"...... he had been eight years upon a project for extracting sunbeams out of cucumbers, which were to be put in vials hermetically sealed, and let out to warm the air in raw inclement summers.........

...... I made him (the Projector) a small present, for my lord had furnished me with money on purpose, because he knew their practice of begging from all who go to see them."

Jonathan Swift in Gulliver's Travels; A Voyage to Laputa - A visit to the Grand Academy of Lagado (1726).
A STUDY OF STRESS-INDUCED WHITENING

IN GLASS FIBRE REINFORCED EPOXY LAMINATES

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SYNOPSIS

The aim of this study has been to investigate stress-induced whitening in glass fibre/epoxy (0,90)_s laminates and to develop a technique to monitor the low strain damage associated with it. The effect of resin cure, laminate geometry, heat treatment and surface finish of glass fibres on the extent and development of damage has also been studied.

It has been found that the whitening is caused by the development of micro-cracks in the resin. The micro-cracks developed in the 90° ply and occurred predominantly at or near points of contact between fibres where the strain magnification in the resin is highest. The cracks occurred near the fibre/matrix interface and extended into the resin with the crack faces lying at 90° to the loading axis.

Careful observation under oblique illumination conditions has shown that the whitening effect is preceded by other colour effects so that the laminate is observed to gradually change colour from an original blue through to red or white depending on the level of cure of the matrix resin. The whitening is a result of ordinary diffuse reflections from cracks that are larger than the wavelength of light and occurs when the level of cure of the matrix system is low while the reddening is the result of Rayleigh or Mie scattering from cracks that are smaller than the wavelength of light and occurs when the level of cure of the matrix is high.

An off-axis LASER diffraction technique has been developed to monitor the amount of damage in the transverse ply of laminates by measurement of the intensity of light diffracted by the micro-cracks. In addition to confirming the results obtained from photomicroscopy, it revealed that decreasing the inner 90° ply thickness in (0,90)_s laminates resulted in a substantial increase in the amount of microdamage in the laminate. Heat treatment of the laminate after testing resulted in the disappearance of whitening and healing of micro-cracks in the resin which continues to cure during heat treatment. Successive heat treatments reduced the size of micro-cracks which developed on reloading. In addition to decreasing the rate of re-development of the original cracks on reloading, the heat treatment reduced the rate of development of "new" cracks formed at higher applied strains.
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LIST OF MAIN SYMBOLS

\( E_{f,m} \) Elastic modulus of fibre, resin
\( E_1 \) Elastic modulus of 0° unidirectional lamina
\( E_t \) Elastic modulus of 90° unidirectional lamina
\( E_c \) Elastic modulus of laminate
\( \Delta E \) Mean reduction in laminate modulus before transverse cracking
\( G_t \) Shear modulus of 90° ply

\( \sigma_a \) Applied stress
\( \sigma^1 \) Stress parallel to fibres in the 0° ply
\( \sigma^2 \) Stress parallel to fibre in the 90° ply
\( \sigma_{db} \) Debonding stress
\( \sigma_{mn} \) Axial stress on minimum section of testpiece
\( \sigma_y \) Yield stress
\( \sigma_c \) Stress at critical distance ahead of crack
\( \tau \) Interlaminar shear stress
\( P \) Applied load

\( \varepsilon_a \) Applied strain
\( \varepsilon_t \) Transverse strain in 0° ply
\( \varepsilon_1 \) Longitudinal strain in 90° ply
\( \varepsilon_f \) Fracture strain of resin
\( \varepsilon_{db} \) Debonding strain
\( \varepsilon_{tc} \) First transverse ply cracking strain
\( \varepsilon_{th} \) Thermal strain in the transverse ply in the longitudinal direction

\( \nu_{f,m} \) Poisson's ratio of fibre, matrix
\( V_{f,m} \) Volume fraction of fibres, matrix
\( V_0 \) Volume fraction of fibres in the 0° ply
\( V_{90} \) Volume fraction of fibres in the 90° ply

\( G_c \) Critical strain energy release rate
\( G(L) \) Strain energy release rate parallel to fibres in 90° ply
\( G_c(L) \) Critical strain energy release rate parallel to fibres in the 90° ply
$K_c$ Critical stress intensity factor
$\gamma_f$ Fracture surface energy per unit area of transverse ply
$l_r$ Length of slow crack growth region in resin
$r_c$ Radius of Dugdale plastic zone
$
\alpha_{f,m}$ Thermal expansion coefficient of fibre, matrix
$
\alpha_f$ Thermal expansion coefficient of 0° ply
$
\alpha_t$ Thermal expansion coefficient of 90° ply
$D_t$ Density at temperature, $T$
$D_{f,m}$ Density of fibre, matrix
$T_g$ Glass transition temperature
$T_1$ Stress free temperature
$T_2$ Temperature of measurement
$\tan \delta$ Loss tangent
$\log k$ log of dynamic modulus
$W_c$ Weight of composite
$W_f$ Weight of fibres
$W_r$ Weight of resin
$N$ Number of plies
$C$ Number of tows per unit width
$F$ Fibre tow weight per metre
$s$ Distance between fibres
$r$ Radius of fibre
$V$ Volume
$U$ Elastic strain energy
$w$ Size of crack along width of laminate
$a$ Size of crack along edge of specimen
$n$ Number of cracks
$2l_{crit}^{'}$ Critical length of flaw parallel to fibres, [73]
$2a_{crit}$ Critical length of flaw perpendicular to fibres, [73]
$b$ Thickness of 0° ply
$2d$ Total thickness of 90° ply
$2c$ Total thickness of constraint zone
\( \lambda \)  Wavelength

I  Detector output

\( I_n \)  Normalised detector output

K  Rate of increase of \( I_n \) as a function of applied strain

\( K' \)  Rate of increase of \( I_n \) as a function of applied strain above 0.4% strain after heat treatment

A  Pre-exponential factor
CHAPTER 1

INTRODUCTION

Composite materials are characterised by their relatively high specific stiffness and strength and have been developed to meet the specific requirements of advanced technology. Fibre reinforced materials offer the additional advantages of design flexibility so that the materials can be "tailored" for a particular purpose through control of fibre and matrix composition and fibre orientation.

Although fibre orientation allows a high modulus and strength to be achieved along the principal loading axis the properties of continuous unidirectional fibre reinforced composites are anisotropic and the transverse modulus and strength are an order of magnitude lower than the longitudinal modulus strength. This is often a cause for concern since transverse stresses are unavoidable in most real applications. As a consequence the properties of a continuous fibre reinforced composite are usually optimised by 'stacking unidirectional laminae at various specified angles. The properties of the laminates formed by this process depend not only on the properties of the individual laminae but also on their thickness and stacking sequence.

Glass fibre reinforced laminates are excellent materials for fundamental studies on the fracture behaviour of composites since they can, by the correct choice of resin, be made transparent and any fracture phenomena may then be studied using optical methods. These have the advantage of being direct and do not require the specimen to be treated in any way as is necessary, for example, in X-ray radiography performed on carbon fibre composites, which relies on the effectiveness of a radio opaque penetrant.

Cross-ply \((0,90)_s\) laminates represent model systems which allow the effects of transverse tension to be studied since a single fracture of the transverse ply at one location does not result in total failure of the laminate. Instead failure of the transverse ply may be regarded as sub-critical damage because the transverse ply can still be loaded through the zero degree plies. Transverse ply cracks are generally considered to be the first characteristic form of damage which may be observed in such laminates. However, in many laminates, it is possible to observe other forms of damage in the transverse
ply prior to the onset of transverse ply cracking. For example, Manders et al [1] have reported the observation of stress-induced "whitening" in (0,90)s glass/epoxy laminates, prior to transverse cracking.

This study is based on the reported occurrences of "stress-whitening" and "reversible debonding" in (0,90)s cross-ply glass/epoxy laminates [1,2]. In (0,90)s cross-ply laminates with relatively thick inner 90° plies (1 mm) this "debonding" effect was identified by a decrease in laminate modulus shown as a "knee" in the stress/strain diagram (Figure 1(a)). The "knee" appeared at a strain, $e_{db}$, much below the strain, $e_{tc}$, at which the first easily visible macroscopic failure event, the transverse ply crack, occurred. After heat treatment of the laminate for 30 mins. at 100°C, the modulus was seen to recover (Figure 1(b)). The laminate also appeared to "whiten" at the debonding strain. In situ experiments, using a straining stage placed inside a scanning electron microscope, on cross-ply laminates containing relatively thin inner plies (0.5mm) showed fibre/resin debonding at the interface. However, a "knee" corresponding to debonding in the stress/strain curve was not visible in these laminates [3], possibly because the stress/strain response of these laminates is dominated by the outer 0° plies.

These observations provided an opportunity to study debonding as an event occurring prior to the widely studied macroscopic phenomenon of transverse ply cracking in cross-ply laminates. Furthermore, the recovery of the laminate modulus after heat treatment merited further investigation on possible rebonding mechanisms at the interface. Although the phenomenon of debonding and its possible reversibility were reported, no quantitative data regarding the corresponding modulus changes were provided. In addition, no microscopic evidence of the reversible phenomenon had been presented. Black and white photographs of "stress-whitening" in laminates made from the same glass fibres but a more highly cured matrix system (compared to the system reported in reference 2) were published by Manders et al [1].

The objective of this work was to investigate the low strain damage in glass/epoxy (0,90)s laminates, develop techniques to monitor and characterise the damage, and establish the mechanism of "reversible debonding" and "stress-whitening". To this end, transparent (0,90)s cross-ply laminates were fabricated from continuous E-glass fibres and epoxy resin with varying inner ply thickness and matrix cure levels. The properties of both the matrix and the laminates were characterised. A variety of optical techniques including colour macro-photography, polished edge transmission microscopy and
in situ optical microscopy were used to observe the onset and development of damage under uniaxial tension. A LASER diffraction technique was developed in which the intensity of light diffracted by micro-cracks was used as a measure of damage. The effects of heat treatment on the development of damage within the laminates were studied both quantitatively and by microscopic techniques.
Figure 1 (a). Stress/strain diagram of a (0,90)_s glass/epoxy laminate, from Parvizi et al [2], reportedly showing two "knees"; the first observed at 0.3% strain was associated with a whitening effect and the second "knee", at 0.55% strain, was associated with the appearance of a transverse ply crack.

Figure 1 (b). Load/unload curves for a (0,90)_s glass fibre/epoxy laminate, from Parvizi et al [2] who observed that "Upon reloading, the annealed composite behaved exactly like an "as new" specimen with the "whitening" and the "knee" both appearing at the same strains as observed in a new specimen."
CHAPTER 2

LITERATURE REVIEW

In this chapter, the properties of the individual phases of the glass fibre reinforced epoxy laminates and their behaviour as a composite system are reviewed in relation to the available literature. There are two main processes during the manufacture of a given fibre/resin composite system which control the nature of the interfacial bond and hence, affect the transverse properties of the composite. The first is the surface treatment of the fibres and the second is the in situ curing of the resin around the fibres. The glass fibre surface is treated with film formers, and other compounds such as lubricants and anti-statics to ease processing and protect the fibre surface during manufacture. Coupling agents are also used to improve the bonding between the fibre surface and the matrix. The interface which develops between the two constituents may be considered as a finite region having specific properties. Thus, it is often referred to as the interphase and regarded as a third component of the composite system.

The resin is brought into contact with the fibres when it is in the liquid state and normally cured at an elevated temperature. The resin shrinks as it cures and internal stresses can arise due to the presence of the glass fibres which do not undergo any chemical shrinkage. The direction of these stresses can vary depending on the fibre packing geometry. The unidirectional lamina is cooled to room temperature after curing or post-curing and this gives rise to further internal stresses in the composite because the differential thermal contraction of the two constituents is resisted by the adhesive bond between them. The stresses become inherent in the lamina. In angle-ply laminates, such as the (0,90), laminates, further internal stresses are developed since the thermal expansion coefficients of the laminae, in a given direction, vary with fibre orientation. The differences in the properties of the fibre and the resin and of the individual laminae, the fibre size and packing geometry, and the fibre volume fraction govern the stress distribution around the interface and within the laminate prior to external loading and also when under an externally applied load.
The adhesive strength of the fibre/matrix bond and the above mentioned factors are important considerations in the understanding of the micromechanics of failure in cross-ply laminates and are discussed in the following sections. Transverse ply cracking in cross-ply laminates has been widely studied and is related to the debonding and micro-cracking which precedes it and is, therefore, also discussed in this chapter.

2.1. Glass Fibres

The high ideal strength of covalently bonded brittle materials, such as glass, can only be realised if they are free from surface and internal flaws. In order to minimise the probability of flaws, glass is often used in a fibrous form and is then suitable for use as reinforcement in matrix materials such as polyester and epoxy resins. E-glass fibres are the most commonly used. The fibres or filaments are grouped into strands, each strand usually containing 102 or 204 filaments. The filaments may be twisted into yarns and then woven into cloth or they may be collected into rovings, usually 20 to 60 parallel strands in a bundle. They may be further processed into mats of either continuous or chopped rovings. The diameters of commercial glass fibres are normally of the order of 10 microns. During the manufacture of the fibres, damage to them is minimised by treating the glass surface with a "size" or "finish" consisting of an emulsion or solution of lubricants, anti-statics, coupling agents and film formers.

The surface of glass fibres is relatively smooth compared to fibres such as carbon which in addition to having a rough surface also contain micro-pores. The surface free energy of the glass fibre depends on its chemical composition and governs the wettability of the fibre and its chemical reactivity. Owing to the curved surface and small size of the fibres, critical surface energy data is difficult to obtain and appears to depend on the technique used for measurement [4]. As a result, quantitative correlation between fibre wettability and the strength of the interfacial bond between glass fibre and resin has been difficult to establish conclusively. There are also difficulties in accurately assessing the interfacial bond strength. Nevertheless, it has been shown qualitatively that the interfacial bond is influenced by fibre wettability and chemical reactivity [4]. The chemical reactivity of the fibre governs its ability to form chemical bonds and thus, influences the vulnerability of the glass surface to attack from the environment.
E-glass is a soda-free calcia-alumina-borosilicate glass. A typical composition is 54% silica, 14% alumina, 17% calcium oxide, 8% boron oxide and 4% magnesium oxide. Iron, sodium, and potassium oxides may be present in very small amounts [B1]. The composition of metal oxides near the fibre surface is different from that of the bulk [5]. The external environment can affect the non-silicate portion of the glass fibre. Calcium, for example, can diffuse towards the surface at high temperatures and aluminium can be leached out by acids. The glass surface is also hygroscopic in nature and after contact with water the surface oxides become hydrated. Koenig et al [6], using LASER Raman spectroscopy, have demonstrated the presence of spectral lines corresponding to silanols on the glass surface, hydrogen bonded to absorbed water molecules. The glass surface can also have a catalytic effect on chemical reactions and this can influence the curing reaction of the resin. Infra-Red spectroscopy has shown the preferential absorption of an amine catalyst in an epoxy resin system onto the glass surface [7].

The properties of the glass fibres are generally believed to be isotropic since the physical structure of glass is amorphous and based on a three-dimensional random network of covalently bonded silica. The metal ions are attached ionically to oxygen on the network. The Youngs modulus of the fibres is approximately 72 GPa. [B2]. The fibres remain linearly elastic to failure which is brittle (glass is a nearly ideal Griffith solid). Commercial E-glass fibres have tensile strengths in the range of 1.4 to 2.5 GPa [B2]. This variability arises from surface flaws which inevitably result from handling during the various stages of processing and testing. The strength of glass fibres is, thus, usually described using Weibull statistics. The properties of glass fibres are stable and reversible up to a temperature of 250°C. Elongation to fracture is typically 1.8 to 3.2% strain. The thermal expansion coefficient of glass fibre at 20°C is 4.9 x 10^{-6} K^{-1} [B2]. This is lower than that of the resin used in this study which has a thermal expansion coefficient of 63 x 10^{-6} K^{-1} [8] and leads to the development of residual thermal stresses in the laminate. The refractive index of the glass is 1.55.

2.2, Epoxy Resins

The term epoxy or epoxide refers to a chemical group consisting of an oxygen atom bonded with two carbon atoms already united in some way. The simplest
epoxy is a three membered ring to which the term α-epoxy or 1,2-epoxy is applied. Ethylene oxide is an example of this,

\[
\begin{array}{c}
\text{O} \\
\text{CH}_2 - \text{CH}_2
\end{array}
\]

Many of the common mono-epoxies have trivial names such as epichlorohydrin,

\[
\begin{array}{c}
\text{O} \\
\text{CH}_2 - \text{CH} \text{CH}_2 \text{Cl}
\end{array}
\]

epichlorohydrin

\[
\begin{array}{c}
\text{O} \\
\text{CH}_2 - \text{CH} \text{CH}_2
\end{array}
\]

glycidyl group

The term glycidyl is used to refer to the terminal epoxy group (see above), the name being modified by ether, ester, amine, etc., depending on the nature of the group attached to the third carbon.

An epoxy resin is defined as any molecule containing more than one α-epoxy group capable of being converted into a useful thermoset form. The term is used to indicate the resins in both the uncured and the cured state.

The materials first called epoxy resins were synthesised by Castan in 1936 in Switzerland [B3]. His work was later licensed to Ciba Ltd. The resins, reaction products of epichlorohydrin and Bisphenol-A, were produced commercially in 1947. By 1960 over 25 distinct types of resins were commercially available and the term epoxy resin became generic and is now applied to a wide family of materials.

The resin used in the present work was Shell Epikote 828, a diglycidyl ether of Bisphenol-A (DGEBA). It is synthesised by the reaction of epichlorohydrin and Bisphenol-A in a caustic liquid. The molecular weight of the resulting resin depends on the ratio of epichlorohydrin to Bisphenol-A; the greater the proportion of epichlorohydrin, the lower the molecular weight. Epikote 828 has a molecular weight of approximately 380. The chemical structure is shown in Figure 3.1(a). The cured structure is a heteropolymer composed of epoxy resin molecules linked together through reactive sites of the curing agent. The epoxy group can react either anionically or cationically. The formation
of anions and cations is a complex process. The reactivity depends on whether the epoxy group is terminal, internal or ring-situated.

2.2.1 Curing of epoxy resins

The basic curing agents employed in epoxy resin technology are Lewis bases, inorganic bases, primary and secondary amines and amides. The acid curing agents are carboxylic acid anhydrides, di-basic organic acids, phenols and Lewis acids. The organic bases such as tertiary amines represent the more reactive type Lewis bases suitable for curing epoxy resins. Tertiary amines react preferentially with anhydrides and are used as accelerators in epoxy resin systems where an anhydride is employed as the hardener. Cyclic anhydrides cannot react directly with epoxy groups and in order for the reaction to occur, the anhydride ring must be opened. This function is performed by a tertiary amine which reacts with the anhydride to generate a carboxyl ion. The carboxyl ion then reacts with the epoxy group to release an ion which opens another anhydride ring and an alternating copolymer is formed.

In the present work Epikote 828 was cured with 'Nadic' methyl anhydride (NMA) at 80 parts per hundred of resin and benzyl dimethyl amine (BDMA) as the accelerator in small amounts (0.5 to 3.0 %). NMA, normally a solid, is made into a yellow liquid by the addition of 0.1% Phosphoric acid. The reaction rate is dependent on the accelerator concentration [9]. The chemical structure of NMA, BDMA and the resulting material are shown in Figure 3.1(b), (c), and (d) respectively. Table 2.1 shows some physical properties of a DGEBA resin cured with NMA and BDMA. The table shows that the resin is a bi-modular material in which the tensile and compressive modulus are different.

Curing of epoxy resins is normally carried out at an elevated temperature. With anhydride curing systems, the exotherm is reported to be only 20 to 30°C above the cure temperature [10]. During the early stages of cure of an epoxy, before the molecules are all cross-linked, the resin exists as a 'gelled' or B-stage resin. It is hard but frangible and soluble in solvents such as acetone. At this point the cure reaction has been initiated at a number of reactive points in the mass. Additional curing makes the cross-linking more general and the resin reaches its thermoset stage. In general, post-curing the resin at temperatures higher than the cure temperature produces an improvement in some properties because the diffusion
controlled cure reactions become more probable above the glass transition temperature of the resin.

In epoxy resin technology, the degree of cure has come to refer to the extent to which the epoxy groups have been consumed. For practical purposes, a fully cured resin is considered to be one in which the degree of cross-linking is sufficient to provide optimum properties for a particular application. During cure, two processes occur: Conversion, which is the consumption of reactive groups, and cross-linking which is the coupling of molecules into a three-dimensional network through reactive sites (as opposed to the mere formation of long linear non-cross-linked resins). The nature of the network and the extent of cross-linking of an epoxy system cured with a tertiary amine will depend on the concentration of the curing agent as well as the temperature of cure. The extent of conversion of the cured resin may be the same under both conditions. The different cross-linking densities which may arise, however, means that the properties of the two cured systems will differ significantly.

The post-cured resin is a rigid amorphous glass-like solid with a network structure developed through cross-linking via the reactive epoxide groups and the reactive groups on the hardener. The hardener becomes part of the network so that the amount and type of hardener affects the properties of the resulting material, as does the curing schedule. The glass transition temperature, \( T_g \), of the resin indicates the extent of cross-linking. The \( T_g \), associated with the glass-rubber transition, is a second order transition caused by the thermal agitation freeing parts of the resin chain allowing, it to rotate around its bonds.

2.2.2. Shrinkage

One of the important changes which occur in the resin mixture during curing and subsequent heat treatments is shrinkage. This is the reduction in volume or linear dimensions which occurs while the system transforms from the liquid state through to the solid state. The shrinkage is of two kinds. The first is curing shrinkage which is caused by the reaction and re-arrangement of the molecules into a more compact configuration. The second is thermal shrinkage which occurs when the resin is cooled down to room temperature from the higher processing temperature. A distinction should also be made between shrinkage changes in the liquid phase and those in the gelled or solid phase. So long as the changes occur in the liquid phase, no internal stresses can be
generated. In the gelled or solid phases stresses can appear and are unavoidable if materials which do not have the same expansion coefficient as the resin are embedded in it. There remains the possibility that curing shrinkage stresses occurring in the gelled state can be annealed out since the resin still has a viscous component. Thermal shrinkage stresses cannot be annealed out.

Shrinkage and density changes can be understood with reference to Figure 2.1 which is reproduced from 'The handbook of epoxy resins' [B3]. The figure shows the density and percentage linear shrinkage (with reference to the cured resin at 20°C) against temperature for a DGEBA resin cured with phthalic anhydride. The effect of time at temperature has been ignored for simplification. The uncured resin mixture has a density of 1.229 (extrapolated to 20°C). Assuming that the heating up is very rapid and that no reaction occurs during this time, the decrease in density with increasing temperature will be linear (line AB) according to the equation [B3],

\[ D_t = 1.229 \left[ 1 - 6.8 \times 10^{-4} (T - 20) \right] \]  \hspace{1cm} (2.1)

where \( T \) is the temperature at which the density is being calculated and \( D_t \) is the density. If curing is carried out at a constant temperature of 120°C, the density will now increase until curing is complete (point D). When the cured resin is cooled down to room temperature, two different expansion or contraction coefficients must be taken into account. Down to a temperature of about 105°C (DE) the change in density is given by,

\[ D_t = 1.205 \left[ 1 - 5 \times 10^{-4} (T - 110) \right] \]  \hspace{1cm} (2.2)

Below 105°C, the density changes according to,

\[ D_t = 1.23 \left[ 1 - 2.2 \times 10^{-4} (T - 20) \right], \text{ line EF.} \]  \hspace{1cm} (2.3)

The point E at the intersection of the two lines is, by definition, the glass transition temperature, \( T_g \). At 20°C, the density of the cured and uncured mixture is practically identical but this is not always the case. In the above resin mixture, the isothermal shrinkage due to curing is distributed equally between the liquid and solid phase (this is not always the case). A gel line can, thus, be drawn as shown in Figure 2.1. The shrinkage which causes stresses to build up occurs below this line (represented by CG).
The observations made above are only valid if the heating up time, as assumed, is very rapid and curing is carried out at a constant temperature. This may be true for small quantities of resin but for larger quantities a partial reaction can occur during heating up and an exotherm is inevitable. The density curve is then non-linear and goes from A to M. From here, if the reaction is very fast so that after passing the gel line the decrease in density caused by the rise in temperature (due to the exotherm) is greater than the increase in density caused by the chemical reaction, then the curve follows the dotted line MN and the shrinkage in the solid or gelled phase is determined by the maximum temperature reached during cure (line NO). On the other hand if after heating up to point M the chemical reaction shrinkage is greater than the expansion caused by the rise in temperature, then the density shows a continuous increase and the rise in temperature no longer causes shrinkage (MPQ). Shrinkage in the solid or gelled phase in this case is determined by the temperature at the intersection of the gelled line (point P) and is represented by the line PR.

To minimise shrinkage, therefore, the exotherm should pass the gel line at the lowest possible temperature and on passing this line the reaction should proceed slowly so that chemical shrinkage is always greater than the thermal expansion caused by the rise in temperature [B3].

2.2.3. Fracture of epoxy resins

The room temperature tensile stress/strain properties of typical epoxies generally show a linear relationship. Near to the glass transition temperature, the resin shows signs of visco-elastic behaviour and plastic deformation is observed prior to failure. Depending on the mode of loading, the room temperature brittle behaviour can be suppressed. In uniaxial tension the resin is brittle and fails at low strains since its behaviour is flaw sensitive. In uniaxial compression or pure shear, significant plastic deformation and yield can occur.

The fracture behaviour of epoxy resins, like most brittle solids, can be described by two well known parameters. These are the critical strain energy release rate, $G_c$, often referred to as the fracture energy and the critical stress intensity factor, $K_c$, often referred to as the fracture toughness. In molecular terms, fracture involves the rupture of primary covalent bonds or secondary Van der Waals bonds through molecular "pull-outs". In network polymers such as epoxy resins the extent to which the latter can occur is
limited as a result of the chemical cross-links and so fracture occurs mainly by primary bond rupture. The measured fracture energy, $G_0$, of the resins has been found to be even higher than that required to break primary bonds and has to be corrected to allow for all the bonds between cross-links of a chain, through which a crack is propagating, to be stressed to their breaking point before the chain breaks [B4].

Fracture even in the most brittle polymers is believed to involve visco-elastic or plastic energy dissipative processes under the high stresses experienced near the crack tip. The term, $G_c$, is then used to encompass all energy losses. Thus,

$$G_c = G_0 + Q$$  \hspace{1cm} \text{(2.4)}$$

where $Q$ is the visco-elastic component [B4]. $Q$ for a given resin composition depends on the rate and temperature of testing and the crack growth rate. The differences between values of $G_c$ shown in the literature compared to those of $G_0$ indicate that the yield criterion is exceeded in regions near the crack tip suggesting that flow processes occur [11].

Fracture in glassy polymers is believed to occur when highly localised yielding due to local stress concentrations generates an area of highly strained material. The most highly strained molecules are broken and preferential chain disentanglements occur. Micro-voids are then nucleated and can increase in size and number with increasing strain producing crazes or micro-cracks. A craze is a thin plate-like region, containing material composed of oriented polymer and void. The craze structure in thermoplastics has been well characterised and has been shown to result from localised molecular orientation [B5]. In thermosetting polymers such as epoxy resins where flow is restricted due to the cross-linked network, the same process of molecular orientation would require bond rupture. Crazing is, therefore, less energetically favourable and experimental evidence has suggested that crazing does not occur [12]. Yamini and Young [13] found no evidence of craze debris on the fracture surfaces of epoxy resin (Epikote 828) hardened with different amounts of Triethylenetetramine (TETA). Crazing at the tip of cracks in thin films of undercured epoxy resins has been reported [14] but the evidence for this was inconclusive because the crazes were difficult to distinguish from micro-cracks.
"Craze" like behaviour has also been reported by Lilley et al [15] in a "fully" cured Epikote 828, NMA and BDMA system similar to the one used in the present study. A pattern of "craze" like features was observed at the tip of a wedge loaded crack. The crack-like defects were formed perpendicular to the principal loading axis. Tensile surfaces of loaded cantilever beams were also reported to show these features with denser arrays near notches and near crack arrest points. Lilley et al suggest that as there was little apparent interaction between closely spaced features these must be load bearing, which satisfies the phenomenological criterion for crazes. Their results suggest that regions of intense localised plastic strain might occur in fully cured resins. The internal structure of the craze-like features is not reported but from a structural viewpoint might be expected to be dissimilar to that found in thermoplastics. This might explain why fracture surfaces showing "typical" craze debris have not been observed in epoxy resin systems.

Since epoxy resins are cured by the addition of a hardener, it has been suggested that there could be inhomogeneities in the resin at a microscopic level. The resin is believed to contain a microstructure of nodules of highly cross-linked material surrounded by a less cross-linked matrix. Mijovic and Koutsky [12] have shown such a nodular structure on replicas taken from the fracture surfaces of diethylenetetramine (DETA) cured resin. The nodular size was found to decrease with increasing concentration of DETA. Yamini and Young [13] have shown that for Triethylenetriamine (TETA) cured Epikote 828, the nodule size is also affected by post-cure temperature such that it is large (100nm) for an undercured resin and small for a more highly cured resin. It is not known whether the size of the nodules directly affects the mechanical properties of the resin.

Yamini et al [13] also examined the flow and crack propagation behaviour of the epoxy resins cured with TETA. The variation of $K_{IC}$ (critical stress intensity factor) with temperature showed that below 0°C, crack propagation was continuous while above room temperature crack jumping occurred by a stick/slip process. When propagation occurred in a stick/slip manner, the resulting fracture surface appeared featureless up to the crack arrest point. This was followed by a region of slow growth (of length $l_p$) in which closely spaced striations parallel to the crack growth direction were observed. Beyond this, there was a rougher hackled region where the crack accelerated during the slip process. After this, the crack would be arrested again and so forth.
The magnitude of, $l_r$, appeared to approximate to $r_c$, the radius of the Dugdale plastic zone. This can be calculated using

$$r_c = \pi/8 \left( K_{IC}/\sigma_y \right)^2$$ (2.5)

where $\sigma_y$ is the yield stress of the resin.

Although a plastic zone as such was not observed, Yamini and Young suggested a close relationship between $r_c$ and $l_r$. The slow growth region was then taken to be in the plastic zone.

Gledhill et al [17] have found that if $\sigma_y$ was high then crack propagation was continuous while if $\sigma_y$ was lowered due to formulation changes or testing conditions, then propagation became stick/slip in nature. Using the concept of crack blunting, Yamini and Young [13] derived a failure criterion which implied that a stress, $\sigma_c$, of the order of three times the yield stress had to be reached at a critical distance ahead of the crack for failure to occur. It was found that increasing the amount of hardener (TETA) in the DGEBA epoxy resin system caused a large increase in the critical distance and a small reduction in $\sigma_c$. The modulus and yield stress also decreased with increasing amounts of hardener [16]. In a composite, the glass fibres are surrounded by the epoxy matrix. Due to the difference in properties of the two materials the resin is in a complicated triaxial stress state. On loading, therefore, the matrix resin behaves differently to bulk resin. For example, Gaggar et al [18] have suggested that crack tip deformation may be restricted to a thin layer of resin if the interfibre spacing is smaller than the size of the plastic zone.

The processes of fracture and plastic deformation in the resin are important in the understanding of transverse cracking behaviour and micro-cracking in laminates. The appearance of the resin on transverse ply fracture surfaces in laminates is believed to be a good indication of the degree of adhesion of the fibre/matrix bond. A high degree of adhesion results in a fracture surface in which the glass fibres are found to be coated with resin, showing substantial signs of plastic deformation. A poor fibre/matrix bond results in a fracture surface where the fibres appear to be relatively free of resin [22].

The surface energy for separating fibre/resin interfaces is calculated to be of the same order of magnitude as that for generating cohesive matrix cracks.
[19], which is of the order of 1 Jm$^{-2}$ for polymers such as epoxies [20,21]. However, the total fracture energy consumed by a transverse crack is greater than 100 Jm$^{-2}$ [3]. Thus, it appears reasonable to assume that there are other energy dissipative processes taking place during transverse failure, for example, extensive plastic deformation of the matrix.

Lee [19] used the analogy between the fracture behaviour of adhesive bonds and fibre composites to develop a theoretical model to describe a restricted plastic zone size in composites. The concept of the restricted zone size has been successfully used in adhesives technology to describe the dependence of $G_c$(adhesive) on the thickness, 'h', of the adhesive layer [23]. As 'h' is decreased, the constraint on the crack tip deformation is increased. Wang et al [24] found that as the bond thickness decreased the stress ahead of the crack decayed more slowly than in the bulk adhesive material. Based on the results of Wang et al, Kinloch and Shaw [23] postulated that at large values of 'h' (h>>2$r_c$, where 2$r_c$ is the diameter of the plastic zone in the bulk material), the constraint on the zone is negligible and $G_c$(adhesive) is equal to that of the bulk material. When 'h' is of the order of 2$r_c$ the maximum value of $G_c$(adhesive) is achieved. For h < 2$r_c$, the constraint results in diminishing overall zone volume and $G_c$(adhesive) steadily decreases as 'h' is reduced to below 2$r_c$ where 2$r_c$, in plane strain condition is given by,

$$2r_c = \frac{E \sigma_g}{3\pi (1-\nu^2)}$$

(2.6)

Where $G_c$(resin) is the fracture toughness of the resin, $\nu$ is the Poissons ratio of the resin, E is the Youngs modulus and $\sigma_g$ is the yield stress of the resin.

By analogy, in the laminate, 'h' is replaced by 's', the average fibre spacing. The above argument implies an optimum fibre spacing equivalent to 2$r_c$. For values of $G_c$(resin) between 100-200 Jm$^{-2}$, this implies an optimum volume fraction of fibres of between 64 to 48% and the optimum fibre spacing is between 2 to 4 microns. Thus, for the high fracture energy resin the "optimum" volume fraction is lower (assuming a hexagonal array and modulus of 3.8 GPa and a yield stress of 140 MPa.). The adherends are fibres in this case and are assumed to have overall laminate properties. A plane crack is then considered in the centre of the adhesive (resin). Lee's analysis [19] indicated that in order to resist transverse cracking in a desired resin system, the resin should have a large plastic zone and a high $\sigma_g^2/E$ value in
the zone, so that $\sigma_y^2/E$ is at least as important as $G_C(resin)$ in contributing to $G_C(comp)$, the fracture energy of the composite. In the presence of thermal residual stresses, it is considered that part of the fracture energy can be provided by the resulting stored energy. Lee [19] incorporates this into his model. His experimental results indicated that the measured values of $G_C(comp)$ for four different glass/epoxy resin systems increased with increasing volume content of resin, $V_r$. A plot of $G_C(comp)$ versus $G_C(resin)$ for the four systems showed that at the same $V_r$, the fracture energies of the neat resins were not proportional to those of the corresponding composite. The results also showed that in a laminate with a severe build-up of thermal residual stress, the contribution to toughness by the resin alone can be significantly offset. Comparison between measured and estimated values of $G_C(comp)$ did show a trend but there was some scatter in the results, particularly for the system with the lowest measured value of $G_C(comp)$.

The work described above outlines the important resin variables that contribute to fracture such as transverse cracking. However, it must be stated that the approach employed above is limited. The constants used cannot be derived analytically but are assumed. It must also be noted that in a real laminate there is a distribution of fibre spacings and that the resin volume fraction measured is only an average value. The variations in fibre spacings result in variations in the stress distribution and become very significant when considering fracture processes. Finally, as Lee [19] points out this is a three dimensional problem which has been reduced to two dimensions for simplification and ignores the triaxial stress state which is known to exist.

2.2.4. Crack healing

An interesting aspect of polymeric materials reported in the literature is the process of craze and crack healing [25-27]. The experimental investigations of this effect usually involve the measurement of mechanical or optical properties of the material in its original undamaged state. The material is then subjected to a tensile or other type of load so that crazes, voids or cracks are produced. The same properties are re-measured. The material is then given a "healing" treatment which involves a healing time, temperature and pressure. The properties of the healed material are then measured. Jud and Kausch [26] measured the fracture toughness of healed fracture surfaces of a poly (methyl methacrylate) (PMMA) using compact tension specimens. The authors found that depending on the time, $t_p$, allowed
for healing and the healing temperature, T_p, the fracture toughness was found to vary from very low values (of the order of the surface free energy) to the fracture toughness of the original material. Wool [27] has also reported a number of healing experiments. In cases where microscopy, spectroscopy or scattering effects confirmed the presence of crazes or cracks, these were observed to disappear while healing occurred with the restoration of mechanical properties. A variety of polymers were investigated including filled elastomers, carbon and glass reinforced poly(carbonate), poly(sulphone) and even epoxies. Although healing experiments on epoxies are reported, no experimental evidence has been presented. Nevertheless, the principles of the work of Jud and Kausch and Wool and O'Conner are considered here since this aspect of crack closure and healing is of interest in connection with the disappearance of stress-whitening after heat-treatment of the glass/epoxy laminates.

Wool and O'Connor [25] have postulated five stages of healing which influence mechanical and spectroscopic measurements. These are surface rearrangement, surface approach, wetting, diffusion and randomization. Wetting and diffusion determine the mechanical property development via an intrinsic healing function and a wetting distribution function. Jud and Kausch [26] use the three concepts of polymer-polymer inter-diffusion, adhesion between rough surfaces and jointing by flow of molten material to evaluate quantitatively the time dependent joint strength of two surfaces.

In the diffusion model it is assumed that at T_p, the molecular chains have a mobility which allows chain segments to cross the crack interface by inter-diffusion. With increasing contact time the chains form new physical cross-links between molecules on different sides of the interface and the strength of the interface increases with time. If the inter-penetration is sufficiently extensive, the interface disappears optically and mechanically so that forces can be transmitted across it. In the adhesion model the gradual reduction of surface irregularities (increasing contact area) by local flow of polymer material under the action of adhesive forces is considered. The strength depends again on the interchange of material across the interface. Using these concepts, Jud and Kausch [26] derived the following relationship for K_i, the stress intensity factor for the healed interface, in terms of K_i0, the original stress intensity factor,

\[ \frac{K_i}{K_{i0}} = \left( \frac{G_c}{G_{c0}} \right)^{1/2} = \left( \frac{t}{t_0} \right)^{1/4} \]  

(2.7)
where \( t = \) contact time and \( t_0 = \) the characteristic time at \( T_p \), necessary for the diffusion of molecules to establish \( N_0 \) links per unit contact area. \( N_0 \) is concentration of physical links at full strength. The experimental results for the styrene acrylonitrile and PMMA agreed well with their predictions.

2.3. The Fibre/Matrix Interface

The fibre/matrix interface may be defined as the contact area between the glass fibre and the resin. The contact between the two may be physical, chemical or mechanical or a combination of all three. The contact is at an atomic level. Generally, the interfacial bond formed between a clean glass fibre surface and a polymer resin is relatively weak and is rapidly destroyed by water even at room temperature. Bjorksten and Yaeger [28] and Witt [29] discovered early in the 1950's that the application of "coupling agents" such as methacrylate-chromium complexes or unsaturated silanes onto the glass fibre surface, before bringing into contact with the resin, resulted in a fibre/resin bond which was much stronger. Hence, laminates made from surface treated glass fibres and the resin matrix had higher dry flexural strengths and also retained their properties after exposure to a wet environment. They proposed that this was due to the "chemical unification" brought about by the coupling agent acting as a link between the glass and the resin. Although this theory was not rigorously proven, it had a large impact on development work.

The exact nature of the "chemical unification" and its contribution to the interfacial bond strength and bond permanence has been the subject of intensive research. The work done in establishing the nature of the interface and the most popular theories of bonding are reviewed in the following sections. The mechanical requirements of the interface, the measurement of interfacial bond strength, and the current understanding of the distribution of thermal and applied stresses in the composite at and near the interface are also reviewed.

2.3.1. Bonding at the interface

One of the most obvious requirements for a strong adhesive bond between the fibre and matrix would appear to be complete wetting of the fibre by the
liquid resin. Poor wetting would produce voids at the interface which would act as stress concentrators and initiate cracks. In order to achieve complete wetting, the resin must initially have a low viscosity and its surface tension must be lower than the critical surface tension of glass. For most resins in contact with clean dry glass this requirement is met. However, during processing the glass surface is covered with at least a monolayer of water since the surface is hydrophilic. The water becomes attached to the metal oxides on the surface of glass as hydroxide groups (M-OH) and as molecular water hydrogen bonded to surface hydroxyl groups. The critical surface tension is therefore lowered. Lee [30] showed that the wettability of glass could be controlled by the use of hydrolysable silane coupling agents. However, it was found that some silanes were ineffective bonding agents despite appearing to optimise wetting, while others produced good bonding without improving wettability. Plueddemann [31] on comparing an extensive series of silanes on glass for polyester laminates found no correlation between the polarity of silane or wettability of the treated glass and its performance in the laminates. In contrast, on comparing a series of good coupling agents for epoxy resins Lotz et al [32] found that silanes providing the highest critical surface tension also gave the best laminates. This suggested that wetting was not the primary requirement for good bonding but that wetting aids bonding by improving the chances of bond formation.

In theory, physical adsorption of resin on high energy surfaces can provide adhesive strengths in excess of the cohesive strength of organic resins [33]. In practice, however, the resin must compete with water, and other contaminants which will also interfere with adsorption. Physical adsorption alone is, therefore, not enough to produce or maintain an adequate bond. The primary requirement of a coupling agent is, thus, believed to be that it should contain chemical functional groups which can react with silanol groups present on the glass surface and form chemical bonds. It should also contain chemical functional groups which can co-react with the laminating resin during cure.

Silane coupling agents used today are usually trialkoxysilanes and are applied to the glass surface from aqueous solutions. The concentrations employed vary from 0.025% by weight to 2% by weight, depending on the specific coupling agent, in order to deposit two to three monolayers. Under mildly acidic conditions the alkoxy silanes hydrolyze to form monomeric silane triols. Shih et al [34] studied these silane triols in aqueous solutions
using LASER Raman Spectroscopy (LRS) in conjunction with Fourier Transform Infra-Red (FT-IR) Spectroscopy. They showed that the spectral bands originally produced by the triols disappeared in time with the appearance on the spectra of another band corresponding to the position of an Si-O-Si siloxane linkage. Thus, the silane triols appeared to condense to polymeric organic siloxanols. Siloxane formation has also been studied on E-glass fibre [35]. This work showed that the coupling agent near the glass surface had a high degree of molecular orientation, and that the siloxanol condensation was enhanced by the glass surface. Cross-condensation between the coupling agent and glass was also observed during drying.

Lee [36] proposed that in the extremely mild aqueous conditions under which the coupling agent is applied to the glass surface, hydrogen bonding between silanols of the coupling agent and the glass must be the predominant mode of reaction. Infra-Red evidence supports this postulate [37]. Chamberlain et al [38] attached organofunctional groups covalently onto a fluorinated glass surface. The mechanical strength of epoxy laminates prepared from this type of glass, in which 1.3% of the surface silanols were converted, compared well with standard silane treated glass laminates. However, laminates made with glass fibres where 9% of the surface silanols were converted proved to be inferior. A high degree of covalent bonding, therefore, appeared less effective than the type of bond obtained by surface deposition from water.

