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LIFE ASSESSMENT AND PREDICTION

Accelerated Test Methods for Assessing Environmental Degradation of Composite Laminates

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W.R. Broughton, M.J. Lodeiro and S. Maudgal
Centre for Materials Measurement & Technology
National Physical Laboratory
Teddington
Middlesex, TW11 0LW, UK

ABSTRACT

This report provides an assessment of accelerated test methods evaluated within the "Composites Performance and Design (CPD2) Project - Life Assessment and Prediction". The project is directed towards the development and validation of test methods and predictive methodologies that can be used for characterising the long-term properties and residual life/strength of polymer matrix composites. The report considers convenient methods for obtaining basic strength-time data for unconditioned and environmentally conditioned glass and carbon fibre-reinforced laminates. Environmental data from tensile and flexural tests conducted on unidirectional and cross-ply laminates are evaluated. The report examines methods for monitoring damage (i.e. transverse cracking) in cross-ply laminates and assesses elastic and strength property degradation as a function of degree of damage.

The report considers: (i) tensile testing of hot/wet conditioned unidirectional and cross-ply glass fibre-reinforced epoxy laminates (70 °C/85% RH for periods up to 12 weeks); (ii) tensile testing of chemically conditioned unidirectional glass fibre-reinforced epoxy laminates (sodium hydroxide and sulphuric acid solutions); (iii) static fatigue testing of unconditioned glass fibre-reinforced laminates; (iv) flexural properties of hot/wet conditioned unidirectional laminates at ambient and elevated temperatures (immersion in deionised water at 60 °C for periods up to 42 days); and (v) autoclave conditioning of flexural and tensile specimens manufactured from carbon and glass fibre-reinforced laminates (steam environment at 136 °C and 2.2 bar for periods up to 72 hours).

The principal conclusions that can be drawn from the results are: (i) standard test geometries in the international standards ISO 527-4 and ISO 527-5 are suitable for assessing the combined effects of environmental conditioning and/or static loads on tensile properties; (ii) transverse flexural properties are particularly sensitive to the combined effect of moisture and elevated temperature; (iii) autoclave conditioning can accelerate moisture absorption by a factor of 100 and is suitable for use with materials designed for hot/wet conditions; and (iv) classical laminate analysis combined with micromechanics can be used to predict elastic and strength properties of moisture conditioned materials. The report provides a summary of the results, including recommendations on preparation, testing and inspection of composite laminates.

The report was prepared as part of the research undertaken at NPL for the Department of Trade and Industry funded project on "Composites Performance and Design - Life Assessment and Prediction".

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National Physical Laboratory
Teddington, Middlesex, UK, TW11 0LW

Approved on behalf of Managing Director, NPL, by Dr C Lea,

Head of Centre for Materials Measurement and Technology.

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1. INTRODUCTION

This report provides an assessment of techniques that can be employed to accelerate environmental degradation in glass and carbon fibre-reinforced composite laminates. The research described forms part of the DTI funded project "Composites Performance and Design (CPD2) - Life Assessment and Prediction". This project is directed towards the development and validation of test methods and predictive models that can be used for characterising the behaviour of polymer matrix composites (PMCs) exposed to combined aggressive environments and applied loads. Tensile and flexural tests have been carried out on both glass and carbon fibre-reinforced systems to obtain basic strength-time data for unconditioned and environmentally conditioned unidirectional and cross-ply (0°/90°) laminates. Throughout this report comparison is made between predictive analysis and experimental data, however, the report is essentially directed towards test methodology. Future reports will include an evaluation of predictive methodologies developed within the CPD programme and existing analytical models.

The report is divided into six sections including the introduction (Section 1). Section 2 describes the materials used to validate the test methods in this programme, specimen geometry and specimen preparation. Tensile test results for hot/wet conditioned and chemically conditioned epoxy resin, unidirectional and cross-ply laminates are presented in Section 3. This section also examines methods for monitoring damage (i.e. transverse cracking) in cross-ply laminates and assesses elastic and strength property degradation as a function of degree of damage. The combined effect of temperature and moisture on the flexural properties of unidirectional laminates is evaluated in Section 4. The use of a high temperature and pressure autoclave as a means of inducing accelerated moisture degradation is examined in both Sections 3 and 4. Section 5 considers stress rupture behaviour of unconditioned unidirectional and cross-ply glass fibre-reinforced laminates. Conclusions are given in Section 6. **Throughout this report, statements of particular importance or relevance are highlighted in bold type. Test data will generally be expressed as an average value ± one standard deviation.**

2. MATERIALS CHARACTERISATION

2.1 MATERIALS DESCRIPTION

The materials used to develop and validate the test methods in this programme are listed below:

(a) Continuous unidirectional glass fibre-reinforced epoxy prepreg sheet (E-glass/Fibredux F922).

(b) Continuous unidirectional carbon fibre-reinforced epoxy prepreg sheet (Tenax HTA/Fibredux F922).

(c) Continuous unidirectional glass fibre-reinforced epoxy prepreg sheet (E-glass/Fibredux 913).

(d) Continuous unidirectional carbon fibre-reinforced epoxy prepreg sheet (Torayca T300/Fibredux 924).

Unidirectional and cross-ply (0°/90°) laminates were autoclaved (including post cured) at the National Physical Laboratory (NPL) to Hexcel Composites specifications. All panels were visually inspected for evidence of damage or processing defects.

Several cross-ply configurations (i.e. $[0°/90°]_{4S}$, $[0°_2/90°_2]_S$, $[0°_2/90°_4]_S$, $[0°_2/90°_6]_S$ and $[0°_2/90°_8]_S$) have been included in the programme to assess the predictive methodology being developed within the CPD programme.

2.2 FIBRE CONTENT AND COMPOSITE DENSITY

Fibre volume fraction, $\mathbf{V_f}$, fibre weight fraction, $\mathbf{W_f}$, and composite density, $\boldsymbol{\rho_c}$, were measured for all materials (Table 1). Composite density measurements were carried out using method A (zeroed pan immersion) specified in ISO 1183 [1]. Fibre volume and weight fraction measurements for the glass fibre-reinforced epoxy laminates were carried out according to the ISO 1172 standard [2], which uses a resin burn-off technique. In this technique, the composite is dried to constant mass and then subjected to 600 °C in a furnace for at least an hour to remove all traces of resin. The fibre volume and weight fractions of carbon fibre-reinforced epoxy panels were determined according to BS ISO 11667 [3]. Resin removal was achieved using concentrated sulphuric acid and hydrogen peroxide. This process was carried out using a Prolabo Microdigest 401 digester.

Table 1: Composite Density, Fibre Volume Fractions and Fibre Weight Fractions

Material	Composite Density (kg/m^3)	Volume Fraction (%)	Weight Fraction (%)
Aligned GRP			
E-glass/F922	2,122 ± 53	65.41 ± 4.46	78.84 ± 3.01
E-glass/913	1,883 ± 39	50.95 ± 0.19	69.26 ± 0.26
Aligned CFRP			
HTA/F922	1,562 ± 17	58.64 ± 2.21	66.41 ± 1.79
T300/924	1,555 ± 10	61.49 ± 1.44	68.48 ± 1.24
Cross-Ply GRP			
E-glass/913 $[0°/90°]_{4S}$	1,957 ± 62	56.47 ± 0.41	72.16 ± 0.48
E-glass/F922 $[0°_2/90°_2]_S$	2,060 ± 6	60.73 ± 0.73	75.48 ± 0.62
E-glass/F922 $[0°_2/90°_4]_S$	2,042 ± 21	59.70 ± 1.08	74.61 ± 0.58
E-glass/F922 $[0°_2/90°_8]_S$	1,966 ± 4	53.32 ± 0.56	69.45 ± 0.49
Cross-Ply CFRP			
HTA/F922 $[0°_2/90°_2]_S$	1,543 ± 6	57.52 ± 1.96	65.90 ± 2.00
HTA/F922 $[0°_2/90°_4]_S$	1,548 ± 8	57.80 ± 0.86	65.94 ± 0.75
HTA/F922 $[0°_2/90°_6]_S$	1,537 ± 3	56.02 ± 2.34	64.47 ± 2.69

2.3 SPECIMEN GEOMETRY AND PREPARATION

This section describes the test methods and specimen geometries used for tensile and flexural testing of unidirectional and cross-ply laminates, and tensile testing of bulk resin specimens. Details of specimen preparation for each method are also covered in this section.

2.3.1 Unidirectional and Cross-Ply Laminate Tensile Specimens

Specimen preparation and testing of unidirectional laminates was carried out to BS EN ISO 527-5 [4] specifications. Both longitudinal (i.e. fibres parallel to loading direction) and transverse (i.e. fibres perpendicular to loading direction) specimen geometries were used to determine the tensile properties of the unidirectional composite materials. Longitudinal specimens (Figure 1) were 250 mm in length, 15 mm wide and 1 mm (i.e. 8 plies) thick. Transverse specimens were 250 mm long, 25 mm wide and 2 mm thick (i.e. 16 plies). The overall gauge-length (i.e. region between grips) was 150 mm for both specimen geometries.

End tabs (50 mm long), manufactured from a plain woven glass fabric/epoxy laminate (1.6 mm thick) with the fibre axes of the fabric set at ±45° to the specimen axis, were adhesively bonded to all the specimens. The tab angle was 90° (i.e. not tapered). An epoxy film adhesive with a cure temperature of 120 °C was used to bond the end tabs to the specimen. **A high elongation adhesive is recommended for bonding the end tabs to the specimen. The use of a film adhesive with carrier to bond the end tabs was found to reduce both preparation time and adhesive wastage. Specimen preparation was also relatively clean in comparison to paste adhesives. It is essential to dry the end tabs before bonding to remove moisture, which can compromise the adhesive bond.**

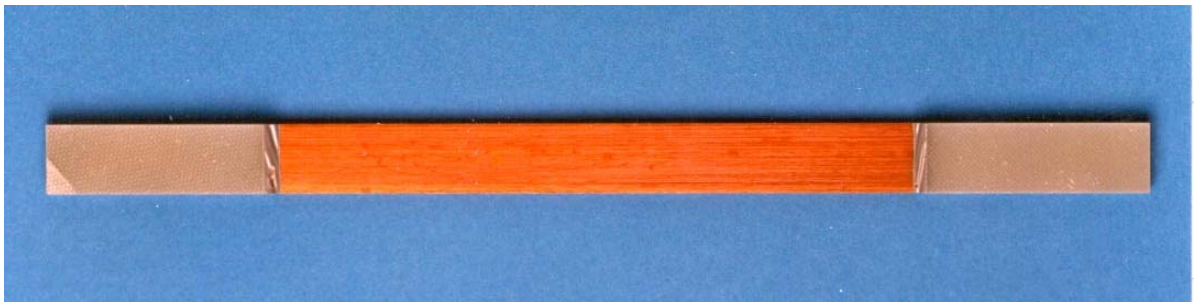

Figure 1: Continuous unidirectional glass fibre-reinforced laminate.

The cross-ply laminates were prepared and tested according to BS EN ISO 527-4 [5] specifications. Specimens (Figure 2) were 250 mm in length, 25 mm wide and 2 mm (i.e. 16 plies) thick. The overall gauge-length (i.e. region between grips) was 150 mm. End tabbing was identical to that used for the unidirectional specimens.

Figure 2: Cross-ply glass fibre-reinforced laminate.

2.3.2 Unidirectional and Cross-Ply Laminate Flexure Specimens

Preparation and testing of flexure specimens was carried out to BS EN ISO 14125 [6] specifications. Flexure specimens were cut from 2 mm thick continuous unidirectional glass and carbon fibre-reinforced epoxy laminates in both the longitudinal and transverse directions. The specimens were tested in four-point bending. An outer to inner span ratio of 3:1 was employed. The longitudinal and transverse specimens were 100 mm and 60 mm in length, respectively. The width for both specimens was 15 mm.

