></td>
<td></td>
<td>Mean = 2.4</td>
</tr>
<tr>
<td>1.2% EPDM</td>
<td>2.0236 2.0275</td>
<td>2.0422</td>
<td>0.91 0.72</td>
</tr>
<tr>
<td></td>
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<td>Mean = 0.8</td>
</tr>
<tr>
<td>3.4% EPDM</td>
<td>2.0025 1.9939</td>
<td>2.0367</td>
<td>1.68 2.10</td>
</tr>
<tr>
<td></td>
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<td>Mean = 1.9</td>
</tr>
<tr>
<td>8.2% EPDM</td>
<td>1.9436 1.9474</td>
<td>2.0045</td>
<td>3.04 2.85</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>Mean = 2.95</td>
</tr>
</tbody>
</table>