Molecular water at the interface is believed to play a vital role in the bonding mechanism at the interface. In 1974, Plueddemann [39] proposed a reversible hyrolysable bond mechanism, where in the presence of molecular water, the covalent bond between the silicon (or the metal) and oxygen hydrolyses. The hydrolysis was considered to be reversible so that the covalent bonds could reform when the water diffused away. In the presence of a shear stress parallel to the interface, the surfaces could slide past each other without permanent interfacial bond failure. Reversible hydrolysis and condensation of the bond through a siloxane-silanol equilibrium could, therefore, actually benefit composite performance by providing a chemical mechanism for stress relaxation across the interface. Evidence to support this mechanism is provided by both mechanical property data and by LASER Raman (LR) Spectroscopy [40,41]. The reversibility of mechanical strength of the laminate, after a boiling water or methanol treatment, followed by drying in vacuo at an elevated temperature has been demonstrated [40]. Koenig and Shih [41] using LR spectroscopy also observed a reversibility in the intensity of the Si-O-Si symmetric stretching mode line in the spectra.
Indirect evidence for chemical bonding between the organofunctional group of the coupling agent and thermosetting resins was first obtained by Plueddemann [42]. On comparing an extensive series of unsaturated functional trimethoxysilanes as coupling agents for polyester resins, it was observed that the effectiveness of the silanes was directly related to the reactivity of the functional group in copolymerising with the resin. The chemical reaction in the silane interphase region of treated glass fibres in a polyester has been observed during curing using FT-IR spectroscopy [43]. A methacrylate functional silane formed a multilayer on an E-glass fibre and polymerised completely during cure while a vinyl silane layer did not react completely. The carbonyl frequency of the polymerised coupling agent differed from that of the homopolymerised material indicating that true polymerisation had occurred.

The treated surface generally comes into contact with the matrix while the siloxanols still have some degree of solubility. Bonding with the matrix can, therefore, take two forms. The siloxanol layer may be compatible in the liquid matrix and form a true copolymer during cure or it may only have partial solubility in which case it would form an inter-penetrating polymer network. In the latter case the siloxanols and matrix resin cure separately with a limited amount of copolymerisation. It is believed that the bonding in thermosetting resins is probably a combination of the two forms [44].

In order to provide a complete description of the interface, the optimum number of chemical bonds required to achieve the highest strength, the most favourable equilibrium conditions for the siloxane-silanol reversible hydrolysis, and the physical solubility of the siloxanol layers in the resin must be known. An understanding of the interface and its exact role can lead to the development of improved composite systems.

2.3.2. Physical and mechanical properties of the interface.

Marom and Arridge [45] showed experimentally that the transverse tensile strength of a model steel reinforced epoxy matrix material compared to that of the matrix alone could only be improved if a thin flexible interlayer was introduced between the inclusion and the matrix. The shear modulus of the layer had also to be lower than that of the matrix. Broutmann and Agarwal [46] showed, however, that this modulus must not be too low. Using finite element analysis, the authors made a theoretical study of the effect of
interfacial layers, with a range of moduli, on the strength and modulus of a model composite. The modulus of the interphase was varied and given values ranging from high, close to the fibre modulus, to much lower than that of the matrix. Although certain assumptions were made, such as perfect bonding at the interface, and the model was limited to short fibres, the study served to illustrate the role of interphase modulus. The conclusions of the study were that a much lower modulus than the matrix modulus contributed little to strength or the modulus of the composite and was equivalent to no bonding at the interface, and, therefore, no stress transfer. An interphase modulus close to or higher than that of the matrix allowed the stress to build up at the interface within a couple of fibre diameters from the fibre ends and the resulting composite modulus was higher. When the interphase modulus was only one order of magnitude lower than that of the matrix the highest maximum stress in the fibre was built up within four fibre diameters from the fibre ends. The slower rate of decay of the shear stresses from the ends allowed the stress transfer to occur with maximum efficiency. By increasing the modulus of the interphase further the composite strength was not improved although the composite modulus was. Tryson and Kardos [47] have reported that the transverse tensile strength of a glass-epoxy laminate with a flexibilised epoxy layer at the interface showed a 67% increase.

In the above study, perfect bonding was assumed at the interface and indeed adequate "adhesive" strength must be developed evenly along the interface so that maximum stress transfer from matrix to fibre is attained. In addition the adhesive strength must be sufficient to withstand the thermal stresses developed at the interface in a cured composite. However, it will be shown later that in cases where the bond is good, thermal stresses can lead to fibre splitting. The actual "adhesive" strength of a bond remains, in many cases, a theoretical concept since a true adhesive failure is difficult to establish. For example, if the adhesive strength of the bond is high, then the initial micro-failure may not occur at the interface but in the resin or glass near the interface where the critical stress concentration may have been exceeded. It may seem appropriate then to assign an interfacial strength, as opposed to an adhesive strength, where the failure may occur in the resin, in the interphase or at the glass-interphase interface. The subsequent propagation path of the initial crack may also be similarly controlled by the strength of the bond. It may continue to avoid the interface if the most favourable path is through the resin. The resulting fracture surface is, thus, a good indicator of the adhesive strength of the bond.
The possible adhesion mechanisms have already been discussed in section 2.3.2. From the viewpoint of fracture mechanics, the measurement of the interfacial strength and a knowledge of the magnitude and distribution of stresses is useful. In principle the interface in a transverse unidirectional laminate under the action of tensile stresses can fail by stresses normal to the plane of the interface or by shear stresses acting in the interface. Two types of interfacial bond strengths are, therefore, measured. These are the interfacial tensile and shear strength. Measurements can be divided into two types: Direct measurements involving model specimens with single fibres embedded in resin, or indirect tests such as the measurement of the interlaminar shear strength and the transverse strength of a laminate.

One of the direct methods for assessing the bond strength is the single filament pull-out test, of which various configurations exist. Essentially, a short length of a single filament is partly embedded in resin and pulled in uniaxial tension. A graph of force versus distance pulled out is obtained and from this the interfacial bond strength and the pull-out processes can be assessed. The interpretation of the graphs can be rather involved but measurements of the interfacial shear stress, the interfacial yield stress and even energy absorption terms for the interfacial fracture can be obtained. The frictional shear strength arising from frictional forces existing after bond breakage can also be estimated. These frictional forces are due to the residual curing pressures resulting from matrix shrinkage and the differential thermal expansion coefficients of the two components. Poisson's shrinkage also affects the frictional forces. A large number of tests must be performed with different embedded lengths of fibre since the required embedded length is influenced by fibre strength. A detailed analysis of this test has been provided by Chua and Piggot [48]. The test set-up must be rigid and sufficient control of embedded and free lengths is required in order to correctly estimate the quantities described. Piggot and Andison [49] have recently reported the results of pull-out experiments on carbon fibres in epoxy resin and epoxy copolymer resin blocks. They suggest three modes of interface failure resulting from the different levels of matrix shrinkage stresses. It is suggested that brittle fracture occurs at intermediate shrinkage stresses while at high shrinkage stresses failure by shear yielding is observed. A length independent fracture was observed at the lowest shrinkage stresses.
A more direct method of measuring the interfacial shear strength and interfacial tensile strength makes use of single filaments completely embedded in resin. The model specimens were specifically designed by Broutmann [50] to cause either shear failure or tensile failure of the interface. A rectangular specimen was designed to fail the interface in shear when loaded in uniaxial compression while a curved neck specimen was designed to simulate a tensile debonding failure at the interface when loaded in compression. The compressive load causes a radial expansion governed by the Poisson's ratio of the resin. The resin expands more than the glass and in order to preserve continuity a tensile stress is generated at the interface.

Although single fibre tests are valuable, it is accepted that they do not simulate the state of stress at the interface found around fibres randomly packed and often closely spaced or even touching as in a real composite. Indirect methods of determining the interfacial "adhesive" strengths using laminates are preferred. A number of different tests have been used to determine the interfacial strength while others are designed to measure the interfacial contribution to fracture toughness of the composite. The most commonly used method is the interlaminar shear strength (ILSS) method and the transverse strength test.

The ILSS test is a three point bend test where the shear stress, $\tau$, is related to the applied load, $P$, by the following equation,

$$\tau = \frac{3P}{4ab} \quad (2.8)$$

where 'a' is the thickness of the specimen and 'b' is its width.

Whether a specimen fails in flexure or shear is governed by the span to depth ratio, $a/s$, where $s$ is the distance between the support reaction points. The most commonly used ratios range from 4:1 to 6:1. Three common failure modes occur in such tests; interlaminar shear, compression and flexure. The interlaminar shear crack, in which fibres are rarely broken, is the specified mode of failure required by this type of test. A compression failure is a sharp, coherent, buckling failure of the fibres within the sample and represents an invalid test. A flexural failure is the nominal failure mode when the three point bend test is conducted at a span to depth ratio in excess of 40:1.
Johnson [51] comments that often aspects of all three failure modes are seen in a large proportion of samples even when careful control of test parameters is maintained to restrict the failure mode to a valid interlaminar shear crack. The significance of such failure phenomena are now recognised and ascribed to a function of the fibre/matrix interface. In a careful study of the behaviour and mechanisms of crack formation in cross-plied carbon/epoxy laminates tested in three-point bend Johnson observed from polished sections, incipient cracks whose origins were found to lie close to the fibres but were actually in the resin. Examination of fracture surfaces showed filmy residues on fibres. From this Johnson concluded that an important contribution was made by unidentified flaws in the resin and this suggested that when the interface bond was of sufficiently high strength, the ILSS test was a resin strength limited test.

Classical estimates of shear strength are not adequate for the interpretation of the ILSS test since the actual deformation, even in unidirectional composites is not the same as that predicted by the beam theory or finite element analysis. The fracture process occurs under complicated conditions of combined shear and compression [52]. Consequently, the ILSS test can only be used for comparative purposes and not to determine absolute values of the adhesive strength of the fibre/resin bond. The data must be carefully interpreted and fracture surfaces analysed.

The transverse tensile strength of the composite is also used as an indirect measure of the interfacial bond strength. The transverse tensile strength of the composite depends on the adhesive strength of the interfacial bond, the presence of flaws and the internal stress and strain distribution which in turn is governed by fibre volume fraction, fibre diameter, fibre packing geometry and thermal history. The strength of the matrix relative to that of the interfacial bond is also important. If failure occurs predominantly at the fibre/matrix interface rather than in the matrix enclosed by fibre, then the interface quality can be determined by transverse tension test data. In contrast, when the fibres are strongly bonded to the matrix, the matrix may fail first or simultaneous failure of the matrix and fibre/matrix interface may occur. The area under the transverse stress/strain diagram is also likely to provide more information on bond quality and deformation processes before transverse fracture.
2.3.3. The state of stress at the interface.

The glass fibre/epoxy laminate is inherently a pre-stressed material. The pre-stressed state arises from shrinkage of the resin as it cures, and the difference between thermal expansion coefficients of the resin and glass. Similarly, in a laminate composed of individual laminae with different fibre orientations the thermal expansion coefficients vary giving rise to thermal stresses. During the curing process of a composite, changes taking place in the chemistry of the matrix result in shrinkage which continues even during post-cure. As the laminate cools, the adhesion between the resin and the fibres prevents free shrinkage when the physical state of the resin is such that its viscous component is unable to relax the stresses in the available time. As a consequence, the laminate is put under a complicated state of stress. Similar considerations apply to time at temperature.

The residual thermal stresses are three dimensional in nature and their presence has been demonstrated experimentally with the use of photoelastic techniques [53]. Complex fringe patterns relating to biaxial and triaxial stresses have been observed. Model laminates are, therefore, often used for their study. Two and three dimensional photoelastic analysis on model unidirectional laminates shows that the direction and magnitude of stresses depends critically on fibre packing geometry and the fibre volume fraction [54]. Most laminates show local variations in fibre volume fraction and geometry. This is reflected in the distributions of fibre spacings. McGarry and Wilner [55] measured fibre pair spacing and plotted the result as a function of the number of fibre pairs. The largest population was found at zero fibre spacing, i.e. fibres in contact, with the second largest population at 0.51 micron spacing. A significant population was found at spacings above 10 microns (the fibre diameters were approximately 10 microns). In view of this, two extreme cases of fibre packing can be identified. The first is when a single fibre is surrounded completely by resin such that the residual stress near or at the interface is affected little by the presence of other fibres and is, therefore, expected to be compressive while the resin around the fibre is in tension, both radially and axially. The axial tension has been shown by Outwater [56] to be about 200 times the radial component and leads to kinking of the fibre which is in compression.

The second case occurs when the resin is surrounded completely by fibres in contact so that a tricorn of resin is formed. Here the fibre/matrix
interface is under tension and the resin is also under radial and axial
tension, provided the bonding between the fibre and the matrix is maintained.
In this case the axial and radial stresses have been shown by Haslett and
McGarry to be comparable [57]. The two extreme cases are good illustrations
but the state of stress at the interface is much more complex, due to the
variation in fibre spacings which can vary at a single fibre/matrix interface
since the nearest neighbour spacing can vary with angular position within the
matrix.

Various authors have examined the internal stress state both theoretically
and experimentally. Most analyses consider two types of fibre packing
geometry, namely square and hexagonal arrays. (Most real laminates exhibit a
mixture of both types). The fibre volume fraction or fibre spacing (to which
fibre volume fraction is inversely proportional) is varied and the stresses
in the fibre and in the resin in the region of the interface are examined.
The stresses generally considered are radial, tangential or hoop, and axial
stresses. The occurrence of debonding and the existence of any surface
forces between the fibre and matrix after debonding are related to the sign
and magnitude of the shrinkage and differential contraction stresses.

In a paper by Asamoah and Wood [58], the stress distributions were analysed
both theoretically, using a plane strain model, by the finite element method
and experimentally using photo-thermoelasticity. Their results showed that
for most real composites both compressive and tensile radial stresses are
present within the matrix if the composite is cured at a temperature above
ambient. The closer the spacing of the fibres, the larger the area in
tension. The tensile region develops first from within the resin tricorn and
as the spacing decreases the tensile region spreads towards the interface and
beyond. For all fibre spacings the radial stresses remain compressive along
a line joining the centres of any two adjacent fibres and they increase with
decreasing fibre spacing. The radial stresses around the interface remain
nearly constant for widely spaced fibres but they change from compressive to
tensile for closely packed fibres. If the packing is symmetrical the change
is cyclic occurring three times for triangular packing and four times for a
square arrangement. It must be pointed out that even if the thermal stresses
generated do not cause direct failure, they provide an initial state which
requires only small external loads to produce failure. The distribution of
these stresses is therefore important in determining the micromechanisms of
failure.
Asamoah and Wood [58] also suggest that when fibres are brittle and the 
interface strong, fibre cracking (or fibre splitting) can occur, the planes 
of failure forming arcs around the compressively loaded contact lines along 
fibres. The magnitude and direction of thermal stresses are very sensitive 
to fibre spacing which should therefore be optimised, particularly in the 
transverse ply in which the strength is dominated by flaws.

In cross-ply or angle-ply laminates, thermal strains arising due to a 
mismatch in thermal expansion of plies of different orientation are 
superimposed on the already existent thermal strains which result from a 
mismatch in the thermal expansion between fibre and matrix. The thermal 
strains arising from differences in ply properties are referred to as thermal 
restraint strains. Thus, if a laminate is made up of two laminae only, such 
as a 0° ply and a 90° ply, the asymmetric beam cut from this laminate will, 
at the stress free temperature, remain flat exhibiting no effect of the 
mismatch in expansion coefficients. As the beam cools below this 
temperature, the 90° lamina, whose properties are dominated by the matrix, 
will contract more than the 0° lamina, the properties of which are fibre 
dominated. The beam is, therefore, forced into balance by forming an arc. 
The radius of curvature of this arc is related to the amount of thermal 
strain which would develop in an equivalent symmetric laminate, i.e. a 
(0,90)_s laminate. The second outer ply in a symmetric configuration is able 
to restrain the contraction of the 90° ply. The magnitude of the thermal 
restraint strain depends on the ratio of the ply moduli (E₁, Eₜ), the 
thickness of the plies (b, d), the difference in thermal expansion 
coefficients (αₜ - α₁), and the temperature interval between the stress free 
temperature and the temperature of measurement (T₁ - T₂). The thermal strain 
in the transverse ply in the longitudinal direction, eₜ₁, is given by,

\[ e_{t1} = \frac{E_1 b (\alpha_t - \alpha_1) (T_1 - T_2)}{(E_1 b + E_t d)} \]  

(2.9)

It has been noted [8] that the residual stresses within a ply must be 
equilibrated with interlaminar shear stresses transmitted from adjacent plies 
which may result in ply separation. Finite element calculations have 
suggested that interlaminar shear stresses and interlaminar normal stresses 
increase significantly at the free edge of finite width specimens and might 
affect the level of thermal strain. However, the equations used to predict 
thermal strains give good agreement with experimental results [8] for systems 
similar to those used in the present study without including edge effects, 
suggesting that such effects are small.

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2.3.4. The distribution of stress on external loading

Following the observation of stress-whitening believed to be caused by "crazes" in resin-rich regions of glass/epoxy pressure chambers, Rawe [59] advanced a qualitative theory of the connection between "craze cracking" and resin-rich areas. The theory supposed that transverse stresses caused large strains to be formed in resin rich regions leading to the development of craze cracks* because the modulus of the resin was much lower than that of the glass. The strain was therefore concentrated in resin rich regions.

* Although in the original literature "crazing" is referred to, there was no evidence to suggest that the cracks were crazes which are caused by polymer orientation forming fibrils in highly strained localised regions. The whitening could equally have been caused by fine matrix cracks.

Kies and Shultz [60] calculated, using an approximate method, the maximum stress generated in the resin of a composite with regularly arranged fibres. Using the simple model illustrated in Figure 2.2, the strain magnification factor (SMF) in the resin along the line AB of a square array subjected to a tensile strain was shown to be,

\[
\text{SMF} = 2 + \frac{s}{r} / \left[ \frac{s}{r} + 2\left(\frac{E_m}{E_f}\right) \right]
\]  

where \( s \) is the fibre spacing and \( r \) is the fibre radius, \( E_m \) is the matrix modulus and \( E_f \) is the fibre modulus.

\( s \) is related to \( r \) and \( V_f \), the volume fraction of fibres (for a square array) in the following way [B2],

\[
s = 2\left[\left(\frac{\pi}{4V_f}\right)^{1/2} - 1\right]r
\]  

At high volume fractions, the strain magnification factor (SMF) is higher. The SMF will vary locally with volume fraction variations. The non-uniform distribution of stress, in a unidirectional laminate, on transverse loading can be shown using photoelastic techniques [61]. The fringe patterns obtained show that the magnitude and direction of the stresses vary.
throughout the matrix and depend on the volume fraction and fibre arrangement. Provided the fibre and resin remain bonded the strain magnification in the resin causes failure of the resin in the laminate at a lower applied stress than would otherwise result from testing unreinforced resin.

In a theoretical analysis, by Tirosh et al [62], of a well bonded, rigid, circular fibre in an elastic matrix subjected to a transverse load, the stress solution obtained showed two features. The first was that the radial tensile stress component was higher than the tangential component. The second feature was that the locality, \( r^* \), measured from the centre of the fibre at which the maximum stress occurred was not at the interface but a small distance ahead, depending on the Poisson's ratio of the matrix and was given by;

\[
\begin{align*}
  r^* &= \frac{6}{K(K-1/2)+4} r \\
  &\text{where } K = (3-\nu), \text{ where } \nu \text{ is the Poisson's ratio of the resin, and } r \text{ is the fibre radius.}
\end{align*}
\]  

For an epoxy resin with \( \nu = 0.35 \), \( r^* \) is 1.02\( r \). According to the equation with a glass fibre radius of 5-6 microns, the maximum stress would occur at a distance of 0.1 to 0.12 microns from the fibre circumference. Thus, providing the bonding between the fibre and the matrix is sufficient, micro-cracks may extend under load without debonding at the fibre/matrix interface and the fracture path may by-pass a well bonded fibre altogether. It should be noted that in [62], \( r^* \) is quoted to be 1.2\( r \) for a Poisson's ratio of 0.35. This is not consistent with the equation quoted above in the same paper. No erratum concerning this inconsistency has been reported to date.

2.4. Laminate Properties.

The longitudinal strength of unidirectional laminae tested in tension, parallel to the fibres depends primarily on the strength and volume fraction of fibres. However, at low fibre volume fractions, the longitudinal strength depends also on the failure stress of the resin since after matrix fracture the load transferred to the fibres cannot be sustained. At high volume fractions, the majority of the load is carried by the fibres and so failure of the resin is not catastrophic and instead multiple matrix cracking occurs [64].

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The transverse tensile strength of a unidirectional lamina depends on a large number of factors such as the fibre/matrix interface strength, the properties of the fibre and matrix, and the presence of thermal residual stresses. When the interface bonding is good the transverse strength is dependent on the strength of the matrix and/or the strength of the bond. If the bond does not fail there is a strain and stress magnification in the resin as discussed in section 2.3.3. Eventual failure depends on the full triaxial stress state.

The properties of angle-ply laminates may be determined from the properties of the individual unidirectional laminae using classical lamination theory. This allows specific expressions to be derived for the stiffness of laminates in terms of laminate thickness, the angle of orientation of the fibres, the stacking sequence and elastic constants. The expressions, which can be found in standard texts [B2], show that for a cross-ply laminate, with $V_0$ (volume fraction of the 0° plies) equal to $V_{90}$ (volume fraction of 90° plies), longitudinal modulus of 40 GPa., transverse modulus of 10 GPa. and Poisson's ratio of 0.3, tested in uniaxial tension, an externally applied stress, $\sigma_a$, in a direction parallel to the fibre direction in the 0° plies produces a stress, $\sigma_{t0}$, of 1.61 $\sigma_a$ parallel to the fibres in the 0° plies. A tensile stress, $\sigma_{te}$, of 0.07 $\sigma_a$ is produced perpendicular to the 0° ply because of the constraint imposed by the 90° ply preventing Poisson contraction of the 0° ply. In the 90° ply, the external stress produces a stress, $\sigma_{t90}$, of 0.39 $\sigma_a$ perpendicular to the fibres (parallel to the loading axis) and the Poisson effects lead to a compressive stress, $\sigma_{c90}$, of 0.073 $\sigma_a$ parallel to the fibres. The main part of the applied load is, thus, carried by the 0° plies. Transverse ply cracking will occur when the stress on the laminate is equal to $\sigma_a/0.39$ where $\sigma_a$ is the critical stress for transverse fracture. The expressions however, only apply if the constraint effects due to the presence of neighbouring plies are neglected and so only applies to laminates with relatively thick plies.

2.5. Transverse Cracking in (0,90)$_s$ Laminates.

Transverse ply cracking in (0,90)$_s$ cross-ply laminates has been widely studied in both glass/epoxy and carbon/epoxy systems. A transverse ply crack is the first macroscopic failure event in the 90° ply of the (0,90)$_s$ laminate under uniaxial tension. The crack is visible in transparent or translucent systems and can also be detected by techniques such as acoustic emission and polished edge microscopy. For opaque laminates, such as those made with
carbon fibres, acoustic emission or penetrant enhanced X-Ray radiography has been used [66]. The transverse ply crack, often referred to as a matrix crack, spans the width and thickness of the 90° ply and ideally lies in a plane normal to the loading axis. The crack is responsible for the "jump" or "knee" in the stress/strain diagram of a (0,90)s laminate. Puck [67] made one of the first references to it and attributed the knee to craze-cracking. The transverse crack is usually arrested at the 0/90 ply interface. The presence of the crack necessitates a redistribution of load in the 0° and 90° plies of the laminate since an additional stress is thrown onto the the longitudinal ply region adjacent to the transverse crack and indeed, Jamison [68] has shown a higher density of fibre breaks in the longitudinal plies in the plane of the transverse crack.

Hahn and Tsai [69] suggested that the presence of a transverse crack led to an ineffective length over which the transverse ply carried no load. The transfer of load back to the 90° plies is assumed to occur by shear of the constituent plies according to the shear lag theory developed by Aveston and Kelly [64] and applied to cross-ply laminates by Garrett and Bailey [65]. In this, the stress in the longitudinal ply has a maximum value in the plane of the transverse crack. The load is transferred back into the transverse ply by shear and reaches a maximum value between two existing cracks. Thus, the remainder of the transverse ply is still able to sustain loads such that with increased loading further cracks continue to form. The crack spacing at a specified applied stress depends on the thickness of the 90°ply [3] such that a thinner inner ply results in more closely spaced cracks at a given strain. The laminate stress and crack spacing relationship has been predicted by Bader, Bailey, Curtis and Parvizi [70] using the shear lag theory giving good agreement with experimental results.

The crack density is believed to approach an asymptotic value or a saturation density. However, often sufficiently high stresses are generated in the 0° plies by Poisson restraint effects so that longitudinal splitting of the 0° plies occurs before the saturation crack density can be reached. Delamination between plies and tensile failure of the 0° plies usually follows rapidly and the laminate fails. The build-up of transverse ply cracks causes a gradual loss in the stiffness of the laminate [71] and alters its thermal expansion properties [72]. They can also precipitate delamination under long term service conditions.
An interesting aspect of transverse cracking is that the threshold strain for the first crack increases as the thickness of the transverse ply relative to the 0° plies is reduced. Aveston and Kelly [64] postulated that when the 90° ply is very thin, the threshold strain for transverse cracking is raised because insufficient elastic strain energy is released by crack nucleation and growth for fast fracture to occur. Bader et al [70] compared their experimental data on strains to first transverse crack as a function of 90° ply thickness with predicted values using the energetics arguments of the multiple cracking theory and obtained good agreement at small ply thicknesses. The data presented by Bader et al [70] has been subsequently used by several workers [73,74] to validate their analyses. Korczynskyj and Morley [75] determined the stress field around assumed pre-existing cracks modified by the constraint of the neighbouring plies and found good agreement over a range of ply thicknesses. Ogin et al [73] have derived a stress intensity factor from which the strain to the first transverse crack can be obtained. Based on a critical flaw size concept, the authors have calculated a critical value of the 90° ply at which the threshold strain for transverse ply failure is increased dramatically. This work is discussed further in section 5.1.2.

It is generally accepted that transverse ply cracks initiate at the laminate edge as a result of local stresses associated with the free edge. However, there is evidence to suggest that transverse ply cracks can also occur in the bulk of the ply especially during fatigue loading [73] and in laminates with small inner ply thickness where crack propagation is largely controlled and proceeds slowly. In order to elucidate the exact mechanisms of transverse ply cracking, an in situ test inside a scanning electron microscope was performed by Parvizi [3] on a constrained (total 90° ply thickness = 0.3 mm) cross-ply laminate (outer plies = 0.25 mm). Fibre/resin debonds were observed on the edge, of which some were seen to coalesce at higher strains. It is generally assumed that such a group of debonds form the critical flaw which initiates transverse ply cracks, although the particular laminate examined by Parvizi [3] had a very high transverse ply cracking strain and was not tested to this cracking strain.

While many references to a 'knee' (or modulus drop) due to transverse cracking are available [67,71], Parvizi and Bailey [2] and Manders et al [1] make the only reference to a knee due to debonding. The magnitude of the modulus drop was not reported. The phenomenon of stress-whitening prior to transverse cracking, believed to be associated with fibre/resin debonding,
was reported by Manders et al [1] and black and white photographs of the effect were presented. Whitening in glass fibre/epoxy laminates has been reported by other workers on angle-ply laminates and associated with deformation in the resin [76]. Whitening due to debonding resulting from the accumulation of bulk water at the interface has also been observed [77].
Figure 2.1. Density and shrinkage changes during cure of a DGEBA resin/phthalic anhydride system (see text for details).
Figure 2.2. The Kies square array model for calculating strain magnification in the resin along the line AB where "s" is the spacing between fibres and "r" is the fibre radius.

<table>
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<tr>
<th>Property</th>
<th>Value</th>
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</tr>
<tr>
<td>Tensile strength (MPa)</td>
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<tr>
<td>Elongation (%)</td>
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<td>Flexural strength (MPa)</td>
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<tr>
<td>Flexural modulus (GPa)</td>
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<tr>
<td>Compressive strength (MPa)</td>
<td>118.0</td>
</tr>
<tr>
<td>Compressive modulus (GPa)</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 2.1. Physical properties of Epikote 828 epoxy resin with 84 phr NMA and 2.2 phr BDMA, cured for 4 hrs. at 80°C and post cured for 15 hrs. at 150°C.
The primary objectives of the experimental work have been: (a) to observe and establish the cause of stress-whitening and "reversible debonding" in laminates and (b) to develop a quantitative technique to monitor the development of stress whitening during tensile loading.

To this end, high quality, transparent laminates and resin specimens were fabricated. The properties of both resin and laminate specimens were characterised using established test methods. Several new techniques were used to observe stress-whitening in the laminates. These included colour photography, macro-photography, high power microscopy and in situ tensile testing and microscopy. A number of techniques were developed for the quantitative measurement of stress-whitening. A LASER light diffraction method was found to give reproducible results for the quantitative measurement of stress-whitening. Laminates fabricated with three different 'degrees of cure', four different geometries and two different glass fibre surface finishes were examined.

3.1. Specimen Preparation

3.1.1. Materials

(a) Matrix

The matrix material used in this study consisted of a three-part epoxy resin system. The resin was based on the diglycidyl ether of Bisphenol-A (DGEBA) epoxy pre-polymer, Epikote 828 (Shell Chemicals Co. Ltd.), and was cured with 80 phr (parts per hundred of resin) of nadic methyl anhydride (NMA) hardener. Benzyl dimethyl amine (BDMA) was used as the accelerator to facilitate cure. Three different levels of BDMA were used to produce matrices with varying 'levels of cure'. Only small amounts of accelerator are required and the three levels used were 0.5 phr, 1.5 phr, and 3.0 phr. The 'level of cure' was assessed using a Dynamic Mechanical Thermal Analyser (Polymer Laboratories Ltd) as described in Section 3.2.2.
The curing conditions were kept constant for all the resins regardless of the accelerator level. Curing was carried out at 100°C for a period of 3 hours and this was followed by post-curing at 150°C for a further 3.5 hours. This resin system, when used with glass fibres, produces laminates of high transparency due to the closeness of its refractive index to that of glass. The resins do, however, have a yellow colour and this is also imparted to the laminates.

The chemical formulae of the constituents and the resulting matrix are shown in Figure 3.1.

(b) Reinforcement

The glass fibres used in this study were made of E-glass and were coated with a commercial silane coupling agent compatible with epoxy resins. The fibres were supplied by Silenka Ltd. in the form of a continuous roving consisting of parallel strands of individual fibres. Initial work was carried out using 1200 tex roving. Tex refers to the weight of fibres per kilometre of roving and gives an indication of the number of fibres (approximately 6000 fibres) present in the roving since the fibre diameters are approximately constant. The fibre diameters were of the order of 10 microns as measured from the graduated eyepiece of a microscope. In order to improve the packing of these fibres, particularly in thin (< 1 mm) inner ply laminae, a lower tex (600) roving was later used to fabricate another complete set of laminates and characterisation of these laminates was repeated before any further tests were done. A limited quantity of continuous E-glass fibre coated with a starch finish was also used for some experiments in which poor bonding between the glass fibres and resin was required. These fibre rovings were of a lower tex (120) and the fibre diameters were smaller than the silane coated glass fibres.

3.1.2. Resin specimens

In order to obtain specimens of matrix material for characterisation purposes, samples of the bulk resin with three different accelerator levels were cast in an aluminium mould of approximate dimensions 215 mm x 120 mm x 6 mm. The mould assembly consisted of two flat rectangular aluminium plates separated on three sides by blocks of 6 mm thickness. The fourth side of the mould was left open to allow the activated liquid resin to be poured in.
Prior to assembly of the mould all the internal surfaces were polished with a proprietary metal polish to obtain a smooth finish and then coated with a mould release agent (Slip-wax).

It was found that in order to facilitate the release of the cured resin block from the mould it was necessary to first heat each component of the mould to allow the Slip-wax to melt and coat the surfaces evenly. The mould was then assembled using metal screws. The edges of the mould were sealed using silicone rubber to prevent seepage of the resin, since prior to gelation, the resin viscosity is reduced considerably with increasing temperature.

All three components of the resin are liquid at room temperature and together produce an activated viscous mix. The mix was heated to a temperature of 50°C to reduce its viscosity and de-gassed in a vacuum oven. It was then poured gently into the mould and cured in an air-circulating oven for 3 hours at 100°C and post-cured for an additional 3.5 hours at 150°C. Specimens suitable for testing were then cut from the cured block of resin using a water-cooled rotary diamond wheel.

3.1.3. Laminates

Unidirectional and cross-ply (0,90)₅ laminates were fabricated from continuous E-glass fibres and the epoxy resin using a three stage process consisting of dry filament winding followed by resin impregnation and cure.

Continuous glass fibre was wound onto a rotating open square metal frame using an automated filament winding machine. The glass roving was passed through a tensioning unit via a guiding hook and then onto two separate low friction guiding rollers manufactured from poly(tetrafluoroethylene) (PTFE). The roving was then attached to one end of the open square metal frame using masking tape, Figure 3.2. A slight tension on the roving was necessary in order to prevent fibres from bowing out during cure under the high temperature and pressure. Under these conditions the resin viscosity is reduced and surplus resin is forced to flow outwards. If the fibres are not adequately tensioned they will start to bow in the direction of resin flow.

The PTFE rollers were attached to a runner which traversed back and forth on a rotating threaded mandrel. The rotation of the mandrel was controlled by a variable speed motor and the speed of rotation of the metal frame was independently controlled by a fixed speed motor. A known number of tows were
laid down across the frame on each traverse. The number of traverses and the speed of rotation of the mandrel controlled the total amount of glass wound on the frame for any given tex of roving. Thus, the thickness of the ply could be controlled for any tex. To make the cross-ply laminates, the frame was rotated by 90° after the first layer of fibres had been wound on. The winding procedure was then repeated and fibres were laid down on both sides of the first direction layer and at 90° to it.

The glass fibres were then impregnated with resin. Two different impregnation techniques were investigated. In both methods impregnation of the wound frame was carried out under vacuum. The first method of impregnation was identical to that employed by Manders et al [1] and involved freezing the de-gassed resin mix in a single layer over a thin sheet of silicone-coated polyester (Melinex). The sheet of Melinex was placed on top of the glass-wound frame with the frozen resin layer in contact with the fibres. The assembly was then quickly transferred to a vacuum box and placed on a Melinex covered hot metal plate (100°C) inside the box. Evacuation was begun immediately so that a good vacuum was achieved before the resin softened. Impregnation was therefore vacuum assisted, reducing the chances of the formation of micro-voids and air pockets. The general arrangement is shown schematically in Figure 3.3.

Freezing the resin on a sheet of Melinex did, however, cause a layer of water droplets to develop on the surface of the resin through condensation from the atmosphere. It was believed that this layer of condensation might affect the laminate properties under investigation and so an alternative method of resin impregnation was devised so that the condensation layer could be avoided. The vacuum box was modified to allow direct impregnation of the liquid resin. The wound frame was placed inside the box as before and liquid resin was slowly dripped in from a reservoir, after the box had been evacuated. The results achieved from both methods were found to be identical. All laminates were then fabricated using the first method, where the resin was easier to handle.

After impregnation, the laminate was removed from the box and inspected. Any obvious entrapped air on the surface was driven out by wiping the release film with a plastic spatula. The laminate was then sandwiched between two smooth glass plates and cured in an air-circulating oven under a pressure of about 3 kPa at 100°C for 3 hours. At the end of this period, the laminate was allowed to cool. It was then cut out of the metal frame using a water
cooled rotary diamond saw (600 grit) with a movable head. The metal frame was left intact while cutting the laminate so that it could be cleaned and re-used. Test coupons of approximate dimensions 230 mm x 20 mm x t (where t is the thickness of the laminate) were then cut in the desired orientation and post-cured for 3.5 hours at 150°C. This procedure was adopted since experience had shown that post-curing on the frames could lead to the development of cracks in the laminates.

In order to prevent premature failure of the specimen by the indentation action of the grips during testing, chromic acid etched aluminium end tags (1.5 mm thick) were attached to the end regions of both laminate and resin specimens. This was done by first abrading the end regions lightly with Emery cloth, cleaning the end regions and the end tags with Methanol and then using a 24 hours epoxy adhesive to glue the tags on. (The strain gauges and aluminium end tags were fixed to the specimens at the same time and these were allowed to cure at room temperature for at least 72 hours prior to testing, Figure 3.4(a)).

The formulation and configuration of all the laminates fabricated are shown in Table 3.1.

3.1.4. Polishing of laminate specimens.

For any microscopic observations of debonding and matrix cracking on or through the edge of laminate specimens, well polished surfaces are essential to obtain good images and avoid artifacts in the micrographs. It was necessary to polish both edges of each laminate specimen to prevent failure from initiating at an unpolished edge. Specimens of two different sizes were polished. Those for testing on a straining stage (Section 3.3.4) had maximum dimensions of 45 mm X 10 mm X 5 mm. 5 mm was the maximum thickness that could be accommodated by the grip section of the straining stage and includes the thickness of end tags. Specimens for tensile testing on an Instron 1175 (Section 3.2.1) had nominal dimensions of 230 mm X 20 mm X t, where, t, is the laminate thickness. The specimens were polished prior to the attachment of end tags and strain gauges. The types of end tags and strain gauges used are discussed in section 3.2.1. The following polishing methods were found to give the best results;
a) Short specimens (45 mm X 10 mm X t).

The specimens were ground and polished automatically on a Struers Planopol-2, 150/300 machine fitted with a motor operated rotating disc into which the specimens were clamped. The specimens were then ground and polished according to the schedule outlined in Table 3.3. The silicon carbide papers used for grinding were placed on plane Aluminium discs. For the final two stages of polishing, a silk cloth surface was used with Struers OP-S suspension. This is a mildly alkaline suspension of magnesium oxide particles, and gives a final finish of below 0.3 microns.

(b) Long specimens (230 mm X 20 mm X t)

These specimens had to be polished by hand, since the automatic specimen holder could not accommodate the long edges of the specimens. A hand held jig was designed so that specimens could be held with their edges flat on the polishing wheel, thus preventing bevelling of the edges. In the initial stages of polishing, a spirit level was used to ensure that the jig was level. The polishing procedure employed was similar to that shown in Table 3.3, except that the time required to achieve good results was longer. The specimens had to be inspected under the microscope for the quality of polish achieved after each stage of grinding and polishing.

3.2. Characterisation of Resin and Laminate Properties.

3.2.1. Tensile property measurements

Tensile testing of both resin and laminate specimens was carried out using an Instron 1175 universal tensile testing machine. In this test the specimen is gripped between a top fixed jaw at one end and one attached to a moving cross-head driven at a constant displacement rate. A cross-head speed of 0.5 mm min\(^{-1}\) was used for all tests which corresponds to a strain rate of 0.5 \times 10^{-4} \, \text{s}^{-1} for the specimen gauge length used. The load on the specimen registered by an electrically calibrated tension load cell located above the top jaw. The output of this cell was used to drive the Y-axis of an X-Y-Y' chart recorder.

The longitudinal strain in the specimens was measured using an electrical resistance strain gauge (Techniméasure PL10-11-120) The gauge was aligned
parallel to the tensile axis and attached to the specimen surface using a 24 hours epoxy adhesive. The change in the resistance of the strain gauge was monitored through a Wheatstone bridge circuit connected to the integral strain amplifier unit of the Instron. The output from this unit was used to drive the X-axis of the X-Y-Y' chart recorder. In order to measure the Poisson's ratio of the resins, a second strain gauge was also attached to the specimen and was aligned at 90° to the tensile axis. This strain gauge was connected to a strain measuring bridge, whose output was used to drive the second Y'-axis of the X-Y-Y' chart recorder. A simultaneous record of the transverse strain was obtained in this way.

Each tensile test produced a graph of load as a function of strain. The values of load were converted to stress using the original cross-sectional area of the specimen and it was, thus, possible to determine the stress/strain curve and the corresponding elastic modulus for each specimen. Owing to the non-linear stress/strain response of laminates, the secant moduli were determined at intervals of strain as illustrated in Figure 3.4(b). The secant modulus was used in preference to the tangent modulus since it can be measured more accurately. Poisson's ratio was determined directly from the ratio of the measured transverse strain to the longitudinal strain, \( \nu = -\varepsilon_t/\varepsilon_l \). All tensile tests were performed at room temperature.

The specimens were, in general, not tested to destruction, although a number of preliminary tensile tests were carried out on both resin and laminate specimens in which specimens were taken to failure on a single loading. The preliminary tests were done in order to establish the threshold for the failure strains of resin specimens and the first ply transverse cracking strains for cross-ply and 90° unidirectional specimens. The remaining specimens were loaded repeatedly for several cycles below these threshold levels so that any hysteresis or permanent set could be recorded at the end of each cycle. Measurements could also then be made of the changes in moduli of the specimens after repeated loadings, below the transverse cracking strain threshold for laminates, and below the failure threshold for the resin specimens.

The cycling procedure for resin specimens involved loading to just below their failure threshold and then unloading by reversing the cross-head movement at the same cross-head speed and then reloading to failure on the second loading. The laminate specimens were loaded to an upper limit which was determined by the first transverse crack strain threshold, \( e_{tc} \), of the
specimen. Each specimen was strained up to a value of about 0.2% below $e_{tc}$ and the cross-head movement reversed. On reaching zero load the specimen was extended again to the same strain. The specimens were cycled three or four times. Some specimens were then removed from the grips and heated in an air circulating oven for 20 mins. at 100°C. After this the specimen was allowed to cool to room temperature and re-tested for two further cycles. At the end of this second cycle the maximum strain limit was increased but still kept to below the transverse cracking strain, $e_{tc}$. The specimen was again cycled up to the new strain limit for several cycles.

For each specimen, a set of curves was obtained of load as a function of strain for consecutive cycles as well as a record of any permanent deformation at zero load. The effect of heat-treating the specimens on the load/strain diagram was also examined. Corresponding stress/strain curves and elastic moduli were determined for each cycle as described above.

3.2.2. Dynamic mechanical thermal analysis

The glass transition temperature, $T_g$, and the stress-free temperature, $T_I$, of all three resins were obtained using a Polymer Laboratories Dynamic Mechanical Thermal Analyser (DMTA). This is a fixed frequency, variable amplitude analyser and consists of a dynamic measuring head, a microprocessor controlled analyser and a temperature programmer. The apparatus applies a sinusoidally varying displacement via a driven arm clamped centrally on a thin rectangular specimen, of approximate dimensions 6 mm x 3 mm x 30 mm, fixed at both ends in a passive frame. The analyser is programmed to apply a fixed frequency of specimen flexure. This is achieved by varying the current supplied to a large electromagnet to which the driven arm is connected. The resultant displacement of the driven arm is controlled by the visco-elastic response of the specimen and is monitored by an electro-optical device operating from a small 'flag' attached to the arm.

For a linear visco-elastic material the strain and the stress will vary sinusoidally but the strain is out of phase with the stress. The phase lag results from the time necessary for the rearrangement of molecules, generally known as relaxation phenomena. The molecular rearrangements also result in the dissipation of a certain amount of energy. By comparing the phase angle, $\delta$, between the drive signal and the response of the driven arm, the analyser is able to determine the loss tangent, $\tan \delta$, which is the ratio of the
energy dissipated to the maximum energy stored per cycle. \( \tan \delta \) is defined by the equation,

\[
\tan \delta = \frac{E''}{E'}
\]

(3.1)

where \( E'' \) is the loss modulus, which is the out-of-phase or non-elastic component related to the loss of energy (heat) during deformation and \( E' \) is the real part of the modulus which is the elastic component and is related to the storage of potential energy and its release during periodic deformation. When the apparatus has been calibrated for the specimen dimensions, the analyser can also determine the real modulus, \( E' \). Both \( \tan \delta \) and \( E' \) are dependent on the structure of the polymer and any structural changes such as the extensive molecular motions occurring at the glass transition temperature, \( T_g \), result in a dramatic increase in the value of \( \tan \delta \) on reaching this temperature and a corresponding decrease in the value of the real modulus.

The frequency of specimen flexure used in these tests was chosen to be 1 Hertz and this was kept constant. The amplitude of specimen displacement was determined by the microprocessor controlled analyser which was set to operate in its 'auto' strain control mode. This enables the analyser to operate under optimum conditions allowing for changes in the specimen response at high temperatures. The temperature of the specimen was controlled by a temperature programmer connected to a large cylindrical heater placed around the dynamic measuring head. A heating rate of 2K per minute was used in the temperature range 23°C to 200°C.