2.3.3 Bulk Resin Tensile Specimens

Dumbbell-shaped (type 1B) tensile specimens were machined from F922 epoxy plaques with a 2.5 mm nominal thickness. Preparation and tensile testing of the bulk resin specimens was carried out to BS EN ISO 527-2 [7] specifications. Specimen thickness was "as cast" (i.e. specimens were not machined to reduce the thickness). The overall length of the resin specimens was 75 mm. The gauge section was 25 mm long and 10 mm wide. **Care needs to be taken to ensure the specimens are free of voids and machine defects (i.e. nicks and cuts). The presence of defects will reduce the tensile strength of the material.**

3. TENSILE TESTS

This section presents the results from tensile tests that were conducted to evaluate the effects of hostile environments on the tensile stiffness and strength of unidirectional and cross-ply laminates, and bulk resin specimens. Tests were carried out under standard laboratory conditions (i.e. 23 °C and 50% relative humidity (RH)) after the conditioning stage. Specimens were subjected to one of the following:

(i) Hot/wet conditioning at 70 °C and 85% RH for periods up to 12 weeks.
(ii) Immersion in deionised water at 25 °C for a period of 2 weeks.
(iii) Exposure to a 1.0 M (or 1 N) solution of sodium hydroxide (1 M concentration of OH^- ions) for 2 weeks.
(iv) Exposure to a 0.5 M (or 1 N) solution of sulphuric acid (1 M concentration of H^+ ions) for 2 weeks.

Note. A one normal (1 N) solution contains one gram-equivalent weight of a particular substance dissolved in 1 litre of solution.

Laminate and bulk resin specimens were also immersed in deionised water at 25, 40 or 60 °C for various periods of time in order to determine diffusion rate and the effect of moisture on the glass transition temperature, $\mathbf{T}_g$, for these materials.

3.1 HOT/WET CONDITIONED F922 EPOXY RESIN

Tensile tests were conducted on dry and hot/wet conditioned F922 epoxy dumbbell specimens (see Section 2.3.3). The tests were carried out in order to generate material property data for the predictive modelling work in this project. The specimens were conditioned in a Climatic Test Systems Ltd environmental chamber at 70 °C and 85% RH. Batches of specimens were withdrawn at selected intervals over a period of 6 weeks and then tested within an hour of removal from the conditioning environment. A period of 6 weeks (≈ 1,000 hours) is commonly used by industry for accelerated ageing of composite coupon specimens. Specimens were pre-dried to a constant weight at 50 °C, weighed, conditioned and reweighed. Test specimens were weighed prior to testing.

Tensile testing was carried out under standard laboratory conditions at a constant displacement rate of 2 mm/min using an Instron series 4500 screw-driven test machine fitted with wedge-action manually tightened grips. Instron Series IX software was used to control the servo-hydraulic test machine and to collect the test data. Contact extensometers were used for measuring strain parallel (i.e. longitudinal) and perpendicular (i.e. transverse) to the direction of applied load. Tests were conducted on at least 6 specimens per condition.

Table 2: Tensile Properties of Hot/Wet Conditioned F922 Epoxy

Exposure Time (Weeks)	Moisture Content (Weight %)	Tensile Strength (MPa)	Tensile Modulus (GPa)
0	0.00	62.0 ± 5.4	3.75 ± 0.04
1	2.44	52.9 ± 5.2	3.47 ± 0.09
2	2.85	42.8 ± 5.9	3.44 ± 0.04
3	3.02	42.9 ± 13.4	3.47 ± 0.05
6	3.20	55.4 ± 8.9	3.54 ± 0.05

Tensile strength and Young's modulus for unconditioned and hot/wet conditioned F922 epoxy are shown in Table 2. Although tensile strength and modulus of the epoxy resin decreased with increasing moisture content, the rate of degradation was moderate. Poisson's ratio was 0.41 for the dry material. This value remained constant as moisture content increased.

Dynamic mechanical analysis (DMA) measurements were carried out on hot/wet conditioned F922 specimens to determine the change in the glass transition temperature, $\mathbf{T}_g$, as a function of moisture content. ISO 6721-1 [8] specifies a method of using DMTA for plastics and composites (see also [9]). Each specimen was immersed in deionised water at elevated temperatures (i.e. 25, 40 or 60 °C) for a select period (either 1, 2, 3 or 6 weeks).

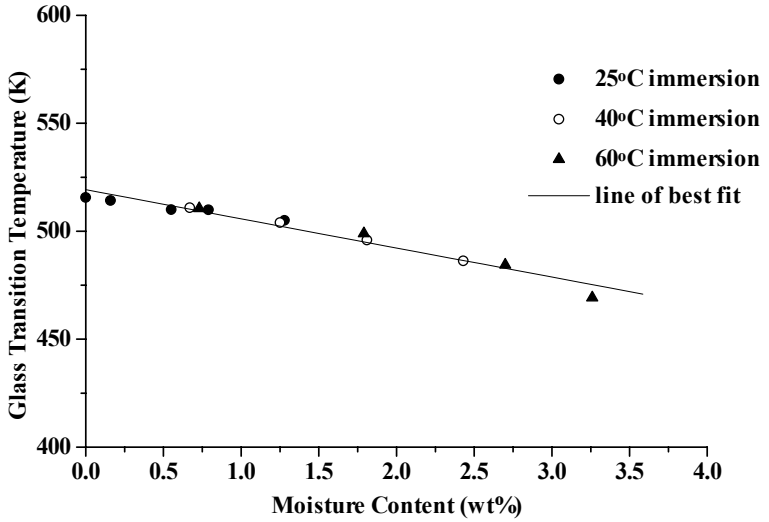

Figure 3: Glass transition temperature of F922 as a function of moisture content.

The results, presented in Figure 3, show that moisture reduces $\mathbf{T}_g$ with the shift in temperature being related to moisture content by the following linear relationship [10]:

$$T_{gw} = T_{gd} - gM \quad (1)$$

where $\mathbf{T}_{gd}$ is the glass transition temperature of the dry material, $\mathbf{T}_{gw}$ is the glass transition temperature of the conditioned (or wet) material, **g** is the temperature shift (in K) per unit moisture absorbed and **M** is the amount of moisture absorbed (wt %). The value of **g** in this case is 13.5 K. The measured and projected (i.e. Y-intercept of linear regression best fit) values of $\mathbf{T}_{gd}$ for F922 epoxy were 515.6 K (242.6 °C) and 519.2 K (246.2 °C), respectively.

3.2 HOT/WET CONDITIONED LAMINATES

Unidirectional and cross-ply laminate specimens were conditioned at 70 °C and 85% RH and then tested under standard laboratory conditions. Batches of specimens were withdrawn at selected intervals over a period of 6 or 12 weeks and then tested within an hour of removal from the conditioning environment. Tensile specimens were loaded at a constant displacement rate of 2 mm/min using an Instron 8501 servo-hydraulic test machine fitted with servo-hydraulic grips. Data collection and analysis was identical to that employed for the bulk resin tensile specimens. Tests were conducted on at least 5 specimens per condition. Traveller specimens accompanying the test specimens were used to monitor moisture content.

Travellers are required to monitor specimen moisture content throughout the environmental history (i.e. manufacture, storage, pre-conditioning and testing). Traveller specimens should have identical material properties, geometry and processing history as the test specimen. It is essential that moisture content prior to pre-conditioning be established. Prior to environmental conditioning, test specimens and travellers were pre-dried in an oven maintained at 50 ± 2 °C until specimen weight reached a constant value. The process of determining the moisture content within the gauge-length of conditioned specimens is described below:

(i) The end tab regions were removed using a diamond-cutting wheel (**dry cut - no lubrication to be used**).
(ii) The separated gauge-length was then weighed to determine the weight of the conditioned section.
(iii) The gauge-length was dried in an oven (50 ± 2 °C) until specimen weight reached a constant value.

The difference between the weights recorded for (ii) and (iii) is the moisture weight gain due to hot/wet conditioning; **providing there is no loss of material to the surrounding environment.**

3.2.1 Unidirectional Laminates

This section presents the tensile test data for unidirectional laminates that have been subjected to hot/wet conditioning (i.e. 70 °C/85% RH). Tables 3 to 5 show the residual strength and stiffness loss as a function of exposure time (see also Figure 4).

Table 3: Longitudinal Tensile Properties of Hot/Wet Conditioned E-glass/913

Exposure Time (Weeks)	Moisture Content (Weight %)	Tensile Strength (MPa)	Tensile Modulus (GPa)
0	0.00	1215 ± 20	41.1 ± 1.4
1	0.70	1026 ± 24	40.6 ± 0.7
2	0.92	949 ± 101	41.0 ± 1.0
3	1.03	918 ± 63	40.6 ± 0.6
6	1.13	783 ± 95	39.7 ± 0.4

Table 4: Tensile Properties of Hot/Wet Conditioned Unidirectional E-glass/F922

Exposure Time (Weeks)	Moisture Content (Weight %)	Tensile Strength (MPa)	Tensile Modulus (GPa)
Longitudinal			
0	0.00	1087 ± 29	43.0 ± 0.9
1	0.79	983 ± 12	45.6 ± 3.0
2	0.82	806 ± 35	36.2 ± 1.0
3	0.84	782 ± 69	35.9 ± 1.8
6	1.00	797 ± 75	37.2 ± 1.4
12	1.14	763 ± 42	38.2 ± 2.4
Transverse			
0	0.00	58.6 ± 5.1	13.9 ± 1.2
6	0.61	64.1 ± 6.2	14.3 ± 1.5

Table 5: Tensile Properties of Hot/Wet Conditioned Unidirectional HTA/F922

Exposure Time (Weeks)	Moisture Content (Weight %)	Tensile Strength (MPa)	Tensile Modulus (GPa)
Longitudinal			
0	0.00	1684 ± 132	126 ± 5
1	0.83	1661 ± 60	117 ± 3
2	0.84	1589 ± 103	121 ± 2
3	0.87	1768 ± 71	121 ± 3
6	1.06	1728 ± 132	130 ± 4
12	1.24	1615 ± 138	129 ± 10
Transverse			
0	0.00	46.2 ± 9.1	9.9 ± 0.5
6	0.79	48.6 ± 4.9	8.9 ± 0.7

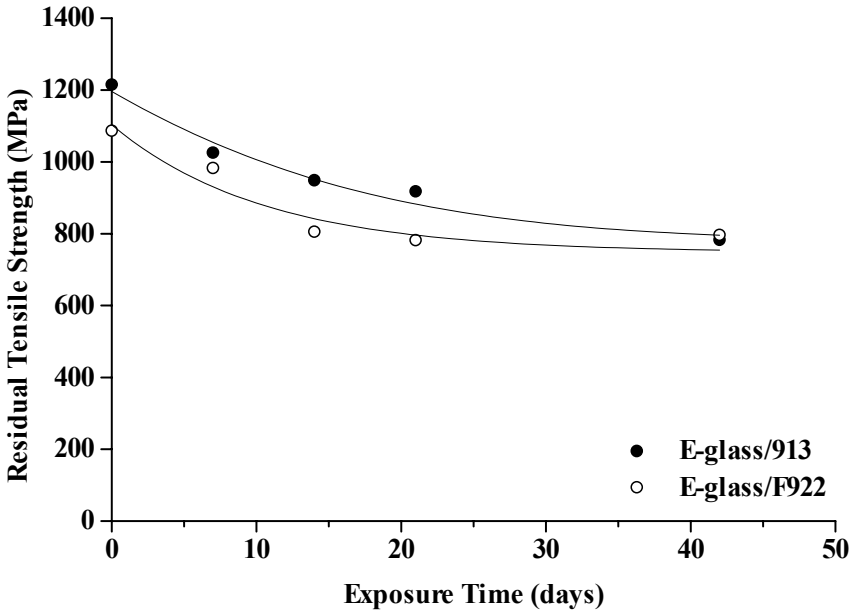

Figure 4: Longitudinal tensile strength of hot/wet conditioned glass/epoxy laminates.

A number of points to note on the tensile behaviour of conditioned unidirectional material tested at room temperature:

- Longitudinal and transverse tensile properties of HTA/F922 carbon/epoxy were unaffected by moisture. **In general, any changes in tensile properties that occur in carbon/epoxy systems through moisture ingress are likely to be due to matrix plasticisation. The loss of mechanical properties is reversible on drying**.

- Longitudinal tensile properties of the glass/epoxy systems decreased with increasing moisture content. The loss of tensile strength can be attributed to the corrosion/leaching of the glass fibre reinforcement rather than matrix or interfacial degradation. After 6 weeks exposure at 70 °C and 85% RH, the longitudinal tensile strength of E-glass/F922 had been reduced from 1087 ± 23 MPa to 797 ± 75 MPa. When dried, the tensile strength of the conditioned material was 960 ± 134 MPa (approximately 88% of the virgin strength of the material). The tensile strength is not fully recoverable.

- There was no deleterious effect on the transverse tensile properties of E-glass/F922 due to the presence of low levels of moisture (i.e. 0.6 wt%). As expected, moisture uptake was slower in the transverse specimens compared with the longitudinal specimens due to the transverse specimens larger size.

- The rate of moisture absorption decreases with increasing fibre content. The higher rate of strength loss observed for E-glass/913 compared with E-glass/F922 can be partially attributed to its higher resin content (see Table 1).