Each test produced a plot of the real modulus (log \( E' \)) and \( \tan \delta \) as a function of specimen temperature. A decrease in the real modulus was observed before reaching the glass transition temperature. The temperature at which this occurred was regarded as the stress-free temperature of the laminate. The glass transition temperature, \( T_g \), was identified as the maximum of the \( \tan \delta \) peak. Typical traces of \( \tan \delta \) and \( E' \) as a function of temperature are shown in Figure 3.5, which also shows how \( T_g \) and \( T_1 \) were measured. \( T_1 \) was obtained by drawing tangents to the real modulus versus temperature curve as shown.
3.2.3. Determination of the volume fraction of fibres in laminates

The volume fraction of fibres, $V_f$, in the laminates was determined using the "Burn-off" method, and from thickness measurements. The "Burn-off" method involved the thermal decomposition of the resin in a known weight, $W_c$, of a laminate. The specimen was heated overnight in a furnace at 600°C in a pre-weighed crucible. The resin was allowed to burn off and escape while the fibres remained unaffected. After cooling the crucible to room temperature, the contents were re-weighed and the weight of fibres, $W_f$, and resin lost, $W_r$, was determined. From a knowledge of the fibre and resin densities, the volume fraction of fibres, $V_f$, was calculated using the equation,

$$V_f = \frac{(W_f/D_f)}{[(W_f/D_f)+(W_r/D_r)]}$$

(3.2)

where $D_f$ is the density of fibre and $D_r$ is the density of the resin (2550 kgm$^{-3}$ and 1230 kgm$^{-3}$ respectively)

The volume fraction could also be determined simply from a measurement of the laminate thickness. During filament winding a known number of tows are laid down over a given width of each ply. For a laminate with $N$ plies, the volume fraction of fibres, $V_f$, is related to the thickness, $t$, of the laminate according to the following equation,

$$V_f = \frac{(NCF)}{tD_f}$$

(3.3)

where $N$ = Number of plies, $C$ = Number of tows per unit width, $F$ = Fibre tow weight per meter, and $D_f$ = Fibre density.

The volume fractions of fibre were converted to percentage values for convenience. Both methods gave values of volume fraction which agreed closely (+ 2%).

3.2.4. Measurement of the tensile debonding stress

In order to obtain a direct measure of the stress required to cause tensile debonding between a single fibre and the resin matrix, test pieces were prepared in which a single continuous fibre was embedded through the centre of a necked specimen as shown in Table 3.2. A mould was designed to produce five complete specimens. The surfaces of the mould were first coated with a release agent and a single fibre was then aligned down its centre through two
guiding holes, one at each end of the mould. Each fibre end was glued to the base of the mould with a quick-setting epoxy adhesive and the guiding holes sealed with silicone rubber. De-gassed resin was then poured into the mould and the specimens given the same cure schedules as the laminates. The specimens were designed to simulate a tensile stress state at the fibre/matrix interface [50].

On axial compression of the testpiece, the higher Poisson's ratio of the resin causes it to expand radially more than the glass, causing a transverse tensile stress to develop at the glass/resin interface in order to preserve continuity. This stress can then cause debonding in the necked region of the specimen where the stresses are the most concentrated. In the case of a transparent glass fibre/epoxy specimen, the discontinuity would cause light to be scattered at the interface and fibre prominence or stress whitening would be observed making the debond visible. The tensile debonding stress, $\sigma_{db}$, is given by,

$$\sigma_{db} = \sigma_{mn} (\nu_m - \nu_f) \frac{E_f}{1 + \nu_m} \frac{E_f}{(1 - 2\nu_f - 2\nu_f^2)E_m}$$

where $\sigma_{mn}$ = axial stress on minimum section at failure and $\nu_{f,m}$ = Poisson's ratio of fibre and resin respectively, $E_f$ = Modulus of fibre, $E_m$ = Modulus of resin.

### 3.2.5. Measurement of the yield stress of the resin matrices

In order to obtain a better knowledge of the change in mechanical properties of the resin matrices, brought about by increasing the level of cure of the resins, the yield stress of the resins was measured in addition to the Young's modulus and Poisson's ratio. The yield stress of the epoxy resins had to be obtained in compression. Tests in tension were not suitable since the epoxy resins were brittle at room temperature and failed prematurely from defects. The room temperature brittle behaviour can be suppressed, however, using different modes of loading. In uniaxial compression or pure shear, for example, plastic deformation can occur at room temperature. Two methods were used to determine the yield stress. These were the plane strain compression test developed by Williams et al [78], and the uniaxial compression of cylindrical specimens [13].
a) Plane strain compression test

A schematic diagram of the test apparatus used is shown in Figure 3.6. The apparatus consisted of a pair of flat, highly polished parallel dies of known width which were inserted into a sub-press. Each half of the press contained vertical columns to ensure that the dies were aligned, held rigid and parallel. The sub-press was placed on a compression anvil attached to a load cell fitted to the compression beam of a universal tensile testing machine (Instron TTD). A smaller diameter anvil was attached to the moving cross-head above the press. The resin specimen in the form of a flat plate was placed between the lubricated dies. These dies were forced into the testpiece from either side by lowering the moving cross-head at a constant rate of 0.5 mm min\(^{-1}\) in the direction shown (direction 1) in Figure 3.6. Deformation along the axis of the die (direction 2) is prevented by the unstrained material outside the dies. The material displaced in direction 1 is, thus, forced to move in direction 3 only. This results in a constant area under load and a state of plane strain since the width of the testpiece under the die is prevented from increasing (while only the thickness changes).

The friction and geometry of the dies are important considerations. The dies and the specimens had, therefore, to be cleaned and lubricated thoroughly. The specimen width had to be at least four times that of the die to eliminate end effects due to bowing and thereby ensuring plane strain conditions. The ratio of the specimen thickness to die width (h/b) had to be within 0.5 and 0.25 in order to minimise the corrections which may have been necessary for the changing h/b ratio. A set of interchangeable dies of different widths were available so that values could be corrected and normalised. No corrections were made, however, since the inconsistencies in material behaviour were comparatively large. These resulted largely from premature cracking of the material lying outside the dies (see section 4.1.1 (d)).

A typical form of the trace obtained is shown in Figure 3.7. An initial inflexion was always observed because of the extrusion of excess lubricant and the general consolidation of the testpiece and press. An effective origin, \(A'\), was obtained by extrapolating the curve linearly as shown in Figure 3.7.
b) Uniaxial compression of cylindrical specimens.

The cylindrical specimens required for these tests were machined from samples of bulk resin (see section 3.1.2) so that they had nominal diameters of 5mm and lengths of about 10 mm. Each specimen was cleaned and lubricated at the ends and placed between the lubricated compression anvils attached to the moving cross-head (containing the load cell) and the stationary compression beam respectively. The cross-head was then lowered at a constant rate of 0.5 mm min⁻¹. A typical form of the curve obtained is shown in Figure 3.8. The maximum load achieved was converted to stress using the initial cross-sectional area of the specimen and was taken to be the yield stress.

3.2.6. Determination of resin refractive index

The change in refractive index of all three resin matrices with cure was measured so that the apparent change in the transparency of the resulting laminates with increasing cure could be correlated with the closeness of the resin refractive index to that of glass. Two parallel surfaces of resin specimens were polished. The refractive index was then determined using the real and apparent depth method [79]. A travelling microscope was focused on some lycopodium particles on a sheet of paper (point 0, see Figure 3.9) and a reading of the vertical scale on the microscope recorded. The resin block was then placed on the particles and the microscope raised until the particles were in focus again at an apparent depth of I. More particles were then sprinkled at M on top of the block and the microscope raised to bring these into focus. The real depth of O is OM while the apparent depth is IM. The refractive index, N, is given by,

\[ N = \frac{\text{real depth (OM)}}{\text{apparent depth (IM)}} \]  

3.3. Observations of Stress-whitening

3.3.1 Colour photography

While undergoing tensile tests, the laminate specimens were photographed at strain intervals to record any change in their appearance. As the laminates were mostly transparent, the lighting conditions were specifically set so that the small optical inhomogeneity of the specimens could be exploited and
a scattered image of the entire specimen could be recorded. The lighting arrangement is shown in Figure 3.10. Two tungsten angle poise lamps were used as the light sources and the light was directed at an oblique angle to the specimen. A black screen was placed behind the specimen. A Chinon CE4 camera fitted with a macro lens and mounted on a fixed tripod was used to record the sequence of images on an ordinary (125 ASA) daylight colour film. A colour film was used since it was observed that the specimen exhibited certain colour changes as well as the whitening effect. With tungsten lighting, it was necessary to use a blue tungsten to daylight filter on the lens to ensure that the correct colours were recorded. The lighting conditions were critical for the observations of both colour changes and stress-whitening.

Photographs of the specimens were taken at every 0.05% interval of strain during both the loading and the unloading cycles of the tensile test and after heat treating the specimens.

3.3.2 Macro-photography

The experimental set-up for observing the specimens at higher magnifications during tensile testing is shown in Figure 3.11. A Zeiss Tessovar photomacrographic zoom system capable of magnifying up to 12.6 times was used. This was the highest magnification available on a portable unit which could be fixed to the Instron testing machine and covered the range between an ordinary zoom lens and a photomicroscope. A variable intensity halogen light source was used in which the light was passed through two fibre optic cables. Both cables were positioned so that the light could be directed onto the specimen at an oblique angle. The specimen was observed through a lens at the side of the attachment. It was photographed using a camera attached to the back of the unit. A fast black and white film (400 ASA) was used as the exposures tended to be long even at maximum lamp settings. Photographs of sections of the 'face' (width) of the specimen were taken at every 0.05% intervals of strain at magnifications of 0.8 times and 3.2 times during both the loading and unloading cycles of the tensile test. The system could not resolve individual debonds on the edge or thickness of the coupon. In order to resolve individual micro-cracks in situ microscopy had to be employed.
3.3.3. Polished edge microscopy

A number of laminate specimens with polished edges were tensile tested and their edges examined in transmission on a Zeiss photomicroscope. The specimen was first examined prior to tensile testing and several areas were photographed. It was then tested in uniaxial tension and the test interrupted on reaching a given strain level when it was removed from the grips of the Instron and re-examined under the microscope, with particular reference to the known areas. The procedure was continued so that the specimen was examined over an applied strain range of 0.0% to 0.6% or until micro-cracking near the fibre/matrix interface was observed. The specimen was then heated in an air-circulating oven at 100°C for 20 mins. It was allowed to cool to room temperature, re-examined under the microscope and photographed prior to re-testing. The above test procedure was then repeated.

A series of photographs showing the appearance of micro-cracks and their disappearance on heat treating the specimen were, thus, obtained. This test procedure was not successful for all specimens since it relied on the visibility of micro-cracks at zero load - i.e. the micro-cracks had to remain sufficiently 'open' at zero load so that stress-whitening was 'retained' after unloading. The retained stress-whitening was most apparent in the laminates with thin (0.5 mm) inner 90° plies and hence the specimens from these laminates were used for the above experiments. The same specimens were also photographed using colour photography as described in section 3.3.1. Thus, the appearance, retention and disappearance of stress-whitening before and after heat treatment was also recorded. Later, all laminates were examined in situ when this became possible.

3.3.4. In situ observation of the polished edge of specimens in uniaxial tension

In situ observations of the polished edges of laminate specimens were made using a hydraulically operated straining stage. This was designed to fit on a microscope stage and was capable of applying a tensile force of up to 40 kN on a specimen of approximate dimensions of 45 mm x 10 mm. (The total thickness, including the end tags, must not exceed 5 mm.) The straining stage was designed to fit inside the chamber of a scanning electron microscope (SEM, Cambridge S100) so that continuous observations of the initiation and growth of micro-cracks in the specimen could be made during a tensile test.
Hence, all laminate specimens could be examined under load. Examination under load presented a considerable advantage since a great deal of detail is lost due to crack closure upon unloading the specimen.

The straining stage was designed and built at the University of Surrey. The device was machined from a single block of high grade 18/8 stainless steel, favoured in high vacuum systems. One end of the block was machined to produce, internally, a highly polished hydraulic cylinder. PTFE cup seals were used inside the cylinder and a hydraulic line was connected to the cylinder. The other end of the hydraulic line was connected to a footpump which was used to actuate the hydraulics. The hydraulic line was made of a reinforced thermoplastic tubing to withstand the high pressures required for extending high modulus specimens and provide a degree of flexibility so that the straining stage could be manoeuvred through the port-hole in the door of the specimen chamber of the SEM. (The dimensions of the straining stage were thus dictated by the size of the port-hole and the size of the specimen chamber itself.) The remainder of the stainless steel block was machined as shown in Figure 3.12. The specimen was gripped by wedge-action inserts and a screw adjustment positioned on the end of the block opposite the hydraulic cylinder allowed a slight pre-tensioning of the specimen. This was necessary so that the specimen could be securely gripped at the beginning of the test.

The strain on the specimen was monitored by an electrical resistance strain gauge, attached to the specimen with an epoxy adhesive, aligned parallel to the tensile axis. The strain gauge leads were soldered to connecting wires attached to the inside of the the port-hole cover. Terminals on the outside of the port-hole cover allowed connections to be made to a portable strain gauge meter which was capable of giving a direct reading of the longitudinal strain. The load on the specimen could not be monitored directly.

The use of the straining stage in the SEM had limited success. Although the problems encountered with its use were soluble they could not be solved in the limited time available for these experiments. The SEM was initially preferred to an optical microscope because of its superior resolution at high magnifications. The optical microscope, however, did have an advantage in that the transparent laminate specimens could be examined in transmission which was found to be more informative than examining in reflected light. The device was, therefore, simply adapted for use under an optical microscope (Zeiss photomicroscope). This was achieved by drilling an elliptical hole in the base of the straining stage so that the specimen could be observed in
transmitted light. The straining stage was then positioned on a microscope stage capable of providing X, Y, and Z movements, three mutually perpendicular directions. Experiments using this method were successful.

Three problems were encountered with the straining stage. The first was specific to its use in the SEM while the other two occurred when using either microscope. The problem encountered when using the straining stage in the SEM was concerned with the flexibility of the hydraulic hose. The hose was not flexible enough to allow permanent positioning of the stage onto the existing stage of the SEM. Specimens for examination in the SEM are usually mounted on stubs which fit into the microscope stage and are held in position by a grub screw. The straining stage was fitted with a similar but larger stub so that the X, Y, Z and tilt movements already available in the microscope could be utilised. The inflexibility of the hose made it difficult to position the hose inside the chamber. It could not be forcibly positioned because it applied a torque on the straining stage which in turn rotated the microscope stage. This would have eventually led to premature wear of the mechanisms providing the X, Y and other movements. The second problem was the occasional leakage of hydraulic fluid. This cannot be tolerated in a vacuum apparatus.

The third problem was concerned with small inaccuracies in the machining of the grip housing. During initial testing under the optical microscope it was observed that transverse cracks always initiated on the edge of the specimen furthest from the lens, despite the uniform polish given to both edges. It became apparent that this was the result of small variations in the dimensions of the grip housing. This had the effect of applying an uneven load to the specimen across its width which led to the preferential cracking of the specimen on one edge. A finely machined aluminium specimen inserted in the grips and tensioned showed jaw marks on the bottom edge only, making the effect apparent. In order to even out the grip pressure thin strips of aluminium packing were inserted between the wedge inserts and the grip housing. This was successful.

3.3.5. Fractography

(a) Optical microscopy

The polished edges of fractured specimens were examined in transmission under a Zeiss microscope so that the path of a transverse fracture (90°
unidirectional specimens) or a transverse crack [(0,90)s specimens] could be studied in detail.

(b) Scanning electron microscopy

The fracture surfaces of transverse failures were examined under a scanning electron microscope (Cambridge S100) to obtain details of the mode of failure and localised deformation. The specimens were mounted on standard aluminium stubs with "Durafix" glue. As with all non-conducting specimens for examination under an electron microscope, the surfaces had to be coated with a conductive coating (gold-palladium alloy, in this case) to prevent charging of the surface. The specimens were sputter-coated over short successive time intervals (1 min.) to prevent the specimen from heating up. A conducting path from the specimen surface to the aluminium stub was painted using silver colloidal paint.

3.4-Quantitative Measurement of Stress-whitening

3.4.1. Preliminary tests

Stress-whitening is a term applied to an optical effect resulting from a change in the transmission characteristics of the laminate, as a result of the application of stress. It is generally used in connection with thermoplastics to describe an effect resulting from the scattering of light, caused by microscopic voids such as crazes, generated during plastic deformation. In glass/epoxy laminates, given the absence of crazes, such an effect can result from the presence of small cracks of the order of the wavelength of visible light. Direct photometry during a tensile test was, therefore, chosen for the measurement of this effect. The measurement required a photometric system consisting of a fixed intensity light source, a photodetector, an amplifying circuit and a chart recorder. The photodetector had to be positioned on or near the specimen to continuously monitor the change in intensity (Wm⁻²) of a fixed intensity of light passed through the specimen. It could be positioned to monitor the attenuation in intensity of the main emergent beam, in the direction of the incident beam, or the increase in intensity of light scattered at an angle to the incident beam as the specimen stress-whitened.
Initial trials were conducted using a simple photodiode—a semiconductor device whose voltage output is known to be related to the intensity of light falling on its sensitive area. Measurements were made in the two transmission modes shown in Figure 3.13. In mode 1, the photosensitive device was encased in a black rubber grommet attached to the wide face of the specimen with an epoxy adhesive. A variable intensity halogen lamp was used as the light source and the light was guided into a second grommet on the opposite side of the specimen using a fibre optic cable. The photodiode was connected to an amplifying circuit whose output was used to drive the second $Y'$-axis of an X-Y-Y' chart recorder. The first $Y$-axis and the X-axis was used to record the load and the longitudinal strain in the usual way. The specimen was positioned in the grips of an 1175 Instron tensile testing machine. A tensile test was then carried out in the usual manner but in darkness. The results obtained using this arrangement are shown in Figure 3.14 for a 0.5% BDMA laminate with a thin inner 90° ply, 2d, of 0.5 mm (outer 0° plies, b, of 0.8 mm). This shows the photodetector output and load as a function of applied strain.

It was clear from these results that the level of light changes being monitored were low and the amplifying circuit was operating at its limit. The signal to noise ratio was high and the results were also difficult to interpret. This method was seen to contain inherent complexities such as the presence of a range of wavelengths as a white light source was used. It was proposed that a better result could be achieved by improving the amplifying circuit and by experimenting with other more efficient light sensitive devices such as photoresistors and phototransistors. Alternative monochromatic light sources were also sought since the specimen had earlier shown some colour changes.

The possibility of using a commercially available scanning monochromator unit was investigated. This device worked on the principle of a rotating diffraction grating which was able to resolve wavelengths in the visible region of the electromagnetic spectrum. The dynamic range of this device was not sufficient for the purposes of accurately monitoring the colour changes or stress-whitening. Use was made of colour filters to provide a narrow band of radiation. Experiments were also done with an infra red emitter and receiver. None of these methods, however, provided satisfactory results. A Ne-He LASER was considered at this stage but in both modes 1 and 2 (Figure 3.13), it led to the saturation of the photosensitive devices at the start of the test.
An improved electronic circuit which could convert current received from a phototransistor to voltage in a range of sensitivities from 50V/A to 5V/mA and amplify it with a selectable gain of 1 to 500 was designed and built in the Materials Science and Engineering Department at the University. A block diagram of the circuit is shown in Figure 3.15 (a) and a full detailed circuit diagram is provided in appendix 1. The amplifying circuit was housed as a single unit referred to as the photometer, Figure 3.15 (b). For experimentation in mode 2, a phototransistor was used in conjunction with the photometer. A special clamp was designed to locate the light source and the phototransistor. The edges of the specimen were polished to minimise light scatter due to the surface roughness of the edges. The clamp was designed so that an optic fibre cable could be guided and brought into contact with a 0.8 mm² area of the 90°ply on the edge of the specimen, while a phototransistor which had a sensitive area of about 0.8 mm² could be positioned at the opposite edge of the specimen, Figure 3.16. A phototransistor is approximately 100 to 1000 times more sensitive then a photodiode. The phototransistor was connected to the photometer whose output voltage was used to drive the second Y'-axis of an X-Y-Y' chart recorder while the first Y-axis was used to record the load on the specimen and the X-axis monitored the longitudinal strain in the usual way. The results obtained in mode 2 for a (0,90)₈ specimen with a thin (0.5 mm) inner 90° ply are shown in Figure 3.17.

Although some noise was still apparent in the trace shown in Figure 3.17, the results were greatly improved with the use of the new amplifying circuit. The trace which shows the intensity of transmitted light and load as a function of applied strain has three characteristic regions. Firstly an increase in the level of the transmitted light is observed as the strain is increased suggesting an improvement in the transmission of light from one edge to the other. This increase is then followed by a plateau despite the increase in strain. A sudden decrease in the detected light is then observed. The decrease in light did not coincide exactly with the strain at which stress-whitening was observed but occurred later. In addition to the complex nature of the trace a further problem was their lack of reproducibility.

Compare, for example, the result obtained for a second specimen from the same laminate, as shown in Figure 3.18, with that shown in Figure 3.17. Although the general form of the traces is similar, the variability was difficult to
interpret. The need for a simple and reproducible method led to the development of the off-axis LASER diffraction technique which is discussed in section 3.4.2.

3.4.2. The off-axis LASER diffraction technique.

The off-axis LASER diffraction method was found to give the most reproducible results on the quantitative measurement and development of low strain damage in the glass fibre/epoxy specimens. The results correlated with both the visual effect of stress-whitening and microscopic observations of cracking in the 90° ply. The principal experimental arrangement is shown in Figure 3.19 (a). In this method a 5 mW Ne-He LASER beam (wavelength = 632.8 nm) was projected onto the surface of the specimen at an angle of 45° to the tensile axis as shown in the schematic diagram, Figure 3.19 (b). A phototransistor was positioned behind the specimen at 90° to, and in the same vertical plane as, the incident beam. The phototransistor was attached to the specimen. The photodetector housing is shown in Figure 3.19(c) in position on the specimen. The position of the detector could be varied from the 90° position to any point on an arc described by arms 'A' and 'B' on the housing which were of equal length. The majority of tests were performed with the photodetector fixed at 90° to the incident beam, position 1. Some tests were carried out to study the effect of varying the angular position of the detector. The angular positions scanned are shown in Figure 3.19(d). The voltage output from the phototransistor, which was proportional to the intensity of light, was fed to the photometer (amplifying circuit) which in turn was used to drive the Y'axis of an X Y Y' chart recorder. The angle of incidence of the LASER could also be varied and so diffraction patterns were recorded with the LASER at both 90° and 45° to the specimen. Figure 3.19(b) shows the two orientations of the LASER beam with respect to the specimen at which diffraction patterns were recorded. The patterns obtained are discussed in section 5.3 (a).

At the start of the tensile test when there is little damage in the specimen the majority of the beam is transmitted straight through the specimen and little or no light reaches the detector. As the specimen begins to develop damage, a number of gaps or interfaces develop which interfere with the passage of light. As a result, the light is diffracted and is able to reach the detector. This effect can be directly observed by positioning a screen behind the specimen to show the change in the diffraction pattern as the specimen is loaded. At the beginning of the tensile test, a small diffuse
spot is observed on the screen at a position corresponding to that of the transmitted LASER beam. When the specimen is loaded, the LASER beam is diffracted and a vertical band of light is observed on the screen, see section 5.3 (a). The band continues to increase in length and intensity with increasing strain, depicting the angular distribution of the diffracted light. A typical trace of the change in the intensity of detected light (with the detector fixed at 90° to the incident beam and the LASER at 45° to the specimen) as a function of the longitudinal strain is shown in Figure 3.20 which also shows the load on the specimen as a function of strain.

3.4.3. The reversibility of stress-whitening.

Results on the observation of stress-whitening in the laminate had already indicated that the stress-whitening effect was reversible after heat-treatment for 30 mins. at 100°C. An experiment was, therefore, undertaken to investigate this reversible effect using the off-axis LASER diffraction method. A low cure (0.5% BDMA accelerator level), thin (0.5 mm) 90° ply, cross-ply specimen was tested in tension in conjunction with the off-axis LASER diffraction method. The specimen was strained until stress whitening was observed and then unloaded and removed from the grips. It was then heat-treated at 120°C for 20 mins. and allowed to cool and then re-tested as described above. This procedure was repeated 4 times. A fifth and final heat-treatment where the specimen was heated at 120°C for 12 hours was then given to the specimen and the specimen was re-tested, after cooling to room temperature.

Any change in the glass transition or stress-free temperatures of the specimen was investigated at the same time by including specimens for DMTA analysis during each heat-treatment. A total of 6 DMTA specimens were, therefore, tested. The first specimen had no heat-treatment while the sixth specimen had been heat-treated 5 times (i.e. it received a total of 13 hours and 10 mins. at 120°C.) A slightly higher temperature (120°C compared to 100°C for earlier work) was used in order to accelerate the effects of any curing processes which may be occurring. The effect of increasing time of heat-treatment on the reversibility of stress-whitening and the role of the curing processes of the resin were investigated using the above methods.
(a) Epikote 828 resin - diglycidyl ether of bisphenol-A (DGEBA).

(b) Epikote NMA - nadic methyl anhydride (NMA).

(c) Benzyl dimethyl amine (BDMA).

(d) Cured epoxy resin.

Figure 3.1. Chemical structure of (a) resin (b) hardener (c) accelerator and (d) cured epoxy matrix.
Figure 3.2. Filament winding apparatus showing glass fibre roving being wound on an open square metal frame.

Figure 3.3. Schematic diagram showing laminating lay-up in vacuum box.
Figure 3.4 (a) Schematic illustration of tensile test specimen with end tags and strain gauge.

Figure 3.4 (b) Schematic diagram illustrating the measurement of secant moduli from a stress/strain diagram.
Figure 3.5. Schematic diagram showing typical traces obtained during dynamic mechanical thermal analysis. T_g is the glass transition temperature, T_1 approximates to the stress-free temperature.

Figure 3.6. Plane strain compression rig for the measurement of yield stress (after Williams and Ford [78]).
Figure 3.7. Typical trace of load against cross-head movement obtained during a plane strain compression test. The discontinuities in the trace are the result of tensile cracks which originated outside the compression region. \( \sigma_y \) is the yield stress of the resin.

Figure 3.8. Typical trace of load against cross-head movement obtained during uniaxial compression of resin cylinders. \( \sigma_y \) is the yield stress.
Figure 3.9. Measurement of refractive index using the real and apparent depth method where, OM is the real depth of the object under the resin block, IM is the apparent depth and T is the graduated scale of a travelling microscope.

Figure 3.10. Oblique illumination conditions for colour photography with a black screen positioned behind the specimen.
Figure 3.11. Experimental set-up for macro-photography during tensile testing showing the Zeiss Tessovar zoom system and the halogen light source behind the specimen.

Figure 3.12. Straining stage in position on a photo-microscope stage showing a small specimen with attached strain gauge, held in the grips.
Figure 3.13. Schematic illustration showing light transmission modes 1 and 2 with respect to the (0,90)_s laminate and the loading axis.

Figure 3.14. Typical result showing transmitted light in terms of millivolts and load, as a function of strain in mode 1 for a (0,90)_s laminate (0.5% BDMA) with an inner 90° ply thickness, 2d, of 0.5 mm and outer 0° plies, b, of 0.8 mm).
Figure 3.15 (a). Block circuit diagram showing the main components of the amplifier (photometer), see also appendix 1.

Figure 3.15 (b). The photometer connected to the phototransistor.
Figure 3.16. Transmission clamp designed to hold the phototransistor at one end and the light guide at the other (mode 2).

Figure 3.17. Light detected, in terms of millivolts, and load as a function of strain for a specimen from a 0.5\% BDMA (0,90)\textsubscript{5} laminate with an inner 90° ply thickness, 2d, of 0.5 mm, and outer 0° ply thickness, b, of 0.8 mm (mode 2).
Figure 3.18. Light detected, in terms of millivolts, and load as a function of strain for a specimen from a 0.5% BDMA (0,90)₉ laminate with an inner 90° ply thickness, 2d, of 0.5 mm and outer 0° ply thickness, b, of 0.8 mm (mode 2).

Figure 3.19(a). Experimental arrangement of the off-axis LASER diffraction technique showing LASER at 45° to the specimen.
Figure 3.19(b). Schematic diagram of the experimental arrangement of the LASER diffraction technique, showing the positions at which diffraction patterns were obtained (90° and 45° to the specimen).

Figure 3.19(c). Photodetector housing in position on specimen showing arms "A" and "B".
Figure 3.19(d). Schematic diagram showing angular positions of the photodetector at which light intensity was monitored.

Figure 3.20. Typical traces of light detected, in terms of millivolts, and load as a function of applied strain obtained with the LASER at $45^\circ$ to the specimen and photodetector in position 1 (see Figure 3.19(d)).
<table>
<thead>
<tr>
<th>Laminate code</th>
<th>Fibre finish</th>
<th>Fibre tex</th>
<th>BDMA Level (%)</th>
<th>Laminate lay-up</th>
<th>Ply thickness 'b' (mm)</th>
<th>Ply thickness '2d' (mm)</th>
<th>Volume fraction (Vf)</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Silane</td>
<td>600</td>
<td>0.5</td>
<td>(90)_s (0)_s</td>
<td>-</td>
<td>2.0</td>
<td>57.5</td>
<td>(0,90)_s laminate</td>
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<tr>
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<td>0.5</td>
<td>(0,90)_s</td>
<td>0.65</td>
<td>2.0</td>
<td>60.3</td>
<td></td>
</tr>
<tr>
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<td>(0,90)_s</td>
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<td>1.0</td>
<td>63.5</td>
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</tr>
<tr>
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<td>0.5</td>
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<td>0.8</td>
<td>0.5</td>
<td>59.9</td>
<td></td>
</tr>
<tr>
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<td>Silane</td>
<td>600</td>
<td>1.5</td>
<td>(90)_s (0)_s</td>
<td>-</td>
<td>2.1</td>
<td>58.0</td>
<td></td>
</tr>
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<td>Silane</td>
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<td>(0,90)_s</td>
<td>0.6</td>
<td>1.8</td>
<td>60.3</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Silane</td>
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<td>1.5</td>
<td>(0,90)_s</td>
<td>0.8</td>
<td>1.0</td>
<td>61.5</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Silane</td>
<td>600</td>
<td>1.5</td>
<td>(0,90)_s</td>
<td>0.9</td>
<td>0.5</td>
<td>54.1</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Silane</td>
<td>600</td>
<td>3.0</td>
<td>(0)_s (90)_s</td>
<td>-</td>
<td>2.9</td>
<td>44.0</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Silane</td>
<td>600</td>
<td>3.0</td>
<td>(0,90)_s</td>
<td>0.7</td>
<td>1.8</td>
<td>54.9</td>
<td></td>
</tr>
<tr>
<td>11</td>
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<td>3.0</td>
<td>(0,90)_s</td>
<td>0.65</td>
<td>1.0</td>
<td>54.6</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Silane</td>
<td>600</td>
<td>3.0</td>
<td>(0,90)_s</td>
<td>0.9</td>
<td>0.5</td>
<td>41.1</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Starch</td>
<td>120</td>
<td>0.5</td>
<td>(0)_s (90)_s</td>
<td>-</td>
<td>2.3</td>
<td>41.5</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Starch</td>
<td>120</td>
<td>1.5</td>
<td>(0)_s (90)_s</td>
<td>-</td>
<td>2.1</td>
<td>42.0</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Silane</td>
<td>1200</td>
<td>0.5</td>
<td>(0,90)_s</td>
<td>0.5</td>
<td>2.2</td>
<td>58.0</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Silane</td>
<td>1200</td>
<td>1.5</td>
<td>(0,90)_s</td>
<td>0.5</td>
<td>2.2</td>
<td>56.0</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Silane</td>
<td>1200</td>
<td>3.0</td>
<td>(0,90)_s</td>
<td>0.55</td>
<td>2.6</td>
<td>47.0</td>
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</tr>
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Table 3.1. Formulation and configuration of laminate specimens.
<table>
<thead>
<tr>
<th>Type of test</th>
<th>Specimen configuration</th>
<th>Resin system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile tests: determination of tensile modulus, fracture strain and Poisson's ratio.</td>
<td>a = 20 mm, b = 6 mm, l = 200 mm</td>
<td>All three resin systems (0.5%, 1.5% and 3.0% BDMA.)</td>
</tr>
<tr>
<td>Plane strain compression test: determination of yield stress.</td>
<td>a = 20 mm, b = 2 mm, l = 40 mm</td>
<td>As above.</td>
</tr>
<tr>
<td>Axial compression test: determination of yield stress.</td>
<td>r = 6 mm, l = 10 mm</td>
<td>As above.</td>
</tr>
<tr>
<td>Measurement of refractive index.</td>
<td>a = 2 mm, b = 20 mm, l = 20 mm</td>
<td>As above.</td>
</tr>
<tr>
<td>Dynamic mechanical thermal analysis: determination of glass transition temperature and stress free temperature, T2.</td>
<td>a = 10 mm, b = 3 mm, l = 30 mm</td>
<td>As above.</td>
</tr>
<tr>
<td>Broutman test: measurement of the tensile strength of the single fibre-matrix bond.</td>
<td>r = 25 mm, a = 12.5 mm, h = 37.5 mm, b = 5-6 mm</td>
<td>0.5% BDMA resin only.</td>
</tr>
</tbody>
</table>

Table 3.2. Test schedule for resin specimens.
<table>
<thead>
<tr>
<th>Medium</th>
<th>Grade</th>
<th>R.P.M.</th>
<th>Pressure (N)</th>
<th>Time (min)</th>
<th>Lubricant</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC</td>
<td>500</td>
<td>150</td>
<td>60</td>
<td>1</td>
<td>water</td>
</tr>
<tr>
<td>SiC</td>
<td>1000</td>
<td>150</td>
<td>60</td>
<td>1</td>
<td>water</td>
</tr>
<tr>
<td>SiC</td>
<td>2400</td>
<td>150</td>
<td>60</td>
<td>1</td>
<td>water</td>
</tr>
<tr>
<td>SiC</td>
<td>4000</td>
<td>150</td>
<td>60</td>
<td>1</td>
<td>water</td>
</tr>
<tr>
<td>DP-DUR</td>
<td>-</td>
<td>150</td>
<td>60</td>
<td>2</td>
<td>OP-S</td>
</tr>
<tr>
<td>DP-DUR</td>
<td>-</td>
<td>300</td>
<td>60</td>
<td>1</td>
<td>water</td>
</tr>
</tbody>
</table>

Table 3.3. Polishing schedule for specimens.

4.1.1. Resin properties.

(a) Specimen integrity.

All cured resin samples were transparent. They appeared void free when examined in transmitted light and there were no obvious differences in appearance between the three different cure levels. All three resins had a yellow-brown colouration.

(b) Secant modulus and fracture strain.

The variation of mean secant modulus, \( E \), of the epoxy resin with accelerator level is shown in Table 4.1, as a function of applied strain. The results show that as the level of accelerator in the system is increased from 0.5% to 1.5% the modulus is lowered by 0.4-0.5 GPa. A further increase in accelerator level to 3.0% did not result in a further decrease in the modulus. The moduli appear to remain constant with increasing strain up to 0.5% strain. The mean tensile fracture strains, \( \varepsilon_f \), of the three resins are also shown in Table 4.1. The fracture strain is similar for all three resins and is of the order of 0.5% strain. The value of applied strain at failure is low because the samples were tested as-cut so that the cut edges may have contributed flaws leading to premature failure in tension. An increase in fracture strain was obtained by polishing the edges of the samples. The effect of polishing is shown in Table 4.2 which shows the mean fracture strain of polished edge samples of epoxy resin containing 0.5% accelerator. The mean fracture strain was increased to 1.6% strain. Table 4.2 also shows variation of secant modulus as a function of strain for the resin with 0.5% BDMA. The modulus is seen to decrease continuously from 3.8 GPa at 0.1% strain to 3.4 GPa at 1.5% strain. The stress/strain diagram for the resin showed a small amount of hysteresis but no significant permanent set was observed. The stress/strain diagrams for the resins with higher
levels of BDMA (1.5% and 3.0% BDMA) showed linear behaviour and no significant hysteresis was observed up to the fracture strains.

(c) Poisson's ratio.

The effect of accelerator level in the resin on the Poisson's ratio is shown in Table 4.3 as a function of applied strain. The mean values of Poisson's ratio for the resin containing 0.5% BDMA appear slightly lower than those for the resin containing 3.0% BDMA but the difference, 0.02, is small relative to the observed variation in Poisson's ratio for each resin. The increase in Poisson's ratio with increasing level of BDMA must, therefore, be regarded as tentative. Similarly, while the Poisson's ratio for each resin appears to increase with applied strain, this change is of the same order as the observed variation in Poisson's ratio and so lies within experimental error.

(d) Yield stress.

The yield stress, \( \sigma_y \), of the resin was measured using two methods. Table 4.4(a) shows the results obtained using the plane strain compression test. The results indicate that the yield stress of the resin decreases as the level of BDMA increases. The results obtained for the 1.5% and 3.0% BDMA resins were identical, within experimental error. When the specimens were examined after testing, a series of tensile cracks could be seen in the regions outside the compression region, see Figure 4.1. The cracks occurred because the epoxy resins are very brittle under tension. In restraining the movement of the compressed material parallel to the dies, the undeformed material which provides the restraint, is put under tension and so can crack, leading to a reduction in the restraint imposed on the material under test. This test method was, therefore, not ideal for brittle, low-strain-to-failure materials, since the results obtained do not actually reflect small differences in the properties of the high cure resins (1.5 and 3.0% BDMA).

The uniaxial compression of resin cylinders gave a more consistent result for the yield stress, as reflected by the standard deviation, and also by the difference obtained in the values of yield stress for the 1.5% and 3.0% BDMA resins. The results are shown in Table 4.4(b). These results confirm those obtained previously and show clearly that as the level of BDMA in the resin is increased the yield stress decreased. Figure 4.2 illustrates the decrease in yield stress as a function of accelerator level and Figure 4.3 shows the test specimens after yielding.
(e) Dynamic mechanical thermal analysis.

The glass transition temperature, $T_g$, of the resin was determined from the curve of $\tan \delta$ as a function of temperature. The temperature at which a maximum in the values of $\tan \delta$ was obtained was taken to be the glass transition temperature. The "stress free temperature", $T_1$, was determined from the curve of $\log E$, the loss modulus, versus temperature as shown in Figure 3.5. The stress-free temperature is taken to be the temperature above which there are no thermal stresses present. Below this temperature thermal stresses may be locked into the laminate. Alternatively, it may be determined by measuring the temperature at which an unbalanced (0,90) beam begins to develop a curvature. Previous experience has shown that both methods provide values of $T_1$ which are in close agreement [8].

The values of $T_g$ and $T_1$ obtained for the three resin systems are shown in Table 4.5. The results show that as the level of BDMA in the system increased, $T_g$ and $T_1$ are both increased. The $T_g$ achieved for the resin containing 3.0% BDMA is close to the post-cure temperature of 150°C.

(f) Refractive index.

In the literature on epoxy resins [B3], several examples exist which demonstrate that the level of cure of the epoxy resin can be determined by its refractive index. Table 4.6 shows the values of refractive index of the resins obtained with three different levels of accelerator using the method described in section 3.2.6. It is evident that it is not possible to distinguish any difference in the refractive index of the resins. Any small differences present are well within the standard deviations obtained using this method. To monitor the small differences, a high degree of accuracy and reproducibility of the scale reading and focusing of the particles is required and this could not be achieved using the travelling microscope employed.

(g) Tensile debonding stress of the epoxy/glass interface.

At an early stage of this investigation attempts were made to measure the tensile debonding stress of a single glass fibre in epoxy resin using a necked resin specimen, see section 3.2.4. If debonding failure had been detected, the specimen could then have been annealed and the 're-bonded'
specimen tested again to measure the strength of the 'healed' bond. A parallel study could then be made on single fibres along with the study of debonding in laminates. Unfortunately no debonding failure could be detected prior to compression failure of the entire specimen at the neck. The specimens failed at a stress of 140 MPa. This is in agreement with the yield stress measured using other methods, see section 4.1.1(d). Experiments with embedded bundles of glass fibres gave the same result. It is possible that the interface bond had a high strength and that failure could not occur before resin failure. In such a case, it can be deduced from equation 3.4 that the tensile debonding stress is at least greater than 5.0 MPa. It is also possible, however, that failure of the bond, prior to specimen yielding was simply not detected because the amount of light scattered was too small.

There are several ways in which the method could have been investigated further and improved to achieve the desired result. For example, an in situ microscope could have been set up for detecting the debond more easily and a powerful illumination source, such as a LASER, could have been used to make the debond more visible through scattering or diffraction of the light by the gap created. The adhesion of starch coated glass fibres to the epoxy resin could have been investigated to re-assess the feasibility of the method since the adhesion is expected to be very low for these fibres. This method is known to have been successful for large (100 microns) diameter fibres [50]. The priority of this investigation, however, was to detect debonding in laminates and improvement of the test is recommended for future work.

4.1.2. Laminate properties

(a) Specimen integrity.

The laminates were found to vary in clarity depending on the level of cure of the matrix resin. Laminates made from resin containing 0.5% BDMA were slightly cloudy while those made with resin containing 3.0% BDMA were quite clear. The laminates manufactured with 1.5% BDMA were of intermediate clarity. All the laminates appeared yellow when placed flat on a white sheet of paper, a colour imparted to them by the resin. Varying the angle of the light with respect to the specimen led to the presence of various colours being observed. These colours ranged from blue for laminates made with resin containing 0.5% BDMA to blue with tinges of violet or red in some regions of laminates made with resin containing higher cure resins. The colours are discussed in section 4.2.1.
Microscopic examination of the polished edges of laminates prior to testing showed several interesting features. Laminates made with epoxy resin containing 0.5% BDMA showed poor contrast between glass fibre and resin, Figure 4.28. This was not the case for the 1.5% BDMA laminates or the 3.0% BDMA laminates where the individual fibre cross-sections in these laminates were well defined, Figure 4.30. This suggests that the level of contrast was in some way associated with the level of cure of the laminate.

Another feature observed in laminate specimens was the presence of fibre splits which normally occurred where a group of fibres, usually in contact, was surrounded on one side by a resin-rich region. It was noticed that occasionally such regions survived fibre splitting, presumably due to the higher strength of the fibres. These fibre splits did not occur in the 90° unidirectional laminates even in the most highly cured resin, see Figure 4.4. However, they did occur to a very significant extent in the 90° plies of (0,90)s laminates. Figure 4.5 shows a large number of fibre splits concentrated at the 0/90 ply interfaces and they also satisfy the condition of being in contact and near resin rich regions. It shows how these also occurred in the middle of the ply tending to form characteristic arcs. The higher cure (1.5% and 3.0% BDMA) (0,90)s laminates showed more fibre splits as did the low cure cross-ply laminates with relatively thin inner plies. Thus, these fibre splits appear to be associated with the thermal restraint stresses present in a (0,90)s laminate, prior to testing. They were not polishing defects as all laminates were given exactly the same polishing treatment.

Figure 4.29 shows a polished section of the laminate containing fibres with a starch finish. Considerable de-wetting is observed around the fibres as seen by the dark tricorns. The contrast between fibre and resin is very poor and the transmission light image appears to be like an image obtained in reflected light. The light is poorly transmitted due to the large amount of poor bonding which results in the light being scattered in all directions.

(b) Volume fraction of glass fibres.

The volume fraction of glass fibres in the laminates was determined by the burn-off method described in section 3.2.3. The results obtained for all laminates are shown Table 4.7(a-f). For laminates made with 0.5% and 1.5% BDMA resin, the fibre volume fractions achieved were between 50-60%. The
fibre volume fraction achieved for laminates made with resin containing 3.0% BDMA were somewhat lower in the range of 40-55%. The 3.0% BDMA laminates gelled very quickly so that as the temperature of the laminate was increased there was very little time during which the viscosity of the resin was low enough for excess resin to flow out. Once the resin begins to gel its viscosity is increased rapidly so that flow of resin is greatly retarded and more resin is retained resulting in a laminate with a lower volume fraction of glass fibres.

Laminates made from the textile roving containing the starch finish also had low fibre volume fractions of the order of 40%. The glass roving was of a much lower tex (120 as opposed to 600) and although this was allowed for during filament winding, the smaller fibre diameter was not taken into account. The amount of glass fibre laid down was, thus, much lower. Also, the poor wetting of the resin may have affected the volume fraction result.

(c) Secant modulus.

The mean values of secant moduli of the laminates are presented in Tables 4.7(a-f) as a function of applied strain, prior to transverse ply cracking. The tables also show the volume fraction of fibres, $V_F$, in the individual laminates and the mean values of the first transverse ply cracking strain, etc. The experimentally obtained values of moduli shown in Tables 4.7(a-f) are compared with predicted values obtained using the Halpin-Tsai equations in conjunction with laminated plate theory equations to show the validity of the experimental results. The experimentally obtained values of the secant moduli at 0.2% strain are compared with the predicted values in Table 4.8. The equations and material properties used in the calculations are shown in Appendix 2. The experimental results agree well with the predicted values. For each group of laminates (0.5%, 1.5% and 3.0% BDMA laminates) the modulus was seen to increase in proportion with the reduced thickness of the transverse ply and in accordance with the matrix properties used in the Halpin-Tsai equations. The experimental error is considered to be of the order of 10%.

The reduction in modulus as a function of applied strain for each laminate was also examined. The change of modulus observed is tabulated as $dE$ which represents the difference between the modulus at 0.2% strain and the modulus at 0.35% strain or just before transverse ply cracking if this occurred below 0.35% strain. Any modulus drop due to the presence of the transverse crack
was, therefore, excluded. The mean values of dE are shown in Tables 4.7(a-f). The magnitude of dE is small - ranging from 0.3 GPa, which is the maximum accuracy of reading the scale on the axes, to approximately 2.0 GPa. Individual results for dE showed wide deviations from the mean values, often as large as the mean value itself due to sample to sample variation. However, a reduction in modulus does occur in some laminates prior to transverse ply cracking and is apparent in the load/strain traces obtained for the laminates. For 90° unidirectional laminates made with resin containing 0.5% BDMA, for example, the load/strain diagram is continuously non-linear and just before fracture there is a more pronounced reduction in the gradient. This is shown in Figure 4.6. For this particular specimen the reduction in modulus, just before fracture at 0.45% strain, amounted to 1.9 GPa.

90° unidirectional laminates.

The 90° unidirectional laminates made with resin containing 0.5% BDMA have shown the highest reduction in modulus with a mean value of 0.8 GPa at 0.35% strain. For the unidirectional 90° laminates made with resin containing 1.5% BDMA the mean reduction in modulus at 0.35% strain was 0.4 GPa. Individual specimens showed a reduction of 0.8 GPa at 0.45% strain, see Table 4.7(b). The reduction was lower than that for the 0.5% BDMA laminates. The 3% BDMA 90° unidirectional laminates showed a mean reduction in modulus of 0.1 GPa at 0.35% strain which is negligible. However, one specimen showed a reduction of 0.6 GPa at 0.35% strain. This increased to 0.9 GPa at 0.45% strain and 1.0 GPa at 0.55% strain. It also had an unusually high fracture strain (0.575 %).

(0,90)s laminates (0.5% BDMA).

Figure 4.7 shows the load/strain diagram for laminate 2 (see Table 4.7(a)). This was a (0,90)s laminate with an inner 90° ply thickness of 2 mm (outer 0° plies = 0.65 mm) and should be compared with Figure 4.6 which shows the load/strain diagram for the 90° unidirectional laminate which also had a 90° ply thickness of 2 mm. In a (0,90)s laminate the contribution of the modulus of the transverse ply to the overall modulus of the laminate is proportional to its thickness relative to the thickness of the 0° plies. A reduction in modulus of the transverse ply in a (0,90)s laminate is less noticeable. Thus, for laminate 2, a mean reduction in the modulus of the transverse ply of 0.8 GPa is expected to reduce the overall laminate modulus by only 0.5 GPa. The
The mean value of \( \frac{dE}{d} \) obtained for laminate 2 is 0.4 GPa, at 0.35% strain. The load/strain trace shown in Figure 4.7 does not show a pronounced reduction in modulus prior to transverse cracking as observed by Parvizi et al [2]. The reduction is gradual and small. A load/strain trace for laminate 3 (Table 4.7(a), \( b = 0.7 \) mm, \( 2d = 1.0 \) mm) is shown in Figure 4.8. No significant reduction in modulus was recorded for this laminate.

Figure 4.9 shows a load/strain trace of a specimen from laminate 4 which had a very thin inner 90° ply (\( 2d = 0.50 \) mm). The modulus of this specimen is dominated by the 0° plies. The stress/strain gradient is linear up to a strain of 0.8%, after which multiple transverse cracking occurs. As the density of the transverse cracks increases the gradient is seen to gradually fall. The reduction in the gradient, in this case, was clearly due to the presence of the transverse cracks which affects the load bearing capacity of the laminate.

\((0,90)_s\) laminates (1.5% BDMA)

No apparent reduction in modulus was detected for \((0,90)_s\) laminates made with resin containing 1.5% BDMA and with an inner ply thickness, \( d = 1 \) mm or with \( d = 0.5 \) mm prior to transverse cracking (laminate 6 and 7, Table 4.7(b)). Laminate 8 (\( 2d = 0.50 \) mm ), however, showed a very small reduction in modulus at 0.35% strain with a mean value of 0.5 GPa.

\((0,90)_s\) laminates (3.0% BDMA).

\((0,90)_s\) laminates with 3 % BDMA resin (Laminates 10, 11 and 12 with \( 2d = 1.8 \) mm, 1.0 mm and 0.50 mm respectively) showed no significant reduction in modulus. Figure 4.10 shows a load/strain trace obtained for laminate 10 with \( 2d = 1.8 \) mm. The trace is linear and should be compared with the trace shown in Figure 4.7 which is of an equivalent laminate but with 0.5% BDMA matrix resin.

90° unidirectional laminates (starch finish)

The mean Youngs modulus of the 90° unidirectional laminates made with the 120 tex textile roving (starch glass fibre finish) and epoxy resin containing 0.5% and 1.5% BDMA are shown in Table 4.7 (d) and (e) respectively. Both laminates showed no reduction in modulus with increasing applied strain.
The results obtained for laminates made with 1200 tex glass fibres and epoxy resin containing 0.5%, 1.5% and 3.0% BDMA are shown in Table 4.7(f). The values of moduli are in good agreement with the predictions of the Halpin-Tsai equations if a packing factor of 2 is used. This is in agreement with the results of previous workers [3,8] who used the same fibre tex and resins. In Table 4.7(f) the moduli are shown as a function of applied strain. The laminates have inner 90° ply thickness, 2d, of approximately 2 - 2.5 mm. The results show a small reduction in modulus with strain for the 0.5% BDMA laminates (0.7 GPa at 0.35% strain) while the laminates containing 1.5% and 3.0% BDMA do not show a reduction.

The effect of load cycling (prior to transverse cracking) and annealing on the secant modulus.

Table 4.9 shows the effect of repeated load cycles (upto a strain of 0.35% or just before transverse ply cracking) on (0,90)_s laminates made from 1200 tex fibres and epoxy resin containing 0.5%, 1.5% and 3.0% BDMA resin (2d = 2.2 mm). After five cycles the specimen was given a single annealing treatment for 30 minutes at 100°C. The effect of the annealing treatment on the modulus of the specimens is shown in Table 4.9. For the 0.5% BDMA laminates the effect of cycling on the modulus is negligible while the effect of annealing is to cause a very slight reduction in the modulus. The effect of cycling and annealing on the moduli of the 1.5% and 3.0% laminates is negligible.

Summary.

In summary, the moduli (secant modulus at 0.2% strain) for the above laminates were found to be in good agreement with the predictions of the Halpin-Tsai equations. There is a reduction in modulus with increasing applied strain which is noticeable for the 90° unidirectional laminates made with resin containing 0.5% BDMA (mean value at 0.35% strain = 0.8 GPa). A smaller reduction also appears in the 90° unidirectional laminates containing 1.5% BDMA resin (mean value at 0.35% strain = 0.4 GPa). The mean reduction in modulus for the 90° unidirectional laminates made with 3.0% BDMA resin was 0.1 GPa. This is negligible. However, individual specimens did show a
reduction of 0.6 GPa at 0.35% strain. This is lower than for the 0.5% BDMA unidirectional laminates. The \((0,90)_s\) laminate containing 0.5% BDMA resin with \(2d = 2\) mm, also showed a small gradual reduction in modulus (mean value = 0.4 GPa at 0.35% strain). The reduction in modulus for the remaining laminates was found to be negligible. The effect of annealing on the \((0,90)_s\) laminate (0.5% BDMA) was to slightly reduce the modulus.

(d) Transverse ply fracture strains.

90° unidirectional laminates.

The mean transverse failure strains of the 90° unidirectional laminates and the strain to the first transverse ply crack in \((0,90)_s\) laminates as a function of the inner 90° ply thickness are presented in Table 4.10. The volume fraction of fibres in the individual laminates is also shown. The mean values of fracture strain for the unidirectional laminates (0.5%, 1.5% and 3.0% BDMA) are all approximately between 0.3 and 0.4% strain. The 3.0% BDMA unidirectional laminate showed the lowest fracture strain of the three. One of the 3.0% BDMA specimens also showed the highest value of fracture strain.

The unidirectional laminates containing 120 tex glass fibres with the starch finish show lower transverse failure strains due to poor adhesion/wetting of the epoxy resin matrix. The 1.5% BDMA starch finish laminate shows a lower failure strain compared to the 0.5% BDMA starch finish laminate at similar volume fractions. The difference in fracture strain may be attributed to differences in resin properties which depend on the level of cure of the matrix.

Although failure strains of individual 90° unidirectional specimens showed a variation, the mean values indicated that the transverse failure strains decreased as the level of cure of the matrix resin increased. It was also observed that poor wetting/adhesion reduced the failure strains.

\((0,90)_s\) laminates.

The cross-ply laminate made with resin containing 0.5% BDMA with an inner 90° ply thickness of 2 mm showed a lower strain to first transverse ply crack when compared to a 90° unidirectional laminate of identical 90° ply thickness. This can be explained by the presence of thermal restraint strain.
in the 90° ply. The calculated value of thermal strain for all laminates is shown in Table 4.10. The equations and material properties used in the equation are shown in Appendix 2. As the thickness of the inner 90° ply of cross-ply laminates is reduced, the first transverse ply cracking strain is seen to increase even after the thermal restraint strains have been taken into account.

4.2. Observations of Stress-whitening.

4.2.1. Colour photography.

(a) 0.5% BDMA laminates.

During tensile testing, laminate specimens were photographed at short intervals of strain (0.05%) to record any change in their appearance with increasing strain. All specimens were transparent and appeared yellow when placed flat on a white sheet of paper. The yellow colour is imparted to the laminate by the resin which is also yellow. When a specimen was placed in the jaws of the tensile testing machine in front of a black screen and obliquely illuminated with tungsten lighting (95% white light) as shown in Figure 3.10, it appeared to be of a different colour as light was scattered by the 90° ply of the specimen in the direction of the camera.

The 0.5% BDMA laminate specimens were cloudy and had a blue colour at zero load. Figure 4.11 (a-1) shows a series of photographs of a single specimen, taken at intervals of strain during a tensile test. The specimen was a (0,90)s laminate with an inner 90° ply thickness of 2.2 mm (outer plies = 0.65 mm). As the specimen was strained it lost its initial cloudiness and appeared more blue. A careful examination of the specimen at the top of the photograph, Figure 4.11 (b), showed a faint tinge of red. At 0.25% strain, "whitening" appeared in the specimen and can be seen clearly in Figure 4.11 (c) which was obtained at 0.3% strain. At this stage the load on the specimen was decreased and the whitening partially disappeared indicating the reversibility of the whitening effect. At zero load, the specimen retained some whitening as shown in Figure 4.11 (d) which should be compared with Figure 4.11(a). On reloading the specimen, the whitening appeared at 0.2% strain (compare Figure 4.11(e) with Figure 4.11(b)) and the specimen was intensely whitened at 0.4% strain, Figure 4.11(f). On unloading, the whitening diminishes but at the end of the second cycle the specimen appears...
whiter than at the end of the first cycle (compare Figure 4.11(d) with Figure 4.11(g)).

At the end of the second cycle the specimen was removed from the jaws of the Instron tensile testing machine and 'annealed' in an oven at 100°C for 30 mins. After this period it was allowed to cool to room temperature and then replaced in the jaws. Figure 4.11(h) shows the appearance of the specimen after this treatment. The specimen can clearly be seen to have almost entirely lost its residual whitening and can be compared with Figure 4.11(a) which is very similar. The whitening effect, therefore, appeared to be reversible with heat-treatment. As the specimen was loaded for the third time, it was observed that at 0.2% strain, Figure 4.11(i), the specimen showed less stress-whitening than at the beginning of the second cycle, Figure 4.11(e). The specimen also showed more of the red colour and less of the blue when compared to Figure 4.11(b) so that the specimen had a magenta hue. During this third cycle a transverse ply crack appeared at 0.35% strain and as the strain was increased to 0.4% more transverse ply cracks appeared, Figure 4.11(j). On unloading the specimen, the whitening partially disappeared, Figure 4.11(k). After a second annealing treatment for 30 mins. at 100°C the whitening again disappeared while the transverse ply cracks remained. The specimen also appeared clearer (less cloudy) and a magenta hue was observed (compare Figure 4.11(l) with Figure 4.11(a)).

Figure 4.12 shows a series of photographs of a 0.5% BDMA laminate similar to the one described above but with a 1.3 mm thick 90° ply. The initial appearance of the specimen in Figure 4.12(a) at zero applied strain, is similar to that of the specimen in Figure 4.11(a). At 0.3% strain, however, the specimen shows less whitening when compared to the specimen with an inner ply thickness of 2.2 mm (compare Figure 4.12(b) with Figure 4.11(c)). A slow growing transverse ply crack was seen to develop at 0.4% strain (Figure 4.12(c)) while the transverse ply cracks in the laminate with the 2.2 mm inner ply were instantaneous. Figure 4.12(d) shows an increased number of transverse ply cracks in the laminate at 0.6% strain.

Figure 4.13 shows a 0.5% BDMA (0,90)s laminate with an inner ply thickness of 0.5 mm. The fabrication of this ply involved hand laying individual tows of the glass fibres (1200 tex) on an open square metal frame. The tows were fixed to the frame using a cyanoacrylate glue. The outer 0° plies were then wound on as described in section 3.1.3. An outer ply thickness of 0.6 mm was achieved on either side of the 90° layer after curing. Figure 4.13(a) shows
the specimen at zero applied strain. The blue transverse bands that appear in the specimen are fibre rich regions (or tows) while the areas in between the bands are resin rich regions containing a poor distribution of fibres so that the blue colour is not visible in these areas. At 0.35% strain the specimen started to appear whiter in the fibre rich regions, Figure 4.13(b). The whitening continued to intensify with increasing strain, Figure 4.13(c) and (d). Transverse ply cracks appeared at 0.8% strain. The specimen was strained to about 1.5% during which the density of transverse cracks increased. Figure 4.13(e) shows the same specimen after unloading, and the whitening is still apparent. The specimen was removed from the grips of the Instron tensile testing machine and annealed for 30 mins. at 100°C and then allowed to cool to room temperature. Figure 4.13(f) shows the dramatic change in the appearance of the specimen. The stress-whitening had been completely reversed while the transverse cracks were still apparent.

Specimens from the same laminates were re-tested after straining and annealing. The results showed that the whitening reappeared at similar strains as before annealing. Edge polished specimens from the same laminate were also examined under a transmission optical microscope before and after heat-treatment. The results of this experiment are presented in section 4.2.3.

The 90° unidirectional laminates made with resin containing 0.5% BDMA showed similar behaviour to the two thicker (0,90)s laminates (2d = 2.2 mm and 1.3 mm respectively) but at higher strain levels. Figure 4.14(a) shows a specimen at zero applied strain. The specimen is blue but appears cloudy. At 0.4% strain, Figure 4.14(b) the specimen appears less cloudy and a magenta hue is observed. When the specimen is unloaded, it regains its cloudy appearance, Figure 4.14(c). After reloading, some whitening is observed on the edge of the specimen at 0.4% strain, Figure 4.14(d), and continues to increase. Just after 0.55% strain, Figure 4.14(e), the specimen failed in the grips which relieved it of load, Figure 4.14(f). The original appearance of the specimen is regained and the whitening does not appear to have been retained (compare Figure 4.14(f) with Figure 4.14(a)).

(b) 1.5% BDMA laminates.

A series of photographs taken of a 1.5% BDMA (0,90)s laminate with an inner 90° ply thickness of 2.2 mm, outer plies = 0.6 mm, is shown in Figure 4.15. This specimen is geometrically equivalent to the 0.5% BDMA specimen shown in Figure 4.11. At 0.0% applied strain, Figure 4.15(a), the specimen appeared
blue. At 0.2% strain it showed a strong magenta colour, Figure 4.15(b). As the strain was increased to 0.25% the specimen started to whiten. The specimen was then unloaded and at zero applied strain, the magenta colour was completely removed, Figure 4.15(c). On reloading the magenta colour returned and whitening appeared between 0.2 and 0.25% strain and was clearly observed at 0.3% strain, Figure 4.15(d). As the strain was increased the original blue colour was eliminated and replaced by a red colour superimposed by a whitening effect. At 0.35% strain, 'instantaneous' transverse ply cracks developed across the width of the specimen, Figure 4.15(e). This resulted in the appearance of blue bands on either side of the transverse cracks, blue being the original colour of the specimen at zero load. The appearance of the blue bands amidst the red and white colours indicated that the colours were a property of the laminate and not simply a function of the relative movements of the specimen or cross-head with respect to the camera. This also confirms that the colour effects are associated with the state of stress in the 90° ply. On unloading the specimen, the colours disappeared and at zero applied strain the specimen appeared blue while the transverse ply cracks appeared as white lines, Figure 4.15(f).

On reloading the specimen a slight magenta hue was present and more whitening was observed at 0.4% strain, Figure 4.15(g). The whitening continued to increase and at 0.45% strain more transverse cracks were produced with blue bands on either side of the cracks. As the load was increased, the red colour and the stress-whitening in the 90° ply decreased with increasing number of transverse ply cracks, Figure 4.15(h). After longitudinal splitting and fracture of the 0° plies the blue colour between the transverse ply cracks was observed again showing that it had been obscured by whitening or brightening of the 0°plies prior to fracture, Figure 4.15(i)).

The 1.5% BDMA laminate with an inner 90° ply thickness of 1.3 mm (outer plies = 0.55 mm) showed similar behaviour to the laminate with an inner ply of 2.2 mm. Figure 4.16(a) shows the specimen at zero applied strain, in which a faint blue colour can be seen. At 0.2% strain, Figure 4.16(b), the specimen shows the development of a red colour which appeared initially at 0.1% strain. The red colour developed over the entire specimen and by 0.3% strain, Figure 4.16(c), whitening had appeared in the specimen. At 0.35% strain, Figure 4.16(d), a slow growing transverse crack appeared in the specimen accompanied by blue bands on either side of the crack. The bands are not as wide as those observed for the specimen with an inner ply thickness of 2.2 mm (compare with Figure 4.15(e)). The width of the blue
bands, therefore, appeared to be proportional to the thickness of the inner 90° ply of the laminate.

Upon unloading the specimen, the intensity of the red colour diminished, Figure 4.16(e) and the specimen returned to its original blue colour, Figure 4.16(f). The transverse crack was still apparent but no whitening could be seen. On reloading the specimen the colours reappeared, while the region around the transverse ply crack remained blue suggesting that this area remained unaffected by the load. At 0.4% strain a second slow-growing transverse crack was observed, Figure 4.16(g). As the strain was increased further the specimen behaved similarly to the specimen with an inner ply thickness of 2.2 mm, Figure 4.15, and showed instantaneous transverse ply cracks, the number of which increased until longitudinal splitting and fracture occurred in the 0° plies.

(c) 3.0% BDMA laminates.

The 3.0% BDMA laminates (0,90)s laminates with an inner 90° ply of 2.2 mm (outer plies = 0.55 mm) behaved in a similar manner to the 1.5% BDMA laminate of equivalent geometry. Figure 4.17 shows the 3.0% BDMA laminate at 0.4% strain. The blue bands on either side of the transverse ply cracks are clearly observed along with the presence of the red colour and some whitening.

Figure 4.18 shows a 3.0% BDMA laminate with an inner 90° ply thickness of 1.3 mm (outer plies = 0.55 mm). Figure 4.18(a) shows the specimen at zero applied strain. The specimen was the most transparent of all the cross-ply laminates. A large number of fine transverse striations were seen in the specimen, representing isolated cases of 'inherent' whitening. The specimen also had a red tinge at zero load. This developed as the strain was increased to 0.25%, Figure 4.18(b). At 0.35% strain, slow-growing transverse cracks appeared in the specimen with associated blue bands. These were narrower than those shown in Figure 4.17 showing again that the width of these bands is proportional to the thickness of the inner 90° ply. Very little, if any, whitening was observed prior to transverse cracking. The specimen was loaded further to 0.35% strain where an additional transverse ply crack occurred, Figure 4.18(c). The specimen was then unloaded. However, transverse ply cracks continued to develop during unloading up to 0.25% strain after which they stabilised, Figure 4.18(d, e) and (f)). At zero applied strain, the specimen retained some redness in areas between
widely spaced cracks, Figure 4.18(g). Annealing the specimen at 100°C for 30 mins, and cooling to room temperature diminished the redness, Figure 4.18(h)).

**Summary.**

**0.5% BDMA laminates.**

From an original cloudy blue before loading the specimen changed to magenta after loading, followed by whitening which was partially reversible on unloading. Annealing the specimen restored it to its original colour but the magenta became more visible on the second loading. The whitening that developed generally across the specimen could be removed by annealing while the transverse cracks remained visible. In the cross-ply laminate with the thinnest inner ply, transverse cracks occurred on either side of stress whitened regions i.e. near the boundaries of resin-rich and resin-poor areas. The 90° unidirectional laminate shows similar colour effects to the cross-ply laminates but the strain range over which they occur is larger.

**1.5% BDMA laminates.**

These laminates showed a wider range of colour effects. From an original blue, the specimen changed colour on loading to magenta followed by red. These colours were reversible on unloading. On further loading, whitening of the specimen was observed. When transverse cracks developed a small region on either side of the crack was immediately turned blue. The width of the blue bands was larger for larger thicknesses of the inner ply. On reloading, the specimen showed colour changes again except in the areas near to a transverse crack which remained blue. Whitening of the 0° plies was observed at higher strains. The laminate specimens with thick inner plies showed instantaneous crack growth while those with thinner inner plies showed slow, controlled growth of transverse cracks with increasing strain.

**3.0% BDMA laminates.**

The 3.0% BDMA laminate with the thicker inner ply (2d = 2.2 mm) showed similar behaviour to the 1.5% BDMA laminate with an equivalent inner ply thickness. The specimen with the thinner inner ply (2d = 1.3 mm) was the most transparent of all the specimens and at zero load was blue with a red tinge in places. As the specimen was loaded the specimen developed a red
colour and no significant whitening was apparent before transverse ply cracking occurred. The transverse cracks had blue bands on either side. Transverse cracking continued for sometime during unloading. A most interesting observation was that the red colour which developed during loading was still apparent in places at zero load, but could be removed by annealing the specimen for a short time at a 100°C.

4.2.2. Macro-photography.

Macro-photography (as described in section 3.3.2) was employed in order to obtain a more detailed view of the whitening in laminates, previously observed by eye. The method was used only on selected laminates to highlight some interesting features, such as 'texture', of the whitening effect. Figure 4.19 shows the results obtained for a 0.5% BDMA (0,90)s laminate (600 tex fibres) with an inner 90° ply thickness of 0.5 mm (outer 0° plies = 0.8 mm). At zero applied strain, the specimen showed some 'inherent' whitening and fine bright lines were observed across the coupon, Figure 4.19(a). As the specimen was loaded, it developed additional whitening. This effect was resolved by the macro-zoom system. The whitening was observed to be made up of a series of bright lines, Figure 4.19(b). The bright lines appeared in short discrete lengths suggesting that either the damage occurred in short discrete lengths or that the width of the specimen was traversed by the damage but not always in a straight line parallel to the surface of the specimen. This could be associated with imperfect alignment of the transverse fibres if the damage followed the fibre surface and direction.

At about 0.6% strain, slow transverse ply cracks developed from the edge of the specimen and traversed along the width of the coupon. Figure 4.19(c) shows the specimen at zero load after applying a strain of 0.7%. The areas on either side of the transverse ply cracks show less whitening compared to the rest of the laminate. Whitening was still visible and was retained at zero load in the rest of the laminate. Figure 4.19(d) shows a magnified view of a crack tip. The crack tip appears branched and splayed suggesting that the transverse ply crack front grew unevenly in length across the thickness and width of the 90° ply. The resemblance of the fine bright lines on a more localised scale to the appearance of a transverse ply crack suggests that the whitening occurs through a similar mechanism responsible for making the transverse crack visible, i.e. scattering of light at new interfaces, created in the laminate as a result of an applied stress. As the strain is
increased, the density of transverse ply cracks increases and whitening in the 0° plies obscures the 90° ply. Longitudinal splits were observed in the 0° plies at strains greater than 2.0%, Figure 4.19(e). This was followed closely by delamination between plies, Figure 4.19(f). The relief of stress in the 0° plies allows the transverse ply to become visible again.

A 90° unidirectional laminate made with resin containing 0.5% BDMA was also tested and observed through a macro-zoom lens. Figure 4.20(a) shows the specimen at zero applied strain. Some whitening was present in the laminate at zero load. As the strain was applied the specimen began to whiten further at 0.2% strain. A 'texture' could be seen so that it appeared that the whitening was a result of discrete individual events. At 0.45% strain the specimen appeared intensely whitened, Figure 4.20(b). The specimen failed at 0.5% strain, relieving the load. The whitening in the specimen disappeared on the release of load, Figure 4.20(c).

Unidirectional 90° laminates made with resin containing 3.0% BDMA were also tested. The "whitening" seen in the black and white photographs was actually produced by a reddening effect. Figure 4.21(a) shows a 3.0% BDMA specimen at zero applied strain where some "whitening" is observed. Additional "whitening" occurred at about 0.2% strain and the level of "whitening" increased with increasing applied strain. Figure 4.21(b) shows the specimen at 0.35% strain. The "whitening" appeared more diffuse than in the 0.5% BDMA specimens and no fine lines could be resolved at the magnification available suggesting that the damage causing the "whitening" was smaller in size for these laminates. After failure, the "whitening" was reversed as the specimen reached zero load, Figure 4.21(c).

The 90° unidirectional laminate made with 0.5% BDMA resin and the 120 tex glass fibres, with the starch finish, showed considerable whitening at zero load. This is shown in Figure 4.22(a). Figure 4.22(b) shows the laminate at 0.2% strain. The specimen shows little additional whitening which appeared to be retained after failure, Figure 4.22(c).

Summary.

Macro-photography showed that the whitening consisted of a series of fine, bright lines of short lengths in the 90° ply similar in appearance to transverse ply cracks but on a more localised scale. These were retained or
remained visible after unloading to zero load in the 0.5% BDMA cross-ply laminate with an inner ply thickness of 0.5 mm, except in areas near a transverse ply crack. The transverse ply crack tip (or front) appeared splayed and grew unevenly in length across the width and thickness of the 90° ply. The bright lines were not very visible on removal of load in the 0.5% BDMA unidirectional laminate. The 90° unidirectional laminates made with resin containing a higher level of accelerator (3.0% BDMA) appeared to contain damage of a much finer scale than that shown by the 0.5% BDMA laminate, so that a texture could not be easily discerned. The "whitening" effect in the black and white photographs of the high cure laminate was actually produced by a reddening effect in the specimens.

4.2.3. Polished edge microscopy - healing of micro-cracks.

The edges of some tensile test specimens had been polished prior to testing as described in section 3.1.4. so that the specimens could be examined under a transmission optical microscope. Transmitted light was used because it proved more informative than reflected light by providing sub-surface information. In addition, the contrast between the glass fibres and the resin was poorer in reflected light than in transmitted light. Figure 4.23(a) shows a micrograph of a section of the 90° ply of a 0.5% BDMA (0,90)_s laminate with an inner ply thickness of 0.5 mm (outer ply thickness = 0.6 mm). The micrograph was taken at zero load prior to testing. Cracked fibre cross-sections or fibre splits are observed at zero load. This type of damage has already been shown in section 4.1.2(a) and is thought to be the result of a combination of weak fibres and high internal thermal strains and strong fibre/resin bonds, section 4.2.4.

The specimen was strained to 0.45% resulting in significant whitening of the specimen, see Figure 4.13(c). On removal of the load, the specimen retained whitening and was re-examined under the microscope. Figure 4.23(b) is a micrograph of the same section of the 90° ply shown in figure 4.23(a) after straining. Additional damage is observed associated with fibres and in areas where the fibres appear to be in contact. The micro-cracks were associated with fibres and extended into the resin. After examination under the microscope, the specimen was annealed in an oven at a temperature of 100°C for 30 mins., allowed to cool to room temperature, and then re-examined under the microscope. Figure 4.23(c) shows the result obtained. Most of the cracks which had developed in the laminate after straining were not visible.
This was accompanied by the disappearance of stress-whitening on the macroscopic scale as shown in Figure 4.13 (f).

Figure 4.23(d) shows the specimen after re-testing to a strain of 0.35%. At this stage the original cracks did not reappear. The specimen was then strained further to 0.6% strain at which point the cross-head was reversed and the specimen unloaded. Figure 4.23(e) shows the unloaded specimen after straining to 0.6%, and shows the presence of resin cracks. On comparing with Figure 4.23(b), the cracks appeared much smaller and fainter. Not all cracks originally observed in Figure 4.23(b) had reappeared so that some of the original cracks must have been healed. In some regions, for example, near the crack marked 'a' in the micrographs, the annealed matrix appears stronger than the original material since a crack which initially appeared at 0.45% strain did not reappear even after straining to 0.6%. Figure 4.23(e) also shows crescent shaped debonds around some fibres previously associated with matrix cracks. On re-annealing the specimen, the resin cracks disappeared again while the regions around the glass fibre/resin interface still showed crescent shaped debonds, Figure 4.23(f). This suggests that the healing occurred only between resin surfaces and not at the interface.

These experiments showed that the appearance of a whitening effect in laminates could be correlated with the formation of micro-cracks close to the fibre/resin interface. This was confirmed by the fact that the disappearance of stress-whitening was associated with the concomitant disappearance of the micro-cracks. Further evidence of resin cracking was provided by in situ microscopy using a straining stage (See section 4.2.4.).

Summary.

Stress-whitening was found to be associated with localised micro-cracks which developed in the resin between closely spaced fibres after straining. The cracks were tangential and the crack faces generally lay in a direction normal to the loading axis and parallel to the longitudinal axis of the fibres in the 90° ply. The cracks often extended some way into the resin. After heat-treatment at 100°C for 30 mins. many of the cracks which had developed during straining became invisible and the observed whitening was found to disappear. After reloading and applying a strain of 0.35 %, most of the original cracks still remained invisible. After straining to 0.60 % strain, a small proportion of the original cracks reappeared but were
smaller. Cracks were then observed only around fibres when previously they had extended into the resin. Relatively long resin cracks which had originally appeared at 0.45 % strain failed to reappear after the specimen had been taken to a higher strain (0.6 %). Re-annealing the specimen removed the fine cracks. However, some cracks near the fibre/matrix interface remained visible. Thus, it would appear that while cracks in the resin could be healed by heat treatment, the adhesion around the fibre/matrix interface could not be reinstated.

The observations were only possible because stress-whitening was retained at zero load.

4.2.4. In situ optical microscopy.

In situ microscopy using a straining stage represented a considerable advantage over the method of microscopy described in section 4.2.3 since it allowed continuous observation of the development of low strain damage in the laminates. Several laminates were examined using the straining stage and the results obtained are outlined below.

(a) (0,90)_s cross-ply laminate, 0.5% BDMA, b = 0.8 mm, 2d = 0.5 mm.

Figure 4.24 shows an edge on view of a section of the 90° ply in a (0,90)_s laminate (0.5% BDMA) with a total 90° ply thickness of 0.5 mm and outer 0° ply thickness of 0.8 mm (laminate 4). Figure 4.24(a) was taken prior to testing and shows that the laminate contains a substantial amount of damage in the form of fibre splits. An area of very closely spaced fibres on the right hand side of the photograph shows damage in the resin which appears as dark regions between fibres. The contrast between fibres and resin is poor. Several bright spots of light are observed between fibres that are close to each other suggesting that the glass fibres are separated by a very thin layer of resin. The glass fibres themselves do not transmit as much light because the light travelling through the glass fibres is diffused into the surrounding resin.

On straining the specimen, the contrast between fibre and resin improved as shown in Figure 4.24(b) which shows the section at a strain of 0.27%. As the specimen was strained further, the image became streaked with 'shadows' and it became difficult to focus due to the development of sub-surface damage.
This made the additional damage difficult to observe. This effect is shown in Figure 4.24(c) which was taken at 0.6% strain. At 0.8% strain, the fibre cross-sections were very prominent and the image had good contrast, Figure 4.24(d). Additional damage, in the form of micro-cracks, was clearly observed between fibres in contact. Most damage is perpendicular to the loading axis and is not crescent shaped around the fibre in a classic 'debond' style but appears to extend into the resin. Figure 4.24(e) was taken at 0.94% strain and is a clear high contrast image showing more micro-cracking. Many of the bright spots observed earlier between glass fibres are not visible. Figure 4.24(f) shows the image as the load was reduced to zero. The majority of damage is not very visible although in some places faint shadows remain. Some of the bright spots between fibres reappear as the cracks lose up suggesting very good contact between cracked faces, for example, the region between fibres 'a' and 'b' in Figure 4.24(e) and (f). The contrast between the glass fibre and resin is again reduced. Figure 4.24(g) shows another region at zero load where the micro-cracks were retained and were more easily visible.

**Summary.**

The 90° ply in the above cross-ply laminate contained a substantial amount of damage prior to testing. Fibre splitting was observed where fibres were close together and bounded by a resin-rich area on one side. The contrast between fibre and resin improved as the specimen was strained. As micro-cracking developed, the image became streaked since the damage had not yet reached the surface. It is possible that this specimen had been loaded slightly unevenly since during the course of earlier trials, it had been observed that specimens were gripped more tightly on one edge due to a slight machining fault (see section 3.3.4). A high density of micro-cracks were observed. The majority of cracks were not of the "half moon" debond shape commonly observed in glass fibre/polyester laminates [B2], but extended into the resin, and were also found between closely spaced fibres. The fibres appeared very prominent under strain. Very little coalescence between micro-cracks was observed. When coalescence was observed it occurred in densely packed regions or at the tip of a group of split fibres. When the strain is removed the fibres lose their prominence as contact between cracked surfaces is re-made. Some micro-cracks are retained at zero load, after testing.
Figure 4.25 shows a series of micrographs obtained for a (0,90)s, 0.5% BDMA, specimen with an inner 90° ply thickness of 1 mm (outer 0° plies = 0.7 mm) (laminate 3). This specimen showed similar behaviour to the specimen with an inner ply thickness of 0.5 mm. Figure 4.25(a) shows a representative section of the 90° ply, at zero load, near the 0/90 ply interface. The contrast between glass and resin is again low. Some fibre splitting is observed in the 90° ply, although not as much as that observed in the cross-ply laminate with the thinner transverse ply. Again the splits usually appear where fibres which are close together are surrounded by resin-rich regions. A group of three or more fibre splits usually showed a characteristic arc shape as shown in Figure 4.25(a). As the load was applied to the specimen, micro-cracks appeared at about 0.2% strain and increased in size and number as the strain was increased further. The fibre cross-sections became brighter and more prominent. This effect is shown in Figure 4.25(b) which was taken as the strain reached 0.27% (Note that the region being examined has moved slightly towards the right).

Figure 4.25(c) shows a transverse ply crack which developed instantaneously across the specimen edge on further loading. The crack was arrested at the 0/90 interface. The fibres in the vicinity of the transverse crack lost their prominence and micro-cracks in the region of the transverse crack closed up, shown by the reappearance of the bright spots in between fibres. The closing up of cracks here was not entirely even, since cracks near the fibres marked 1, 2, 3, for example, on the far right of the micrograph closed up while those near fibres 4 and 5 did not. The size of the stress relieved region was, therefore, difficult to determine at the microscopic level. A certain amount of spatial distortion compared to Figure 4.25(b) was also observed indicating the relaxation of the matrix around the cracks. Figure 4.25(d) shows the left branch of the transverse crack. The specimen was moved towards the right. Again the area on the left of the transverse crack appeared relaxed and the fibre cross-sections were not as prominent as those on the far right of the crack. The area near the crack, therefore, showed a certain amount of stress relief while the remainder of the specimen was still loaded (0.3% applied strain). Figure 4.25(e) shows the opposite end of the crack on the same edge. The crack is branched and the associated micro-cracks are clearly observed. Crescent shaped debonds are seen at the 0/90 ply interface. Figure 4.25(f) gives an overview of the crack at a lower magnification and shows the area examined.
Summary.

Fibre splits were observed in regions where closely spaced fibres were bound on one side by resin-rich areas. A group of three or more fibre splits showed a characteristic arc shape. As the strain was increased, fibres became more prominent. Micro-cracks developed between closely spaced fibres. A transverse ply crack developed instantaneously in the region under examination. The transverse crack caused a spatial distortion and relaxation in the nearby regions. It also had fine branches and was made up of resin cracks, debonds and fibre splits.

(c) \((0,90)_5\) cross-ply laminate, 0.5 % BDMA, \(b = 0.65\) mm, \(2d = 2\) mm.

Figure 4.26 shows a section of a 0.5% BDMA, \((0,90)_5\) laminate, with an inner 90° ply of 2 mm (outer 0° plies = 0.65 mm) taken at zero load after straining to 0.35% strain. Fig.4.26(a) and (b) show the edge of the laminate including both 0/90 ply interfaces. Both micrographs show how the damage is concentrated near the 0/90 ply interfaces and how the cracks associated with the fibres decrease in size and number towards the middle of the ply. This suggests that the stresses near the ply interfaces are higher than those towards the middle of the 90° ply. Such a stress distribution could be the result of thermal stresses which may be higher near the ply interfaces, particularly at the free edge. Micro-cracks in their initial stages, in which dark 'shadows' appear around points of contact between fibres, are distributed throughout the ply, Figure 4.26(c). The initial stages of micro-cracking are examined much more closely for a 1.5% BDMA, \((0,90)_5\) laminate with an inner 90° ply 1 mm and outer 0° plies of 0.8 mm since the majority of micro-cracks in this laminate did not proceed beyond this stage prior to transverse ply cracking.

Summary.

The most important result that emerged from these observations was the concentration of micro-cracking near the 0/90 ply interface. The cracks near both 0/90 ply interfaces were more advanced and numerous while toward the middle of the ply very few advanced cracks were observed and only some 'shadows' were observed between fibres.
(d) $(0,90)_s$ cross-ply laminate, $1.5\%$ BDMA, $b = 0.8\, \text{mm}$, $2d = 1\, \text{mm}$.

Figure 4.27(a) shows a section of the $90^\circ$ ply near the $0/90$ ply interface at zero applied load prior to testing. Some fibre splits appear near the $0/90$ ply interface but dark 'shadows' near the glass fibre/resin interface and around the points of contact between fibres are also observed showing that some cracking had already occurred prior to loading. Further away from the ply interfaces the laminate showed very little damage. Figure 4.27(b) shows the same section at a strain of $0.15\%$ (Some fibre cross-sections are marked by numbers for easy reference). Additional damage was observed between fibres in contact. The damage occurred first near the $0/90$ ply interface. The micro-cracks near the ply interfaces grew with increasing applied load. Figure 4.27(c) shows a magnified view of Figure 4.27(b).

At $0.2\%$ strain, Figure 4.27(d)) micro-cracks were seen to develop further away from the ply interface (compare regions near fibres 7 and 8, and 9 and 10 in Figure 4.27 (d) with the same in Figure 4.27(c)). Figure 4.27(e) shows the micro-cracks at $0.25\%$ strain. The cracks continued to grow in size while others initiated in regions away from the ply interface. Figure 4.27(f), obtained just before reaching $0.3\%$ strain, shows a shear distortion of the section towards the right of the micrograph due to the occurrence of a transverse ply crack nearby. This distortion makes the micro-cracks that were in their initial stages much more visible, see fibres marked 11 and 12 in Figure 4.27(e) and (f). When the section was moved towards the right, the distortion was more visible and the transverse ply crack could be observed, Figure 4.27(g). It can be seen that the transverse ply crack path has gone through fibre splits, around fibre/matrix interfaces (classic debond) and through resin. Figure 4.27(h) shows the whole transverse ply crack. Figure 4.27(i) shows the transverse ply crack region at zero load. Many of the micro-cracks have closed up and only 'shadows' are now visible in their place. The shear distortion is also removed at zero load.

Summary.

The specimen contained small resin cracks near the $0/90$ ply interface prior to testing. Some fibre splits were also observed. The fibre cross-sections were more prominent at zero load compared to the equivalent $0.5\%$ BDMA laminates and the contrast between fibre and resin was better. (The specimen
appeared less cloudy on a macroscopic scale). As the specimen was strained, 'shadows' appeared between closely spaced fibres, first near the 0/90 ply interface and then near fibres towards the centre of the transverse ply. The cracks were smaller in size compared to those in the 0.5% BDMA laminates and were more difficult to observe. An instantaneous transverse ply crack appeared near the region under examination causing a spatial distortion and relaxation in the region. At zero load the majority of cracks appeared to close up.

(e) 3.0% BDMA laminates.

The observation of micro-cracks in the 3.0% BDMA laminates was difficult using optical microscopy and only initial stages of micro-cracking were observed prior to transverse ply cracking.

4.2.5. Fractography.

(a) Optical microscopy.

The transverse fracture path in unidirectional 90° specimens was examined using a transmission optical microscope to see if the underlying micro-cracking behaviour was reflected in the fracture path taken. Figure 4.28 shows part of a transverse fracture for a 90° unidirectional, 0.5% BDMA laminate (laminate 1). The regions, both near the fracture and away from the fracture show the presence of micro-cracks perpendicular to the loading axis. The fibres on the fractured edge still adhere to the rest of the laminate. Figure 4.29 shows the fracture path through a 90° unidirectional specimen of the laminate made with 120 tex glass fibres coated with starch in a resin containing 0.5% BDMA (laminate 13). The fracture shows a number of loose and completely debonded fibres and consists mainly of well defined impressions of fibres where they had been in contact with the resin. The fracture path has fine branches made up of crescent shaped debonds. The fracture path confirms that the laminate with the starch finish glass fibres had a poor fibre/matrix bond so that instead of resin cracks a large number of crescent shaped debonds were observed and also a number of loose fibres.

Figure 4.30 shows a fracture path through a 90° unidirectional specimen made with resin containing 1.5% BDMA resin and silane coated glass fibres (laminate 5). The immediate difference on comparing the micrograph with that
shown in Figure 4.28 is that no micro-cracks are visible near the fracture. The contrast between fibre and resin is better than in the 0.5% BDMA matrix. The fracture in the 0.5% BDMA matrix has caused the fractured edge of the specimen to deform so that the specimen surface near the edge is not on the same level as the rest of the surface. The fracture in the higher cure resin (1.5% BDMA) appears to be more brittle in nature and the surface near the fractured edge is level with the surface further away from the fracture.

Figure 4.31 shows a section of a fracture from the 90° unidirectional laminate with 0.5% BDMA resin matrix in transmission mode, Figure 4.31(a), and in reflection mode, Figure 4.31(b). The two micrographs illustrate the depth of information that can be obtained using transmission optical microscopy and the extent to which detail is lost using reflection microscopy in which only the surface is examined.

(b) Scanning electron microscopy.