- **Pre-conditioned carbon/epoxy and glass/epoxy laminates do not necessarily have to be tested immediately after hot/wet conditioning. Specimens can be stored in a refrigerator for at least 6 weeks at 5 °C with minimal change in the tensile properties of the degraded composite**. After 6 weeks exposure at 70 °C and 85% RH, the longitudinal tensile strength of E-glass/F922 was 797 ± 75 MPa. Following 6 weeks storage at 5 °C, the tensile strength of the conditioned material was 800 ± 114 MPa.

Figure 5 shows an example of a failed unidirectional glass/epoxy specimen that has been loaded in monotonic tension. The fibrous (or brush-like) appearance of the failure indicates that substantial fibre debonding and fibre pull out have occurred. The sequence of damage development and failure modes observed for the unidirectional glass/epoxy laminates was as follows: (i) fibre breakage; (ii) interfacial and matrix cracking; and (iii) longitudinal splitting, which extends along the entire gauge-length of the specimen. The failure mode remained unaltered with increasing moisture content. In comparison, unidirectional carbon/epoxy specimens disintegrate into brittle splinters (wet or dry).

Figure 5: Typical tensile failure for unidirectional E-glass/913 laminate.

Dynamic mechanical analysis (DMA) measurements were carried out on environmentally conditioned unidirectional E-glass/F922 and HTA/F922 specimens to determine the permanent change in the glass transition temperature, $\mathbf{T_g}$, as a function of moisture content (Table 6). Each specimen was conditioned for a select period of time (either 1, 2, 3 or 6 weeks) at 70 °C and 85% RH and then removed from the hot humid environment and dried to a constant weight. The moisture content (wt %) values given in Table 6 correspond to the maximum moisture uptake in the conditioning environment prior to drying the specimens. The procedure for measuring the glass transition temperature was similar to that employed for the F922 epoxy (see Section 3.1).

Table 6: Permanent Change in T_g for Hot/Wet Conditioned HTA/F922 Carbon/Epoxy

Exposure Time (days)	Moisture Content (Weight %)	Glass Transition Temperature (°C)	
		E-glass/F922	HTA/F922
0	0.00	232.4	219.2
7	0.83	-	235.7
14	0.84	225.3	236.0
21	0.87	232.3	234.4
42	1.24	225.8	239.8

The results in Table 6 show that for the HTA/F922 carbon/epoxy there was a permanent change in $\mathbf{T}_g$ with exposure time. Possible reasons for the increase in $\mathbf{T}_g$ are antiplasticisation of the F922 epoxy due to leaching of uncured monomer from the unmodified epoxy resin system and/or post-curing of the F922 epoxy during conditioning. Although both processes may have occurred in E-glass/F922, there was no evidence to suggest that the glass transition temperature was affected as a result of prolonged exposure to the hot/humid environment. Corrosion/leaching of the glass fibres and hydrolysis at the fibre-matrix interface, resulting in fibre degradation and debonding, probably counteracted the antiplasticisation process.

3.2.2 Residual Strength and Stiffness of Cross-Ply Laminates

This section presents the tensile test data (see Tables 7 to 9) for dry and hot/wet conditioned cross-ply glass/epoxy and carbon/epoxy laminates with different lay-ups. Test conditions, data collection (i.e. strain and load measurements) and data analysis were identical to those employed for tension tests conducted on the unidirectional laminate specimens. The lay-ups tested for each material are shown below:

(i) E-glass/913 ($[0°/90°]_{4S}$)
(ii) E-glass/F922 ($[0°_2/90°_2]_S$, $[0°_2/90°_4]_S$ and $[0°_2/90°_8]_S$)
(iii) HTA/F922 (($[0°_2/90°_2]_S$, $[0°_2/90°_4]_S$, and $[0°_2/90°_6]_S$)

The E-glass/F922 cross-ply laminate $[0°_2/90°_2]_S$ was tested in both the longitudinal and transverse directions (see Table 9). For convenience, the transverse direction in Table 9 is labelled as $[90°_2/0°_2]_S$.

Table 7: Tensile Properties of Hot/Wet Conditioned Cross-Ply E-glass/913

Exposure Time (Weeks)	Moisture Content (Weight %)	Tensile Strength (MPa)	Tensile Modulus (GPa)
0	0.00	545 ± 7	27.7 ± 0.5
1	0.08	498 ± 8	27.1 ± 0.6
2	0.35	503 ± 18	27.1 ± 0.1
3	0.51	492 ± 27	26.5 ± 0.7
6	0.68	476 ± 22	26.5 ± 0.5
12	0.75	469 ± 16	26.1 ± 0.7

Table 8: Tensile Properties of Hot/Wet Conditioned Cross-Ply E-glass/F922 Laminates

Exposure Time (Weeks)	Moisture Content (Weight %)	Tensile Strength (MPa)	Tensile Modulus (GPa)
$\underline{[90_2/0_2]_S}$			
0	0.00	395 ± 23	25.7 ± 1.5
6	0.61	368 ± 14	24.8 ± 1.3
$\underline{[0_2/90_2]_S}$			
0	0.00	486 ± 31	29.4 ± 1.0
6	0.61	340 ± 34	25.3 ± 1.9
$\underline{[0_2/90_4]_S}$			
0	0.00	316 ± 16	26.2 ± 1.2
6	0.79	282 ± 22	26.8 ± 0.8
$\underline{[0_2/90_8]_S}$			
0	0.00	170 ± 6	20.2 ± 0.5
6	0.80	159 ± 19	19.2 ± 0.7

Table 9: Tensile Properties of Hot/Wet Conditioned Cross-Ply HTA/F922 Laminates

Exposure Time (Weeks)	Moisture Content (Weight %)	Tensile Strength (MPa)	Tensile Modulus (GPa)
$[0_2/90_2]_S$			
0	0.00	814 ± 42	64.4 ± 1.3
6	1.02	864 ± 48	66.4 ± 3.0
$[0_2/90_4]_S$			
0	0.00	516 ± 13	46.7 ± 1.0
6	0.98	569 ± 44	47.0 ± 1.1
$[0_2/90_6]_S$			
0	0.00	407 ± 27	37.6 ± 0.8
6	0.86	413 ± 32	38.1 ± 0.8

It is apparent from the results presented in Tables 7 to 9 that the rate of moisture uptake decreases with increasing exposure time, laminate thickness and fibre volume fraction. For example, the fibre volume fractions (see Table 1) for all three cross-ply HTA/F922 laminates were almost identical, and hence the expected trend of decreasing rate of moisture uptake with increasing laminate thickness. This trend, however, was not observed for E-glass/F922. The rate of moisture uptake was higher for the thicker laminates. The higher diffusion rate can be partially attributed to the fact that the fibre volume content was lower for the thicker laminates, particularly the 20 ply thick $[0°_2/90°_8]_S$ laminate, which had a fibre volume fraction of 53.32% compared with 60.73% for the 8 ply thick $[0°_2/90°_2]_S$ laminate.

A number of points worth noting in relation to the tensile behaviour of hot/wet conditioned cross-ply laminates tested at room temperature are as follows:

- Tensile properties of the cross-ply carbon/epoxy laminates were not adversely affected by moisture. In fact, tensile strength was higher for the conditioned laminates. Absorbed moisture produces hygroscopic residual stresses. These stresses partially counteract the deleterious effects that thermal residual stresses (induced during processing) have on the tensile strength properties of individual layers.

- Although there were adverse changes in the tensile strength of the glass/epoxy laminates following hot/wet conditioning, the reduction in strength was small (typically 5 to 15%). Elastic modulus and Poisson's ratio values for the cross-ply glass/epoxy laminates were unaffected by increasing moisture content (Tables 7 and 8).

- For the same moisture content, the strength reduction observed for the glass/epoxy laminates was generally more significant for the unidirectional materials (15.6% for E-glass/913 and 30% for E-glass/F922) compared with the cross-ply laminates. This suggests that the **degradation occurs primarily to the glass fibres and that transverse plies probably protect and support the longitudinal layers**.

- The results suggest that a substantial conditioning period of 6 to 12 months, or more, is required to induce significant changes in the tensile properties of the cross-ply laminates. **Although the environmental conditions used in this study can be considered harsh in comparison to most service conditions, the degradation process was slow. The mechanical and physical properties of the bulk material in larger and more realistic structures should remain unaffected for a considerable period of time in temperature climates, such as those experienced by many European countries.**

3.2.3 Progressive Transverse Cracking of Cross-Ply Laminates

The appearance of transverse cracks in the 90° plies is usually the first visible indication of damage in cross-ply laminates (see Figure 6). Transverse cracking will often cause adverse affects, such as stiffness and strength reduction. An experimental study was carried out to investigate progressive transverse cracking in the 90° plies of dry and hot/wet conditioned cross-ply laminates resulting from monotonic tensile loading. The laminate lay-ups used in the study were identical to those described in Section 3.2.2. This section presents the results of this study in which the transverse crack density, longitudinal modulus and Poisson's ratio were measured as a function of applied stress. Optical techniques and acoustic emission (AE) were used to monitor transverse crack formation.

Laminates were cracked using a step-wise monotonic mechanical loading technique. This method consisted of loading specimens to a specific stress level and then unloading, at which time the resultant crack density and elastic property data were measured. The specimen was then reloaded to a higher stress level and the process was repeated until the applied stress approached the ultimate tensile strength of the material. It was not possible to monitor crack formation optically during constant monotonic loading of the specimens.

Figure 6: Transverse cracking of a cross-ply E-glass/F922 laminate.

In the case of the glass/epoxy specimens, transverse cracks can be directly observed by illuminating the back of the specimen with a light source (Figure 6). This transmission technique, however, cannot be applied to carbon/epoxy and therefore an alternative approach was adopted. This consisted of smoothing the longitudinal edges of the coupon specimen with 1200 grade silicon carbide paper, wiping the surfaces with acetone and then coating the surfaces with a film using an Edding white paint marker. Specimens were left for several hours to dry. The marker pen produces a thick brittle layer that clearly shows crack formation in the cross-ply laminates (see Figure 7). A Vickers optical microscope (x 50 magnification) was used to count the transverse cracks (see Figure 7). This technique however, was not entirely satisfactory. A test conducted on a $[0_2/90_2]_S$ glass/epoxy laminate showed that the number of cracks detected along the specimen edge was slightly less than the number of transverse cracks detected by the transmission technique (see Figure 8). **The transmission technique is a more reliable method for transverse crack density measurements, and hence its preferred use for glass/epoxy laminates.**

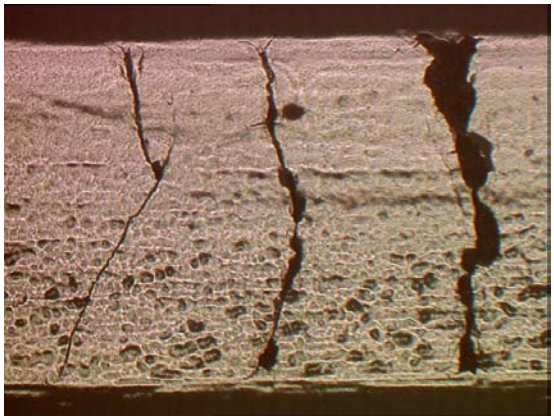

Figure 7: Magnified image of transverse cracks along an edge of a cross-ply laminate.

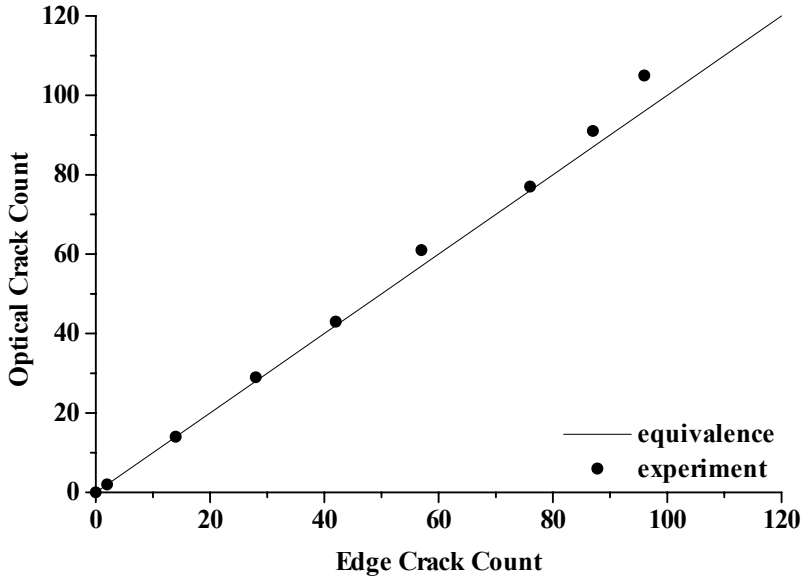

Figure 8: Comparison of edge crack and optical crack counts for $[0_2/90_2]_S$ E-glass/F922.

A MISTRAS AE system (Physical Acoustics Corporation) was also used to monitor the damage progression in the glass/epoxy during testing. **As it was not possible to differentiate between causes of AE events with increasing damage, the technique proved of limited use in detecting transverse cracking.** The results shown in Figures 9 to 11 clearly indicate that the reliability of the technique deteriorates with increasing thickness of the internal 90° plies. **Bifurcation of transverse cracks, which occurred frequently in the thicker laminates, could not be identified using acoustic emission.**

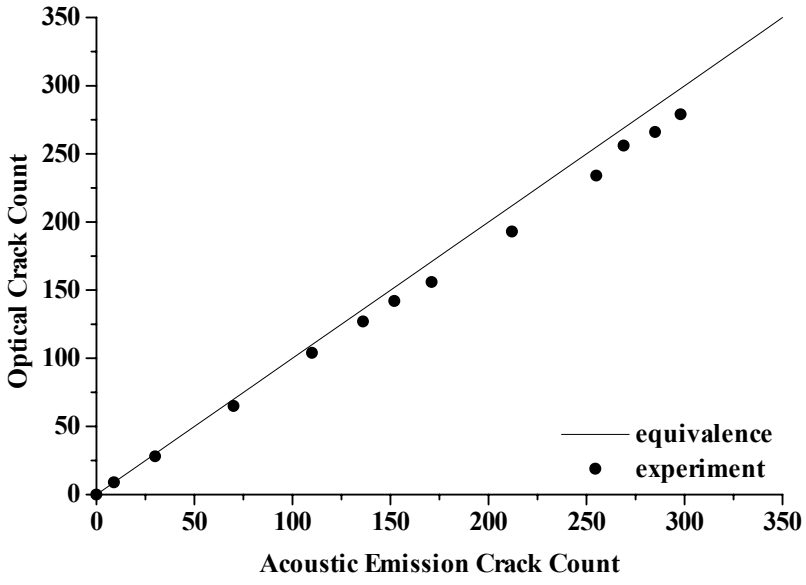

Figure 9: Comparison of optical and AE crack count data for $[0_2/90_2]_S$ E-glass/F922.

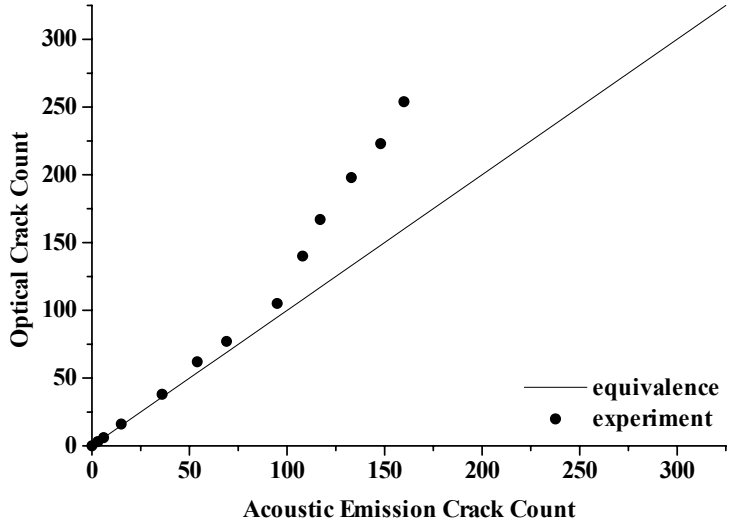

Figure 10: Comparison of optical and AE crack count data for $[0_2/90_4]_S$ E-glass/F922.

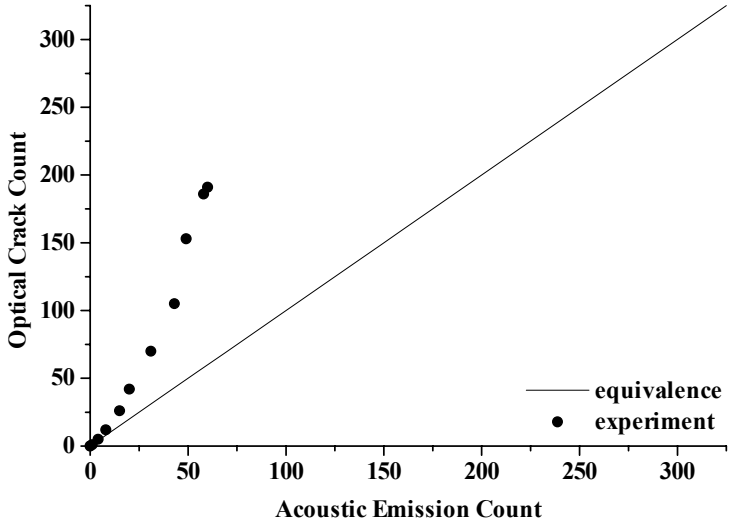

Figure 11: Comparison of optical and AE crack count data for $[0_2/90_8]_S$ E-glass/F922.

A number of points to note in relation to the initiation and accumulation of transverse cracks in E-glass/F922 and HTA/F922 cross-ply laminates (see Table 11, and Figures 12 and 13):

- Onset of transverse cracking (i.e. first ply failure (FPF)), rate of transverse cracking and maximum crack density are dependent on the total thickness of the internal 90° plies. Crack density monitored only to a stress level close to onset of longitudinal splitting in the 0° plies and not to failure. **Increasing the number of 90° plies reduces both the stress level at which first ply failure occurs, rate of transverse cracking and the maximum crack density.**

- **Increasing the stiffness of the fibre reinforcement (i.e. substituting E-glass fibres with HTA carbon fibres whilst maintaining the same-lay-up and fibre content) will increase the FPF stress, increase the rate of transverse cracking and reduce the maximum crack density.**

- Transverse cracking occurred at higher stress levels following exposure to 70 °C and 85% RH for 6 weeks. The effect of absorbed moisture is to decrease the stress experienced by the 90° plies due to the combined effect of hygrothermal and mechanical loading. Also, maximum crack density decreases with moisture uptake.

- There was no indication that crack saturation had occurred in any of the laminate configurations that were tested.

Table 11: Transverse Cracking Data for E-glass/F922 and HTA/F922 Laminates (Dry/6 weeks conditioning at 70 °C and 85% RH)

Material	FPF Stress (MPa)	Tensile Strength (MPa)	Maximum Crack Density (cracks/mm)
E-glass/F922			
$[0_2/90_2]_S$	150/178	486/340	1.90/1.55
$[0_2/90_4]_S$	99/134	316/282	1.75/1.18
$[0_2/90_8]_S$	65/98	170/159	1.27/1.07
HTA/F922			
$[0_2/90_2]_S$	360/399	814/864	1.12/0.87
$[0_2/90_4]_S$	135/267	516/569	0.84/0.79
$[0_2/90_6]_S$	149/189	407/413	0.81/0.77

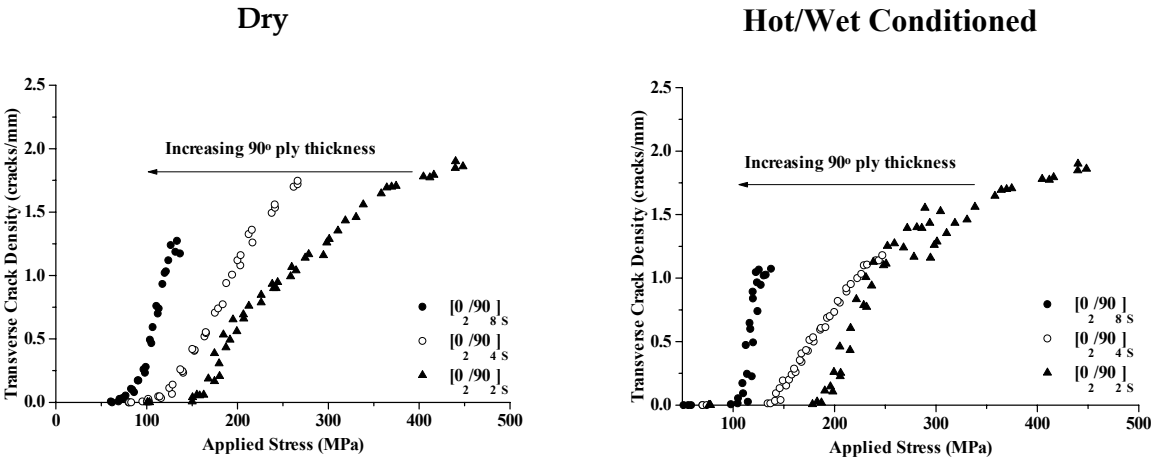

Figure 12: Crack density as a function of applied stress for E-glass/F922 laminates.

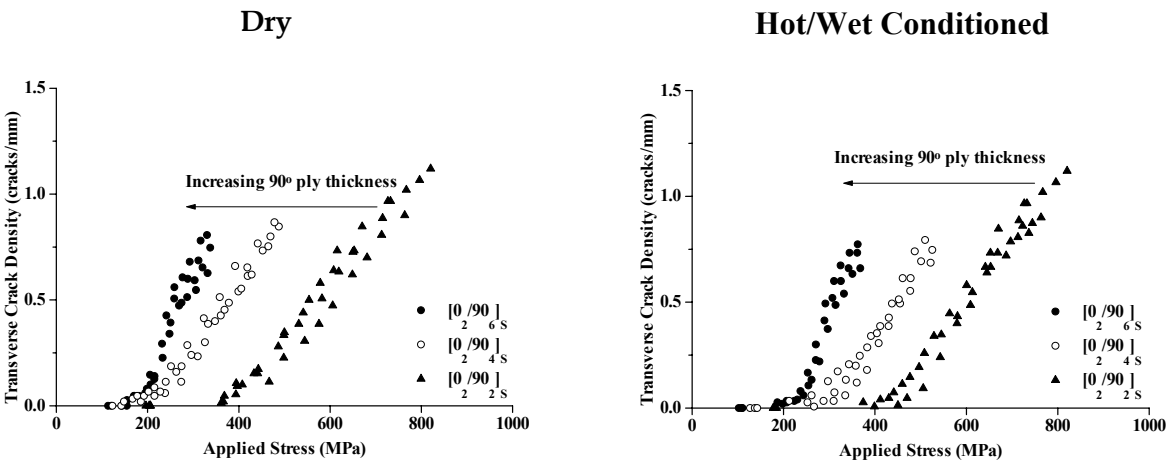

Figure 13: Crack density as a function of applied stress for HTA/F922 laminates.

As previously mentioned, the formation of transverse cracks causes stiffness reduction. Experiments were carried out to determine the effect of progressive transverse cracking on elastic properties of dry and hot/wet conditioned cross-ply E-glass/F922 and HTA/F922 laminates. The results are shown in Table 12, and Figures 14 and 15. Longitudinal stiffness, $\mathbf{E}_{xx}$, and Poisson's ratio, ν_{xy}, values in Figures 14 and 15 are normalised by the undamaged stiffness, $\mathbf{E}_{xxo}$, and Poisson's ratio, ν_{xy}, values.