Figure 4.32 compares the transverse fracture surfaces of 90° unidirectional specimens. Figure 4.32(a) shows the fracture surface of a laminate made with silane coated glass fibres containing 0.5% BDMA resin while Figure 4.32(b) shows the fracture surface of the laminate made with the same fibre but with 1.5% BDMA resin matrix. Figure 4.32(c) shows the transverse fracture surface of a laminate made with the starch coated fibres in 0.5% BDMA resin matrix. Figure 4.32(a) shows a substantial amount of plastic deformation of the resin with the formation of 'hackles' which are seen in the resin still adhered to the fibres and in the resin on either side of a 'channel' or impression left by the glass fibre in the resin. The amount of deformation observed on the fracture surface of the laminate made with resin containing 1.5% BDMA is much less. The resin fracture appears more brittle although a few hackles are still observed. Figure 4.32(c) shows some plastic deformation but most fibres appear 'clean' and free of resin showing the poor glass fibre/resin bond obtained in the laminate with starch finish glass fibres.
4.3. Quantitative Measurement of Stress-whitening.

4.3.1. Preliminary results.

(a) Transmission mode 1.

Figure 3.14 shows the change in intensity of light (measured in terms of millivolts to which it is directly proportional) transmitted through the plies of a (0,90)_s laminate, in a direction perpendicular to the fibre axis in the 90° ply (mode 1, Figure 3.13), as a function of applied strain. The specimen had a total inner ply thickness of 0.5 mm and an outer ply thickness of 0.8 mm on either side of the 90° ply. Immediately after loading, the transmitted light intensity increased slightly. At about 0.2% applied strain it was reduced to the original level at the start of the test at zero applied load. At about 0.4% strain, the transmitted intensity began to decrease and continued to do so with increasing applied strain. Although stress-whitening first appeared at about 0.2% strain, it was most visible at 0.4% strain and above. The results indicated that the method did not allow the monitoring of stress-whitening prior 0.4% strain. The decrease in intensity after 0.4% strain was associated with stress-whitening and was probably due to the scattering of light away from the main beam.

(b) Transmission mode 2.

Figure 4.33 shows the change in transmitted light intensity as a function of applied strain for a specimen from the laminate described above but tested in mode 2, where the light was transmitted through the 90° ply only and in a direction parallel to the longitudinal axis of the fibres (mode 2, see Figure 3.13). The specimen was subjected to three loading cycles in which the specimen was taken to a higher strain level each time. At the end of the third cycle, the specimen was removed from the grips of the tensile testing machine and annealed in an oven at 100°C for 30 mins. It was then allowed to cool to room temperature and then re-tested (4th cycle).

Trace 1 in Figure 4.33 shows that as the specimen was strained for the first time the transmitted light intensity increased. At about 0.2% strain, the intensity reached a plateau and remained level up to a strain of 0.4%. After 0.4% strain, the light intensity was seen to decrease rapidly to below the original base line signal at zero load. At 0.55% strain, the cross-head was reversed. The transmitted light intensity continued to decrease but at a
much slower rate. At zero load the intensity remained below the base line so that there was a 'permanent' decrease in the light transmitted by the specimen in a direction parallel to the longitudinal axis of the fibres. This coincided with the presence of residual whitening in the specimen at zero load after testing. The rapid decrease in the intensity of transmitted light which occurred at 0.4% strain was again associated with the scattering of light away from the main beam causing the stress-whitening.

During the second cycle, a much smaller increase in transmitted light was recorded below 0.2% strain. This reached a plateau at 0.2% strain and remained level suggesting that no additional damage occurred until after the maximum strain limit in the first cycle was reached (0.55% strain). Above this strain, there was a rapid decrease in the transmitted light intensity, similar to that observed in the first cycle, due to the development of additional damage (and hence, increased stress-whitening). On reversing the load, the transmitted light intensity continued to decrease at a decelerated rate until about 0.3% strain after which it remained level and was again below the original base line value.

During the third cycle, there was a negligible increase in the transmitted light intensity until after the maximum strain limit of the second cycle was reached (0.7% strain). Above 0.7% strain, there was a rapid fall in the level of the transmitted light intensity. As the load was reversed, the intensity continued to decrease at a very slow rate until the applied strain had reached about 0.5% after which it remained constant. At the end of the third cycle the specimen was annealed at 100°C for 30 mins. Trace 4 in Figure 4.33 was recorded after cooling to room temperature and re-testing. The trace appears very similar to trace 1. There is an increase in the intensity of transmitted light which reaches a plateau at 0.2% strain and remains constant until a strain of about 0.45% is reached. A decrease in intensity is then observed. The rate of decrease is less rapid than that achieved during the first cycle (trace 1) until after the maximum strain limit of the third cycle (about 0.8% strain) is exceeded. Above 0.8% strain the intensity begins to fall as rapidly as in the first cycle. This set of results illustrates the effect of heat treatment on the specimen. The specimen is seen to have returned to almost its original state except that the rate of decrease of the intensity after 0.4% strain is lower. This suggests that after annealing the nature of the damage induced is changed resulting in less scattering away from the main beam and so the decrease in intensity is less rapid after annealing.
4.3.2. The off-axis LASER diffraction technique.

In this section, the results obtained using the Ne-He LASER light (wavelength = 632.8 nm) diffraction technique are presented. All laminates were examined with the photodetector at position 1, Figure 3.19 (d), which was at 90° to the incident beam. One laminate was tested with the photodetector in all the positions (1 to 6) shown in Figure 3.19 (d) so that more detailed information about the diffraction pattern could be obtained.

Figure 3.20 shows a typical plot of the detector output, \( I \), measured in millivolts (to which the intensity is directly proportional) as a function of applied strain, obtained with the detector in position 1. All plots obtained were characterised by a flat portion over a short initial strain range during which no light was detected in the direction of the detector, Figure 3.20, line AB. The flat portion was followed by a very rapid increase in the light detected (BC) which continued to increase with increasing strain and in some cases the sensitivity of the photometer had to be reduced to accommodate the trace. A minimum of 4 specimens were examined from each laminate. In some cases, the specimens were tested or cycled three times and a record of the output, \( I \), as a function of strain was obtained each time during loading and unloading. For clarity, only the mean voltage readings and the standard deviation obtained for each laminate for the loading part of the first cycle are presented initially. The results obtained after cycling are presented in section 4.3.2(e).

The mean values of detector output, \( I \), obtained as a function of applied strain were then converted to Ln/linear plots. A straight line relationship was obtained indicating that the experimental curves could be closely approximated by an equation of the form,

\[
I = Ae^{K\varepsilon} \quad (4.1)
\]

where 'K' is the rate of increase of the detected light, \( \varepsilon \) is the applied strain on the specimen, \( I \) is the detector output in millivolts, and \( A \) is a pre-exponential factor.

The detector output, \( I \), was normalised prior to taking logarithms to allow for the effects of the thickness of the 90° ply when comparing laminates with varying inner ply thickness. The normalised values, \( I_n \), are presented in tabular form, Tables 4.11 to 4.20. Any differences in the detected signal
arising due to a different type of damage mechanism could then be discerned. Since the beam diameter was constant in all cases, normalisation was defined by the voltage reading obtained at each unit of strain divided by the distance (mm) travelled by the incident beam in the 90° ply. The distance travelled is given by $2d/\cos \theta$, where $2d$ is the total thickness of the 90° ply and $\theta$ is equal to 45° and is the angle by which the incident beam is inclined to the horizontal. It is assumed that the 0° plies do not affect the detector output obtained from the 90° ply after loading (see section 5.3). Thus,

$$I_n = I \cos 45° / 2d$$

(4.2)

The slope and intercept on the Y-axis of the straight line obtained by plotting the logarithm of $I_n$ against applied strain is related to $K$ and $A$ since,

$$\ln I_n = \ln A + Ke$$

(4.3)

Linear regression analysis was used to obtain the 'best fit' and determine values of $K$, the slope of the line, and the intercept on the Y-axis, $\ln A$.

(a) 0.5% BDMA laminates.

Figure 4.34(a) shows a plot of the detector output, $I$, as a function of applied strain for a 90° unidirectional laminate ($2d = 2.1$ mm, laminate 1) made with resin containing 0.5% BDMA, with the photodetector in position 1. After the strain applied had reached about 0.2%, the voltage reading showed a rapid increase. A logarithmic plot of the normalised voltage against applied strain is shown in Figure 4.34(b). The values of $K$ and $A$ are shown in Table 4.11(a). The slope $K$ which gives a measure of the rate of increase in the voltage has a value of 35.0 for the unidirectional 90° laminate. The amount of light detected per millimetre of inner 90° ply thickness at various strains is shown in Table 4.11(b).

Figure 4.35(a) shows a plot of detector output, $I$, as a function of applied strain for a $(0,90)_s$ laminate with a total inner 90° ply thickness of 2.0 mm. Light is detected in position 1 just before reaching a strain of 0.2%. The rate of increase is shown in Figure 4.35(b), which is a plot of the $\ln I_n$ against strain. The slope $K$ has a value of about 18.0, Table 4.11(a). This is half that of the 90° unidirectional laminate described above despite the
similarity in the thickness of the 90° plies. The amount of light detected per millimetre of inner 90° ply thickness at various strains is shown in Table 4.11(b). The amount of light detected is initially higher for the cross-ply laminate when compared to the unidirectional 90° laminate at the same strain. However, the difference in the mean voltage reading between the two laminates is reduced as the strain is increased and is lower for the cross-ply laminate at a strain of 0.375%.

Figure 4.36(a) shows a plot of the detector output, I, as a function of applied strain for a (0,90)s laminate with a total inner 90° ply thickness of 1.0 mm (laminate 3). After about 0.2% strain the voltage increases rapidly and the value of K was found to be 22.0, Figure 4.36(b), Table 4.11(a). This is slightly higher than that for the (0,90)s laminate with an inner ply thickness of 2.0 mm but still lower than that of the unidirectional laminate described above. The amount of light detected per millimetre of inner 90° ply thickness at various strains is similar to that of laminate 2, with the 2.0 mm thick inner ply, Table 4.11(b).

Figure 4.37(a) shows a plot of the detector output, I, against applied strain for a (0,90)s laminate with a total inner 90° ply thickness of 0.5 mm (laminate 4). Just before 0.2% strain, light is detected and the voltage reading continues to increase. The value of K was found to be 23.0, Figure 4.37(b), Table 4.11(a). This is similar to that of laminate 3. At 0.3% strain the amount of light detected is some 30 times that of the 90° unidirectional laminate at the same strain, Table 4.11(b). This difference is reduced to approximately 20 at a strain of 0.325% and again to 10 at 0.35% strain. Thus, the difference in the detected voltage between laminate 4 and the unidirectional laminate is decreased as the applied strain is increased.

Summary.

0.5% BDMA laminates.

The highest rate of increase, K, in the detector output as a function of strain was shown by the unidirectional 90° laminate, Table 4.11(a). The cross-ply laminates showed lower rates and the amount of light detected at a given strain increased with decreasing inner ply thickness. By far the highest amount of light at a given strain was detected for the laminate with the narrowest inner ply, Table 4.11(b). In general, the difference between
laminates in terms of the amount of light detected at a given strain decreased as the applied strain increased.

(b) 1.5% BDMA laminates.

Figure 4.38(a) shows a plot of detector output, I, against applied strain for a 90° unidirectional laminate with a total thickness of 2.1 mm (laminate 5). After a strain of about 0.15% is reached, light is detected and the voltage reading increases as the strain is increased. The slope of the straight line of $\ln I_n$ against strain, Figure 4.38(b), was found to be about 9.0, Table 4.12(a). This is about four times lower than that for the unidirectional laminate made with resin containing 0.5% BDMA. The amount of light detected is initially higher than for the 0.5% BDMA unidirectional laminate, Table 4.12(b). For example, at 0.3% strain, the amount of light detected is higher for the 1.5% BDMA unidirectional laminate by a factor of 2 compared to the 0.5% BDMA unidirectional laminate. However, the difference between the two unidirectional laminates becomes smaller as the strain applied is increased and beyond 0.3% strain the amount of light detected is higher for the 0.5% BDMA unidirectional 90° laminate. Also, it is to be noted that light was initially detected at a smaller applied strain for the 1.5% BDMA laminate.

Figure 4.39(a) shows a plot of the detector output, I, as a function of applied strain for a (0,90)$_s$ laminate with a total inner 90° ply thickness of 1.8 mm (laminate 6). This result was unusual in that light was detected at a very early stage, 0.025% strain, (or immediately after loading) and rose very rapidly before a strain of 0.2% was reached. The slope of the line of $\ln I_n$ against applied strain, Figure 4.39(b), had a value of 33.0, Table 4.12(a). This is high compared to its unidirectional equivalent (laminate 5) and also compared to laminate 2 which was of equivalent thickness but contained resin made with 0.5% BDMA.

Figure 4.40(a) shows the detector output, I, against applied strain for a (0,90)$_s$ laminate with a total inner 90° ply thickness of 1 mm (laminate 7). Only after a strain of 0.25% had been reached was light detected. The amount of light detected at 0.325% strain, Table 4.12(a), was approximately 4 times lower than its equivalent in the 0.5% BDMA system (laminate 3, Table 4.11(a)). The value of K was found to be 30.0, Table 4.12(a), Figure 4.40(b). This is higher than that obtained for laminate 3 which had a value of 22.0, Table 4.11(a).
The (0,90)s laminate with a total inner ply thickness of 0.5 mm (laminate 8) did not appear to show any effect until a strain of about 0.275% had been reached. This is shown in Figure 4.41(a) which shows the detector output, I, as a function of applied strain. On reaching a strain of 0.325%, the amount of light detected was a factor of 30 lower than its equivalent in the 0.5% BDMA system (laminate 4). The slope of the line of Ln I_n against applied strain, Figure 4.41(b) had a value of 27.0, Table 4.12(a).

Summary.

1.5% BDMA laminates.

The lowest rate of increase, K, in detector output as a function of strain was shown by the unidirectional laminate, Table 4.12(a), and was four times lower than for the 0.5% BDMA unidirectional laminate. The cross-ply laminates with inner plies of 2 mm, 1 mm and 0.5 mm all showed similar rates of increase in voltage. The lowest amount of light was detected for the laminate with the narrowest inner ply, Table 4.12(b), and was approximately 30 times lower than for the equivalent 0.5% BDMA laminate at a strain of 0.325%.

(c) 3.0% BDMA laminates.

The majority of specimens from a 3.0% BDMA 90° unidirectional laminate with a total thickness of 2.9 mm (laminate 9) showed no increase in the voltage with increasing strain except just before failure where a slight inflection in the trace was observed. One specimen, however, did show an increase in voltage and it is this result which is discussed below. Figure 4.42(a) shows the detector output, I, as a function of strain. Light is detected just after a strain of 0.175% is reached. The value of K is obtained from the slope of Ln I_n against strain, Figure 4.42(b). The value is is low, 9.0, Table 4.13(a), and is similar to the value for the unidirectional laminate with 1.5% BDMA and lower by a factor of four compared to that of the unidirectional 0.5% BDMA laminate. The amount of light detected at a given strain is shown in Table 4.13(b). The amount of light detected for this laminate is lower than that detected for the 90° unidirectional laminates containing less BDMA and only starts to increase significantly at higher strains (0.55% strain). The high strain at failure (0.575%) shows unusually
high flexibility for the 3.0% system suggesting that the specimen might not have been adequately cured.

Figure 4.43(a) shows a plot of the detector output, I, as a function of applied strain for a $(0,90)_s$ laminate with a total inner ply thickness of 1.8 mm (laminate 10). The plot of $\ln I_n$ against strain is shown in Figure 4.43(b) and has a slope of 11.0, Table 4.13(a). Figure 4.44(a) shows a plot of I against applied strain for a $(0,90)_s$ laminate with a total inner ply thickness of 1 mm (laminate 11). The slope of $\ln I_n$ against strain, Figure 4.44(b) had a value of 10.0, Table 4.13(a), which is also low. The laminates (9,10 and 11, 3.0% BDMA) all show very similar slopes, Table 4.13(a), and similar values for the amount of light detected as a function of applied strain, Table 4.13(b). The amount of light detected is also the lowest of the three systems. Figure 4.45(a) shows a plot of I as a function of applied strain for a $(0,90)_s$ laminate with an inner ply thickness of 0.5 mm (laminate 12). No light was detected until a strain of 0.3% had been reached. The amount of light detected was the lowest of all the laminates, Table 4.13(b). The slope of $\ln I_n$ against strain, Figure 4.45(b), is the highest of the laminates in the 3.0% BDMA group and has a value of about 21.0, Table 4.13(a).

Summary.

3.0% BDMA laminates.

The 3.0% BDMA laminates show the lowest rates of increase, K, in detector output and have a value of approximately 10.0, Table 4.13(a). The cross-ply laminate with the narrowest inner ply shows the highest rate which is approximately twice that of the other 3.0% BDMA laminates. It also shows the lowest amount of detected light, Table 4.13(b).

(d) Laminates with starch finish glass fibres.

In contrast to the unidirectional laminates manufactured with the conventional glass fibres, the 90° unidirectional laminates containing the starch finish glass fibres diffracted light even at zero applied strain. However, no additional light was detected with increasing strain in either the 0.5% BDMA or the 1.5% BDMA resin systems, prior to failure.
(e) The effects of cycling - 0.5% BDMA laminates only.

Specimens were subjected to three loading/unloading cycles over a strain range of 0.0 to 0.4%. The characteristic loading/unloading curve for the first cycle is of the general form shown in Figure 4.46, where the points ABCDE mark the different regions on the curves.

Cross-ply laminate (2d = 0.5 mm, b = 0.8 mm)

Figure 4.47 shows a typical set of results of detector output, I, as a function of strain for a specimen from a (0,90)₅ laminate with an inner 90° ply thickness of 0.5 mm. Initially, only the loading curves of the three cycles are described. The first curve is characteristic of an undamaged specimen showing a flat region AB extending to a strain of about 0.2%. Above 0.2% strain an exponential increase in the voltage is observed. A plot of $\ln I_n$ as a function of applied strain gives a straight line with a gradient of about 23.0. The second curve shows that AB now only extends to about 0.1% strain. This is then followed by a region which shows a linear increase in voltage as a function of strain. The third loading curve does not show a flat region. Instead the whole curve can be divided into two portions, both with linear increases in voltage but with two different gradients as shown in Figure 4.47. During the second cycle the specimen was loaded to a slightly higher strain so that towards the end of the loading cycle the gradient rises steeply as additional damage is caused. The values of the gradients are shown in Table 4.14.

The unloading portion of the three curves are also shown in Figure 4.47. An immediate difference between the loading and unloading curves is the 'waviness' of the traces. This is attributed to the slight movement of the LASER spot relative to the specimen so that regions with slightly higher micro-crack density due to differences in fibre packing arrangement, give slightly higher signals. Such areas do not exist in the undamaged specimen so that this effect is not observed in the first loading. In general, the loading curves show less waviness possibly because the increase in intensity with applied strain swamps the relatively small differences in the signal. The reproducible pattern of the 'waviness' confirmed that it was not random noise. In order to make measurements of the gradients, the curves were approximated to straight lines. During unloading the voltage remains approximately constant from a strain of 0.4% to a strain of 0.2%, CD. Below 0.2% strain a steep linear decrease in voltage is observed. The second and
third unloading curves show similar behaviour to the first. The values of the gradients are shown in Table 4.14.

At the end of the first cycle a 'residual' voltage is detected (1350 mV) and this accumulates during the second and third cycles (1950 and 600 mV respectively) to a total of 3900 mV.

Cross-ply laminate (2d = 2.0 mm, b = 0.65 mm)

Figure 4.48 shows plots of the detector output, $I$, as a function of applied strain for a 0.5% BDMA, $(0,90)_s$ laminate with an inner 90° ply thickness of about 2.0 mm. The specimen was cycled three times. The first curve is characteristic of an undamaged specimen. The flat region $AB$ extends to a strain of about 0.2%. Above this strain there is an exponential increase in mean voltage. A plot of $\ln I_n$ as a function of applied strain gives a straight line. The value of the slope is 18.0. Upon unloading the voltage reading is seen to remain constant from 0.35% strain to 0.275% strain. Below this strain the voltage decreases linearly. On reloading (second cycle) the voltage does not increase from 0.0% strain to 0.075% strain. Above 0.075% strain there is a straight line increase with a gradient equal to the unloading curve of cycle 1 (note that $AB$ is reduced). On reversing the load, the voltage remains constant from 0.35% strain to 0.275% strain (CD remains unchanged). Below 0.275% strain the voltage decreases linearly with a gradient similar to the unloading curve of cycles 1 and 2. The third cycle gave very similar results to the second but the flat region $AB$ was reduced further still. The values of the gradients are shown in Table 4.15.

At the end of the first cycle a 'residual' voltage is detected (900 mV) and this accumulates during the second and third cycles (325 and 300 mV respectively) to a total of 1525 mV at the end of the third cycle.

Cross-ply laminate (2d = 1.0 mm, b = 0.7 mm)

Figure 4.49 shows plots of $I$ as a function of applied strain for a 0.5% BDMA, $(0,90)_s$ laminate with an inner 90° ply thickness of about 1.0 mm. This specimen was only cycled twice. The first curve is characteristic of an undamaged specimen with the region $AB$ extending to about 0.2% strain after which there is an exponential increase in the voltage reading. A plot of $\ln I_n$ as a function of applied strain gives a straight line. The value of the slope of this line is 22.0, Table 4.16. Upon unloading the voltage is seen
to remain constant from 0.375% strain to 0.35% strain. Below 0.35% strain a linear decrease in voltage is observed. On reloading (second cycle) the voltage does not increase from 0.0% strain to 0.1% strain. Thus, the region AB is reduced. Above 0.1% strain, a linear increase in the voltage was observed. On reversing the load the voltage remains constant from 0.375% strain to 0.35% strain (CD remains unchanged) after which a linear decrease in the voltage is observed with a gradient similar to that obtained for the first cycle. The values of the gradients are shown in Table 4.16.

At the end of the first cycle a 'residual' voltage is detected (350 mV) and this accumulates during the second cycle (200 mV) to a total of 550 mV.

Unidirectional laminate (2d = 2.1 mm)

Figure 4.50 shows plots of I as a function of applied strain for a 0.5% BDMA, 90° unidirectional laminate with a ply thickness of about 2.1 mm. The first curve is characteristic of an undamaged specimen and the flat region AB extends to a strain of 0.25%. Above 0.25% strain there is an exponential increase in voltage and a plot of Ln(In) as a function of applied strain gives a straight line. The value of the slope of this line is 35.0, Table 4.17. Upon unloading the voltage is seen to remain constant from 0.35% strain to 0.3% strain. Below 0.3% strain there is a linear decrease in voltage. On reloading (second cycle) the voltage does not increase from 0.0% strain to 0.15% strain (AB is reduced) after which there is a linear increase in the voltage until the applied strain is equal to the maximum strain reached during the first loading (0.35% strain). Above this strain the voltage began to increase in the manner of an undamaged specimen. On reversing the load, the voltage continued to increase for a short interval of strain (about 0.0325%) after which there was a linear decrease in the voltage. There was no flat region in the curve (i.e. CD = 0.0). As the specimen was reloaded (third cycle), the voltage did not increase from 0.0% to 0.15% strain. An increase in voltage was then observed to be non-linear. The values of the gradients are shown in Table 4.17.

At the end of the first cycle a 'residual' amount of voltage is detected (200 mV) and this accumulates during the second cycle (550 mV) to a total of 750 mV at the end of the third cycle.
Summary.

Cross-ply laminate, \( b = 0.8 \) mm, \( 2d = 0.5 \) mm.

During the first cycle, the specimen shows a characteristic strain range during which no light is detected, \( AB \). Beyond point \( B \) an exponential increase in the voltage is observed, \( BC \). When the specimen is unloaded, a second flat region is observed where the voltage remains fairly constant, \( CD \). Below point \( D \), the voltage shows a linear decrease in value until zero load is reached. At zero load, 'residual whitening' is detected in the specimen. This is marked by the distance \( AE \) in millivolts. Consecutive loading cycles show that the strain range \( AB \) is reduced. At the beginning of the third loading, \( AB \) has a small slope. Above point \( B \), a linear (as opposed to exponential) increase in voltage is observed to point \( C \). During unloading, the strain range \( CD \) remains fairly constant, unlike \( AB \) which is reduced after the first loading. Below point \( D \), a linear decrease in voltage is observed. Residual whitening is again observed at the end of the second and third cycles. The gradients of the straight lines \( BC \) (loading) and \( DE \) (unloading) remain similar for all cycles after the initial loading provided the previous maximum strain limit is not exceeded. Table 4.14 shows the details of the strain range of \( AB \) and \( CD \), and the gradients of the lines \( BC \) and \( DE \). The amount of residual whitening is also shown.

Cross-ply laminate, \( b = 0.65 \) mm, \( 2d = 2 \) mm.

The loading/unloading curves for the laminate are essentially similar to those described for the laminate with the 0.5 mm inner 90° ply. The strain range \( AB \) is reduced during subsequent loading cycles. Above point \( B \), a linear increase in voltage is detected to point \( C \) after the initial loading cycle. The strain range \( CD \) is much smaller for this laminate but still appears to remain constant for all cycles. A linear decrease is observed below point \( D \). At zero load, residual whitening is detected for each cycle but at the end of the third cycle is only one third of the amount detected at the end of the first cycle. Again the gradients of the lines \( BC \) and \( DE \) are similar after the initial loading cycle. Table 4.15 shows the details of the strain ranges \( AB \), \( CD \) and gradients \( BC \), \( DE \). The magnitude of \( AE \) is also shown.
Cross-ply laminate, \(b = 0.7 \text{ mm}, 2d = 1.0 \text{ mm}\)

The loading/unloading curves for this laminate follow the same form as that obtained for the cross-plies mentioned above, but the changes appear on a much smaller scale. The strain range \(AB\) extends to about 0.25%. Above point \(B\), an exponential increase is observed \(BC\). When the specimen is unloaded from point \(C\) the strain range \(CD\) over which the voltage remains constant is the smallest of all the three laminates. Below point \(D\), a linear decrease is observed to point \(E\) at zero load. The amount of residual whitening is small compared to the other laminates. Consecutive cycles show a decrease in \(AB\), while \(BC\) and \(DE\) show linear behaviour. \(CD\) remains unchanged. Table 4.16 shows the details of the strain ranges \(AB\), \(CD\) and the gradients \(BC\) and \(DE\).

Unidirectional laminate, \(b = 0, 2d = 2.1\text{mm}\)

The unidirectional laminate behaved slightly differently in that during the second unloading cycle the range \(CD\) was not apparent. Instead, from point \(C\), on unloading, the voltage continued to increase slightly before showing a linear decrease \(DE\). The strain range \(AB\) was reduced on the second and third loading but the region \(BC\) showed a non-linear increase particularly during the third loading. Residual whitening was detected at the end of the cycles but was small considering the high voltage obtained during loading. Table 4.17 shows details of the strain ranges and gradients.

(f) The effect of heat-treatment after cycling.

Figure 4.51 shows the effect of heat-treating the specimen shown in Figure 4.48 for 30 mins. at 100°C after three load/unload cycles. (The specimen was a 0.5% BDMA cross-ply laminate with an inner ply of 2.0 mm). It was observed that the strain range \(AB\) (during which no light is detected) is re-instated and extends to a slightly higher applied strain than that obtained during the first cycle. The slope, \(K\), of the exponential increase from point \(B\) to \(C\) is reduced slightly from about 18.0 to about 16.0. The range \(CD\) is reduced and the slope of the linear region, \(DE\), has decreased from \(7 \times 10^3\) to \(4 \times 10^3\) (despite the additional straining). The heat treatment, therefore, appeared to return the specimen to its original state but it reduced the rate of increase in the amount of light detected as a function of strain. The effect of heat treatment is described in more detail in section 4.3.3.
Angular distribution of detected light.

Figure 4.52 shows a plot of the detector output, I, as a function of applied strain for a 0.5% BDMA specimen (laminate 4). The detected light was monitored at the positions shown in Figure 3.19(d), positions 1 to 6. Positions 5 and 6 remained saturated throughout the test (due possibly to their closeness to the direct beam) so that no further results are presented for these two positions. Positions 1 to 4 showed a characteristic flat portion AB during which no light was detected. Above point B an exponential increase in the voltage was detected. The strain at which light was first detected (the extent of AB) increased as the angle through which the light is diffracted is increased and so AB is largest for position 2 which was the furthest away from the transmitted beam.

The amount of light detected at 0.4% strain was recorded so that all four curves (for position 1 to 4) could be compared at a given strain. The voltage decreased as the angle through which the light was diffracted increased so that at position 2, the furthest away from the transmitted beam, the lowest amount of light was detected. The voltage reading for all positions is shown in Table 4.18(a).

The exponential plots of voltage as a function of applied strain were converted to plots of \( \ln I_n \) against applied strain from which values of \( K \) were obtained. The results are shown in Table 4.18(b). It is interesting to note that the value of \( K \) for each position is approximately the same. It is only the amount of light and the strain at which it is first detected that varies with angle.

4.3.3. Reversibility of stress-whitening.

Section 3.4.3. described some specific experiments undertaken to investigate the reversibility of stress-whitening using the off-axis diffraction technique and DMTA. The results of these experiments are presented in this section. The tests were carried out on a \((0,90)\) laminate with an inner ply thickness of 0.50 mm and outer ply thicknesses of 0.8 mm, manufactured with resin containing 0.5% BDMA.
(a) Quantitative measurement of stress-whitening.

Figure 4.53 shows plots of the detector output, \( I \), as a function of applied strain. Trace 1 shows the results of the first loading while traces 2, 3, 4, and 5 show the first loading after each successive annealing treatment given to the specimen. Trace 'ON' shows the voltage reading obtained after the specimen had been heat treated overnight at 120°F. The amount of light detected is tabulated at two different strains from traces 1, 2, 3 and 'ON', Table 4.19. These were 0.4% strain and 0.55% strain. The voltage readings from traces 4 and 5 were not tabulated since these differed very little from traces 2 and 3.

The traces in Figure 4.53 show an extension of the flat portion \( AB \) of the traces towards higher strains after each anneal. The voltage for a given strain is also reduced as the number of anneals is increased. This is shown in Table 4.19. After the first annealing treatment the voltage reading at 0.4% strain was reduced by a factor of approximately 6. During the first loading the specimen was only taken to a strain of 0.4%. In the following cycles the specimen was strained to about 0.55%. After annealing for a total of about 13 hours, the voltage reading at 0.4% strain was found to be reduced by a factor of 25.

Figure 4.54(a) shows the relationship between \( \ln I_n \) and applied strain for the first loading before any annealing (plot 1) and after the first anneal (plot 2). Plot 1 shows a straight line relationship between \( \ln I_n \) and applied strain and the slope, \( K \), has a value of about 30.0. Plot 2 shows that the slope of the line after the first anneal is the same between 0.0 and 0.4% strain but is reduced above a strain of 0.4% to a value of about 13.0 (\( K' \) in Table 4.20). It is interesting to note that 0.4% was the maximum strain to which the specimen was taken during the first cycle and that only after this strain is reached does the slope change.

Figure 4.54(b) shows the plot of \( \ln I_n \) against strain obtained after the third and overnight anneals (plot 3 and plot 'ON' respectively). Plot 3 and plot 'ON' both show changes of slope although the transition is less sharp and appears to occur at a slightly higher strain than 0.4%. After the third anneal (plot 3) the initial slope, \( K \), is about the same until a strain of 0.45% is reached. Above this value of strain the slope, \( K' \), had a value of 10.0. This is lower than that obtained after the first anneal, above 0.45% strain. After annealing for about 13 hours at 120°F, the slope below 0.475%
strain is about 23.0 and above this strain it changes to 10.0. These results are shown in Table 4.20.

The results show that initially, before annealing, a straight line is obtained by plotting \( \ln I_n \) as a function of strain. After annealing once, the gradient of the straight line is retained up to the previous maximum applied strain, at which point a distinct reduction in the gradient is observed. Both slopes then continue to decrease after several loading/annealing cycles and the transition between the two slopes becomes less obvious.

(b) DMTA.

Figure 4.55(a) shows the traces of \( \tan \delta \) as a function of temperature for the specimens described above. It can be seen that the initial glass transition temperature, \( T_g \), of 107 ± 5 °C, is gradually increased as the number of anneals is increased and after the fifth anneal, the \( T_g \) is 115 ± 5°C. After annealing for about 13 hours the glass transition temperature increases to 131 ± 5 °C. A similar result is obtained with the temperature \( T_1 \), described in section 3.2.2. This is shown in Figure 4.55(b) which shows \( \log k \) (dynamic modulus) as a function of temperature. \( T_1 \) is increased from 93 ± 5°C to 101 ± 5 °C after the fifth anneal and after the overnight anneal it is increased to 116 ± 5 °C.
Figure 4.1. Epoxy resin specimens after testing in plane strain compression mode showing tensile cracks which originated outside the compression zone.

Figure 4.2. The variation of yield stress, $\sigma_y$, of epoxy resin as a function of BDMA accelerator level in the system.
Figure 4.3. Cylindrical epoxy resin specimens after yielding in uniaxial compression.

Figure 4.4. Resin rich regions in a 90° unidirectional laminate with 3.0% BDMA resin matrix. No fibre splitting is observed despite the presence of resin rich regions.
Figure 4.5. Fibre splitting near 0/90 ply interfaces and resin rich regions in a (0,90)_s laminate with 1.5% BDMA resin matrix and inner 90° ply thickness, 2d, of 1.0 mm and outer 0° ply thickness, b, of 0.8 mm.

Figure 4.6. Load as a function of applied strain for a 90° unidirectional laminate with 0.5% BDMA resin matrix showing non-linearity.
Figure 4.7. Load as a function of applied strain for a (0,90)_s laminate with 0.5% BDMA resin matrix and inner 90° ply thickness, 2d, of 2.0 mm, outer ply thickness, b, of 0.65 mm.

Figure 4.8. Load as a function of applied strain for a (0,90)_s laminate with 0.5% BDMA resin matrix and inner 90° ply thickness, 2d, of 1.0 mm, outer ply thickness, b, of 0.7 mm.
Figure 4.9. Load as a function of applied strain for a $(0,90)_s$ laminate with 0.5\% BDMA resin matrix and inner 90° ply thickness, 2d, of 0.5 mm, outer ply thickness, b, of 0.8 mm (note: change of strain scale).

Figure 4.10. Load as a function of applied strain for a $(0,90)_s$ laminate with 3.0\% BDMA resin matrix, inner 90° ply thickness, 2d, of 1.8 mm, outer ply thickness, b, of 0.7 mm.
Figure 4.11. Colour changes as a function of strain for a (0,90)_5 laminate with 0.5% BDMA resin matrix, inner 90° ply thickness, 2d, of 2.2 mm, outer 0° ply thickness, b, of 0.65 mm. (a-c) first cycle, (d-g) second cycle, (h) after first heat treatment, (h-k) third cycle, (l) after second heat treatment.
Figure 4.12. Colour changes as a function of strain for a $(0,90)_s$ laminate with 0.5% BDMA resin matrix, inner 90° ply thickness, $2d$, of 1.3 mm, outer 0° ply thickness, $b$, of 0.65 mm. (Position of transverse ply cracks indicated by arrows.)
Figure 4.13. Colour changes as a function of strain for a (0,90)\textsubscript{s} laminate with 0.5% BDMA resin matrix, inner 90\textdegree ply thickness, 2d, of 0.5 mm, outer 0\textdegree ply thickness, b, of 0.8 mm. (a - e) first cycle, (f) after heat treatment. Note: whitening is removed while transverse ply cracks are still apparent.
Figure 4.14. Colour changes as a function of strain for a 90° unidirectional laminate with 0.5% BDMA resin matrix. (a-c) first cycle, (c-f) second cycle.
Figure 4.15. Colour changes as a function of strain for a $(0,90)_s$ laminate with 1.5% BDMA resin matrix, inner 90° ply thickness, $2d$, of 2.2 mm, outer 0° ply thickness, $b$, of 0.6 mm. (a-c) first cycle, (c-f) second cycle, (f-i) third cycle.
Figure 4.16. Colour changes as a function of strain for a (0,90)_s laminate with 1.5% BDMA resin matrix, inner 90° ply thickness, 2d, of 1.3 mm, outer 0° ply thickness, b, of 0.55 mm. (a-f) first cycle, (f-g) second cycle. Note: (d) and (g) show blue bands associated with the transverse ply cracks.

...(Continued on next page.)
Figure 4.16. Colour changes as a function of strain for a \((0,90)_s\) laminate with 1.5% BDMA resin matrix, inner 90° ply thickness, \(2d\), of 1.3 mm, outer 0° ply thickness, \(b\), of 0.55 mm. (a-f) first cycle, (f-g) second cycle. Note: (d) and (g) show blue bands associated with the transverse ply cracks.

Figure 4.17. Specimen from a \((0,90)_s\) laminate with 3.0% BDMA resin matrix, inner 90° ply thickness, \(2d\), of 2.2 mm, outer 0° ply thickness, \(b\), of 0.55 mm at 0.4% strain showing wide blue bands on either side of transverse ply cracks.
Figure 4.18. Colour changes as a function of strain for a (0,90)_s laminate with 3.0% BDMA resin matrix, inner 90° ply thickness, 2d, of 1.3 mm, outer 0° ply thickness, b, of 0.55 mm. (a-g) first cycle, (h) after heat treatment. Note: blue bands on either side of transverse ply crack are relatively narrow compared to Figure 4.17.
(a) at zero applied strain (magnification X 3).

(b) at 0.45% strain (magnification X 10).

Figure 4.19. Macrographs showing the development of whitening in a (0,90)_s laminate with 0.5% BDMA resin matrix, inner 90° ply thickness, 2d, of 0.5 mm, outer 0° ply thickness, b, of 0.8 mm. Note: Direction of applied load shown by arrows.
Figure 4.19. Macrographs showing the development of whitening in a (0,90)_s laminate with 0.5% BDMA resin matrix, inner 90°ply thickness, 2d, of 0.5 mm, outer 0° ply thickness, b, of 0.8 mm. Note: Direction of applied load shown by arrows.
(e) > 2.0% strain showing longitudinal splitting. Note: the 90° ply is obscured by the 0° ply (magnification X 3).

(f) > 2.0% strain showing delamination between 0/90 plies. Note: 90° ply is now seen more clearly (magnification X 3).

Figure 4.19. Macrographs showing the development of whitening in a \((0,90)_s\) laminate with 0.5% BDMA resin matrix, inner 90°ply thickness, 2d, of 0.5 mm, outer 0° ply thickness, b, of 0.8 mm. Note: Direction of applied load shown by arrows.
Figure 4.20. Macrographs showing the development of whitening in a 90° unidirectional laminate with 0.5% BDMA resin matrix. (a) at zero applied strain (magnification X 3). (b) at 0.45% strain (magnification X 3). (c) at zero load after failure (magnification X 3).
Figure 4.21. Macrographs showing the effect of load on a 90° unidirectional laminate with 3.0% BODA resin matrix. (a) at zero applied strain (magnification X 3). (b) at 0.35% strain (magnification X 3). Note: change of "texture", compare with Figure 4.20(b). (c) at zero load after failure (magnification X 3).
Figure 4.22. Macrographs showing the development of whitening in a 90° unidirectional laminate with 0.5% BDMA resin matrix and starch coated glass fibres. (a) at zero applied strain showing extensive whitening (magnification X 3). (b) at 0.2% strain with little additional whitening (magnification X 3). (c) at zero load after failure (magnification X 3).
(a) at zero load prior to testing showing the presence of fibre splits (magnification X 400).

(b) at zero load after straining to 0.45% showing micro-cracks normal to the tensile axis. Note: crack marked 'a' (magnification X 400).

Figure 4.23. Polished edge transmission micrograph of the 90° ply of a (0,90)₅ laminate with 0.5% BDMA resin matrix, inner 90° ply thickness, 2d, of 0.5 mm, outer 0° ply thickness of 0.6 mm.
(c) at zero load after heat treatment at 100°C for 30 mins showing healing of micro-cracks in the resin Note: crack 'a' has not reappeared (magnification X 400).

(d) at zero load after re-testing to a strain of 0.35%. Micro-cracks are still not visible (magnification X 400).

Figure 4.23. Polished edge transmission micrograph of the 90° ply of a (0,90)₅ laminate with 0.5% BDMA resin matrix, inner 90° ply thickness, 2d, of 0.5 mm, outer 0° ply thickness of 0.6 mm.
(e) at zero load after re-testing to 0.6% strain. A small proportion of micro-cracks have reappeared but are finer. Crack 'a' has still not reappeared. Cracks forming dark regions around fibres are visible (magnification X 400).

(f) at zero load after a second heat treatment at 100°C for 30 mins showing further healing of micro-cracks (magnification X 400).

Figure 4.23. Polished edge transmission micrograph of the 90° ply of a (0,90)_s laminate with 0.5% BDMA resin matrix, inner 90° ply thickness, 2d, of 0.5 mm, outer 0° ply thickness of 0.6 mm.
(a) at zero load prior to testing showing fibre splitting (magnification X 400).

(b) at 0.27% strain showing improved contrast between fibre and matrix (magnification X 400). Note: bright regions between fibres, 'a' and 'b'.

Figure 4.24. Polished edge transmission micrograph of the 90° ply of a (0,90)_s laminate with 0.5% BDMA resin matrix, inner 90° ply thickness, 2d, of 0.5 mm, outer 0° ply thickness of 0.8 mm.
(c) at 0.6% strain showing sub-surface damage (magnification X 300).

(d) at 0.8% strain showing excellent contrast between fibre and matrix (fibre prominence) and micro-cracks between fibres in close proximity (magnification X 300).

Figure 4.24. Polished edge transmission micrograph of the 90° ply of a (0,90)$_s$ laminate with 0.5% BDMA resin matrix, inner 90° ply thickness, 2d, of 0.5 mm, outer 0° ply thickness of 0.8 mm.
(e) at 0.94% strain showing further micro-cracking. Bright spots between fibres are no longer visible (compare with Figure 4.24 (b)). Note: regions 'a' and 'b'. (magnification X 400).

(f) at zero load after straining to 0.94%. Very few micro-cracks are now visible and bright spots between fibres have reappeared. See regions 'a' and 'b' (magnification X 400).

Figure 4.24. Polished edge transmission micrograph of the 90° ply of a (0,90)s laminate with 0.5% BDMA resin matrix, inner 90° ply thickness, 2d, of 0.5 mm, outer 0° ply thickness of 0.8 mm.
(g) at zero load after straining to 0.94% showing regions where micro-cracks have remained visible and coalescence of fibre splits, debonds and microcracks has occurred (magnification X 400).

Figure 4.24. Polished edge transmission micrograph of the 90° ply of a (0,90)_s laminate with 0.5% BDMA resin matrix, inner 90° ply thickness, 2d, of 0.5 mm, outer 0° ply thickness of 0.8 mm.
(a) at zero load prior to testing showing fibre splits (magnification X 400).

(b) at 0.27% strain showing micro-cracks and the improvement of contrast between fibre and resin (magnification X 400).

Figure 4.25. Polished edge micrograph of the 90° ply of a (0,90)₅ laminate with 0.5% BDMA resin matrix, inner 90° ply thickness, 2d of 1.0 mm, outer 0° ply thickness of 0.7 mm.
(c) instantaneous transverse ply crack just before reaching 0.3% strain.
Note: loss of contrast between fibre and matrix and closure of micro-cracks in the regions near the transverse ply crack (magnification X 400).

(d) instantaneous transverse ply crack just before reaching 0.3% strain
(section moved to the right to show left branch of crack, magnification X 400).

Figure 4.25. Polished edge micrograph of the 90° ply of a (0,90)_S laminate with 0.5% BDMA resin matrix, inner 90° ply thickness, 2d of 1.0 mm, outer 0° ply thickness of 0.7 mm.
(e) opposite end of transverse crack on the same edge showing crack branching (magnification X 400).

(f) overview of transverse ply crack and the region under examination (magnification X 100).