Table 12: Effect of Transverse Cracking on Elastic Properties of Cross-Ply Laminates (Initial/Final)

Material	Longitudinal Modulus (GPa)		Poisson's Ratio	
	Dry	Conditioned	Dry	Conditioned
E-glass/F922				
$[0_2/90_2]_S$	29.4/23.5	25.3/21.4	0.159/0.084	0.155/0.105
$[0_2/90_4]_S$	26.2/16.1	26.8/16.7	0.134/0.067	0.130/0.060
$[0_2/90_8]_S$	20.2/9.4	19.2/9.5	0.128/0.057	0.119/0.038
HTA/F922				
$[0_2/90_2]_S$	64.4/60.7	66.4/61.0	0.042/0.040	0.042/0.038
$[0_2/90_4]_S$	46.7/41.9	47.0/42.1	0.042/0.027	0.042/0.028
$[0_2/90_6]_S$	37.6/31.8	38.1/31.7	0.039/0.022	0.039/0.021

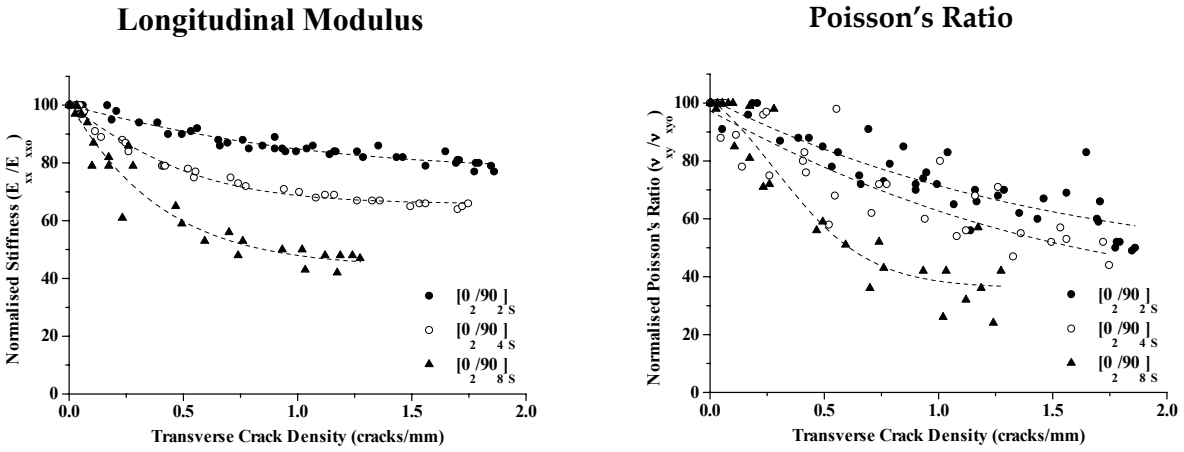

Figure 14: Elastic property reduction in E-glass/F922 laminates. (lines added as a visual aid to show trends)

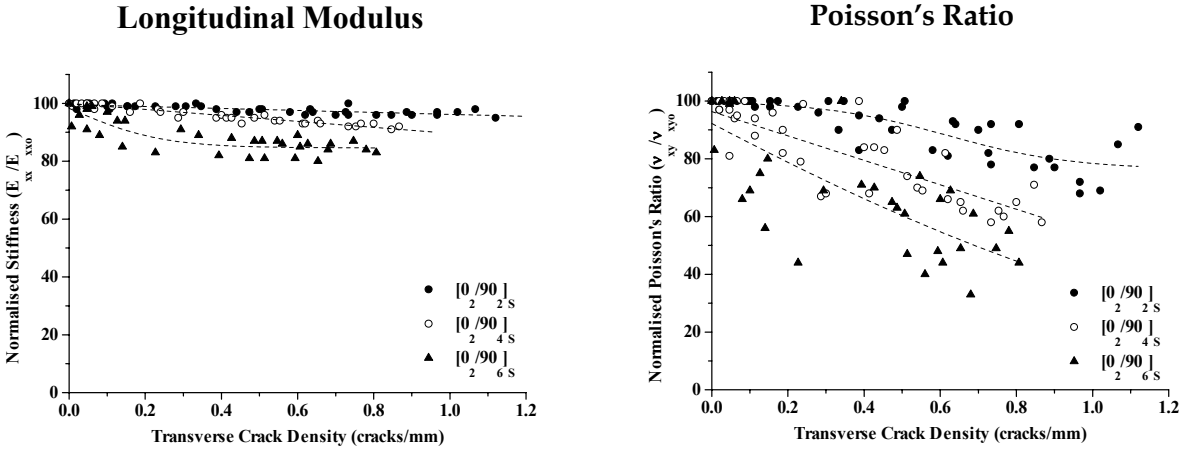

Figure 15: Elastic property reduction in HTA/F922 laminates. (lines added as a visual aid to show trends)

The main observations from the elastic property data are given below:

- **Elastic properties were sensitive to crack formation, particularly Poisson's ratio with the reduction in elastic properties appearing to be directly related to the transverse crack density.** Transverse cracking had a greater effect on the elastic properties of cross-ply glass/epoxy laminates. The combined effect of increased damage and the larger contribution made by 90° plies to the overall laminate stiffness for these materials, compared with equivalent carbon/epoxy laminates, results in a more severe reduction in stiffness for glass/epoxy.

- **Reduction in longitudinal modulus and Poisson's ratio increases with increasing thickness of the internal 90° plies. Although Poisson's ratio is more sensitive to the presence of transverse cracks, the large uncertainty in measurements make it difficult to use this parameter to monitor the level of degradation (see Figures 14 and 15).** Poisson's ratio values are based on very small transverse strain measurements, and hence small fluctuations translate into large errors.

- **Elastic properties were insensitive to moderate levels of moisture (i.e. 0.6-1.0 wt %).**

3.2.4 Predictive Analysis

This section compares the experimental elastic and strength property data with predictive analysis for dry and hot/wet conditioned unidirectional and cross-ply laminates (see Tables 13 and 14). The conditioned specimens have been exposed to 70 °C and 85% RH for 6 weeks. Predicted values were determined using CoDA (Composite Design and Analysis) preliminary design software developed by NPL.

Table 13: Measured and Predicted Tensile Properties for Unidirectional Composites (Measured/Predicted)

Material	Tensile Strength (MPa)	Tensile Modulus (GPa)	Poisson's Ratio
E-glass/913 (dry)			
Longitudinal	1215 ± 20/1178	43.0 ± 0.9/36.6	0.30 ± 0.02/0.33
Transverse	73.1 ± 1.7/56.5	12.5 ± 0.2/10.7	0.094 ± 0.004/0.091
E-glass/F922 (dry)			
Longitudinal	1087 ± 29/1479	43.0 ± 0.9/46.0	0.31 ± 0.01/0.33
Transverse	58.6 ± 5.1/52.9	13.9 ± 1.2/15.4	0.098 ± 0.003/0.102
E-glass/F922 (wet)			
Longitudinal	797 ± 75/1475	37.2 ± 1.4/45.9	0.31 ± 0.01/0.33
Transverse	64.1 ± 6.2/36.5	14.3 ± 1.5/14.5	0.108 ± 0.007/0.096
T300/924 (dry)			
Longitudinal	1723 ± 89/2193	133 ± 2/136	0.34 ± 0.02/0.29
Transverse	92.7 ± 9.1/56.1	8.5 ± 0.2/8.7	0.020 ± 0.003/0.021
HTA/F922 (dry)			
Longitudinal	1684 ± 132/2016	126 ± 5/134	0.32 ± 0.02/0.34
Transverse	46.2 ± 9.1/53.0	9.9 ± 0.5/8.3	0.023 ± 0.003/0.020
HTA/F922 (wet)			
Longitudinal	1728 ± 132/2014	130 ± 4/134	0.33 ± 0.05/0.34
Transverse	48.6 ± 4.9/36.4	8.9 ± 0.7/7.9	0.022 ± 0.007/0.022

Table 14: Strength and Elastic Moduli of E-glass/F222 and HTA/F922 Laminates

Material	First Ply Failure Stress (MPa)		Tensile Strength (MPa)	
	Measured	Predicted	Measured	Predicted
E-glass/F922 (dry)				
$[0_2/90_2]_S$	150	110	486	431
$[0_2/90_4]_S$	99	91	316	253
$[0_2/90_8]_S$	65	76	170	135
E-glass/F922 (wet)				
$[0_2/90_2]_S$	178	80	340	312
$[0_2/90_4]_S$	134	65	282	181
$[0_2/90_8]_S$	98	54	159	98
HTA/F922 (dry)				
$[0_2/90_2]_S$	360	455	814	972
$[0_2/90_4]_S$	135	322	516	649
$[0_2/90_6]_S$	149	255	407	484
HTA/F922 (wet)				
$[0_2/90_2]_S$	399	455	864	972
$[0_2/90_4]_S$	267	322	569	649
$[0_2/90_6]_S$	189	182	413	454
Material	**Initial Modulus (GPa)**		**Final Modulus (GPa)**	
	Measured	Predicted	Measured	Predicted
E-glass/F922 (dry)				
$[0_2/90_2]_S$	29.4	28.6	23.5	22.1
$[0_2/90_4]_S$	26.2	23.1	16.1	14.5
$[0_2/90_8]_S$	20.2	16.8	9.4	8.5
E-glass/F922 (wet)				
$[0_2/90_2]_S$	25.3	28.1	21.4	22.0
$[0_2/90_4]_S$	26.8	22.5	16.7	14.5
$[0_2/90_8]_S$	19.2	16.1	9.5	8.5
HTA/F922 (dry)				
$[0_2/90_2]_S$	64.4	70.2	60.7	66.3
$[0_2/90_4]_S$	46.7	49.8	41.9	44.4
$[0_2/90_6]_S$	37.6	39.1	31.8	32.3
HTA/F922 (wet)				
$[0_2/90_2]_S$	66.4	70.0	61.0	66.2
$[0_2/90_4]_S$	47.0	49.8	42.1	44.4
$[0_2/90_6]_S$	38.1	38.9	31.7	31.8
Material	**Initial Poisson's Ratio**		**Final Poisson's Ratio**	
	Measured	Predicted	Measured	Predicted
E-glass/F922 (dry)				
$[0_2/90_2]_S$	0.159	0.162	0.084	0.084
$[0_2/90_4]_S$	0.134	0.138	0.067	0.047
$[0_2/90_8]_S$	0.128	0.122	0.056	0.027
E-glass/F922 (wet)				
$[0_2/90_2]_S$	0.155	0.154	0.105	0.080
$[0_2/90_4]_S$	0.133	0.130	0.060	0.044
$[0_2/90_8]_S$	0.119	0.115	0.038	0.026
HTA/F922 (dry)				
$[0_2/90_2]_S$	0.042	0.040	0.040	0.019
$[0_2/90_4]_S$	0.042	0.031	0.027	0.010
$[0_2/90_6]_S$	0.041	0.028	0.022	0.007
HTA/F922 (wet)				
$[0_2/90_2]_S$	0.049	0.038	0.038	0.019
$[0_2/90_4]_S$	0.042	0.031	0.028	0.010
$[0_2/90_6]_S$	0.039	0.027	0.021	0.007

In summary, the preliminary design analysis used in CoDA to predict the in-plane laminae (layer) and laminate properties of the unidirectional and cross-ply laminates in tension can be considered satisfactory. As expected, the degree of correlation between the predicted and actual stiffness values are better than that for the strength properties. The degree of correlation between predicted and actual FPF stress could be improved by taking into account hygrothermal residual stresses in the laminate analysis. However, care needs to be exercised when including residual stresses in determining ultimate tensile strength of the laminate as these stresses are considerably diminished after FPF. The large uncertainty associated with Poisson's ratio measurements make it difficult to compare predictive values with experimental results, particularly for the damaged material.

Note. Transverse crack measurement and stiffness loss data will be compared with predictive modelling in future reports. Early indications are that predictions from the plain strain model developed by Dr L N McCartney at NPL are generally in good agreement with the experimental data.

3.3 STEAM AUTOCLAVE CONDITIONING

Longitudinal tensile properties were also measured for steam autoclave conditioned unidirectional E-glass/F922 and HTA/F922 laminates. Specimens were conditioned for periods ranging from 24 to 72 hours at 2.2 bar and 136 °C and then tested under standard laboratory conditions within an hour of removal from the conditioning environment. A Midas 40 bench top autoclave unit, manufactured by Prior Clave Ltd, was used for conditioning the specimens.

The results, shown in Table 15, clearly indicate that moisture saturation is reached within 24 to 48 hours when steam autoclaved with the glass/epoxy absorbing a higher level of moisture. Wicking along the fibre-matrix interface probably contributed to the higher moisture level. The levels of moisture absorbed by the two materials within the 48 hour time period far exceed those recorded after 6 weeks exposure at 70 °C and 85% RH. Tensile properties of the HTA/F922 remain unaltered after 72 hours in the steam autoclave. In contrast, the E-glass/epoxy was highly sensitive to moisture ingress. This material showed a 50% strength loss within 48 hours. No further changes in tensile strength were observed after 48 hours exposure. The loss in strength can be attributed mainly to fibre degradation (i.e. corrosion and leaching). Small blisters were observed on the surface of the glass/epoxy specimens. Tensile modulus was far less sensitive to environmental exposure.