Figure 4.25. Polished edge micrograph of the 90° ply of a (0,90)_s laminate with 0.5% BDMA resin matrix, inner 90° ply thickness, 2d of 1.0 mm, outer 0° ply thickness of 0.7 mm.
(a) at zero load after straining to 0.35% showing concentration of micro-cracks at the 0/90 ply interface (magnification X 400).

Figure 4.26. Polished edge micrograph of the 90° ply of a (0,90)_5 laminate with 0.5% BDMA resin matrix, inner 90° ply thickness, 2d, of 2.0 mm and outer 0° ply thickness, b, of 0.65 mm.
(b) at zero load after straining to 0.35% showing concentration of micro-cracks near the 0/90 ply interface (opposite end). (magnification X 400).

Figure 4.26. Polished edge micrograph of the 90° ply of a (0,90)_s laminate with 0.5% BDMA resin matrix, inner 90° ply thickness, 2d, of 2.0 mm and outer 0° ply thickness, b, of 0.65 mm.
(c) Magnified view of middle region of the 90° ply showing initial stages of microcracking. Dark shadows are observed near fibres in contact (magnification X 1000).

Figure 4.26. Polished edge micrograph of the 90° ply of a (0,90)_s laminate with 0.5% BDMA resin matrix, inner 90° ply thickness, 2d, of 2.0 mm and outer 0° ply thickness,b, of 0.65 mm.
(a) at zero load prior to testing showing fibre splits and micro-cracking near the 0/90 ply interface. Some fibre cross-sections are marked for easy reference (magnification X 400).

(b) at 0.15% strain showing additional damage (magnification X 400).

Figure 4.27. Polished edge micrograph of the 90° ply of a (0,90)_s laminate with 1.5% BDMA resin matrix, inner 90° ply thickness, 2d, of 1.0 mm, outer 0° ply thickness, b, of 0.8 mm.
(c) at 0.15% strain showing additional damage (magnification X 600).

(d) at 0.2% strain showing micro-cracks which develop further from the 0/90 ply interface. See regions near fibre cross-sections marked 7, 8, 9, and 10 (magnification X 600).

Figure 4.27. Polished edge micrograph of the 90° ply of a (0,90)₅ laminate with 1.5% BDMA resin matrix, inner 90° ply thickness, 2d, of 1.0 mm, outer 0° ply thickness, b, of 0.8 mm.
(e) at 0.25% strain showing further development of micro-cracks.

(f) just before 0.3% strain showing a distortion of the matrix as a result of transverse ply cracking in the nearby region (magnification X 400).

Figure 4.27. Polished edge micrograph of the 90° ply of a (0, 90)_s laminate with 1.5% BDMA resin matrix, inner 90° ply thickness, 2d, of 1.0 mm, outer 0° ply thickness, b, of 0.8 mm.
(g) transverse ply crack just before reaching 0.3% strain (section moved towards the left, magnification X 400).

(h) overview of the transverse ply crack and area being examined (magnification X 100).

Figure 4.27. Polished edge micrograph of the 90° ply of a (0,90)₅ laminate with 1.5% BDMA resin matrix, inner 90° ply thickness, 2d, of 1.0 mm, outer 0° ply thickness, b, of 0.8 mm.
(i) at zero load after testing showing that most of the micro-cracks have closed up and only shadows are now visible in their place (magnification X 400).

Figure 4.27. Polished edge micrograph of the 90° ply of a (0,90)_S laminate with 1.5% BDMA resin matrix, inner 90° ply thickness, 2d, of 1.0 mm, outer 0° ply thickness, b, of 0.8 mm.
Figure 4.28. Transverse fracture path of a 90° unidirectional specimen with 0.5% BDMA matrix showing the presence of micro-cracks. Fibres still adhere to the resin after fracture (magnification X 400).
Figure 4.29. Transverse fracture path of a 90° unidirectional specimen with 0.5% BDMA matrix and starch coated glass fibres showing loose and completely debonded fibres. The fracture path has many fine branches and is made up of crescent shaped debonds (magnification X 400).
Figure 4.30. Transverse fracture path of a 90° unidirectional specimen with 1.5% BDMA matrix. No residual micro-cracks can be seen (magnification X 400).
Figure 4.31. Micrographs showing the same section of a transverse fracture of a 90° unidirectional laminate with 0.5% BDMA resin matrix (magnification X 400). (a) in transmission mode showing micro-cracking (b) in reflection mode where micro-cracking is difficult to determine, illustrating the extent to which information is lost by observing only in reflection.
(a) Laminate with 0.5% BDMA resin matrix showing the formation of "hackles" in the resin.

(b) Laminate with 1.5% BDMA resin matrix. The deformation in the resin is less extensive.

Figure 4.32. Scanning electron micrographs of fracture surfaces of 90° unidirectional laminates.
(c) Laminate with 0.5% BDMA resin matrix and starch coated glass fibres. The glass fibres appear free of resin.

Figure 4.32. Scanning electron micrographs of fracture surfaces of 90° unidirectional laminates.
Figure 4.33. Transmitted light in terms of millivolts as a function of applied strain in mode 2 for a 0.5% BDMA, (0,90)₅ laminate with inner 90° ply thickness, 2d, of 0.5 mm and outer 0° ply thickness, b, of 0.8 mm. The specimen was subjected to three loading cycles (traces 1, 2, and 3). It was then heat treated for 30 mins. at 100°C and re-tested after cooling to room temperature (trace 4).
Figure 4.34 (a). Light detected in terms of millivolts as a function of applied strain for a 90° unidirectional laminate with a 0.5% BDMA matrix. (b) The logarithm of the mean normalised millivolt readings as a function of applied strain.
Figure 4.35 (a). Light detected in terms of millivolts as a function of applied strain for a \((0,90)_s\) laminate with a 0.5% BDMA matrix and an inner 90° ply thickness, \(2d\), of 2.0 mm and an outer 0° ply thickness, \(b\), of 0.65 mm. (b) The logarithm of the mean normalised millivolt readings as a function of applied strain.
Figure 4.36 (a). Light detected in terms of millivolts as a function of applied strain for a $(0,90)_5$ laminate with a 0.5% BDMA matrix and an inner 90° ply thickness, $2d$, of 1.0 mm and an outer 0° ply thickness, $b$, of 0.7 mm. (b) The logarithm of the mean normalised millivolt readings as a function of applied strain.
Figure 4.37 (a). Light detected in terms of millivolts as a function of applied strain for a (0,90)_s laminate with a 0.5% BDMA matrix and an inner 90° ply thickness, 2d, of 0.5 mm and an outer 0° ply thickness, b, of 0.8 mm. (b) The logarithm of the mean normalised millivolt readings as a function of applied strain.
Figure 4.38 (a). Light detected in terms of millivolts as a function of applied strain for a 90° unidirectional laminate with a 1.5% BDMA matrix. (b) The logarithm of the mean normalised millivolt readings as a function of applied strain.
Figure 4.39 (a). Light detected in terms of millivolts as a function of applied strain for a $(0,90)_s$ laminate with a 1.5% BDMA matrix and an inner 90° ply thickness, $2d$, of 1.8 mm and an outer 0° ply thickness, $b$, of 0.6 mm. (b) The logarithm of the mean normalised millivolt readings as a function of applied strain.
Figure 4.40 (a). Light detected in terms of millivolts as a function of applied strain for a \((0,90)\)\\(_s\) laminate with a 1.5\% BDMA matrix and an inner 90° ply thickness, \(2d\), of 1.0 mm and an outer 0° ply thickness, \(b\), of 0.8 mm. (b) The logarithm of the mean normalised millivolt readings as a function of applied strain.
Figure 4.41 (a). Light detected in terms of millivolts as a function of applied strain for a (0,90)_s laminate with a 1.5% BDMA matrix and an inner 90° ply thickness, 2d, of 0.5 mm and an outer 0° ply thickness, b, of 0.9 mm. (b) The logarithm of the mean normalised millivolt readings as a function of applied strain.
Figure 4.42 (a). Light detected in terms of millivolts as a function of applied strain for a 90° unidirectional laminate with a 3.0% BDMA matrix. (b) The logarithm of the mean normalised millivolt readings as a function of applied strain.
Figure 4.43 (a). Light detected in terms of millivolts as a function of applied strain for a \((0,90)_s\) laminate with a 3.0% BDMA matrix and an inner 90° ply thickness, \(2d\), of 1.8 mm and an outer 0° ply thickness, \(b\), of 0.7 mm. (b) The logarithm of the mean normalised millivolt readings as a function of applied strain.
Figure 4.44 (a). Light detected in terms of millivolts as a function of applied strain for a (0,90)ₙ laminate with a 3.0% BDMA matrix and an inner 90° ply thickness, 2d, of 1.0 mm and an outer 0° ply thickness, b, of 0.65 mm. (b) The logarithm of the mean normalised millivolt readings as a function of applied strain.
Figure 4.45 (a). Light detected in terms of millivolts as a function of applied strain for a (0,90)\textsubscript{s} laminate with a 3.0\% BDMA matrix and an inner 90\(^\circ\) ply thickness, 2d, of 0.5 mm and an outer 0\(^\circ\) ply thickness, b, of 0.90 mm. (b) The logarithm of the mean normalised millivolt readings as a function of applied strain.
Figure 4.46. Schematic diagram showing the characteristic curve of detected light as a function of strain obtained during the first complete load/unload cycle. The characteristic regions are marked, AB, during which no light is detected, BC, during which there is an approximately exponential increase in detected light, CD during which the detected light remains constant despite the decrease in applied load or strain, DE, where a linear decrease in detected light is observed and AE which shows the "residual" light detected at zero applied strain.
Figure 4.47. Typical traces of light detected in terms of millivolts as a function of applied strain obtained from a (0,90)_s laminate with a 0.5% BDMA matrix and an inner 90° ply thickness, 2d, of 0.5 mm and an outer 0° ply thickness of 0.8 mm, during cyclic loading (see also Table 4.14).
Figure 4.48. Typical traces of light detected in terms of millivolts as a function of applied strain obtained from a (0,90)$_s$ laminate with a 0.5% BDMA matrix and an inner 90° ply thickness, 2d, of 2.0 mm and an outer 0° ply thickness of 0.65 mm, during cyclic loading (see also Table 4.15). Traces have been displaced for clarity.
Figure 4.49. Typical traces of light detected in terms of millivolts as a function of applied strain obtained from a (0,90)_s laminate with a 0.5% BDMA matrix and an inner 90° ply thickness, 2d, of 1.0 mm and an outer 0° ply thickness of 0.70 mm, during cyclic loading (see also Table 4.16). Traces have been displaced for clarity.
Figure 4.50. Typical traces of light detected in terms of millivolts as a function of applied strain obtained from a 90° unidirectional laminate with a 0.5% B DMA matrix and a ply thickness, 2d, of 2.1 mm, during cyclic loading (see also Table 4.17). Traces have been displaced for clarity.
Figure 4.51. Typical trace of light detected in terms of millivolts as a function of applied strain obtained from a (0,90)_s laminate with a 0.5% BDMA matrix and an inner 90° ply thickness, 2d, of 2.0 mm and an outer 0° ply thickness of 0.65 mm, after cycling (Figure 4.48) and heat treating for 30 mins. at 100°C, cooling to room temperature and re-testing.
Figure 4.52. Typical traces of light detected, in terms of millivolts, as a function of applied strain obtained for $(0,90)_s$ laminate with a 0.5% BDMA matrix and an inner 90° ply thickness, $2d$, of 0.5 mm and an outer 0° ply thickness of 0.8 mm, for six different angular positions of the detector (see also Table 4.18 and Figure 3.19 (d)).
Figure 4.53. Typical traces of light detected, in terms of millivolts, as a function of applied strain obtained for \((0,90)_s\) laminate with a 0.5% BDMA matrix and an inner 90° ply thickness, 2d, of 0.5 mm and an outer 0° ply thickness of 0.8 mm. Trace 1 was obtained during the initial loading while traces 2, 3, 4, and 5 were obtained during the first loading after each additional heat treatment at a 120°C for 20 mins. Trace ON was obtained after the specimen had been heat treated overnight for 12 hours at 120°C.
Figure 4.54 (a). The relationship between the logarithm of light detected, in terms of millivolts, and applied strain for (0,90)_s laminate with a 0.5% BDMA matrix and an inner 90° ply thickness, 2d, of 0.5 mm and an outer 0° ply thickness of 0.8 mm. Plot 1 shows the initial relationship prior to heat treatment. Plot 2 shows the relationship after the first heat treatment. Note: The line has two different gradients, one before and one after reaching the previous applied strain limit. (see also Table 4.20)

Figure 4.54 (b). The relationship between the logarithm of light detected, in terms of millivolts, and applied strain for (0,90)_s laminate with a 0.5% BDMA matrix and an inner 90° ply thickness, 2d, of 0.5 mm and an outer 0° ply thickness of 0.8 mm. Plot 3 shows the relationship after the third heat treatment. Plot ON shows the relationship after the overnight heat treatment (see also Table 4.20).
Figure 4.55 (a). Traces of $\tan \delta$ as a function of temperature showing the change in the glass transition temperature, $T_g$, with successive heat treatments of 20 mins. at 120°C, of a (0,90)s laminate with 0.5% BDMA matrix, 90° ply thickness, $2d$, of 0.5 mm and 0° ply thickness, $b$, of 0.8 mm. The biggest change is observed after the overnight heat treatment (trace 6).
Figure 4.55 (b). Traces of dynamic modulus as a function of temperature showing the change in the stress free temperature, $T_I$, with successive heat treatments of 20 mins. at 120°C, of a (0,90)s laminate with 0.5% BDM A matrix, 90° ply thickness, $2d$, of 0.5 mm and 0° ply thickness, $b$, of 0.8 mm. The biggest change is observed after the overnight heat treatment (trace 6).
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<th>BDMA accelerator level (%)</th>
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<th>S.D.</th>
<th>( E ) (GPa)</th>
<th>S.D.</th>
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| \( e_f \) (%)    | 0.52                      | 0.26          | 0.53 | 0.04          | 0.64 | 0.2          |

Table 4.1. Variation of mean secant modulus \( (E) \) and fracture strain \( (e_f) \) for unpolished epoxy resin samples with accelerator level as a function of applied strain. Each value is a mean of three samples, S.D. = standard deviation.
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| $e_f$          | 1.6                     | 0.16               |

Table 4.2. Variation of mean secant modulus ($E$) and fracture strain ($e_f$) of polished edge epoxy resin samples with 0.5% BDMA as a function of applied strain. Each result is a mean of 3 samples.
Table 4.3. Variation of mean Poisson's ratio ($\nu$) for epoxy resin samples with accelerator level as a function of applied strain. Each value is a mean of three samples, S.D. = standard deviation.

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</table>

Table 4.4(a) Variation of mean yield stress ($\sigma_y$) with accelerator level (plane strain compression test) of epoxy resin samples. Each value is a mean of 3 samples.

<table>
<thead>
<tr>
<th>BDMA (%)</th>
<th>Mean yield stress (MPa)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>144.0</td>
<td>5.5</td>
</tr>
<tr>
<td>1.5</td>
<td>129.0</td>
<td>8.4</td>
</tr>
<tr>
<td>3.0</td>
<td>128.0</td>
<td>3.2</td>
</tr>
<tr>
<td>BDMA (%)</td>
<td>Mean yield stress (MPa)</td>
<td>Standard deviation</td>
</tr>
<tr>
<td>----------</td>
<td>------------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>0.5</td>
<td>138.0</td>
<td>0.58</td>
</tr>
<tr>
<td>1.5</td>
<td>124.0</td>
<td>2.6</td>
</tr>
<tr>
<td>3.0</td>
<td>119.0</td>
<td>2.16</td>
</tr>
</tbody>
</table>

Table 4.4(b) Variation of mean yield stress ($\sigma_y$) with accelerator level for epoxy resin samples (uniaxial compression of cylinders). Each value is a mean of 3 samples.

<table>
<thead>
<tr>
<th>BDMA (%)</th>
<th>Glass transition temperature (°C)</th>
<th>T1 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>110 ± 5</td>
<td>95 ± 5</td>
</tr>
<tr>
<td>1.5</td>
<td>135 ± 5</td>
<td>125 ± 5</td>
</tr>
<tr>
<td>3.0</td>
<td>155 ± 5</td>
<td>135 ± 5</td>
</tr>
</tbody>
</table>

Table 4.5. Variation of glass transition temperature ($T_g$) and stress-free temperature ($T_1$) with accelerator level for epoxy resin samples. Each value is a mean of three samples.

<table>
<thead>
<tr>
<th>BDMA (%)</th>
<th>Refractive Index</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.53</td>
<td>0.05</td>
</tr>
<tr>
<td>1.5</td>
<td>1.51</td>
<td>0.03</td>
</tr>
<tr>
<td>3.0</td>
<td>1.49</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Table 4.6. Variation of the refractive index with accelerator level for epoxy resin samples. Each value is a mean of at least three samples.
Table 4.7(a) Mean Secant modulus (E), mean change in Secant modulus before transverse cracking (dE), strain to first transverse ply crack ($\varepsilon_{tc}$), and volume fraction of glass fibres ($V_f$) for laminates made with resin containing 0.5% BDMA. Each result is a mean of 4 to 5 specimens.
<table>
<thead>
<tr>
<th>Laminate code</th>
<th>Laminate geometry</th>
<th>Secant modulus, E (GPa)</th>
<th>dE (GPa)</th>
<th>$\varepsilon_{tc}$ (%)</th>
<th>Vf (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>b (mm)</td>
<td>2d (mm)</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>5</td>
<td>b = 0,</td>
<td>2d = 2.1</td>
<td>13.1</td>
<td>13.1</td>
<td>13.0</td>
</tr>
<tr>
<td>6</td>
<td>b = 0.60</td>
<td>2d = 1.8</td>
<td>26.4</td>
<td>26.1</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>b = 0.8</td>
<td>2d = 1.0</td>
<td>33.9</td>
<td>33.9</td>
<td>33.6</td>
</tr>
<tr>
<td>8</td>
<td>b = 0.9</td>
<td>2d = 0.5</td>
<td>35.3</td>
<td>35.5</td>
<td>35.3</td>
</tr>
</tbody>
</table>

Table 4.7(b) Mean Secant modulus (E), mean change in Secant modulus before transverse cracking (dE), strain to first transverse ply crack ($\varepsilon_{tc}$), and volume fraction of glass fibres (Vf) for laminates made with resin containing 1.5% BDMA. Each result is a mean of 4 to 5 specimens.
<table>
<thead>
<tr>
<th>Laminate code</th>
<th>Laminate geometry</th>
<th>Secant modulus, E (GPa)</th>
<th>dE</th>
<th>$\varepsilon_{tc}$</th>
<th>Vf</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>$b = 0$, $2d = 2.9$</td>
<td>10.0 10.0 9.90 9.90</td>
<td>0.1</td>
<td>0.4</td>
<td>44.0</td>
</tr>
<tr>
<td>10</td>
<td>$b = 0.70$, $2d = 1.8$</td>
<td>24.0 24.0 23.5 -</td>
<td>-</td>
<td>0.26</td>
<td>55.0</td>
</tr>
<tr>
<td>11</td>
<td>$b = 0.65$, $2d = 1.0$</td>
<td>31.9 31.5 31.2 31.1</td>
<td>0.4</td>
<td>0.35</td>
<td>55.0</td>
</tr>
<tr>
<td>12</td>
<td>$b = 0.9$, $2d = 0.5$</td>
<td>32.9 32.4 32.0 32.0</td>
<td>0.4</td>
<td>0.33</td>
<td>41.0</td>
</tr>
</tbody>
</table>

Table 4.7(c) Mean Secant modulus (E), mean change in Secant modulus before transverse cracking (dE), strain to first transverse ply crack ($\varepsilon_{tc}$) and volume fraction of glass fibres (Vf) for laminates made with resin containing 3.0% BDMA. Each result is a mean of 4 to 5 specimens.

<table>
<thead>
<tr>
<th>Laminate code</th>
<th>Laminate geometry</th>
<th>Secant modulus, E (GPa)</th>
<th>dE</th>
<th>$\varepsilon_{tc}$</th>
<th>Vf</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>$b = 0$, $2d = 2.3$</td>
<td>9.38 9.10 9.08 -</td>
<td>-</td>
<td>0.31</td>
<td>42.0</td>
</tr>
</tbody>
</table>

Table 4.7(d) Mean Secant modulus (E), mean change in Secant modulus before transverse cracking (dE), strain to first transverse ply crack ($\varepsilon_{tc}$) and volume fraction of glass fibres (Vf) for laminates made with resin containing 0.5% BDMA and 120 tex glass fibres with the starch finish. Each result is a mean of 4 to 5 specimens.
### Table 4.7(e) Mean Secant modulus (E), mean change in Secant modulus before transverse cracking (dE), strain to first transverse ply crack (etc) and volume fraction of glass fibres (Vf) for laminates made with resin containing 1.5% BDMA and 120 tex glass fibres with the starch finish. Each result is a mean of 4 to 5 Specimens.

<table>
<thead>
<tr>
<th>Laminate code</th>
<th>Laminate geometry</th>
<th>Secant modulus, E (GPa)</th>
<th>dE</th>
<th>etc</th>
<th>Vf</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Applied strain (%)</td>
<td>(GPa)</td>
<td>(%)</td>
<td>(%)</td>
</tr>
<tr>
<td>No. b (mm) 2d (mm)</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>( b = 0.55 )</td>
<td>23.2</td>
<td>23.0</td>
<td>22.7</td>
<td>22.5</td>
</tr>
</tbody>
</table>

### Table 4.7(f) Mean Secant modulus (E), mean change in Secant modulus before transverse cracking (dE), strain to first transverse ply crack (etc) and volume fraction of glass fibres (Vf) for laminates made with resin containing 0.5%, 1.5% and 3.0% BDMA and 1200 tex glass fibres. Each result is a mean of 4 to 5 specimens.

<table>
<thead>
<tr>
<th>Laminate code</th>
<th>Laminate geometry</th>
<th>Secant modulus, E (GPa)</th>
<th>dE</th>
<th>etc</th>
<th>Vf</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Applied strain (%)</td>
<td>(GPa)</td>
<td>(%)</td>
<td>(%)</td>
</tr>
<tr>
<td>BDMA (%) 2d (mm)</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>15, (0.5) 2d = 2.2</td>
<td>21.6</td>
<td>21.5</td>
<td>21.4</td>
<td>-</td>
<td>0.2</td>
</tr>
<tr>
<td>16, (1.5) 2d = 2.2</td>
<td>17.7</td>
<td>17.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Laminate code</td>
<td>Secant modulus (0.2% strain) (GPa)</td>
<td>Youngs modulus (calculated) (GPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>-----------------------------------</td>
<td>----------------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>15.5</td>
<td>15.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>28.0</td>
<td>27.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>35.1</td>
<td>36.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>36.9</td>
<td>38.0</td>
<td></td>
<td></td>
<td></td>
</tr>
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</tr>
<tr>
<td>6</td>
<td>26.1</td>
<td>27.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>33.9</td>
<td>34.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>35.5</td>
<td>34.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>10.0</td>
<td>9.85</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>24.0</td>
<td>25.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>31.5</td>
<td>28.7</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>12</td>
<td>32.4</td>
<td>26.7</td>
<td></td>
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</tr>
<tr>
<td>13</td>
<td>9.10</td>
<td>10.4</td>
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</tr>
<tr>
<td>14</td>
<td>8.70</td>
<td>9.60</td>
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</tr>
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</tr>
<tr>
<td>16</td>
<td>21.5</td>
<td>22.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>17.7</td>
<td>19.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.8. Comparison of experimental values of Secant modulus (at 0.2% strain) and calculated values obtained using the Halpin-Tsai equations and classical laminated plate theory.
### Table 4.9. Mean Secant modulus and reduction in modulus (dE) after 4 cycles and after annealing at 100°C for 30 minutes for laminates made with 1200 tex fibres and resin containing 0.5%, 1.5% and 3.0% BDMA (laminates 15, 16 and 17). S.D. = standard deviation. Each result is a mean of at least 4 specimens.

<table>
<thead>
<tr>
<th>Applied strain (%)</th>
<th>Initial value</th>
<th>S.D.</th>
<th>After 4 cycles</th>
<th>S.D.</th>
<th>dE After cycles</th>
<th>S.D.</th>
<th>dE After annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>0.5% BDMA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>23.2</td>
<td>1.1</td>
<td>23.0</td>
<td>1.3</td>
<td>0.2</td>
<td>22.6</td>
<td>1.0</td>
</tr>
<tr>
<td>0.2</td>
<td>23.0</td>
<td>1.3</td>
<td>22.6</td>
<td>1.2</td>
<td>0.4</td>
<td>22.2</td>
<td>0.9</td>
</tr>
<tr>
<td>0.3</td>
<td>22.8</td>
<td>1.2</td>
<td>22.4</td>
<td>1.1</td>
<td>0.4</td>
<td>21.9</td>
<td>0.9</td>
</tr>
<tr>
<td>0.35</td>
<td>22.6</td>
<td>1.2</td>
<td>22.3</td>
<td>1.1</td>
<td>0.3</td>
<td>21.8</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>1.5% BDMA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>21.0</td>
<td>0.4</td>
<td>21.0</td>
<td>0.5</td>
<td>-</td>
<td>20.7</td>
<td>0.4</td>
</tr>
<tr>
<td>0.2</td>
<td>21.1</td>
<td>0.4</td>
<td>20.8</td>
<td>0.5</td>
<td>0.3</td>
<td>20.6</td>
<td>0.4</td>
</tr>
<tr>
<td>0.3</td>
<td>21.0</td>
<td>0.4</td>
<td>20.9</td>
<td>0.5</td>
<td>0.1</td>
<td>20.4</td>
<td>0.4</td>
</tr>
<tr>
<td>0.35</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>3.0% BDMA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>17.7</td>
<td>0.6</td>
<td>17.6</td>
<td>0.6</td>
<td>0.1</td>
<td>17.6</td>
<td>0.4</td>
</tr>
<tr>
<td>0.2</td>
<td>17.7</td>
<td>0.6</td>
<td>17.6</td>
<td>0.6</td>
<td>0.1</td>
<td>17.6</td>
<td>0.4</td>
</tr>
<tr>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.35</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>No.</td>
<td>(% )</td>
<td>(mm)</td>
<td>(mm)</td>
<td>Transverse fracture strain (εtc)</td>
<td>Thermal strain εth</td>
<td>εtc + εth</td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>-------------------------------</td>
<td>-------------------</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>-</td>
<td>1.05</td>
<td>0.40</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.65</td>
<td>1.0</td>
<td>0.30</td>
<td>0.14</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>3</td>
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<td>0.7</td>
<td>0.5</td>
<td>0.30</td>
<td>0.16</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>0.8</td>
<td>0.25</td>
<td>0.70</td>
<td>0.20</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.5</td>
<td>-</td>
<td>1.05</td>
<td>0.34</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.5</td>
<td>0.6</td>
<td>0.90</td>
<td>0.24</td>
<td>0.20</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1.5</td>
<td>0.8</td>
<td>0.5</td>
<td>0.30</td>
<td>0.24</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1.5</td>
<td>0.9</td>
<td>0.25</td>
<td>0.35</td>
<td>0.32</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>3.0</td>
<td>-</td>
<td>1.45</td>
<td>0.30</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>3.0</td>
<td>0.7</td>
<td>0.9</td>
<td>0.25</td>
<td>0.26</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>3.0</td>
<td>0.65</td>
<td>0.5</td>
<td>0.37</td>
<td>0.30</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>3.0</td>
<td>0.9</td>
<td>0.25</td>
<td>0.39</td>
<td>0.44</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>0.5</td>
<td>-</td>
<td>2.3</td>
<td>0.30</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1.5</td>
<td>-</td>
<td>2.1</td>
<td>0.19</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0.5</td>
<td>0.55</td>
<td>1.1</td>
<td>0.38</td>
<td>0.14</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>1.5</td>
<td>0.55</td>
<td>1.1</td>
<td>0.30</td>
<td>0.22</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>3.0</td>
<td>0.65</td>
<td>1.3</td>
<td>0.26</td>
<td>0.28</td>
<td>0.54</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.10. Values of first transverse ply cracking strains corrected for thermal strain. (Thermal strains calculated using equations and material properties shown in appendix 2.)
Table 4.11(a). Values of $A$ and $K$ for the 0.5% BDMA laminates obtained from plots of $\ln I_n (\text{mV/mm})$ as a function of applied strain.

<table>
<thead>
<tr>
<th>Laminate code</th>
<th>$A$</th>
<th>$K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.002</td>
<td>35.0</td>
</tr>
<tr>
<td>2</td>
<td>1.10</td>
<td>18.0</td>
</tr>
<tr>
<td>3</td>
<td>0.35</td>
<td>22.0</td>
</tr>
<tr>
<td>4</td>
<td>1.3</td>
<td>23.0</td>
</tr>
</tbody>
</table>

Table 4.11(b). Light detected as a function of strain for 0.5% BDMA laminates, voltage readings were normalised for inner 90° ply thickness.

<table>
<thead>
<tr>
<th>Laminate code</th>
<th>Strain interval (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0 - 0.3</td>
</tr>
<tr>
<td>1</td>
<td>57.0</td>
</tr>
<tr>
<td>2</td>
<td>240.0</td>
</tr>
<tr>
<td>3</td>
<td>285.0</td>
</tr>
<tr>
<td>4</td>
<td>1700.0</td>
</tr>
</tbody>
</table>
Table 4.12(a). Values of A and K for the 1.5% BDMA laminates obtained from plots of Ln In as a function of applied strain.

<table>
<thead>
<tr>
<th>Laminate code</th>
<th>A</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>7.4</td>
<td>9.0</td>
</tr>
<tr>
<td>6</td>
<td>2.4</td>
<td>33.0</td>
</tr>
<tr>
<td>7</td>
<td>0.007</td>
<td>30.0</td>
</tr>
<tr>
<td>8</td>
<td>0.012</td>
<td>27.0</td>
</tr>
</tbody>
</table>

Table 4.12(b). Light detected as a function of strain for 1.5% BDMA laminates, voltage readings were normalised for inner 90° ply thickness.

<table>
<thead>
<tr>
<th>Laminate code</th>
<th>Strain interval (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0 - 0.3</td>
</tr>
<tr>
<td>5</td>
<td>112.0</td>
</tr>
<tr>
<td>6</td>
<td>&gt;1735.0</td>
</tr>
<tr>
<td>7</td>
<td>67.0</td>
</tr>
<tr>
<td>8</td>
<td>48.0</td>
</tr>
<tr>
<td>Laminate code</td>
<td>A</td>
</tr>
<tr>
<td>--------------</td>
<td>-----</td>
</tr>
<tr>
<td>9</td>
<td>4.5</td>
</tr>
<tr>
<td>10</td>
<td>3.7</td>
</tr>
<tr>
<td>11</td>
<td>2.7</td>
</tr>
<tr>
<td>12</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table 4.13(a). Values of A and K for the 3.0% BDMA laminates obtained from plots of Ln In as a function of applied strain.

<table>
<thead>
<tr>
<th>Laminate code</th>
<th>Light detected Inₙ (mV/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Light detected Inₙ (mV/mm)</td>
</tr>
<tr>
<td></td>
<td>Light detected Inₙ (mV/mm)</td>
</tr>
<tr>
<td></td>
<td>Light detected Inₙ (mV/mm)</td>
</tr>
<tr>
<td></td>
<td>Light detected Inₙ (mV/mm)</td>
</tr>
<tr>
<td>9</td>
<td>79.0</td>
</tr>
<tr>
<td>10</td>
<td>86.0</td>
</tr>
<tr>
<td>11</td>
<td>55.0</td>
</tr>
<tr>
<td>12</td>
<td>26.0</td>
</tr>
</tbody>
</table>

Table 4.13(b). Light detected as a function of strain for 3.0% BDMA laminates, voltage readings were normalised for inner 90° ply thickness.
<table>
<thead>
<tr>
<th>Cycle No.</th>
<th>Strain range (%) and Slope m, X 10^3</th>
<th>Residual signal (mV/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>BC</td>
<td>CD</td>
</tr>
<tr>
<td>1</td>
<td>0.0 - 0.2</td>
<td>0.2 - 0.4</td>
</tr>
<tr>
<td>m = 0</td>
<td>K = 23.0*</td>
<td>m = 0.0</td>
</tr>
<tr>
<td>2</td>
<td>0.0 - 0.1</td>
<td>0.1 - 0.425</td>
</tr>
<tr>
<td>m = 0</td>
<td>m = 12.5</td>
<td>m = 0.0</td>
</tr>
<tr>
<td>3</td>
<td>0.0 - 0.1</td>
<td>0.1 - 0.4</td>
</tr>
<tr>
<td>m = 3.5</td>
<td>m = 16</td>
<td>m = 0.0</td>
</tr>
</tbody>
</table>

Table 4.14 The strain range and gradients of the traces obtained during three consecutive loading and unloading cycles, for a 0.5% BDM A cross-ply laminate with 2d = 0.5 mm. * indicates gradient of Ln I_n against applied strain. All other values are for linear plots of I_n against applied strain.

<table>
<thead>
<tr>
<th>Cycle No.</th>
<th>Strain range (%) and Slope m, X 10^3</th>
<th>Residual signal (mV/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>BC</td>
<td>CD</td>
</tr>
<tr>
<td>1</td>
<td>0.0 - 0.2</td>
<td>0.2 - 0.35</td>
</tr>
<tr>
<td>m = 0</td>
<td>K = 18.0*</td>
<td>m = 0.0</td>
</tr>
<tr>
<td>2</td>
<td>0.0 - 0.1</td>
<td>0.1 - 0.375</td>
</tr>
<tr>
<td>m = 0</td>
<td>m = 7.0</td>
<td>m = 0.0</td>
</tr>
<tr>
<td>3</td>
<td>0.0 - 0.075</td>
<td>0.1 - 0.35</td>
</tr>
<tr>
<td>m = 0.0</td>
<td>m = 7.7</td>
<td>m = 0.0</td>
</tr>
</tbody>
</table>

Table 4.15 The strain range and gradients of the traces obtained during three consecutive loading and unloading cycles, for a 0.5% BDM A cross-ply laminate with 2d = 2.0 mm. * indicates gradient of Ln I_n against applied strain. All other values are for linear plots of I_n against applied strain.
<table>
<thead>
<tr>
<th>Cycle No.</th>
<th>Strain range (%) and Slope m, X 10^3</th>
<th>Residual signal (mV/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AB</td>
<td>BC</td>
</tr>
<tr>
<td>1</td>
<td>0.0 - 0.25</td>
<td>0.25 - 0.4</td>
</tr>
<tr>
<td></td>
<td>m = 0</td>
<td>K = 22.0*</td>
</tr>
<tr>
<td>2</td>
<td>0.0 - 0.125</td>
<td>0.125 - 0.4</td>
</tr>
<tr>
<td></td>
<td>m = 0</td>
<td>m = 2.5</td>
</tr>
</tbody>
</table>

Table 4.16 The strain range and gradients of the traces obtained during two consecutive loading and unloading cycles, for a 0.5% BDMA cross-ply laminate with 2d = 1.0 mm. * indicates gradient of Ln I_n against applied strain. All other values are for linear plots of I_n against applied strain.

<table>
<thead>
<tr>
<th>Cycle No.</th>
<th>Strain range (%) and Slope m, X 10^3</th>
<th>Residual signal (mV/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AB</td>
<td>BC</td>
</tr>
<tr>
<td>1</td>
<td>0.0 - 0.3</td>
<td>0.3 - 0.35</td>
</tr>
<tr>
<td></td>
<td>m = 0</td>
<td>K = 35.0*</td>
</tr>
<tr>
<td>2</td>
<td>0.0 - 0.15</td>
<td>0.15 - 0.385</td>
</tr>
<tr>
<td></td>
<td>m = 0</td>
<td>see text</td>
</tr>
<tr>
<td>3</td>
<td>0.0 - 0.125</td>
<td>0.125 - 0.4</td>
</tr>
<tr>
<td></td>
<td>m = 0.0</td>
<td>see text</td>
</tr>
</tbody>
</table>

Table 4.17 The strain range and gradients of the traces obtained during three consecutive loading and unloading cycles, for a 0.5% BDMA unidirectional laminate with 2d = 2.1 mm. * indicates gradient of Ln I_n against applied strain. All other values are for linear plots of I_n against applied strain.
Detector Light detected, position \( I_n \) (mV/mm)

<table>
<thead>
<tr>
<th>Detector position</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I_n ) (mV/mm)</td>
<td>417.0</td>
<td>55.5</td>
<td>1087.0</td>
<td>2187.0</td>
</tr>
</tbody>
</table>

Table 4.18(a). The amount of light recorded for four different angular positions of the detector measured over a strain range of 0.0 to 0.4%. Voltage readings have been normalised for inner 90° ply thickness.

<table>
<thead>
<tr>
<th>Detector position</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K )</td>
<td>23.6</td>
<td>23.4</td>
<td>20.1</td>
<td>23.0</td>
</tr>
</tbody>
</table>

Table 4.18(b). The values of \( K \) for four different angular positions of the detector.
Table 4.19. The light detected, $I_n$ after successive annealing treatments to a 0.5% BDMA cross-ply laminate with $2d = 0.5$ mm (Laminate 4).

<table>
<thead>
<tr>
<th>No. of annealing treatments</th>
<th>Strain range (%)</th>
<th>Light detected, $I_n$ (mV/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0 - 0.4</td>
<td>4324.0</td>
</tr>
<tr>
<td>2</td>
<td>0.0 - 0.55</td>
<td>706.0</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>441.0</td>
</tr>
<tr>
<td>Overnight</td>
<td></td>
<td>164.0</td>
</tr>
</tbody>
</table>

Table 4.20. Values of $K$ and $K'$ obtained from plots of $\ln I_n$ as a function of applied strain (%) after successive annealing treatments. $K'$ is the slope beyond 0.4% strain.

<table>
<thead>
<tr>
<th>No. of annealing treatments</th>
<th>$K$</th>
<th>$K'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30.0</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>31.0</td>
<td>13.0</td>
</tr>
<tr>
<td>3</td>
<td>30.0</td>
<td>10.0</td>
</tr>
<tr>
<td>overnight</td>
<td>23.6</td>
<td>10.6</td>
</tr>
</tbody>
</table>
The following discussion is divided into three main sections. In the first section the resin properties and the properties of the laminates made with the resins have been assessed. This was done in order to provide a better understanding of laminate properties and to ensure laminate quality. The properties and behaviour of the laminates had to be compared with those obtained by previous workers [1,2] and also checked for their consistency with resin properties. In the second section the phenomenon of stress-whitening is characterised and the factors controlling stress-whitening are discussed. The third section is concentrated on the quantification of stress-whitening using an off-axis LASER diffraction technique in which the intensity of the light diffracted by micro-cracks, which cause the whitening, was used as a measure of the damage. An additional section which discusses the effect of heat treatment on microdamage is also included.


5.1.1. Resin properties.

The results in section 4.1.1 show that as the level of accelerator in the epoxy resin system is increased, the Youngs modulus and yield stress of the resin decrease. This is accompanied by a definite increase in the glass transition temperature, Tg. The tensile fracture behaviour shows that the resins are flaw sensitive and when the surface flaws are partly removed the tensile fracture strain is increased. The Poisson's ratio appears to increases with increased accelerator but this increase is within experimental error and must be regarded as tentative.

The decrease in tensile modulus and yield stress (measured in compression) with increased cross-link density (as indicated by the higher glass transition temperature) appears surprising at first, since generally epoxy formulations are expected to show an increase in modulus with increased cross-linking. However, there is evidence in the literature suggesting that
this is not the case for all formulations. Yamini and Young [13] for example have found that in a resin system consisting of Epikote 828 (DGEBA resin) cured with different amounts of a triethylenetetramine (TETA), but the same cure schedule, both the modulus and yield stress (measured in compression) decreased with increasing amount of hardener. The modulus and yield stress also decreased when the post-cure temperature was increased. The glass transition temperature on the other hand showed an increase with increasing amounts of hardener.

Brown [81] has shown that for glassy polymers increases in modulus occur simultaneously with increases in the yield stress. The ratio of yield stress to Young's modulus (\(\sigma_y/E\)) is approximately constant for a variety of glassy polymers, generally equal to about 0.025 or falling in the range 0.033 to 0.0166. These ratios were determined by Brown using tensile yield stress and modulus data. Epoxy resins are bimodular materials as discussed in Chapter 2 and, thus, the \(\sigma_y/E\) ratio for the epoxy resins used in the experiments cannot be properly evaluated since the yield stress has been measured in compression while the modulus was measured in tension. Nevertheless, the ratio, using the compressive yield stress, is very close to the range quoted for the glassy polymers above, and all three epoxy resins in this study had values of 0.036 ± 0.002. To obtain a true value of the ratio either a compressive modulus is required or a tensile yield stress. It is difficult to obtain a tensile yield stress because the plastic deformation processes exhibited in compression are not evident in tension due to premature fracture. For plastics that yield in tension the ratio of the yield strength in compression to the yield strength in tension is approximately 1.3 [82]. If this ratio is applied to the epoxy resin and a predicted value of yield strength obtained, then the ratio of \(\sigma_y/E\) is found to be 0.028. This is within the range quoted for glassy polymers. Yamini et al [13] have shown that for their epoxy resin system, which bears many similarities to the resin used in the present work, the empirical rule of \(\sigma_y/E\) which governs the yield behaviour of glassy polymers was also obeyed although they also measured a compressive yield strength while the Young's modulus was measured in a three point bend test. They concluded that the yielding behaviour can be explained using the current molecular theories with good agreement at all temperatures up to the glass transition temperature and that the presence of cross-links did not fundamentally affect the yield behaviour of the polymer.

An explanation for the surprising fact that the Youngs modulus and yield stress of some epoxy resins actually decrease with increased cross-linking
has been advanced by Enns and Gillham [82]. Enns et al studied the effect of the extent of cure on the modulus, density, moisture absorption, and the glass transition temperature, \( T_g \), of a stoichiometric mixture of Epikote 828 resin and 4,4' diaminodiphenyl sulphone. The authors used a single cure temperature of 175°C but varied the cure time to obtain resins with different cross-link densities. They found that the room temperature density and modulus decreased with increasing cross-link density whilst the glass transition temperature increased. Further, higher equilibrium moisture contents and, higher absorptivity with increasing cure suggested an increasing free volume and hence, increasing specific volume.

Enns et al [82] explain this apparently anomalous behaviour with reference to schematic plots of specific volume versus temperature for a partially cured and fully cured resin, shown in simplified form in Figure 5.1. In the rubbery state above the temperature \( T_g \), the density of the more cross-linked material is higher but its \( T_g \) is also higher. As a result the specific volume versus temperature curves can cross. This would result in a lower density at room temperature for the more highly cured material. The room temperature modulus is lower since it is directly proportional to density. At room temperature the more highly cured resin is further from equilibrium and therefore, has more free volume than the resin with a lower degree of cure.

The modulus of the resin with the lowest accelerator level is non-linear beyond about 0.5% strain. Figure 5.2 shows the change in modulus of the 0.5% BDMA resin as a function of applied strain. By about 1.5% strain the modulus is reduced by 9% of its initial value. The effect of this decrease on laminate modulus is discussed in the next section.

In conclusion, it has been found that as the level of accelerator in the resin system is increased the tensile modulus of the resin and its yield strength in compression are decreased while the glass transition temperature increases, showing an increase in cross-link density. The resin containing the smallest amount of accelerator showed non-linear behaviour beyond a strain of about 0.5%.
5.1.2. Laminate properties.

(a) Secant modulus.

The measured secant moduli (at 0.2%) of all the laminates were compared with the predictions of the Halpin-Tsai equations combined with the classical laminated plate theory (see Table 4.8). In general, the results were in good agreement, to within 10%. The results were also compared, where possible, with those of other workers using the same glass fibre and matrix systems [3,8] and were found to agree well. Laminates 11 and 12 ((0,90)$_{s}$, 2d = 1.0 mm and 0.5 mm respectively, 3.0% BDMA) were the only exceptions where the calculated values were lower by 2 to 5 GPa compared to the experimental results. This could be attributed to the fact that only an average value of volume fraction of fibres is measured for the (0,90)$_{s}$ laminates and it is this value that is used in the calculation. It is possible that the 0°plies contained more glass fibre than the average value measured, which is in fact quite low (see Table 4.7(c)).