Table 15: Tensile Properties of Hot/Wet Conditioned Unidirectional Laminates

Condition	Moisture Content (wt %)	Tensile Strength (MPa)	Tensile Modulus (GPa)
E-glass/F922			
Dry (unconditioned)	0.00	1087 ± 29	43.0 ± 0.9
70 °C/85% RH (6 weeks)	1.00	763 ± 42	37.2 ± 1.4
Steam autoclave (24 hrs)	2.09	654 ± 22	38.3 ± 1.3
Steam autoclave (48 hrs)	2.94	579 ± 47	38.1 ± 0.8
Steam autoclave (72 hrs)	2.83	585 ± 50	37.6 ± 1.0
HTA/F922			
Dry (unconditioned)	0.00	1684 ± 132	126 ± 5
70 °C/85% RH (6 weeks)	1.06	1728 ± 132	130 ± 4
Steam autoclave (24 hrs)	2.12	1691 ± 91	125 ± 1
Steam autoclave (48 hrs)	1.90	1725 ± 42	128 ± 2
Steam autoclave (72 hrs)	2.20	1784 ± 94	123 ± 9

The results strongly indicate that autoclave conditioning is a viable option for inducing accelerated ageing, particularly for those systems possessing a cure temperature and a glass transition temperature in excess of 120 °C to 140 °C. The technique may prove far too destructive for materials possessing a low Tg value, such as polyester resins. This promising accelerated ageing procedure warrants further consideration.

3.4 CHEMICAL RESISTANCE

Unidirectional E-glass/F922 and HTA/F922 specimens were exposed to either 1 N solution of sulphuric acid, 1 N solution of sodium hydroxide solution or deionised water at 23 °C in an unstressed state for 2 weeks. Immersion in all three liquids results in a substantial reduction in tensile properties of the E-glass/F922 (Table 16), with the sulphuric acid solution having a greater degrading effect than either the deionised water or sodium hydroxide solution. In comparison, HTA/F922 carbon/epoxy shows far superior chemical resistance. Exposure to sodium hydroxide for 2 weeks had no affect on the tensile properties of this material, whilst the reduction in tensile strength after exposure to the acidic solution was relatively small (6.6%). The effect of water immersion on the tensile properties of HTA/F922 carbon/epoxy was not investigated as the tensile properties of this material were unaltered following exposure to 70 °C and 85% RH for longer periods (see Table 4).

Table 16: Chemical Resistance of Unidirectional Laminates

Material	Environment	Tensile Strength (MPa)	Tensile Modulus (GPa)
E-glass/F922	Unconditioned	1087 ± 29	43.0 ± 0.9
	Deionised water	859 ± 59	36.6 ± 8.4
	Sodium hydroxide	875 ± 57	37.8 ± 2.0
	Sulphuric acid	775 ± 59	35.7 ± 1.4
HTA/F922	Unconditioned	1684 ± 132	126 ± 5
	Sodium hydroxide	1670 ± 56	125 ± 3
	Sulphuric acid	1573 ± 61	124 ± 2

Table 17: Permanent Change in T_g for Chemically Aged Unidirectional Laminates

Material	Environment	Tg (°C)
E-glass/F922	Unconditioned	226.8
	Sodium hydroxide	244.6
	Sulphuric acid	249.6
E-glass/913	Unconditioned	176.5
	Sodium hydroxide	170.2
	Sulphuric acid	165.2
HTA/F922	Unconditioned	219.2
	Sodium hydroxide	244.5
	Sulphuric acid	249.2

DMA measurements were also carried out on chemically conditioned material to determine permanent changes in $\mathbf{T_g}$. Specimens were pre-dried to a constant weight at 50 °C, weighed, conditioned and reweighed. Test specimens were weighed prior to DMA tests. The $\mathbf{T_g}$ values of conditioned E-glass/F922 and HTA/F922 after drying were higher than the $\mathbf{T_g}$ measured for unconditioned material, whereas $\mathbf{T_g}$ for E-glass/913 is permanently depressed following conditioning. The reduction in $\mathbf{T_g}$ observed for E-glass/913 can be attributed to a permanent loss in stiffness of the epoxy matrix.

A probable cause for the increase in $\mathbf{T_g}$ observed for the E-glass/F922 and HTA/F922 systems is antiplasticisation of the F922 epoxy through leaching of uncured monomer from the unmodified epoxy resin.

Changes in colour and gloss were also evident in the glass and carbon fibre-reinforced composite laminates. Pigment change was most noticeable for those specimens that had been immersed in the sulphuric acid solution. The predominantly orange E-glass/F922 specimens were tinged green as a result of chemical reactions between the sulphuric acid the glass fibres and the epoxy resin. The colour change of E-glass/913 was more dramatic with the colour of the conditioned specimens being black with an aquamarine hue. **Changes in colour have been used in previous studies (see [11]) as an indicator of degradation of the composite substrate, although colour transformation may be misleading as to changes in mechanical properties.**

The results from this programme and from published literature clearly show that the chemical resistance of epoxy resin systems to acid and alkali solutions depends on the resin chemistry. Chemical resistance of each epoxy system differs for each chemical reagent, and it is not possible to generalise about the chemical resistance of epoxy or any other thermosetting resin system (e.g. polyester or vinyl ester) (see Chapter 3 [11]). It is therefore necessary to evaluate each composite system individually. The results presented in this section, however, demonstrate that it is possible to use the standard specimen geometry prescribed in ISO 527-5 to quantify and rank the chemical resistance of composite systems to different chemical reagents. This can often be achieved within 6 to 12 weeks. **Care is needed to ensure the end tabs remain bonded to the test specimen throughout the conditioning and testing phases of the trials.**

The rate of degradation is dependent on the absorption rate and on the amount of chemical agent absorbed. Large structures are more resistant to environmental attack with equivalent changes in mechanical and physical properties of the composite substrate requiring far longer exposure times compared with coupon specimens. In large structures, chemical deterioration may take many decades to occur, whereas for coupon specimens these changes can be induced in weeks using accelerated testing methods. **It is therefore essential to take account of the rate of diffusion of the chemical agent into the material in order to extrapolate laboratory data from accelerated tests to actual structures. The use of laboratory data obtained from accelerated tests on coupon specimens tends to result in conservative design practices. It would be preferable to use larger test pieces or actual components and to condition these materials for 12 months, or longer, under milder and more realistic conditions than those generally employed to accelerate degradation.**

4. FLEXURE

4.1 HYGROTHERMAL EFFECTS

Four-point flexure tests were carried out on unconditioned and moisture conditioned longitudinal and transverse flexure specimens that were cut from 2 mm thick unidirectional E-glass/913 and T300/924 laminates (see also Section 2.3.2). The flexural properties were measured at five temperatures (23 °C, 50 °C, 100 °C, 150 °C and 200 °C). Specimens were tested in an environmental chamber attached to an Instron 4507 screw-driven test machine. Temperatures were allowed to stabilise for 5 to 10 minutes prior to testing. Instron Series IX software was used to control the test machine and record load and strain during the tests. A 20 kN load cell was used to monitor load.

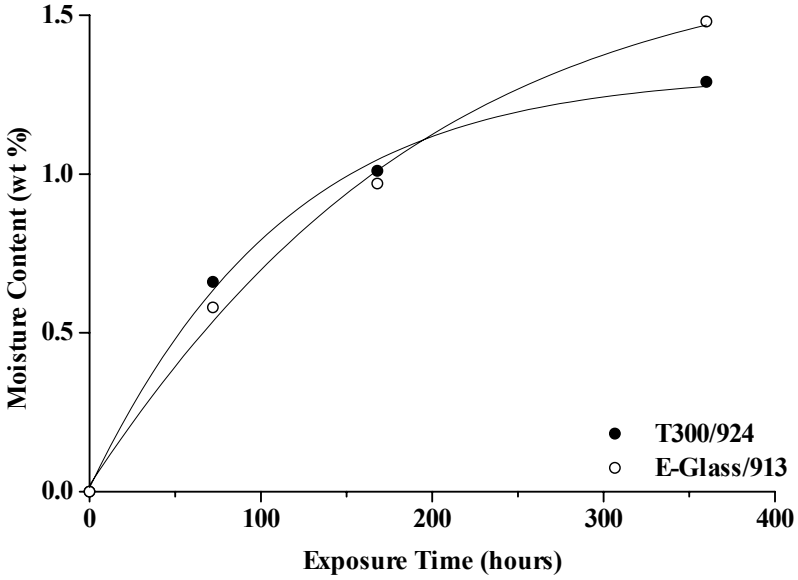

Figure 16: Moisture absorption of longitudinal E-glass/913 and T300/924 specimens.

The flexure specimens were conditioned by immersion in deionised water at a temperature of 60 °C. Specimens were withdrawn at selected intervals over a period of 15 days. Five specimens were tested at each temperature after 0, 3, 7 and 15 days exposure. The moisture content (wt %) was monitored using travellers (Figure 16) [8]. DMA measurements were carried out on dry and conditioned specimens to determine the change in $\mathbf{T}_g$ as a function of moisture content (Figure 17). These results, presented in Figure 18, clearly show that moisture reduces the glass transition temperature with the shift in temperature being related to moisture content by Equation (1). The temperature shift, **g**, is 36.8 K and 28.9 K for T300/924 and E-glass/913, respectively. The corresponding transition temperatures for the unconditioned materials were 430 K (157 °C) and 482 K (209 °C).

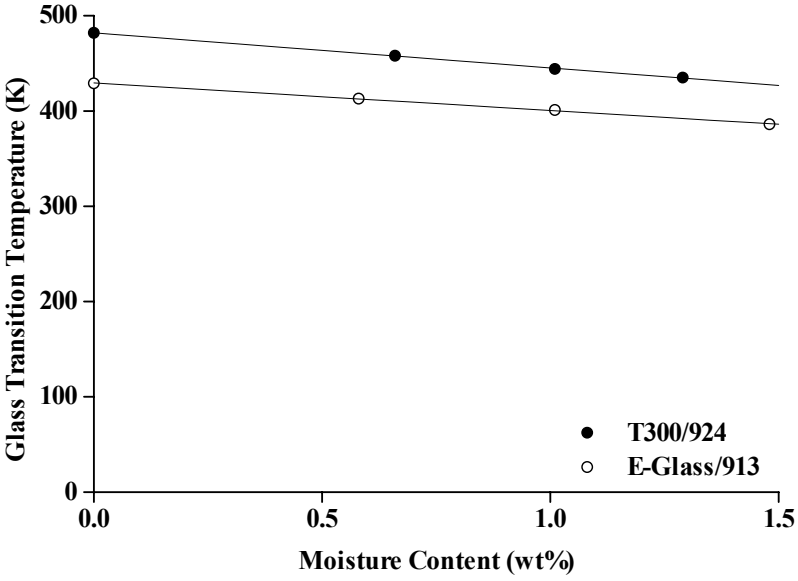

Figure 17: Glass transition temperature for hot/wet conditioned E-glass/913 and T300/924.

Two different values of glass transition temperature were obtained for two different batches of E-glass/913 (see also Table 17) using DMA. The differences can be attributed to differences in: (i) thermal analysis equipment used; (ii) temperature ramp rates; and (iii) techniques of data handling and analysis.

The transverse and longitudinal flexure results for the two composites are presented as a set of graphs (Figures A1 to A4) in the Appendix of this report. The following observations can be made in relation to flexure and moisture absorption results.

- $\mathbf{T_g}$ for both of the epoxy based composites decreases linearly with moisture content. The rate of decrease is approximately 29 °C/wt% for E-glass/913 and 37 °C/wt% for T300/924.

- Rate of moisture absorption was higher for the E-glass/913 laminate (Figure 16). A contributing factor was the higher resin content present within the composite.

- At elevated temperatures the adverse effect of moisture on the flexural properties is exacerbated. A synergism exists between moisture content and temperature.

- Transverse flexural properties are particularly sensitive to changes in moisture content.

- Flexural properties of E-glass/913 are more sensitive to changes in moisture and temperature in comparison with T300/924. This is understandable as the $\mathbf{T_g}$ for unconditioned (i.e. dry) E-glass/913 and T300/924 is 156 °C (429 K) and 209 °C (482 K), respectively.

- **Transverse flexure tests offer a rapid and economic method of assessing environmental degradation. Tests can be carried out under combined environment and applied loading (static and fatigue) conditions.**

4.2 PREDICTIVE ANALYSIS

At present, there are no physics/mechanistic-based theories, which can be used to predict changes in mechanical properties of composite materials caused by environmental exposure. Predictive models tend to be non-mechanistic or empirical in nature (i.e. curve fitting to experimental data). A number of semi-empirical models (both linear and logarithmic) have been suggested [12-16]. These models need experimental data in order to determine the effects of temperature and moisture on the mechanical properties. This section will examine two mathematical relationships used for predicting strength and strength reduction due to hygrothermal ageing: (i) non-dimensional temperature function [13]; and (ii) Kitagawa power-law relationship [14-16]. The two relationships will be used to estimate the longitudinal and transverse flexural properties of unidirectional T300/924 and E-glass/913 for a range of temperatures and moisture contents.