The moduli of the cross-ply laminates increase as the proportion of the 90°ply is decreased, in accordance with the "rule of mixtures" approach of the classical laminated plate theory. The moduli also show a decrease with increasing level of accelerator and the values can be predicted from the measured values of the matrix modulus. This provides some degree of confidence in using the laminates.

(b) Secant modulus as a function of strain.

An interesting aspect of the 90° unidirectional laminates and some cross-ply laminates was the reduction in modulus with increasing strain. Figure 5.3 compares the stress/strain trace of a 90° unidirectional specimen with that of a 0° specimen from the same laminate containing a 0.5% BDMA matrix. The 0° specimen has a modulus value which remains constant up to a strain of 0.4% above which a small increase is observed. This increase with strain may be attributed to the improved alignment of fibres towards the loading axis. The transverse properties of the laminate are matrix dominated and the value of the modulus is much lower than that of the 0° unidirectional laminate. The modulus is also observed to decrease with increasing applied strain. It is noted, however, that the decrease is gradual and a sudden reduction at a specific strain or a "knee" as reported by Parvizi et al [2] is not observed.
The decrease in modulus can occur from two possible sources; (i) the visco-elastic properties of the matrix and (ii) the development of microdamage or cracks normal to the loading axis.

(i) Stiffness reduction due to visco-elasticity of the resin.

The link between the flexibility of the resin and the appearance of non-linearity or visco-elasticity in the stress/strain curves of 90° unidirectional laminates with the same resins has been reported by Hull [B2] for three glass/polyester resin laminates. The plots of stress against strain for the polyester resins and the corresponding unidirectional laminae in transverse tension showed that the non-linearity observed in the resins prior to fracture also appeared in the laminae and was most obvious in the laminate with the most flexible resin. Similar behaviour was also observed when testing in shear mode. The strains at which the 90° unidirectional laminates fractured were an order of magnitude lower than the corresponding failure strains of the resin, although the laminate with the highest strain to failure contained the most ductile resin. It may be argued that the relatively low failure strains of the laminates reflect the strain magnification in the resin due to the presence of fibres, resulting in failure at lower applied strains. The magnification factor depends on the ratio of the fibre modulus to the resin modulus, the fibre spacing and other factors according to the Kies equation (eq.2.10).

The change in modulus as a function of strain for the epoxy resin with 0.5% BDMA is shown in Figure 5.2. The decrease appears to be continuous with increasing strain. Figure 4.6 shows the stress/strain curve of a 90° unidirectional laminate with a volume fraction of 58% glass. The modulus drop observed for the laminate from 0.2% strain to 0.35% strain is approximately 0.9 GPa. In order to estimate whether this reduction in laminate modulus can be accounted for by the drop in the modulus of the resin alone, the strain magnification in the resin has to be estimated. This can be done by assuming that the fibres are arranged in a square array. The strain magnification factor (SMF) is then given by eq.2.10,

\[ SMF = 2 + \frac{s}{r} / \left[ \frac{s}{r} + 2 \left( \frac{E_m}{E_f} \right) \right], \]

where \( r \) = radius of fibres, 6 microns (measured value) \( E_m \) = modulus of the resin, 3.8 GPa. (measured value) \( E_f \) = modulus of the fibres, 72 GPa. (from [B2]) and \( s \) = spacing between fibres, which can be determined from a
knowledge of the volume fraction of fibres and by assuming a square array according to eq.2.11

\[ s = 2r \left[ \left( \frac{\pi}{4V_f} \right)^{1/2} - 1 \right] , \]

where \( s \) and \( r \) have the same meaning as above.

With a volume fraction of 58%, the SMF for the 90° laminate is estimated to be about 8. Thus, for an applied strain of 0.35% on the laminate, the maximum strain in the resin is approximately 2.8%. The modulus of the resin at this strain can be obtained by extrapolation, from Figure 5.2 and is estimated to be about 3.2 GPa. Using this value of resin modulus, \( E_m \), in the Halpin-Tsai equation,

\[ E_t = E_m \left( 1 + \infty \beta V_f / (1 - \beta V_f) \right) \quad (5.1) \]

where \( \infty \) is a packing factor = 2.2, \( E_t \) is the laminate modulus, \( V_f \) is the volume fraction of fibres and \( \beta \) is given by,

\[ \beta = \left[ (E_f/E_m) - 1 \right] / \left[ (E_f/E_m) + \infty \right] \quad (5.2) \]

gives an estimate for the laminate modulus of about 13.6 GPa. This is a reduction of about 2 GPa, from an initial value of 15.5 GPa (laminate 1, 0.5% BDMA). This value is an over-estimate since the Kies strain magnification equation applies only to a very small volume of resin in between the fibres. The resin is expected to fracture before reaching this strain in several places and the packing arrangement is not actually a square array. The only purpose of this calculation is to illustrate that the reduction in laminate modulus may be accounted for by the reduction in the resin modulus.

An alternative argument can be employed to relate the reduction in modulus to the SMF and resin modulus. For example, simply using eqns.5.1 and 5.2; to obtain a drop in the laminate modulus of 0.9 GPa., at 0.35% strain, a drop of 0.28 GPa. is required in the resin modulus and at 0.35% strain this means that from Figure 5.2, the average SMF in the laminate is about 4. This is half the maximum SMF given by the Kies equation which gives the maximum SMF along a line AB (see Figure 2.2) and seems a reasonable value for an average SMF. The actual behaviour of the resin is difficult to predict because of the triaxial stress state, the non-ideal packing geometry and the fact that its fracture behaviour is dominated by the effect of flaws.
(ii) Stiffness reduction due to the presence of flaws.

The development of flaws during tensile testing has been observed in the laminates prior to transverse fracture and it is possible that these contribute to a stiffness reduction, particularly if the crack faces are normal to the tensile axis. In order to estimate the possible contribution to stiffness reduction an estimate of the flaw dimensions is required. It has been shown in section 4.2. that prior to transverse fracture or cracking, the micro-cracks occurred in short discrete lengths, parallel to the longitudinal axis of the fibres in the 90° ply (along the width of the specimen), see Figure 4.19. The short width probably being a function of fibre misalignment and the spacing between two fibres (see section 5.2.3). These cracks developed throughout the specimen, frequently initiating more numerously at the specimen edges (judging from the intensity of stress-whitening, see Figure 4.14) and near ply interfaces, but very quickly developing throughout the 90° ply. In Figure 4.19, it can be seen that there is a wide distribution of crack widths (w) in the direction parallel to the fibre axis. Edge-on views along the thickness of the 90° ply show that the micro-cracks are associated with closely spaced fibres and for the purpose of an approximate calculation of stiffness reduction, the crack lengths (2a) as seen from the edge are estimated to be of the order of a fibre diameter.

The stiffness reduction due to the presence of a distribution of cracks can be estimated using the following approximate argument according to Poursatip et al [83], and with reference to Figure 5.4,

The elastic strain energy in an uncracked volume, V, of a material with a Youngs modulus, $E_0$, held at a constant strain, $e$, is given by,

$$ U_1 = V E_0 e^2 /2 $$  \hspace{1cm} (5.3)

After the introduction of cracks, the energy is reduced to,

$$ U_2 = V E e^2 /2 $$  \hspace{1cm} (5.4)

assuming no change in strain and where $E$ is the modulus of the cracked material.
The energy difference, $U_1 - U_2$, is the energy lost which is roughly contained in a cylindrical volume, $\pi a^2 w$ per crack, since this volume is unloaded when the crack forms (see Figure 5.4). Thus, for $n$ cracks in a volume $V$,

$$U_1 - U_2 = n \pi a^2 w \cdot E_0 e^2 / 2 \quad (5.5)$$

Then, from equations 5.3 and 5.4,

$$V E_0 e^2 / 2 - V E e^2 / 2 = n \pi a^2 w E_0 e^2 / 2$$

and,

$$E/E_0 = 1 - (k/V), \quad (5.6)$$

where $k = n \pi a^2 w$.

If the crack size, $2a$, is taken to be 12 microns (the diameter of the glass fibre) and $w$, the width of the cracks is taken to be half the width of the specimen (i.e. 10 mm), then, for a modulus reduction of 0.8 GPa. (from 15.5 GPa. at 0.2% strain to 14.7 GPa at 0.35% strain, result for laminate 1), $k/V = 0.05$.

Consider a volume of laminate, 1 mm X 20 mm X 2 mm, with a volume fraction of 58% glass (laminate 1), and assume a square packing geometry, then the number of fibres in that volume is 10,368, from eqn. 2.11.

Now, if $k = 0.05$, and $a = 6$ microns and $w = 10$ mm, then $n = 1770$, where $n$ is the number of cracks.

Thus, in order to achieve a modulus reduction of 0.8 GPa., the number of cracks of dimension $a = 6$ microns and $w = 10$ mm is 1770 out of a possible 10,368 which is the number of fibres in the volume near which cracks can occur. Thus, 17% of the fibres must have cracks associated with them. This percentage increases if the width of the crack ($w$) is reduced. Assuming the worst condition where all fibres have cracks associated with them of depth 20 mm, the width of the specimen, the expected modulus drop is about 9 GPa. This gives an approximate lower bound of about 6 GPa. which is slightly higher than the modulus of the resin. The above approximate analysis assumes an isotropic solid.
A more rigorous analysis for an anisotropic solid by Gottesmann et al. [84] gives,

\[ \frac{E}{E_0} = 1 - CD, \]  

where \( D = \frac{n a^2 w}{V} \), and \( C \) is a constant given by,

\[ C = \pi \left( \frac{2 E_1^2}{E_t} \right)^{1/2} \left[ \frac{1}{(E_1 E_t)^{1/2}} + \frac{1}{2} G_1 \sqrt{\frac{\nu}{E_1}} \right]^{1/2} \]  

(5.8)

for cracks normal to the tensile axis but fibres parallel (0° unidirectional laminate where \( E_1 \) is the longitudinal modulus and \( E_t \) is the transverse modulus and \( \nu \) is the Poisson's ratio). For a 90° unidirectional laminate, \( E_1 \) is taken as \( E_t \) and the same applies to the other properties. This gives a value of \( C \), approximately equal to 13 when for a transverse ply,

\[ E_1 = 15.5 \text{ GPa}, \ E_t = 43.0 \text{ GPa}, \]

\[ G_1 = 3.0 \text{ GPa}, \ \nu = 0.1. \]

Using the above analysis with \( a = 6 \) microns and \( w = 10 \) mm, for a modulus drop of 0.8 GPa, 4% of the fibres are required to have cracks associated with them. For smaller widths of crack, the number of cracks is higher and increases by the same order of magnitude as the decrease in width. Thus, if the width is reduced from 10 mm to 1 mm, the number of cracks increase from 427 to 4270 to obtain the same reduction in modulus. It should be noted that as the number of cracks increase the analysis becomes less applicable since the cracks begin to interact and so it cannot be used to predict the modulus reduction at high densities of cracks.

It must be emphasised that it has not been possible to show conclusively that the micro-flaws are responsible for the observed reduction in modulus. The analysis is also not strictly valid for cracks that are smaller than a few fibre diameters since it is assumed in the analysis that the crack sees an effective homogeneous medium and the material at this scale cannot be considered to be homogeneous. A general solution to the problem of even a homogeneous elastic body containing a distribution of cracks is a difficult task. A solution can be approached analytically for the case of non-interacting cracks or numerically for a specific periodic crack geometry. Only upper and lower bounds can normally be obtained. The cracked material is then assumed to be a homogeneous orthotropic sheet which contains cracks.
and the orthotropic moduli are the effective composite moduli as in the argument used above. A similar form has been applied successfully to angle-ply laminates to account for the stiffness reduction arising from the accumulation of fatigue damage in the form of transverse ply cracks, by Poursatip et al [83]. It is not expected to work as well for the micro-cracks for the reasons discussed above.

The purpose of the two estimates of stiffness reduction through (i) visco-elasticity and (ii) development of micro-damage, is to show that either mechanism could account for the magnitude of stiffness reduction monitored for the 0.5% BDMA glass/epoxy laminates. From the experimental observations of cracks, the numbers of cracks estimated using the above approach are reasonable. The two mechanisms are, of course, not mutually exclusive and both probably operate in reality. The above approach can only be applied at very low strains and crack densities. Transverse ply cracking occurs long before all fibres are debonded or have cracks associated with them and thus, the stiffness reduction due to transverse ply cracking is the more dominant effect at higher strains.

The decrease in modulus might also be attributed to plastic deformation or yielding of the matrix. However, such deformation is permanent and not recoverable and might be expected to affect the stress/strain curve of the laminate on re-application of load. This is not observed in practice where on repeated loading and unloading, the secant modulus is affected very little by cycling. In addition the retained or residual strain observed on unloading the specimen is dependent on the time at load and appears recoverable. This is shown in Figure 5.5. in which a 90° unidirectional laminate was cycled seven times in succession. During the fifth cycle the specimen was held at load for about 45 mins. during which time the specimen relaxed. On immediate reloading the specimen did not show any hysteresis (sixth cycle). After 15 mins. at zero load, the specimen appeared to recover and during the seventh cycle some hysteresis reappeared. The specimen showed time-dependent effects due to its visco-elastic nature while the modulus remained unaffected after cycling. The results of this experiment suggest that the most likely cause of the reduction in transverse modulus is the visco-elastic nature of the resin.
The effect of inner 90° ply thickness of cross-ply laminates on the reduction in modulus.

The cross-ply laminates do not show the same reduction in modulus at a given strain, as the unidirectional laminate tested in transverse tension. (see Table 4.7(a)). This is not unexpected since the 90° ply now contributes less to the overall modulus because of the presence of the 0° plies. Based on the classical laminated plate theory, it can be shown that a reduction in modulus of the 90° ply in a cross-ply laminate by 0.8 GPa, would be expected to produce a reduction in the overall modulus of the cross-ply laminate \((b = 0.5 \text{ mm}, 2d = 2.0 \text{ mm})\) of about 0.5 GPa. The contribution of the 90° ply in laminates with thinner inner plies is even less and would be beyond the limit of detection by the experimental method used.

The effect of accelerator level.

The reduction in stiffness prior to transverse cracking is very small (< 0.3 GPa) for the laminates made with resin containing the higher levels of accelerator (1.5% BDMA and 3.0% BDMA). The higher glass transition temperature of these resins indicate higher cross-link densities compared to the 0.5% BDMA laminates. Visco-elasticity is, therefore, reduced and was not detected. The stress-whitening monitored in these laminates by LASER diffraction is also considerably lower (see sec.5.3). The modulus reduction is therefore, not expected to be very significant and this was found to be the case.

The effect of surface finish of glass fibres.

The 90° unidirectional laminates containing the glass fibres with the starch finish showed no reduction in modulus prior to transverse fracture in either the 0.5% or the 1.5% BDMA systems. However, the measured modulus of these laminates prior to testing was lower than the predicted value. This could be the result of debonds present in the laminate. The starch coating does not contain coupling agents nor is it compatible with the resin. Thus, a weak interfacial bond was expected and considerable debonding was observed at zero load. If it is assumed that these debonds affect the modulus in the same way as as fibre-associated cracks, described in section 5.1.2 (b), and that the width of the cracks is the full width of the specimen then the reduced modulus can be accounted for if 25% of the fibres have cracks associated with them. The poor bonding between fibre and resin does not
allow any strain magnification to develop in the resin since no stress transfer occurs. Visco-elastic effects are not apparent prior to fracture.

(c) Transverse ply cracking strains.

The strain at which the first transverse ply crack occurs in the 90° unidirectional laminate is, of course, the fracture strain of the laminate in this particular case. The fracture strains of the 90° unidirectional laminates (0.5% BDMA) were measured during the off-axis LASER diffraction tests and were found to vary from 0.35% to 0.5% strain. A large number of tests have to be carried out to determine a reasonable mean of the fracture strain since often the specimens fail at the grips or near the end tags and these values cannot then be included in the determination of average strains. The limited results available indicated an average fracture strain of about 0.4%.

The strain to first transverse ply crack for the cross-ply laminate (0.5% BDMA) with an inner ply thickness equivalent to the 90° unidirectional ply (2 mm) is expected to be about the same as for the 90° unidirectional laminate after correction for the thermal strains (provided the outer plies have no other effect on the failure strain) and this was found to be the case. The strain to the first transverse crack is relatively easy to determine since failure does not now occur near the end tags due to the protection afforded by the outer 0° plies. The transverse crack in this case is also instantaneous. In laminates with an inner ply 2d < 1 mm, however, the first transverse ply crack appeared at the edge of the specimen (i.e. spanning the thickness of the 90° ply and extending only a short way into the width) and then progressed slowly across the width. The transverse ply cracking strain, $\varepsilon_{tc}$ quoted in Table 4.10 represents the strain at which the crack first appeared on the edge. Continued loading resulted in a rapid increase in the number of transverse ply cracks. For the cross-ply laminate with 2d = 0.5 mm a dramatic increase in the strain at which the first transverse ply crack occurred was observed. Thus, in general, it was observed that $\varepsilon_{tc}$ increased as the thickness of the inner ply decreased with a dramatic increase at 2d = 0.5 mm. Below a transverse ply thickness of 2d = 1 mm, the first few cracks to appear were edge cracks spanning a short way into the width and progressed slowly along the width on continued loading.

The (0,90)$s$ laminates made from resin containing 1.5% and 3.0% BDMA also showed an increase in the transverse ply cracking strain as the thickness of
the inner 90° ply decreased. However, the increase did not appear as
dramatic as the one observed for the 0.5% laminates, before allowing for
thermal strains, over the ply thicknesses investigated.

The form of the increase in $\varepsilon_{tc}$ as a function of inner ply thickness for all
three groups of (0,90)$_5$ laminates is shown in Figure 5.6 (a) before allowing
for thermal strain and (b) after compensating for thermal strains. Figure
5.6 (b) shows that after allowing for the thermal strains, the increase in
$\varepsilon_{tc}$ appears similar for all three groups of laminates. Bader et al [70] have
investigated the variation in $\varepsilon_{tc}$ as a function of inner ply thickness for a
similar glass fibre/resin system (except that the fibre tex of the glass was
1200 instead of the 600 used in the present study). The resin matrix
contained 0.5% BDMA. Their results, after allowing for the thermal strains,
are shown in Figure 5.6(c) along with the results of the present study on the
0.5% BDMA laminates. The results are compared with the predicted values
obtained using the constraint theory of Bailey et al [85], eq.5.9, and the
stress intensity factor approach of Ogin and Smith [73], eq.5.10. The
predicted values for the laminates used in this study using the constraint
theory are similar to those of Bailey et al [85] as shown in Figure 5.7(c).
The predicted values using the approach of Ogin and Smith have been obtained
using a value of $G_c = 240 \text{ Jm}^{-2}$ as obtained by Bailey et al [85] and a value
of transverse modulus = 15.5 GPa, see Table 4.7(a)). All results are in
close agreement.

At ply thickness larger than $2d = 0.25$ mm, the experimental results of Bader
et al [70] show some scatter with values of $\varepsilon_{tc}$ around 0.6 to 0.8% strain
(including thermal strains). A dramatic increase was observed in their
results at $2d = 0.25$ mm from a strain of about 0.7 to 1.2%. At ply thickness
lower than $2d = 0.25$ mm, the laminate fractured before transverse cracking
could be observed. The present results show a small gradual increase in the
$\varepsilon_{tc}$ as $2d$ decreases from 2 mm and a large increase at $2d = 0.5$ mm, which is
the thickness at which the transition from "thick" to "thin" ply behaviour is
expected to occur, according to the model proposed by Ogin and Smith [73].
Hence, the results of this study agree more closely with the predictions of
Ogin and Smith. Allowing for the variation in laminate fabrication
techniques the general trends in results are consistent with those of Bailey
et al [85]. Both the constraint theory [85] and the stress intensity factor
approach [73] describe the experimental results reasonably well despite their
apparently different approaches. However, both theories make certain
simplifying assumptions and these are discussed below. More precise
analysis, especially the effect of thermal strains may provide even better agreement.

Bailey et al [85] use an energy balance argument and obtain an expression for the first transverse ply cracking strain, $e_{tc}$, given by,

$$e_{tc} = \left[2\phi_t \frac{b}{E_t} \frac{\phi}{(b+d) E_t} \right]^{1/2}, \quad (5.9)$$

where $\phi = \left( \frac{E_c G_t}{E_t E_t} \right) \frac{(b+d)}{(b d^2)}$

$\gamma_t$ is the fracture surface energy per unit area of inner ply, $E_c$, $E_t$, and $E_l$ are the laminate modulus, the transverse modulus and the longitudinal modulus, $G_t$ is the shear modulus of the transverse ply and $b$ and $d$ are the thickness of the longitudinal ply and half the thickness of the transverse ply respectively. The expression does not consider the direction of crack propagation in the transverse ply, i.e normal or parallel to the fibre axis.

Ogin and Smith [73] on the other hand derive a stress intensity factor, $K_c$ for an idealised crack which already spans the thickness of the $90^\circ$ ply (but not the width). The crack is then considered to be restrained by the $0^\circ$ plies so that over most of its length the load is transferred by shear into the zero degree plies. The local disturbance near the crack tip is assumed to span a distance $'d'$ where $2d$ is the ply thickness. Because the crack is restrained by the zero degree plies the stress intensity factor is assumed to be less than the conventional $\sigma(\pi d)^{1/2}$ and is taken to be $d(2d)^{1/2}$. They then relate this factor to the stress in the transverse ply in terms of the laminate modulus before cracking, the transverse ply modulus, $E_t$, and the strain energy release rate, $G_c$ (in a direction parallel to the fibres in the $90^\circ$ ply since the crack already spans the thickness) to obtain the strain at cracking,

$$e_{tc} = \left( \frac{G_c}{E_t} \frac{2d}{2} \right)^{1/2} \quad (5.10)$$

Both equation 5.9 and 5.10 apply when $2d$ is "small". Ogin and Smith employ the concept of a critical flaw size to determine the ply thickness at which the transition from thick to thin ply behaviour occurs. A critical flaw size is obtained by proposing that at a critical strain, $e_{crit}$ (the fracture strain of the $90^\circ$ unidirectional laminate), a flaw of 'critical' dimensions is formed by the growth of debonds. The dimensions being $2a_{crit}$, perpendicular to the fibres and $2t'$ parallel to the fibres (where $21'$
This is then an enclosed flaw in the centre of the ply. If the ply thickness $2d$ is large and the condition,

$$
\varepsilon_{\text{crit}} E_t \left( \pi a_{\text{crit}} \right)^{1/2} > K_C
$$

is satisfied, then fast fracture is proposed both across the thickness and width. There is an implicit assumption here that the flaw size in the direction parallel to the fibres is larger than in the direction normal to the fibres. The shape of the flaw chosen ensures that the flaw propagates in such a manner as to make itself 'square' so that propagation occurs simultaneously in both directions. Also once the flaw has formed, $G_C$ is assumed to be the same in a direction parallel and perpendicular to the fibres.

For a ply to be thin, the ply thickness is smaller than $2a_{\text{crit}}$ so that even after the flaw spans the thickness of the $90^\circ$ ply, $2d$, it is still stable. Fast fracture occurs when the laminate strain, $\varepsilon_a$, is increased such that the condition,

$$
\varepsilon_a E_t \left( 2d \right)^{1/2} > K_C
$$

is satisfied. The transition from thick to thin ply behaviour occurs at about $2d = \pi a_{\text{crit}}$. For the laminate system used by Bader et al [85] this was predicted to be 0.5 mm while the transition was actually observed at 0.25 mm. The results of the present study agree more closely with the predictions of Ogin and Smith [73]. Also the transition to high transverse ply cracking strains was observed at an inner ply thickness of 0.5 mm, as predicted by Ogin and Smith.

The treatment of Ogin and Smith considers fast fracture across the transverse ply. In laminates used in the present study, it was observed that the transverse ply cracks invariably initiated at the free edge and for ply thicknesses below 1 mm the crack appeared across the thickness and some way into the width before it was arrested. After continued loading it then progressed slowly along the width. There are a number of reasons for this behaviour. Firstly the tensile tests were carried out in displacement control (as opposed to load control) and the load drop due to the formation of the crack might act to slow the crack. Secondly, the misalignment of fibres in the $90^\circ$ ply create local regions of increased 'toughness' which would act to slow the crack. Indeed, slow transverse ply crack growth
enables the crack tip to bifurcate and, hence, the tip is observed to be splayed and branches ahead of the main crack, see Figure 4.19(d). The third reason is provided by Dvorak and Laws [74] who apply a similar treatment to transverse ply cracking, in terms of a critical flaw, as Ogin and Smith [73]. However, Dvorak et al consider two types of transverse ply cracks. The first is a type 'L' crack where crack propagation is in a direction parallel to the fibre axis which they show to control the strength of thin plies. The second is a type 'T' crack, perpendicular to the fibre direction which determines the strength of thick plies. Since $G(L)$ (strain energy release rate parallel to the fibres) does not depend on crack length (the load is shed into the 0° plies over most of the distance as proposed by Ogin and Smith) type L cracks may be arrested more easily due to a local reduction in applied stress or ply toughness, $G_c(L)$. In thin plies, therefore, where failure depends on type L cracking, cracks are easily arrested. In thicker plies which start to fail by type T cracks, $G(L)$ is still constant but would be much larger than $G_c(L)$ when a type L crack propagates along a wide front [74]. Detailed studies of the fracture surfaces may provide useful information regarding the direction of crack propagation.

Peters [86] has suggested that the presence of the outer 0° plies has a constraining effect on the flaws present in the 90° ply such that the ones in a zone nearest to the 0° plies are more difficult to propagate. The influence of the constraining zone becomes greater as the inner ply thickness decreases. The observations of micro-cracks in this study support this argument in that a large number of stable micro-cracks are seen to develop continually at points of magnified stress in laminates with thin inner plies, in preference to transverse fracture across the thickness. For laminates with a thicker inner 90° ply (2d = 2 mm), stable micro-cracks developed near the 0/90 ply interface (possibly due to high thermal stresses in this region) but fracture always appeared to occur from positions elsewhere in the ply. The strain at which fracture eventually occurs would, therefore, be much higher for the laminates with significant constraint zones. This represents the mechanical analogue of the constraint theory proposed by Bailey et al [85].

The mechanical analogue can be understood with reference to Figure 5.7. Where the two constraint zones of length 'c' on either side of the 0/90 ply interfaces meet in the middle of the 90° ply, represents the ply thickness, 2d, at which constraint becomes effective as shown in Figure 5.7(b). When 2d is greater than 2c, an unconstrained zone is still present (Figure 5.7(a)).
Where $2d = 2c$ is the transition from "thick" to "thin" ply behaviour and it is the point of minimum constraint since the constraining influence itself must have a profile where constraint is highest nearest to the $0^\circ$ plies. Figure 5.7 (c) shows the increasing constraint.

The critical flaw concept of Ogin and Smith [73] and Dvorak and Laws [74] allows the transition thickness $2d$ (equivalent to the length $2c$ of the constrained zones) to be determined. However, it must be pointed out that 'critical' flaws of the type of dimensions referred to by Ogin and Smith (of the order $0.15 \text{ mm}$, which is approximately 15 fibre diameters, have not been observed in these laminates. This supports the view put forward by Wang et al [87] that the idea of critical flaw sizes is a useful conceptual property of the material ply which enables a gross representation of the actual effects of inherent material flaws to be made. The flaws, of course, need not be inherent but as has been shown can develop prior to transverse fracture assisted by the Kies strain magnification in the ply. The distribution of flaws originate in local random differences in fibre packing and can be taken as the source of multiple ply failure.

The form of the increase in the strain to first transverse crack as a function of inner ply thickness for the 1.5% BDMA and 3.0% BDMA cross-ply laminates is shown in Figure 5.6(a) and (b). Before allowing for thermal restraint strains, (Figure 5.6(a)) no dramatic increase in the first transverse ply cracking strain is observed even at $2d = 0.5 \text{ mm}$. Figure 5.6(b) shows the first transverse ply cracking strains after the thermal strains have been added to the measured cracking strains. The resulting general increase in the cracking strain may be dominated by the thermal restraint strains which also increase with decreasing inner ply thickness. It is pointed out that the thermal restraint strains were calculated and in doing so, several assumptions were made. For example, it was assumed that the thermal expansion coefficient of the resin did not change significantly with increasing cure. For a more accurate analysis of the variation in cracking strains with inner ply thickness, the thermal restraint strains should be measured experimentally.
5.2. Observations of Damage.

5.2.1. Colour and whitening effects.

When a beam of light is passed through a material, its propagation is affected by the material. Firstly, its intensity is decreased as light penetrates into the material and secondly, its velocity in the material becomes slower compared to that in air. The loss in intensity is due to absorption. Under certain conditions, scattering plays an important role. General absorption is shown by a material if it reduces the intensity of all wavelengths of light equally. For white light this means that the transmitted light, as seen by the eye, is of no particular colour but reduced in intensity so that the material appears grey. More often, however, selective absorption of wavelength occurs. Thus, a piece of green glass absorbs the red and blue ends of the visible spectrum preferentially and only the green part of the spectrum is seen in the transmitted light and the glass is said to have a green body colour. Surface colour, on the other hand, arises because certain materials, such as gold, have a higher reflecting power for some wavelengths than for others and, therefore, show colour by reflected light while any transmitted light will have the complementary colour.

The basic processes of the scattering of light by a cloud of fine suspended particles can involve reflection and diffraction [B6]. If the particle (or reflector or slit) is small compared to the wavelength of an incident plane wave (see Figure 5.8(a)) the reflected secondary waves are uniform spherical waves and the incident beam is said to be scattered, since the laws of reflection are not applicable. The secondary waves are produced by the induced vibrations of the electric charges in the surface of the particle or slit. If the particle is larger than the incident wavelength, then the secondary spherical wavelets cooperate to produce short segments of plane wavefronts, which are spread out owing to diffraction (see Figure 5.8(b)).

The first quantitative study of the laws of scattering by small particles was made in 1871 by Lord Rayleigh [88]. The scattered intensity was found to be proportional to the incident intensity, the square of the volume of the particle and to the inverse fourth power of the wavelength. The latter implies that for a given size of particle, short wavelengths will be scattered more effectively than long wavelengths. Thus, since red light has a wavelength 1.8 times larger than blue the law predicts ten times greater
scattering for the blue from particles smaller than the wavelength of either colour. If white light is passed through a cloud of sufficiently small particles, the cloud takes on a colour which depends on the size of the particles. With the smallest particles the colour will be blue while with increasing size the light scattered will contain longer and longer wavelengths until finally it becomes white as a result of ordinary diffuse reflections from the surface of the particles. At the same time, the light of the direct beam transmitted through the cloud will appear more and more red until it cannot be seen at all [B7].

The colour effects observed in the laminates may be understood using the following argument. At zero applied load, the specimen when placed flat on a piece of white paper appears yellow, a colour imparted to it by the resin. Under oblique illumination conditions it appears blue due to scattering from small centres in the laminate, where small can be taken as an order of magnitude smaller than 400 nm, the wavelength of blue light. As the strain is applied to the specimen, more scattering occurs due to the development of new scattering centres which may, or may not, be similar to those present at zero load. As more scattering centres, such as cracks, develop and their size increases (but is still smaller than the wavelength of blue or red light) more blue light is scattered away from the main beam compared to the red light which has a longer wavelength so is scattered less. The laminate, therefore, begins to show a magenta colour followed by red as the blue light is scattered away in all directions. As the size of the scattering centres increases with further straining, they become too large for scattering to occur and the specimen then begins to appear white due to ordinary reflections from the surface of the scattering centres. Diffraction effects may also occur but are not easily observed under the conditions of this experiment.

Rayleigh's theory applies to particles that are an order of magnitude smaller than the wavelength of the light. Mie's theory [B7] which is more generalised takes into account the size, shape, dielectric constant and absorptivity of the particle. For Mie scattering the \( \lambda^{-4} \) relationship no longer applies. With increasing particle size the scattered intensity becomes less dependent on wavelength until for sufficiently large particles there is no dependence at all. (Also, the relationship is not a monotonic one). With larger particles or objects the result of the interaction with light is more appropriately described by diffraction. This is discussed further in section 5.3.
The upper limit for particle radius, 'a', for which the Rayleigh equation is presumed valid is set at $a/\lambda = 0.05$, where $\lambda$ is the wavelength of the light. This implies that the colour effects are caused by very small entities or gaps between 20 and 40 nm, which in polymeric systems is of the same order as the molecular size. Thus, it would appear that the onset of whitening can be associated with defects much smaller than can be easily resolved using the optical microscope. That such small gaps can exist in composites was demonstrated by Sargent and Ashbee [77] who reported the presence of small interfacial gaps of the order of 5 nm, between a glass fibre and epoxy matrix. These were measured by studying the effects of light transmitted transverse to the fibre axis, for varying gap sizes where the gaps between the fibre and matrix were filled with either air or water. Characteristic patterns of light and dark bands parallel to the fibre axis were observed when viewing damaged specimens in transmitted light. Individual fibres showed regions of interfacial contrast. Sargent and Ashbee [77] demonstrated that this contrast was a result of the creation of small interfacial gaps between fibre and matrix. The gap width was estimated by comparing calculated and measured intensity distributions of the transmitted light.

It is interesting to note that the red colouration is not observed to any great extent in the laminates containing 0.5% BDMA resin (see Figure 4.11 - 4.14). In situ microscopy showed that the micro-cracks which developed in the above laminates were generally larger than those observed in the laminates made with resin containing 1.5% BDMA or 3.0% BDMA where the red colouration was observed. The lack of a red colouration in the 0.5% BDMA laminates suggests that there was no significant transition stage in which small cracks existed and micro-cracks appear to have "popped" open to a certain size large enough (at least larger than 40 nm) to have simply caused whitening. This also explains why micro-cracks were much easier to detect in the 0.5% BDMA system. On the other hand, whitening was barely detected in laminates made with resin containing 3.0% BDMA although a red colouration was observed. Micro-cracks were hardly visible in these laminates implying that the reddening is associated with smaller crack sizes which could not be resolved easily by photomicroscopy. On annealing a 3.0% BDMA specimen after testing, the residual red colour could be removed, see Figure 4.18(g) and (h)). This implied some rearrangement of structure, possibly closure of the very small gaps.

The colours have been shown to be reversible with load. The return to the blue colour upon stress relief in a short region on either side of a
transverse crack has been shown in section 4.2 to be associated with the closure of small micro-cracks in this region, see Figure 4.19(d) and Figure 4.25(c). The region on either side of the crack corresponds to the ineffective length or the stress transfer length suggested by Hahn and Tsai [69], over which the transverse ply carries no load. Hence the bands remain blue on reloading. (note: since the whitening and colour changes were apparently reversible on removal of load, particularly in the 90° ply it is unlikely that any crazing had occurred because any craze fibrils formed would hinder closure of the crack).

It is recognised that the micro-cracks have a distribution of sizes. This was observed during microscopy and is also expected since there is a distribution of spacings between fibres and, therefore, in the strain magnification factors. Thus, the 'size' referred to in the above discussion is the predominant crack size.

5.2.2. Polished edge microscopy showing healing of cracks.

The reversibility of whitening with annealing at 100°C in a laminate containing 0.5% BDM A resin was shown in Figure 4.13(e) and (f) and shown clearly to be associated with the disappearance of micro-cracks in the resin in Figure 4.23(b) and (c). Crack closure and healing of micro-cracks simply on removal of load has been known to occur in other systems. Obreimoff [89] carried out an experiment on the cleavage of mica in which a glass wedge was inserted beneath a thin flake of mica attached to a parent block, and was used to drive a crack along the cleavage plane. Obreimoff observed that when performing the cleavage test in vacuum, partial withdrawal of the glass wedge caused the crack to retreat and heal. On reinsertion of the wedge a fraction of the cleavage strength was still retained. Interestingly, Griffith's condition for crack equilibrium implies complete reversibility of crack growth. Ideally, relaxing a load system to recover strain and surface energies should ensure closure and healing of a contracting crack. In practice, however, irreversible processes accompany fracture and these act to oppose interfacial bonding. The new surface may also be exposed to an environment and become contaminated.

For small micro-cracks, in which the separating walls do not fully disengage during the loading stage, the surface structure may aid reversibility by "guiding" the crack interface back to it's original configuration. Lateral constraining effects also aid in allowing the crack surfaces to achieve
better contact as would compressive thermal microstresses. Crack closure and healing can be induced, in particular at high temperatures, where the tendency for matter to diffuse to the crack tip interface from the surrounding region of high residual stress may be an important mechanism. The fact that the micro-cracks which healed in the resin did not reappear in the same position at the same applied strain as before annealing, see Figure 4.23(b) and (e), is evidence that a strong bond is formed. This can occur either by chemical reaction across the crack interface since the resin is a partially reacted non-equilibrium system or by some form of inter-penetration or diffusion between the two surfaces or a combination of these two processes. It has been reported by Wool [27] that "healing" has been observed in epoxy resin systems. However, no experimental evidence was presented.

While the whitening effect was almost fully reversible with load in the 90° unidirectional laminates (see Figure 4.20(c)), in the (0,90)s laminates the amount of residual whitening (i.e. the amount of whitening retained at zero load) was found to be only partially reversible. The 0.5% BDMA specimen with an inner 90° ply thickness of 0.5 mm, showed the largest amount of residual whitening, compare Figure 4.19(c) with 4.20(c). This residual whitening may be associated with the thermal restraining effect of the 0° plies, which are responsible for putting the transverse ply under tension even at zero applied load due to the differences in the thermal expansion coefficients of the 0° plies and the 90° plies as discussed in chapter 2. The (0,90)s laminate with the thinnest inner ply experiences the highest thermal restraint. This restraining effect may not allow the micro-cracks to close up even after removal of the load. They do, however, disappear after annealing at 100 °C and do not reappear after cooling to room temperature. This suggests that a strong bond is formed across the crack interfaces. The reversibility of stress-whitening is discussed further in section 5.4.

5.2.3 In situ microscopy.

In situ observations of the edge of the specimen at zero applied strain, in transmitted light, showed that some damage was already present in the laminates, particularly in (0,90)s specimens. The damage was mostly in the form of fibre splits. These were usually found when a group of fibres in contact was bounded on one side by a resin rich region. The fibre splitting is believed to be caused by the presence of residual thermal strains in the laminate. Asamoah and Wood [58] have used a finite element analysis to
calculate the distribution of thermal stresses for closely spaced fibres in a resin matrix. Based on this analysis they have postulated that where the fibres are brittle and the fibre/resin bond is strong, fibre cracks may be expected to occur, the likely failure planes forming arcs between compressively loaded contact lines between fibres. Since most fibre splits were found in $(0,90)_S$ laminates, particularly in the region nearer the $0/90$ ply interfaces, it suggests that the thermal ply restraint strains provide additional stresses which lead to fibre splitting in these laminates.

The majority of damage that developed during loading of the laminates below the transverse ply cracking strain was in the form of micro-cracks which initiated predominantly in regions where the fibres were very close together. This is in accordance with the theory of Kies [60] which predicts that in the presence of an externally applied load the strain in the resin is magnified and is a maximum when the fibres are nearly in contact. McGarry [55] has noted that the distribution of fibre spacings in a composite is often such that the most dominant spacing is zero (fibres in contact) or close to it. Hence, the majority of the damage is concentrated in these regions.

It was also observed that the fibre cross-sections became brighter or more prominent as the strain on the specimen was increased and as micro-cracks developed, Figure 4.25(b). When a transverse crack was formed the micro-cracks closed up and at the same instant the fibres in the vicinity of the crack were observed to lose their prominence. A certain amount of spatial distortion is also observed showing the relaxation of the matrix when a transverse crack is formed. The fibre prominence suggests that as the specimen is strained the light transmission capability of the fibres is improved. Before any cracking the light is diffused away through the resin because of the close contact and match in the refractive index of the resin and fibre. When the cracks develop at or very close to the interface the crack itself appears dark because the light in the gap is lost through multiple reflection and does not reach the upper surface of the specimen. The fibre, however, is able to transmit more light by a process of internal reflection brought about by the change in refractive index of the new medium (air) now present nearest to it.

Examination of the micro-cracks shows the effect of the degree of cure of the resin matrix on the extent of damage. The micro-cracks in the high cure laminates appeared to be at a much earlier stage of formation resulting in a smaller cracked area at the same applied strain. This is also evident in the
photometric traces of light detected as a function of strain, where the higher cure laminates show a much lower intensity of detected light compared to the laminate with a lower cure (0.5% BDMA) matrix, at a given strain. This indicates a smaller amount of damage. The photometric traces are discussed in more detail in section 5.3. In the high cure laminates the smaller size of cracks results in the laminate showing only reddening before transverse ply failure and no whitening while in the laminates with a matrix with a lower degree of cure only whitening was observed and no reddening. It is postulated that the colour effects result from scattering phenomena akin to Rayleigh and Mie scattering from small particles. Thus, the reddening occurs when the cracks in the resin are small relative to the wavelength of light while the whitening is the result of ordinary diffuse reflections and occurs when the gaps are large relative to the wavelength of light. This scattering phenomenon is discussed further in section 5.2.1.

The smaller size of cracks in the higher cure laminates may be a result of the smaller amount of stored elastic energy at failure since it is known that the elastic moduli of the resins decrease with increasing cure. As a result the energy available for crack growth is smaller. Gledhill et al [17] have found that for a variety of epoxy resins, if the yield stress was high then the crack propagation was continuous while if the yield stress was lowered then propagation became stick-slip in nature caused by blunting of the crack, which may explain the smaller size of micro-crack. The cracks in the higher cure resins, which have a lower yield stress, are halted or blunted more easily and hence, would be smaller.

The behaviour may also be related to the 'inherent' or natural flaw size of the matrix material. The size of the inherent flaw can be determined from the fracture strength of an unnotched specimen, its modulus and its fracture surface energy. The natural flaw size for polystyrene, for example, has been calculated to be about 1 mm while that for poly(methyl methacrylate) is about 0.07 mm. Flaws of this size do not exist in the material but can develop during deformation. In the case of polystyrene deformed in tension large crazes of the order of 1 mm are seen while for poly(methylmethacrylate) the crazes observed are much smaller [B5]. In the absence of a larger artificial flaw, the breakdown of one of the crazes leads eventually to failure of the specimen. The inherent flaw size argument may be applicable to the epoxy resin laminates although there is no firm evidence of crazing in epoxy resins and only localised micro-cracking has been observed instead. If this argument is correct then the smaller size of the micro-cracks in the high
cure laminates suggests (according to the Griffith equation) that the fracture surface energy is reduced with increasing accelerator level. The measurement of fracture surfaces energies and its relation to micro-cracking and transverse ply cracking is recommended for further work.


The primary objective of these tests was to obtain a reliable and reproducible measure of the degree of low strain damage in (0,90)\textsubscript{5} cross-ply laminates so that comparisons between the behaviour of different laminates could be made. Microscopic examination of the laminates has shown a range of crack sizes, spacings and distributions and suggests that any diffraction pattern obtained from dynamic testing is likely to be extremely complex. A complete description of the number and size of cracks was not attempted. The tests were carried out to differentiate between laminates. The majority of measurements were made with the photodetector at a fixed angle and distance from the specimen.

5.3.1. Diffraction patterns.

Diffraction effects occur when part of a wave front is removed by an obstacle in an otherwise infinite wavefront or when all but a small part of a wavefront is removed by an aperture. The effects of diffraction become more obvious when the dimensions of the opening or obstacle approach the wavelength of the radiation. Thus, most diffraction effects are best observed with diffracting sources of the order of the wavelength of the radiation. Each point on a larger source produces its own diffraction pattern and when these patterns overlap only general illumination can be seen.