4.2.1 Non-Dimensional Temperature, T*

Constituent (e.g. matrix) stiffness and strength properties can be approximated by the following power-law relationship [12]:

$$\frac{P}{P_o} = \left(\frac{T_g - T}{T_g - T_o} \right)^n \qquad (2)$$

where **P** denotes a material property (e.g. longitudinal tensile strength) at the test temperature **T** (in K), $\mathbf{P_o}$ is the initial property value of the dry material measured at room or reference temperature $\mathbf{T_o}$ (296 K), and $\mathbf{T_g}$ is the glass transition temperature of the material (dry or conditioned). The relationship will only provide a rational solution when $\mathbf{T_g > T}$ and $\mathbf{T_g > T_o}$. The exponent **n** is a constant, which is empirically derived from experimental data. The bracketed term in Equation (2) is the non-dimensional temperature function, **T***.

Chamis et.al [12] suggested a similar relationship to that given in Equation (2). The difference being that the relationship accounts for differences in glass transition temperature between dry and conditioned (i.e. wet) material. According to the authors, strength and stiffness property reduction due to hygrothermal ageing can be approximated using the following simple algebraic relationship [12]:

$$\frac{P}{P_o} = \left(\frac{T_{gw} - T}{T_{gd} - T_o} \right)^n \tag{3}$$

where $\mathbf{T_{gd}}$ and $\mathbf{T_{gw}}$ are the glass transition temperatures of dry and conditioned material. The exponent **n** has a value of 0.5. The above equation results in conservative strength values. This relationship will only provide a rational solution when $\mathbf{T_{gw} > T}$ and $\mathbf{T_{gd} > T_o}$.

The matrix and fibre strength and stiffness properties determined using Equations (2) or (3) when incorporated into micromechanics formulas, such as the Halpin-Tsai equations for in-plane transverse and shear moduli, can be used to derive ply stiffness and strength properties. **An increase in moisture content may cause either an increase or decrease in the properties**. Hygrothermal effects on the flexure properties of the two composite systems were estimated using Equation (3). The empirical formula was applied directly to E-glass/913 and T300/924 flexure data. No attempt was made to predict ply properties using measured properties of hygrothermally aged matrix materials. **It is extremely difficult, if not impossible, to produce void free resin samples from 913 and 924 epoxy.**

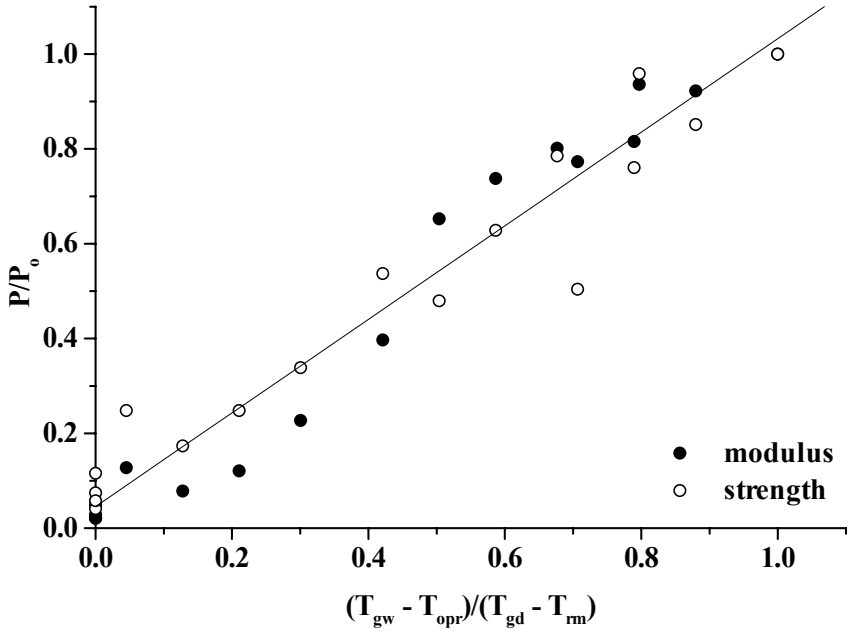

Figure 18: Transverse flexure properties of unidirectional E-glass/913.

Equation (3) was found to be applicable to the transverse flexure data (strength and modulus) for both composite systems. The exponent **n** was estimated to have a value of 1 for E-glass/913 and a value of 0.5 for T300/924. Figure 18 shows a plot of normalised transverse flexure properties of hygrothermally aged E-glass/913 as a function of non-dimensional temperature. The straight line in Figure 18 is a linear regression best fit to all the modulus and strength data, which was obtained at four moisture levels (i.e. 0.0 to 1.48 wt %). The glass transition temperature for the two composite materials, dry or conditioned (i.e. wet), can be determined using Equation (1).

The good agreement between predicted and measured transverse flexure properties is understandable as the power-law formula was originally intended for use in estimating hygrothermally-degraded properties of the resin matrix. Transverse flexural properties are matrix dominated, provided the integrity of the fibre-matrix interface is not compromised.

The non-dimensional temperature approach was also applied to some of the longitudinal flexure data. The results were inconsistent, however, with the value of the exponent **n** being different for the stiffness and strength data. Fibre dominated properties are less sensitive to changes in matrix properties, and hence there is poorer agreement between experimental data and estimates made using the non-dimensional temperature function.

4.2.2 Kitagawa Power-Law Relationship

A model to predict the yield behaviour of glassy polymers was developed by Bowden and co-workers [13]. Kitagawa [14] expanded and generalised the model showing that the relationship between shear yield stress, τ, and shear modulus, **G**, for glassy polymers can be represented by a power law relation of the form:

$$\frac{T_o\tau}{T\tau_o} = \left(\frac{T_oG}{TG_o}\right)^n \qquad (4)$$

where T_o is the reference temperature (in K), τ, and G_o are, respectively, the shear yield stress and the shear modulus at T_o, and the exponent **n** is a constant. The reference temperature T_o is frequently taken as room temperature. The values of log ($T_o\tau/T\tau_o$) are plotted against those of log (T_oG/TG_o), such that the exponent **n** is the gradient of the linear regression best fit through the log-log data. Broughton [15] and Padmanabhan [16] demonstrated that Equation (4) could also be applied to unidirectional carbon/epoxy and glass/epoxy composites.

Figures 19 and 20 show that Kitagawa's power-law relationship can also be used to relate the stiffness and strength data from flexural tests performed on hygrothermally aged unidirectional glass/epoxy and carbon/epoxy composite materials. The relationship can be rewritten in the form:

$$\frac{T_o\sigma_f}{T\sigma_{fo}} = \left(\frac{T_oE_f}{TE_{fo}}\right)^n \qquad (5)$$

where σ_f is the ultimate flexural strength, E_f is the flexural modulus and the subscript **o** relates to the reference condition. Master curves can be fitted to both the transverse flexure and longitudinal flexure data. The slope **n** has a value of 0.52 and 1.35 for the longitudinal and transverse flexure data, respectively.

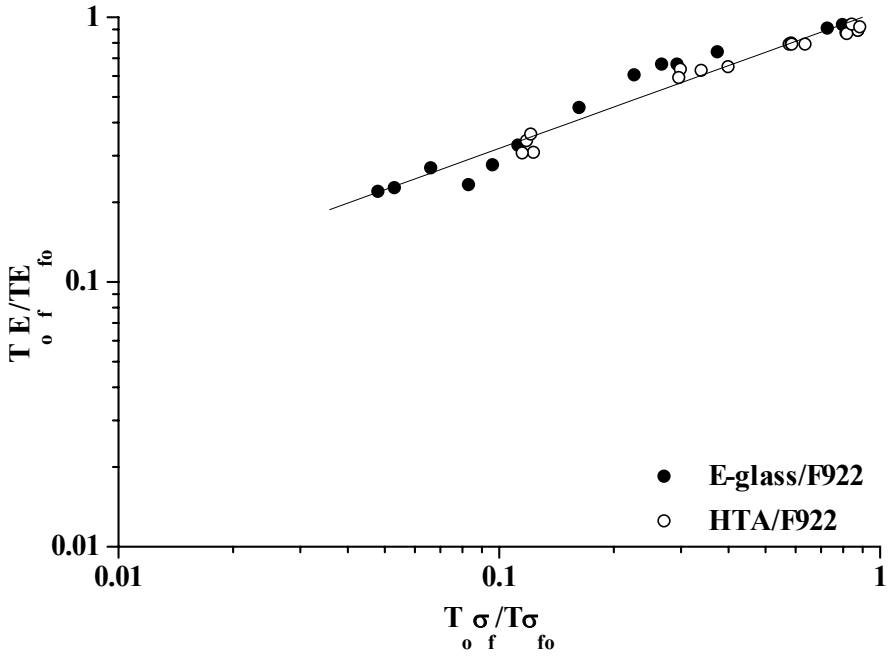

Figure 19: Kitagawa's power-law relationship for longitudinal flexure data.

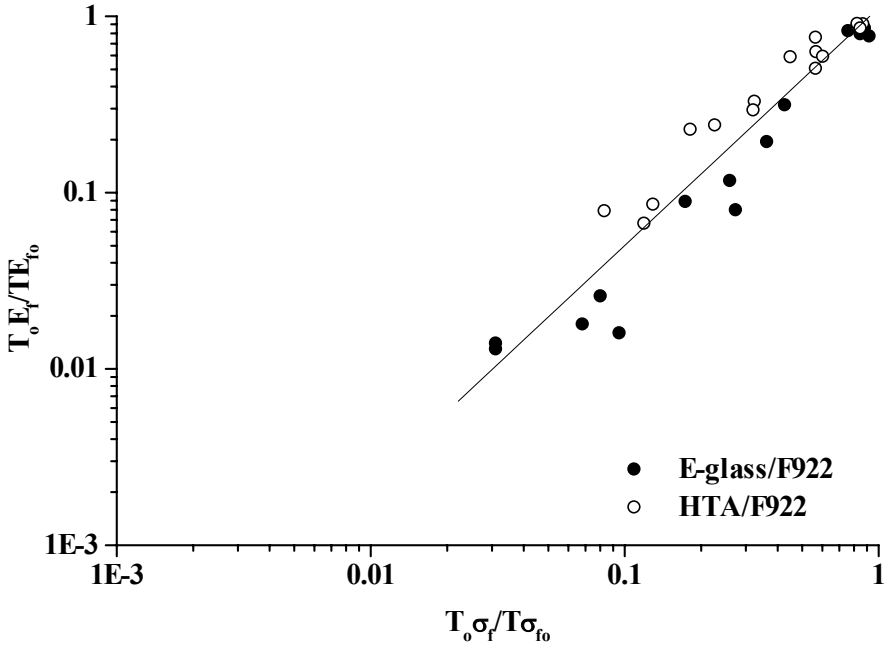

Figure 20: Kitagawa's power-law relationship for transverse flexure data.

4.3 STEAM AUTOCLAVE CONDITIONING

Flexural properties have also been measured for steam autoclave conditioned cross-ply (i.e. 0°/90°) T300/924 carbon/epoxy. Three-point flexure tests were carried out on dry and conditioned specimens under standard laboratory conditions according to BS EN ISO 14125. The flexure tests were simply trials to ascertain the effectiveness of using a steam autoclave to accelerate ageing. Specimens were exposed to the following high temperature and pressure conditions for periods ranging from 6 to 12 hours: (i) 1.05 bar and 121 °C; and (ii) 2.6 bar and 137 °C. The results of the tests are shown in Table 17. The specimens were conditioned in a commercial autoclave unit by LTE Scientific Ltd.

Table 17: Flexural Properties of Autoclaved Conditioned Cross-Ply T300/924

Condition	Moisture Content (%)	Flexural Modulus (GPa)	Flexural Strength (MPa)
Dry	0.19 ± 0.01	92.5 ± 1.1	1332 ± 78
121 °C/1.05 bar/6 hrs	1.10 ± 0.02	90.9 ± 1.1	1,275 ± 73
121 °C/1.05 bar/12 hrs	1.43 ± 0.01	90.0 ± 0.9	1,198 ±97
137 °C/2.60 bar/12 hrs	2.19 ± 0.06	88.9 ± 0.9	1,223 ± 21

The results in Table 17 show that moisture uptake in 12 hours was approximately 2 wt%. The corresponding reduction in $\mathbf{T_g}$ was at least 52 °C. This is equivalent to immersing the specimens in water at 60 °C for approximately 1 to 2 months. Larger coupon specimens would take 3 to 4 months and real structures 1 to 2 years to condition using current procedures. The effect of 12 hours conditioning at 2.6 bar and 137 °C on the cross-ply T300/924 laminate was minimal. Under similar conditions, transverse tensile strength of unidirectional T300/924 had been reduced by 25% within 24 hours.