Diffraction problems are regarded as some of the most difficult in optical physics and there are very few examples of rigorous solutions in diffraction theory [18]. Those that exist are mainly 2 dimensional solutions and approximate methods have to be used in most cases for the sake of mathematical simplicity. Of these the theory Huygens and Fresnel are the most powerful and are considered adequate for the solution of most problems involving diffraction. According to Huygens construction every point on a wavefront may be considered as a source of secondary waves which give rise
to spherical wavefronts. The wavefront at any later stage is regarded as the envelope of these wavelets. Fresnel added the postulate that the secondary wavelets mutually interfere to account for diffraction effects. The combination of these two ideas leads to the Huygens-Fresnal principle. Kirchhoff showed that the principle may be regarded mathematically as an approximate form of a certain integral theorem. The same basic concepts are embodied but the laws governing the contributions from different elements of the surface are more complicated.

Diffraction patterns are generally classified into either Fraunhofer or Fresnel patterns. Fraunhofer patterns are formed when, in the absence of lenses, the source and receiving screen are infinitely distant from the diffracting screen. This is mathematically the simpler case and fortunately represents the most common encountered in practice. Fresnel patterns occur when the source and screen are at finite distances from the diffracting screen relative to the wavelength of light. According to Born and Wolf [B8]

\[
|r'| \gg (x'' + y'')\text{max} / \lambda \quad \text{and} \quad |s'| \gg (x'' + y'')\text{max} / \lambda
\]  

(5.13)

where \( r' \) is the distance from the source to the diffracting aperture and \( s' \) is the distance from the aperture to the screen, \( x'' \) and \( y'' \) are co-ordinates of a point in the aperture, and \( \lambda \) is the wavelength.

The conditions employed for obtaining the diffraction patterns in this study, see Figure 3.19, were those likely to lead to Fraunhofer diffraction.

The diffraction pattern from an infinitely long vertical slit is rotated by 90° relative to the orientation of the slit with the LASER beam and consists of series of fringes. If the slit is horizontal the diffraction pattern is vertical since it is the width of the slit that is the important dimension. If the slit is rotated, the diffraction pattern is rotated by the same amount. A diffraction pattern extending in both the horizontal and vertical directions is a result of the height and width of a slit being of comparable size. In fact, the size of the diffracting object is inversely related to the spread of the diffraction pattern. For a wide slit the diffraction fringes are closer together. It is important to note that according to diffraction theory the aperture may be replaced by a complementary obstacle with the same results. This is known as Babinet's principle [B8]. Watkins [90] has shown that where the obstacle is transparent, such as a glass fibre,
the resulting pattern can be considered as a composite of a diffraction pattern and an interference pattern. The interference pattern is produced by the interaction of the rays refracted through the fibre and that reflected off its surface. Here, the term interference is used to describe the effect when two or more beams of light, separately derived from the same source, are brought together to produce fringes while diffraction is used when the effect is a result of interference of light derived from a continuous portion of a wavefront.

The pattern produced by a single glass fibre, held vertically and illuminated by a LASER beam perpendicular to the fibre axis shows a series of horizontal fringes. The number and separation of these fringes, over a specified range of angles, can be used to determine the diameter of the fibre [90,91]. Watkins [90] has measured the pattern experimentally and shown that the result can be predicted, using a simplified geometric ray-tracing technique in conjunction with wave theory, over an angular range of 5 - 90 degrees. In this range the pattern is a result of the interference between the rays refracted through the fibre and the rays reflected off the surface of the fibre and depends on the size of the fibre, its refractive index and the wavelength of light used. Below an angle of about 5° the pattern could not be easily resolved since it was modified by diffracted light not intercepted by the fibre. The diffracted light is dependent only on the outside diameter of the fibre. It is worth noting that the fibre diameters investigated by Watkins were in the range of 50 to 150 microns and that for smaller diameter fibres, such as the ones used in this study, the diffracted light pattern is likely to extend to angles much larger than 5°.

A bundle of glass fibres, held vertically, produces a bright horizontal band as shown in Figure 5.9(a). Some fibres which were not exactly vertical show the individual fibre patterns rotated at a small angle to the main beam. The pattern produced by an array of fibres depends on the regularity of the array. If the array is regular then the pattern obtained depends on the spacing between fibres and increasing the spacing between fibres by a factor of 'n' decreases the spacing of the fringes in the pattern by a factor of 'n' [B9]. The majority of the fringes found in the pattern of the single fibre cannot be observed since there is both a distribution of spacings and sizes and the resulting fringe patterns overlap each other. This is further complicated by the fact that the bundle has finite thickness. Hence, a very diffuse pattern is expected. Similar arguments apply to the case where fibre bundles are embedded in resin to form a unidirectional coupon. A pattern
similar to that produced by the individual bundles is observed. The pattern produced by a 0° unidirectional coupon with the LASER at 90° to the coupon is shown in Figure 5.9(b). That of a 90° unidirectional laminate is the same but is rotated by 90° (i.e. the pattern is vertical).

The pattern produced by a cross-ply laminate is a result of the interaction of the patterns produced by the individual longitudinal and transverse plies and cannot be obtained by simply overlaying the individual patterns obtained from each ply. The pattern obtained during the loading of such cross-ply laminates will be affected by changes in the arrangement of the fibres and the development of any defects of the appropriate dimensions capable of diffracting light. The previous experiments have shown the formation and growth of small cracks in the transverse ply at strains of about 0.2%. Such cracks were observed to have dimensions in the range 1 to 10 microns and so in principle must be capable of diffracting light. At such low applied strains, any changes in the spacing and arrangement of fibres in the individual plies are expected to be small and unlikely to produce any significant changes in the observed pattern.

A (0,90)₅ cross-ply coupon with a relatively thick inner 90° ply (2d = 2 mm, \(b = 0.65\) mm) shows a very diffuse, almost circular shaped pattern projecting a small distance around the central spot, Figure 5.9(c), LASER oriented at 90° to the specimen. A laminate with a thinner inner ply (2d = 1 mm, \(b = 0.7\) mm) shows that the pattern has a more angular shape, Figure 5.9(d). The diffraction pattern from a cross-ply laminate, with 2d = 0.5 mm, \(b = 0.8\) mm), obtained prior to loading, is shown in Figure 5.9(e) with the LASER beam still at 90° to the specimen. The pattern shows the relatively dominant effect of the 0° fibres in the horizontal direction since the proportion of these is larger. Closer examination reveals a set of fringes spread in the vertical direction. Figure 5.9(f) shows the pattern with the LASER at 45° to the specimen (see Figure 3.19(b)). The central portion of the pattern is bent into an arc. Here, the fringes are observed more clearly confirming that the fringes are present at zero load.

On loading, the development of micro-damage in the 90° ply of a cross-ply laminate will result in changes in the diffraction pattern. The diffraction pattern shows little change until a strain of 0.2% is reached at which point micro-cracks begin to develop. Above this strain, a vertical band is observed which appears to increase in length and intensity. Figure 5.9(g) shows the diffraction pattern produced by a laminate with \(b = 0.8\) mm and 2d =
0.5 mm, at a strain of about 0.5%. The LASER was oriented at 90° to the specimen. A broad vertical band of light, symmetric around the centre is observed and confirms earlier observations that the micro-cracks lie parallel to the fibre axis in the 90° ply, giving rise to the diffraction in the vertical direction. The width or opening of these cracks governs the spread of the diffraction pattern. Superimposed on the vertical band are the fringes observed earlier at zero load. Their mean spacing did not change significantly, under load and was about 0.5 mm with the LASER at 90° to the specimen and about 0.8 mm with the LASER at 45° to the specimen.

With the LASER beam oriented at 45° to the specimen, the diffraction pattern shown in Figure 5.9(h) is observed at a strain of 0.5%. With this orientation the pattern appears to be asymmetric, with a fore-shortening at one end and lengthening at the other. These are the effects of the rotation of the LASER with respect to the specimen in the vertical plane. The apparently longer length of the vertical band compared to the pattern obtained with the LASER at 90° to the specimen may be understood to be the result of a decrease in the apparent spacing between the diffracting objects when the LASER is rotated by 45°. The decrease in the apparent spacing between the diffracting objects or apertures results in the pattern being more spread out or longer. The difference in the spacing of the fringes in the patterns observed earlier at zero load, with the LASER at 90° and at 45° can be accounted for by a decrease in the apparent spacing between diffracting objects as the LASER is rotated. This suggests that the diffracting objects are not glass fibres since their diameters are expected to remain constant and will not appear to change when the LASER is rotated. It is possible for such fringes to be produced by defects or voids in the longitudinal ply. The atlas of optical transforms [92] shows a similar pattern of horizontal fringes produced by randomly sited longitudinal voids in fibres where the void widths and lengths had a Gaussian distribution. However, the apparent spacing or size of the longitudinal defects is not expected to change with the rotation of the LASER in the vertical plane. It is also not likely that the fringes are caused by the development of micro-cracks in the 90° ply since the fringes were apparent at zero load. It is important to note that the fringes are only observed close to the central image and do not effect the pattern at high angles produced by the development of micro-cracks in the 90° ply. The fringes may be a function of the spacing between fibres. Further work is required to establish this.
Since the angle through which light is diffracted from a crack increases with decreasing crack size, much of the diffraction information produced by large cracks is projected into a small region that is already saturated by the forward beam. In contrast, small cracks are capable of diffracting over large angles. This implies that simply increasing the number of small cracks will result in the appearance of light at high angles and might be expected to produce an apparent lengthening of the observed diffraction pattern. However, it must be remembered that if the small cracks start to grow then the light diffracted by these will be redistributed over smaller angles and will be more intense. It may be this light that also contributes to the apparent lengthening of the beam if the intensity at higher angles is still below that which can be detected. The length of the pattern can, therefore, also be increased by the growth of small cracks, into larger cracks. Thus, at any arbitrary position within the diffraction pattern, it is not usually possible to distinguish between an increase in intensity due to crack growth and that due to crack formation.

Figure 5.9(i) shows the diffraction pattern of the specimen on unloading. Comparison of Figure 5.9(i) with 5.9(e) shows the effect of residual damage present in the laminate at zero load. The length and intensity of the vertical band is reduced as small cracks close up. Some large cracks still remain open due to the presence of the tensile thermal stress in the 90° ply as was shown in section 5.2. Hence, some "residual" diffracted light is still observed at angles nearer to the central spot.

The length of the pattern is related to the size distribution of the openings since the smaller the openings the more spread out the pattern will be. For a random distribution of equi-sized slits or particles the intensities from each are additive [B8]. This implies that the length and intensity of the vertical diffraction band is related to the size and number of cracks. In a system where the diffracting objects are of varying sizes, each group of objects of the same size produces a pattern of its own. These patterns overlap and the result is a diffuse blur. The breadth of the vertical diffraction band shown in Figure 5.9(g) is the result of some mis-orientation of the cracks, i.e. the cracks are not always exactly at 90° to the loading axis. Also, the cracks in the 90° ply are distributed through the thickness and so some volume effect in the diffraction band is to be expected. The absence of a diffraction effect in the horizontal direction similar to that found in the vertical direction is probably a result of the length of the crack parallel to the fibres being much larger than the opening of the crack.
i.e. the cracks approximate to infinitely long slits. This is borne out by the observations discussed in section 5.2.

Although the diffraction patterns are complex and must contain a lot of information, they generally confirmed the observations of micro-damage made in section 5.2. For example, the 0.5% BDMA cross-ply laminate with an inner ply thickness of 0.5 mm showed a long, intense vertical band of light, confirming a high degree of damage, while the cross-ply laminate with an inner ply thickness of 2 mm at similar strains produced a much shorter and less intense region of light closer to the central spot. This is shown in Figure 5.9(j) and should be compared with Figure 5.9(g). It was shown in section 5.2 that the cross-ply laminate with an inner ply thickness of 2 mm contained substantially less damage which was mainly concentrated at the 0/90 ply interfaces. Hence, to a first approximation and applying the result that the intensity at any point in the diffraction pattern produced by an irregular array of apertures is \( N \) times the intensity produced by a single aperture at that point [B8], it may be assumed that the amount of damage in a laminate per millimetre of inner ply thickness is proportional to the intensity at any point on the diffraction pattern produced by that laminate. The intensity of diffracted light at a fixed angle was, therefore, monitored with the LASER also at a fixed angle. The level of damage in different laminates could then be compared by comparing the intensities at a given angle.

It was noticed that the projected patterns appeared grainy or speckled. This may be attributed to what is known as the 'speckle' effect and is the result of the LASER light being reflected from a diffuse surface which produces bright speckles where random fluctuations cause constructive interference [B6].

Diffraction patterns similar to the ones obtained in this study have been reported by Cers et al [93] who used a LASER diffraction technique to study horizontal craze cracks in polystyrene. In their work a Ne-He LASER was used to obtain normal transmission diffraction patterns which were projected on a screen and recorded photographically. Comparisons of the patterns with specimens of crazed and uncrazed specimens revealed that when no crazes were present only a circular spot was observed. When perfect parallel crazes (horizontal cracks at 90° to the loading axis) were introduced on the surface of the specimen a sharp vertical diffracted line was observed. Relatively diffused scattering in the vertical direction or broadening of the vertical
line was obtained as the degree of irregularity of the crazes increased. The
diffraction pattern also appeared to register the volume effect regarding the
distribution of crazes (i.e. crazes on front surface, internal to the
specimen and back surfaces ) through broadening of the vertical line. This
led Cers et al [93] to conclude that the diffraction patterns provided
information concerning the distribution of crazes within the specimen.
Unfortunately no work of a quantitative nature is reported.

5.3.2. Quantitative measurement of stress-whitening.

Maxwell and Rahm [94] developed a device, which in principle was very similar
to the one used in the present study. This was used to monitor the
initiation and rate of crazing in polystyrene during creep. A constant
amount of light was beamed at a specimen at an oblique angle of 15° (position
A). When there were no crazes, the light simply travelled in a straight
line. However, rays falling on crazes in the specimen were reflected to a
laterally symmetric position on the other side of the specimen (position B).
The parallelism of the cracks was shown by using a point source of light at
position A, and a well crazed specimen. An image of the source was obtained
at position B. The intensity of the light at B was taken to be a function of
the total cracked area (or the number of cracks times the area of the
individual cracks). They obtained curves of light intensity as a function of
creep time. A simple reflection argument was used to explain the scattered
light. In the case of either reflection or diffraction, the intensity of the
light at a given angle of incidence and diffraction/reflection is
proportional to the amount of damage created.

Figure 3.20 shows a typical trace of the detector output, I, monitored in
position 1 as a function of strain. The detector output is directly
proportional to the intensity of light falling on the sensitive area of the
detector. All the plots obtained were typified by a flat portion over a
short initial strain range during which no light was detected. This was then
followed, usually at about 0.2% strain, by an approximately exponential
increase in the amount of light detected. The rate, K, of this increase was
determined from a plot of Ln I_n against applied strain for each group of
laminates. The normalised light detected, I_n, at any given strain was also
recorded. This gave an indication of the damage intercepting the beam.
(a) Effect of accelerator level and inner ply thickness.

For the (0,90)\textsubscript{s} cross-ply laminates made with resin containing 0.5\% BDMA the strain at which micro-cracks first developed or the strain at which a significant amount of light was first detected did not appear to be affected by the thickness of the inner 90° ply and was found to be about 0.2\%. The micro-cracking strain for the 90° unidirectional laminate was slightly higher and was about 0.275\%. The level of residual thermal stresses present in the (0,90)\textsubscript{s} laminates, therefore, acts to reduce the micro-cracking strain. The rate of development of damage is highest for the 90° unidirectional laminate while for the cross-ply laminates it is somewhat lower. The amount of light detected at a given strain provides the most interesting trend in results in terms of the effect of inner ply thickness of cross-ply laminates. It shows that the amount of damage is the largest in the laminate with the thinnest (0.5 mm) inner ply by a factor of 30 compared to the unidirectional laminate at 0.3\% strain, and by a factor of seven compared to the cross-ply laminate with an inner ply thickness of 2.0 mm. The reason for this may be attributed to the high level of thermal stresses in the thin 90° ply in the (0,90)\textsubscript{s} configuration leading to more damage. In cross-ply laminates with thicker inner 90° plies the level of thermal stresses is lower. The influence of the constraining zone is smaller and the number of large stable cracks are also smaller and confined to the region near the 0/90 ply interface. The amount of damage per millimetre of ply thickness is, therefore, less. The interval between the micro-cracking strain and the transverse cracking strain is the largest for the laminate with the inner 90° ply of 0.5 mm, and so the micro-cracks can continue to form and grow until the conditions are right for transverse cracking to occur. All these factors contribute to the level of damage which is the highest in the cross-ply laminate with an inner ply of 0.5 mm. Hence, although the transverse ply cracking strain is higher for this laminate, the micro-damage in it is actually more severe at a given strain than in the laminate with the relatively thick inner ply which has a lower transverse ply cracking strain.

The laminates made with resins containing a higher amount of BDMA (1.5 and 3.0\%) showed very little change in the diffraction pattern with increasing strain. Any change in the intensity was barely perceptible and no significant lengthening of the diffraction pattern was observed. The amount of light detected at a given strain and with the detector in position 1 is much less for the higher cure laminates, with the 3.0\% BDMA laminates showing the least amount. Whilst this might imply that the cracks in the specimen
were very large and so the diffracted intensity is concentrated at lower angles near to the forward beam, this was clearly not the case since whitening was not observed in these specimens. It may, therefore, be concluded that no large cracks were present and that the number and/or size of small cracks was considerably reduced compared to the laminates made with resin containing 0.5% BDMA resin. The experiments carried out using white light (section 5.2, colour photography) showed that specimens from laminates with 3.0% BDMA resin exhibited a reddening effect prior to transverse cracking, although no whitening was observed. Thus, it would appear that the cracks present in the more highly cured laminates are too small to cause any significant diffraction effects but are big enough to produce a reddening effect through Mie or Rayleigh scattering. The growth of these small cracks must then immediately lead to transverse cracking. This is in agreement with the observations using optical microscopy and in situ microscopy. In interpreting these results all the techniques employed throughout the study are viewed as complementary, providing information about the micro-damage at different stages in its development.

Generally, the 3.0% BDMA laminates show lower values of \( K \), the rate of increase in detector output, compared to the laminates made with resin containing 0.5% BDMA. The 1.5% BDMA laminates represent a case where both reddening and whitening was observed and although the 90° unidirectional laminate showed a low value of \( K \), similar to that shown by the equivalent 3.0% BDMA laminate, the 1.5% BDMA cross-ply laminates showed much higher values. The trend of increasing detector output with decreasing inner ply thickness shown clearly by the 0.5% BDMA laminates is not shown by the 1.5% and 3.0% BDMA laminates (in fact, it is quite the reverse). The reasons for this are not fully understood. Further work on cross-ply laminates with ply thicknesses lower than those investigated may provide more information.

It must be noted that the change in the elastic properties, such as modulus and fracture toughness of the resin as well as the increased level of thermal residual stresses in the high cure laminate may have contributed to the change in cracking behaviour of the laminates. It is also possible that the degree of adhesion of the resin to glass is much better with resin containing higher levels of BDMA. There are indications from the traces of detector output as a function of applied strain that the strain at which micro-cracking is first detected is higher for the higher cure laminates. However, this may be because less light is scattered by these cracks and is, therefore, only detected at higher applied strains.
(b) Laminates with starch finish glass fibres.

Only 90° unidirectional laminates were made with these glass fibres in 0.5% BDMA and 1.5% BDMA resin. No additional light was detected with increasing strain, in either system, prior to failure. The laminates were already heavily whitened as shown in Figure 4.23 since the laminates contained regions of very poor interfacial bonding, shown in Figure 4.29. Only a small applied stress was required to propagate failure from the flaws already present in these laminates.

(c) Angular distribution of light.

Experiments on the angular distribution of diffracted light as a function of strain showed that at any position along the vertical band of light the rate of increase in the detector output was about the same. The amount of light detected varied with angle so that the maximum voltage was recorded closer to the central image and this decreased quite rapidly as the angle through which light was diffracted was increased. Hence, the strain at which the light was first detected increased as the angle through which the light was diffracted was increased. This resembles a single slit diffraction pattern in which the intensity of light furthest away from the central image is lowest although, of course, no maxima or minima were observed.

(d) The effect of cycling- 0.5% BDMA laminates only.

Cyclic tests conducted on both the unidirectional and cross-ply laminates showed some interesting aspects of crack closure and re-opening. For example, the micro-cracks introduced during the first loading do not open immediately on reloading. Thus, no light is detected until after a strain of about 0.1% is reached. This is probably due to a degree of frictional bonding assisted by local compressive residual stresses which may be present. Subsequent cycles showed a decrease in this effect. For all cross-ply laminates the increase in detector output during the second loading cycle is linear after the frictional forces has been overcome, suggesting that no new cracks are introduced prior to reaching the previous maximum applied strain nor do existing cracks grow. Under these conditions the increase in output is then simply related to the opening up of micro-cracks. Beyond this strain the increase in output is returned to an exponential type behaviour.
During the unloading cycle, for a cross-ply laminate, it was observed that the detector output remained constant until the strain on the specimen was reduced by about 0.1 to 0.2% after which there was a linear decrease. On reaching zero load or zero applied strain, the output was not reduced to the original output detected but a residual voltage was recorded. This effect was the most prominent for the laminate with the thinnest inner 90° ply and the least for the 90° unidirectional ply. It has already been shown that there is residual damage in the specimens. This was observed under the microscope (section 5.2, polished edge microscopy) and as stress-whitening (section 5.2, colour photography). The presence of residual damage was also shown in the diffraction pattern. The reason for the presence of these 'open' cracks at zero load was suggested as being associated with a residual thermal restraint stress of a tensile nature in the 90° ply. Although there is local stress relief as the cracks form the ply is still under a tensile stress and the largest cracks are unable to close completely. The restraint on micro-cracks must be overcome before cracks can begin to close up. This may account for the flat portion of the output versus applied strain curve at the start of unloading in a given loading cycle. Hence, a given decrease in strain is required before the cracks close up and their numbers apparently decrease. For the 90° unidirectional laminate, very little decrease in strain is required to close up cracks since no thermal restraint strain is present in these laminates due to the absence of 0° plies and so a flat portion, CD, was not observed.

(e) Effect of heat treatment after cycling.

The effect of heat treatment after three load/unload cycles was to slightly increase the strain at which light was first detected. The increase in voltage which was linear after the third cycle was changed back to an exponential type behaviour. The rate of increase in voltage was slightly lower than that observed during the first cycle. The specimen was, thus, returned to its original state but the cracking behaviour or rate of increase in voltage (damage) had been altered somewhat. This effect of heat-treatment is discussed further in the next section.
5.4 Reversibility of Stress-whitening - the effect of heat treatment.

On the basis of small changes in the stress/strain curves of (0,90)_s laminates, Parvizi et al [2] suggested that the recovery of modulus with heat treatment resulted from re-adhesion between the fibre and matrix and referred to this as "reversible debonding". To support this Parvizi presented a series of scanning electron micrographs (These only allow observation of the specimen edge by reflection) showing the development of crescent shaped debonds at the fibre/matrix interface. However, no evidence was presented to show that on heat treatment the bond in these regions was re-established. As a consequence of these initial observations, experiments were undertaken to investigate the exact nature of the reversible effect on heat treatment, and the mechanism by which it occurs.

The effect of successive heat treatments on specimens from a cross-ply laminate, made with resin containing 0.5% BDMA and with an inner 90° ply thickness of 0.5 mm is shown in Figures 4.53 to 4.55. The changes observed in the behaviour of the specimens were quite dramatic. The stress-whitening effect which was observed at zero load after testing was made to disappear after a single annealing treatment of 30 mins. at 100°C. The micro-cracks which had developed in the resin were shown to have healed and many did not reappear even after reaching the strain at which they first appeared, Figure 4.23(e). This is the first direct microscopic evidence of "reversibility" or crack healing. In contrast to cracks in the resin, the cracks at the fibre/resin interface did not disappear after heat treatment.

The photometric traces showed that, before annealing, a straight line relationship was obtained between \( \ln I_n \) and applied strain. After annealing once, the gradient of the straight line was retained up to the maximum applied strain level. Further loading produced a line with a gradient which had been reduced by a third so that the strain reached during the very first cycle acted as a 'transition point'. Further annealing treatments showed that both gradients, before and after the 'transition point' continued to decrease and the transition point itself became less sharp. The amount of light detected showed a dramatic change. For example, the detector output at 0.4% strain was reduced by a factor of 25 compared to the original output after the specimen had been annealed for a total time of 13 hours and 10 mins. (not a continuous treatment - see section 3.4.3).
Measurements of glass transition temperatures, \( T_g \), performed after each annealing treatment, showed a gradual increase from an original value of 107°C to 131°C. This must mean that the resin continued to cure during the annealing treatments, increasing its cross-link density leading to the higher glass transition temperatures. Thus, it is possible for the micro-cracks to heal if by increasing the temperature of the resin the two crack faces could be brought into contact allowing either the inter-penetration of active mobile species or simply the formation of new bonds across the crack faces. The increase in glass transition temperature is indicative of increased cure. It has been shown that increasing the level of cure of the resin alters its modulus and yield point. It was also shown that the amount of light detected from higher cure laminates (containing 1.5% and 3.0% BDMA resin) during testing was much lower than that detected for the lower cure laminates. The decrease in the detector output after annealing is related to the increased level of cure in the same manner as that achieved by increasing the cure by addition of more accelerator and is not a function of the reversible nature of the interface bond. The cracks that showed 'healing' must have been composed mostly of resin.

The photometric traces in conjunction with microscopy and the observed colour changes suggest that the mechanism of reversible stress-whitening is consistent with the formation and healing of micro-cracks in the resin and not at the fibre/resin interface.
Temperature — ►

Figure 5.1. Schematic plots of specific volume versus temperature for a partially cured and a fully cured resin. Tg is the glass transition temperature of the partially cured resin, Tg∞ is the glass transition temperature of the fully cured resin, RT is room temperature and Tcure is the cure temperature. From [82].

Figure 5.2. The change in secant modulus of a 0.5% BDMA resin with increasing strain.

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Figure 5.3. Stress/strain diagrams of a 0° unidirectional laminate (trace 1) and a 90° unidirectional laminate (trace 2) containing a 0.5% BDMA matrix showing deviations from linearity.

Figure 5.4. Schematic diagram showing micro-crack of length, $2a$, and width, $w$, and the cylindrical volume of unloaded material representing the energy lost by the formation of the crack.
Figure 5.5. Load as a function of applied strain for a 90° unidirectional laminate with a 0.5% BDMA matrix. The laminate was cycled seven times in succession. During the fifth cycle the specimen was held at load for 45 mins. The sixth cycle was performed immediately after unloading. The seventh cycle was performed after 15 mins. at zero load.
Figure 5.6 (a). The first transverse ply cracking strain as a function of inner ply thickness, $2d$, of $(0,90)_{S}$ laminates with 0.5% BDMA matrix (o), with 1.5% BDMA matrix (o), and with 3.0% BDMA matrix (Δ), before compensating for thermal strains.

Figure 5.6 (b). The first transverse ply cracking strain as a function of inner ply thickness, $2d$, of $(0,90)_{S}$ laminates with 0.5% BDMA matrix (o), with 1.5% BDMA matrix (o), and with 3.0% BDMA matrix (Δ), after compensating for thermal strains.
Figure 5.6 (c). The first transverse ply cracking strain as a function of inner ply thickness, 2d, of (0,90)s laminates with 0.5% BDMA matrix, after compensating for thermal strains (▲). The results are compared with the experimental results of [70] shown by circles (○) and the predictions of the constraint theory [85] (—) and those of Ogin and Smith [73] (—is). Dashed lines, 1, and 2, represent fracture strains of 90° unidirectional laminates obtained by [70] and in this study, respectively.
Figure 5.7 (a). Schematic diagrams showing the constraint zones 'c' in the 90° ply of a (0,90)_s laminate with respect to the ply thickness, 2d and b. When 2d > 2c, an unconstrained zone is still present. (b) shows the inner ply thickness at which constraint becomes effective when 2d = 2c, and (c) shows the increasing constraint when 2d < 2c. Note: the constraint profile has not been determined but has been chosen arbitrarily.
Figure 5.8. The reflection and diffraction of light by small objects comparable in size with the wavelength of light (a) object small compared to the wavelength of light and (b) object greater than the wavelength of light. After [B6].
Figure 5.9 (a). Diffraction pattern produced by a bundle of glass fibres held vertically with the LASER at 90° to the fibres.

Figure 5.9 (b). Diffraction pattern produced by a 0° unidirectional laminate with the LASER at 90° to the coupon.
Figure 5.9 (c). Diffraction pattern produced by a $(0,90)_s$ laminate with an inner $90^\circ$ ply thickness, $2d$, of 2.0 mm and outer $0^\circ$ ply thickness, $b$, of 0.65 mm, with the LASER at $90^\circ$ to the coupon.

Figure 5.9 (d). Diffraction pattern produced by a $(0,90)_s$ laminate with an inner $90^\circ$ ply thickness, $2d$, of 1.0 mm and outer $0^\circ$ ply thickness, $b$, of 0.70 mm, with the LASER at $90^\circ$ to the coupon.
Figure 5.9 (e). Diffraction pattern produced by a $(0,90)_s$ laminate with an inner $90^\circ$ ply thickness, $2d$, of 0.5 mm and outer $0^\circ$ ply thickness, $b$, of 0.80 mm, with the LASER at $90^\circ$ to the coupon.

Figure 5.9 (f). Diffraction pattern produced by a $(0,90)_s$ laminate with an inner $90^\circ$ ply thickness, $2d$, of 0.5 mm and outer $0^\circ$ ply thickness, $b$, of 0.80 mm, with the LASER at $45^\circ$ to the coupon.
Figure 5.9 (g). Diffraction pattern produced by a (0,90)_s laminate with an inner 90° ply thickness, 2d, of 0.5 mm and outer 0° ply thickness, b, of 0.80 mm, at an applied strain of 0.5%. The LASER was oriented at 90° to the coupon.

Figure 5.9 (h). Diffraction pattern produced by a (0,90)_s laminate with an inner 90° ply thickness, 2d, of 0.5 mm and outer 0° ply thickness, b, of 0.80 mm, at an applied strain of 0.5%. The LASER was oriented at 45° to the coupon.
Figure 5.9 (i). Diffraction pattern produced by a (0,90)$_s$ laminate with an inner 90° ply thickness, 2d, of 0.5 mm and outer 0° ply thickness, b, of 0.80 mm, at zero load after straining to 0.5%. The LASER was oriented at 90° to the coupon.

Figure 5.9 (j). Diffraction pattern produced by a (0,90)$_s$ laminate with an inner 90° ply thickness, 2d, of 2.0 mm and outer 0° ply thickness, b, of 0.65 mm, at 0.5% strain. The LASER was oriented at 90° to the coupon.
CHAPTER 6

CONCLUSIONS

1. Increasing the "degree of cure" of the Epikote 828 resin, as measured by the glass transition temperature, produces a decrease in the modulus and yield strength of the resin. The degree of cure of the resin increases with both increasing level of accelerator and continued heat treatment. The moduli of glass fibre reinforced laminates made with this resin were in accordance with predictions based on the measured properties of the resin. Changes in laminate modulus with heat treatment were also consistent with the changes in modulus of the resin.

2. There is a small reduction in modulus with increasing applied strain in 90° unidirectional laminates made with resin containing 0.5% BDMA accelerator. A similar reduction in modulus is observed for cross-ply laminates with a relatively thick 90° ply and an equivalent degree of cure. The change in modulus is gradual and in contrast to the results of Parvizi et al [2] no abrupt 'knee' was observed in the stress/strain curve. No significant reduction in modulus could be detected for the laminates made with resin containing higher levels of BDMA. Thus, the observed reduction in laminate modulus, as a function of increasing applied strain, may be attributed to the visco-elastic behaviour of the resin which is most significant in the 0.5% BDMA resin.

3. Stress-whitening and the preceding colour changes result from the development of micro-cracks in the 90° ply of the laminates. In situ microscopy revealed that the micro-cracks are generated in the resin predominantly at or near points of contact between fibres where the strain magnification in the resin is highest. The cracks develop close to the fibre/matrix interface and extend some way into the resin with the crack faces lying normal to the loading axis in accordance with the model described by Tirosh et al [62] for well bonded fibres. Little evidence was found for the formation of whole debonds around the fibre/resin interface.

Under oblique illumination conditions, the laminates appeared blue at zero load. On the application of load, specimens either whitened or reddened depending on the resin system with which the laminate was made. The
formation of a transverse ply crack resulted in the appearance of blue bands on either side of the crack while the rest of the laminate retained a red or white colour. The width of the blue bands was proportional to the thickness of the inner ply. On reloading, the specimen again showed colour changes except in the areas near to a transverse crack which remained blue. It appeared that these areas did not carry load. Within the blue bands, micro-cracks were observed to close up confirming that the colour changes were associated with the development of the cracks. Similarly, the presence of these blue bands amidst the red and white colours in the rest of the laminate confirmed that the colours were a true indication of the level of stresses in the 90° ply. The blue bands are experimental evidence of the stress transfer length or stress relieved regions first proposed by Hahn and Tsai [69], over which no load is carried by the 90° ply.

It is postulated that the colour effects are the result of scattering phenomena akin to Rayleigh and Mie scattering from small particles. The reddening occurs when the cracks in the resin are smaller in size than the wavelength of light while the "whitening" effect is the result of ordinary diffuse reflections and occurs when the gaps are larger than the wavelength of light.

4. The size of the micro-cracks developed in the resin depends on the degree of cure of the resin. The resin with the lowest degree of cure contains the largest micro-cracks. Hence, the laminates made with resin containing 0.5% BDMA showed very little reddening but a large degree of whitening. No micro-cracks could be resolved, using in situ microscopy, in the 3.0% BDMA laminates prior to transverse ply cracking. These laminates showed no whitening, an effect associated with large cracks, but only a reddening effect attributable to scattering from small gaps. It is suggested, therefore, that the 'inherent' flaw size for the laminates made with resin containing the lowest level of accelerator (0.5% BDMA) is much larger than that for the laminates made with resin containing higher levels of accelerator (1.5% and 3.0% BDMA).

5. The amount of damage developed in cross-ply laminates, measured by the intensity of light diffracted by micro-cracks, was found to be related to the thickness of the inner 90° ply and the degree of cure of the resin. In all cases the amount of damage increased exponentially with increasing applied strain and is believed to describe the increase in the number and size of cracks as a function of applied strain.
The laminates made from 0.5% BDMA resin gave the maximum response in terms of the intensity of light diffracted by the specimens. The highest rate of increase in intensity of light was shown by the unidirectional 90° laminate, and the lowest by the cross-ply laminate with a 90° ply thickness of 2 mm. The effect of decreasing the inner ply thickness of the (0,90)_s laminates was to increase the quantity of damage so that a four-fold decrease in inner ply thickness from 2.0 mm to 0.5 mm resulted in a seven-fold increase in the amount of damage per millimetre of inner ply thickness, at a strain of 0.30%. It is to be noted that although the transverse ply cracking strain for the cross-ply laminate with the thinnest inner ply is higher than that of cross-ply laminates with the thicker inner plies, the micro-damage in it is much more severe. Further, it is distributed throughout the 90° ply and a large number of the micro-cracks are held open due to the presence of the thermal restraint stress in the 90° ply which is tensile in nature.

The amount of damage in laminates made with the 1.5% BDMA resin was much lower than in the laminates made with 0.5% BDMA resin. The 3.0% BDMA laminates had the lowest rates of increase in light intensity as a function of applied strain. The overall response of these laminates was very low indicating that they contained the least amount of damage. The effect of inner ply thickness on the laminates made with resin containing 1.5% and 3.0% BDMA are not fully understood and need further work.

6. Fibres treated with a starch size produced laminates with very poor fibre/matrix adhesion and considerable de-wetting was observed. These laminates showed no colour effects and transverse cracking occurred at low applied strains. No significant increase in the intensity of light diffracted with increasing strain was detected in either the 0.5% BDMA or the 1.5% BDMA resin systems, prior to failure. Thus, in systems with initially poor fibre/resin adhesion the cure of the resin will have little effect on the low strain behaviour of the laminate.

7. Cyclic loading/unloading tests conducted on both the unidirectional and cross-ply laminates made with resin containing 0.5% BDMA showed some interesting aspects of crack closure and re-opening. The micro-cracks were able to close up on removal of the load and the stress-whitening diminished as a consequence of this. While the colour changes were almost completely reversible on unloading the whitening in the laminates was only partially reversible suggesting that while small cracks could close up on removal of load the larger cracks remained open. Micro-cracks were observed at zero
load, after testing, near the 0/90 ply interfaces in laminates with thick inner 90° plies and throughout the 90° ply in laminates with thin inner plies. The presence of this residual damage was also shown in the diffraction pattern obtained at zero load, after testing. The reason for these 'open' cracks at zero load is the residual tensile thermal restraint strain in the 90° ply. Although there is local stress relief as the cracks form, the ply is still under a tensile stress and the largest cracks are held open. In cross-ply laminates with the thin inner plies almost the entire 90° ply is under a high level of thermal strain imposed by the 0° plies. For a laminate with thicker inner plies the level of thermal strain is lower and the region nearest the 0/90 ply interfaces experiences the highest thermal strains, especially at the free edge. Micro-cracks, therefore, develop predominantly in these regions assisted by the thermal strains. The micro-cracks in this region are also more stable due to the constraining influence of the 0° plies.

On reloading it appeared that frictional forces between the crack surfaces prevented the immediate re-opening of micro-cracks. Subsequent cycles showed a decrease in this effect. For all cross-ply laminates the increase in intensity during the second loading cycle was linear after the frictional forces had been overcome, suggesting that no new cracks are introduced prior to reaching the previous maximum applied strain. Under these conditions the increase in intensity is then simply related to the opening of existing micro-cracks. Beyond this strain the increase in intensity was returned to an exponential type behaviour and corresponds to the formation of new cracks.

8. The reversibility of stress-whitening with heat treatment is associated with the healing of micro-cracks in the resin and results from continued curing of the resin. There is no evidence of the re-establishment of the bond between fibre and matrix as proposed by Parvizi et al [2]. Microscopic examination showed that after heat-treatment at 100°C for 30 minutes, most of the cracks which had developed in the 0.5% BDMA laminate after straining to 0.6%, were invisible and the residual whitening at zero load had disappeared. After reloading and applying a strain of 0.35%, most of the original cracks remained invisible. After straining to 0.65% strain a proportion of the original cracks reappeared but were smaller in size and even relatively long resin cracks which had originally appeared at 0.45% strain failed to reappear. Re-annealing the specimen removed the fine cracks but some cracks around the fibre/matrix interface were still visible. Thus, while the resin
cracks could be healed, adhesion around the fibre/matrix interface could not be reinstated.

The LASER diffraction technique showed that the effect of successive heat treatments on specimens from a 0.5% BDMA cross-ply laminate were quite dramatic. Prior to annealing, a linear relationship was obtained between the logarithm of the intensity of light detected and the applied strain. After annealing once, the gradient of the line remained the same up to the previous maximum applied strain. Above this strain the gradient of the line was reduced by one third. Thus, the maximum applied strain reached during the first cycle acted as a 'transition point'. Further annealing treatments showed that both gradients, before and after the transition point continued to decrease and the transition point itself became less sharp. Hence, in addition to decreasing the rate of re-development of the original cracks on reloading, the heat treatment reduced the rate of development of 'new' cracks formed at higher strains. The intensity of light detected at a given strain was also reduced. For example, the intensity of light detected at 0.4% strain was lower by a factor of 25 compared to the original intensity after the specimen had been annealed for a total time of 13 hours and 10 mins. Thus, the amount of damage was lower after heat-treatment.

Measurements of glass transition temperature, Tg, performed after each annealing treatment, showed a gradual increase in Tg from an original value of 107°C to 131°C as the number of treatments increased. Hence, the resin continued to cure during annealing. The total amount of light detected from higher cure laminates (containing 1.5% and 3.0% BDMA resin) during testing was much lower than that detected for the lower cure laminates. The decrease in the intensity of light detected after annealing is related to the increased level of cure in the same manner by reducing the "inherent" flaw size as the level of cure of the resin is increased. The cracks that showed 'healing' must have been composed mostly of resin.
CHAPTER 7

SUGGESTIONS FOR FURTHER WORK

1. Further work is suggested in order to establish whether the change in the size of the microcracks with increasing cure is a direct result of a change in the fracture behaviour of the resin or is a result of changes in the fibre/resin bond strength with increasing cure. In this respect measurement of the fracture toughness of the resin and measurement of tensile debonding stresses using curved neck specimens [50] with model large diameter fibres is recommended. This information would also be useful in understanding various aspects of transverse ply cracking behaviour.

2. Experiments on pure resin samples and also on laminates with higher cure resins are recommended in order to establish the regimes of heat treatment temperatures and cure levels at which healing can occur.

3. The measurement of thermal restraint stresses using asymmetric beams [8] in laminates fabricated from resins with the higher levels of accelerator would be useful. The parameters needed in the equations, such as the thermal expansion coefficients can be easily measured by established techniques. Transverse ply cracking strains may then be analysed more accurately and the micro-cracking behaviour of the higher cure laminates may be better understood.

4. The above information may be useful in validating experimentally the set of micromechanics equations recently presented by Chamis [63] to predict the fibre composite micro-stresses in the fibre, matrix and at the interface of a fibre composite for thermal and mechanical loading conditions. The transverse ply cracking model of Ogin and Smith [73] could also be validated for the higher cure laminate systems.

5. The LASER diffraction technique and the optical techniques used in this study can be developed further and employed usefully for systematic studies of micro-cracking behaviour in angle-ply laminates or other suitable composite systems.
Detailed circuit diagram of the photometer.
APPENDIX 2

a) The Halpin-Tsai equations [95] for the calculation of the unidirectional laminate modulus, $E_1$, in the longitudinal direction and $E_t$, in the transverse direction.

(i) $E_1 = E_m (1 - V_f) + (E_f V_f)$

(ii) $E_m = E_m (1 + \alpha \beta V_f / 1 - \beta V_f)$

where $\alpha$ is a constant associated with fibre packing arrangement, and

$$\beta = \left[ (E_f/E_m) - 1 \right] / \left[ (E_f/E_m) + \alpha \right]$$

$\alpha = 2.0$ for laminates made from 1200 tex fibres, and 2.2 for laminates made with 600 tex fibres,

$E_m = 3.8 \text{ GPa}$ for laminates made with matrix containing 0.5% BDMA and 3.4 GPa for laminates made from resin containing 1.5% and 3.0% BDMA,

$E_f = 72 \text{ GPa}$,

and $V_f$ values were obtained from Table 4.7.

The $(0,90)_s$ laminate moduli, $E_c$, were then obtained from,

(iii) $E_c = \left[ E_1 b/(b+d) \right] + \left[ E_t d/(b+d) \right]$

where values of $b$, the $0^\circ$ ply thickness and $d$, half the $90^\circ$ ply thickness were obtained from Table 4.7.

(b) Equations for the calculation of thermal strain in the transverse ply in the longitudinal direction, $\varepsilon_{11}^{th}$ [96].

(i) $\varepsilon_{11}^{th} = E_1 b (\alpha_t - \alpha_1) (T_1 - T_2) / (E_1 b + E_t d)$

(ii) $\alpha_1 = \left( E_m \alpha_m V_m + E_f \alpha_f V_f \right) / \left( E_m V_m + E_f V_f \right)$

(iii) $\alpha_t = \alpha_m V_m (1 + \gamma_m) + \alpha_f V_f (1 + \gamma_f) - \alpha_1$

(iv) $\gamma_{21} = \gamma_m V_m \gamma_f V_f$

where, $\alpha_m(20^\circ C) = 63 \times 10^{-6} \text{ K}^{-1}$

$\alpha_f(20^\circ C) = 4.9 \times 10^{-6} \text{ K}^{-1}$

$\gamma_m = 0.33, \gamma_f = 0.22$

$T_1 = 20^\circ C$ (room temperature),

values of $T_1$ were obtained from Table 4.5.
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