5. STATIC FATIGUE

This section presents the results from static fatigue (creep rupture) tests that were carried out on unidirectional and cross-ply laminates. The test results presented in this report are confined to ambient conditions only. A limited number of tests are being conducted to evaluate the combined effect of environment and applied static tensile stress. Tests on unconditioned coupon specimens were carried out using an Instron 8501 servo-hydraulic test machine fitted with servo-hydraulic grips. Instron Series IX software was used to control the servo-hydraulic test machine and to collect the test data. Tests were conducted under standard laboratory conditions. Strength-time data was obtained for a number of stress levels with one specimen tested per level.

Note: Basic strength-time data can be obtained by conducting dead weight loading tests or using self-stressing fixtures, such as those employed within the CPD2 project for testing fibre bundles and composite rods [17]. Figure 21 shows the long-term environmental fatigue apparatus used for testing fibre strands and composite rods in fluid environments (e.g. water). For short duration tests (i.e. static loads close to the maximum load at failure) load relaxation occurs and it is therefore necessary to continuously manually adjust the screw jack on self-stressing creep frames in order to maintain a constant load. The use of servo-hydraulic controls avoids this problem. Manually operated systems are best suited to long-term testing where loads are relatively low and load relaxation is minimal.

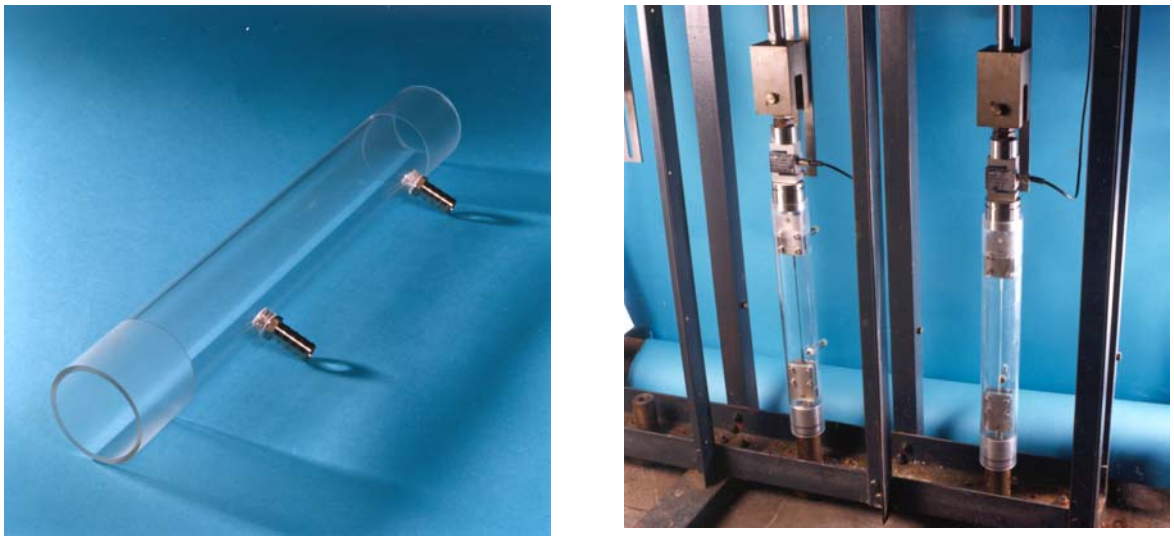

Figure 21: Long-term environmental fatigue apparatus.

The normalised stress rupture data for the unidirectional and cross-ply glass/epoxy laminates when plotted on linear-log plots (Figures 22 to 24) form a sigmoidal or S-shape curve. The unidirectional E-glass/F922 specimens (Figure 22) are capable of sustaining a static load equivalent to 50% UTS under ambient conditions for at least 4 months.

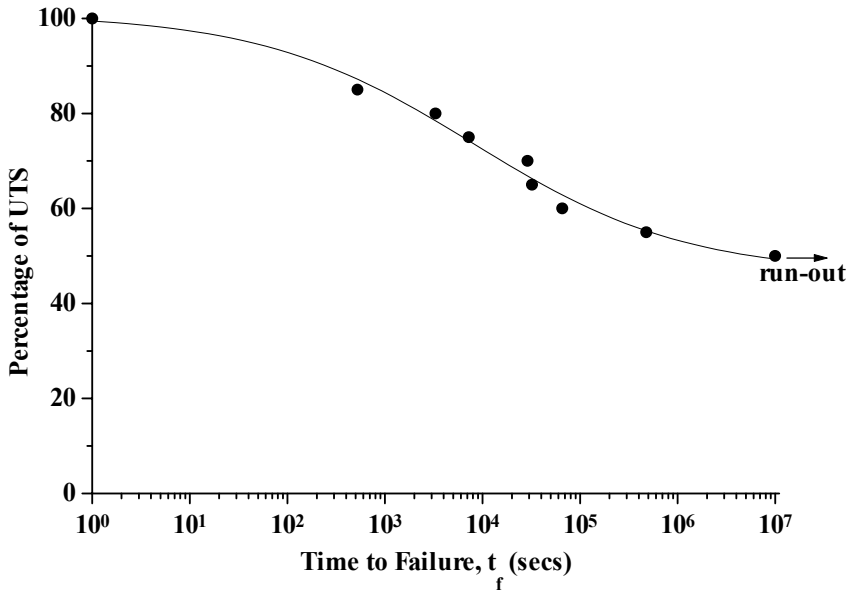

Figure 22: Stress rupture of unconditioned unidirectional E-glass/F922 in air.

The linear-log plots (Figures 22 and 23) of the normalised stress rupture data for the unidirectional and cross-ply glass/epoxy laminates form essentially "S" shaped (i.e. sigmoidal) curves. Aveston and Sillwood [18] obtained similar shaped curves for the stress rupture of unidirectional glass fibre-reinforced laminates subjected to tensile loads whilst immersed in either distilled water or 1 N sulphuric acid solution. The unidirectional E-glass/F922 specimens (Figure 22) displayed a capability of sustaining a static load equivalent to 50% UTS (ultimate tensile strength) for at least 4 months. The strength-time data for the cross-ply E-glass/913 laminate (Figure 23) indicates that this system may also have similar load bearing capabilities.

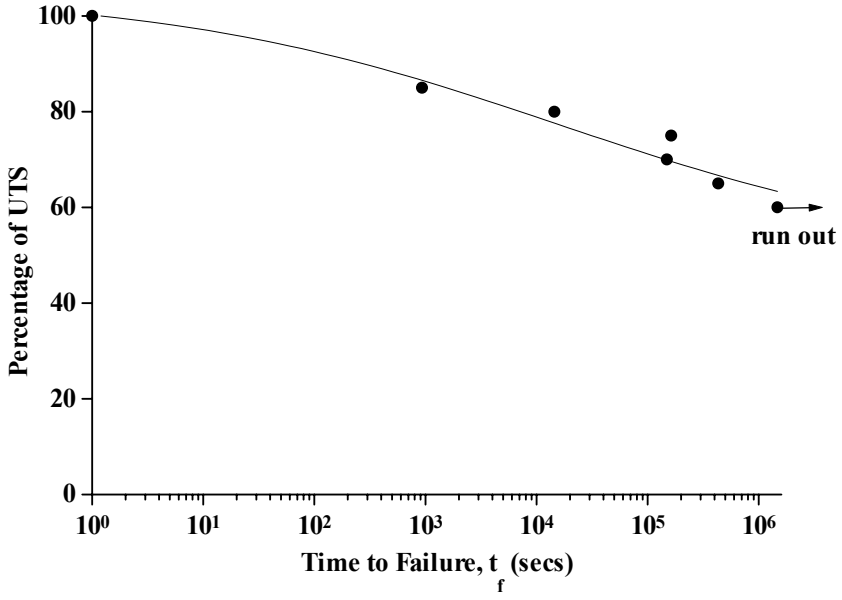

Figure 23: Stress rupture of unconditioned cross-ply E-glass/913 in air.

Tests were also conducted on narrow (3 mm wide) unidirectional specimens in order to assess the suitability of using narrow specimens for accelerated ageing in hostile environments. The normalised stress rupture curve (Figure 24) for 3 mm wide E-glass/F922 specimens when plotted on a linear-log plot can be approximated by the linear relationship:

$$\sigma_{APP} / \sigma_{UTS} = 1 - k \log t_f \qquad (6)$$

where σ_{APP} is the applied load (or stress), σ_{UTS} is the maximum short-term strength of the unconditioned material, **k** is the slope and t_f is time to failure. The value of **k** is 0.09.

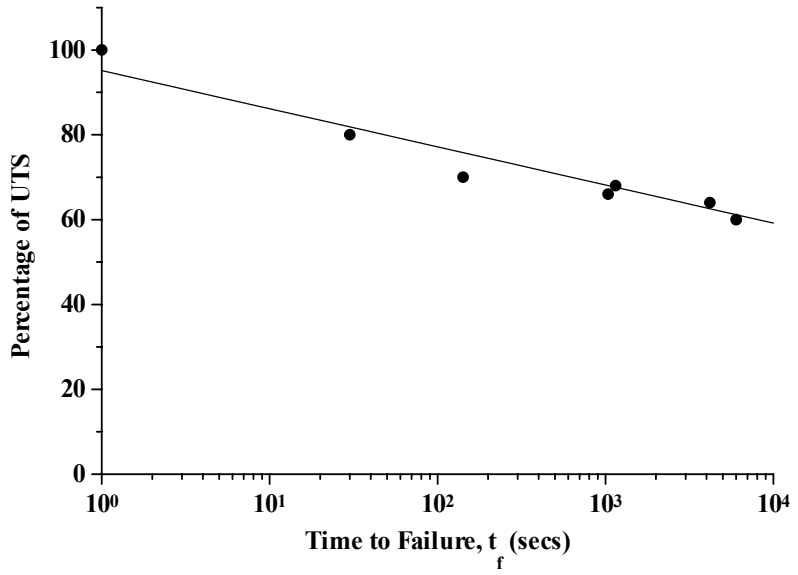

Figure 24: Stress rupture of 3 mm wide unidirectional E-glass/F922 in air.

It can be seen by comparing the results for narrow (Figure 24) and standard (Figure 22) unidirectional E-glass/F922 specimens that the narrow specimens are less robust (i.e. failure time for an equivalent stress level is less). Efforts were made to minimise the possibility of machine-induced damage at the specimen edges from affecting the strength results; particularly for the narrow strips. Although the narrow specimens were cut oversized and then polished to the final width, damage generally initiated at the edges. **The results from the 3 mm wide E-glass/F922 strips cannot be extrapolated to larger coupon specimens.**

The reduction in time to failure observed for the 3 mm wide unidirectional E-glass/F922 specimens may be attributed to a number of factors including:

(i) A higher moisture content in the 3mm wide specimens compared with the wider specimens for the same exposure time;

(ii) Edge effects (including damage through machining) are larger for the narrow specimens; and

(iii) The limited ability of smaller specimens to redistribute load as a result of fibre breakage and matrix and interfacial cracking.

Failure was non-progressive (i.e. catastrophic) with failure consistently occurring within the gauge-length, although often near the end tabs. There was little indication on the load-displacement response that failure was imminent.

6. DISCUSSION AND CONCLUSIONS

Test methods and environmental conditioning procedures have been evaluated with a view to determining the suitability of the techniques for obtaining basic strength-time data for unidirectional and cross-ply glass/epoxy and carbon/epoxy laminates. The principal conclusions that can be drawn from the results are:

Tensile Test Methods/Standards

- Test geometries as specified in the international standards ISO 527-4 and ISO 527-5 are suitable for assessing environmental conditioning (e.g. hot/wet, sulphuric acid and sodium hydroxide solutions) and/or static loads on tensile properties.

Environmental Conditioning Techniques

- Although the hot/wet conditions (excluding the steam autoclave) used in this study can be considered harsh in comparison to most service conditions, the degradation process was slow. The mechanical and physical properties of the bulk material in larger and more realistic structures should remain unaffected for a considerable period of time (e.g. 10-15 years) in temperate climates, such as those experienced by many European countries.

- Steam autoclave conditioning can accelerate moisture absorption by a factor of 100 (or more) and is suitable for use with materials designed for hot/wet conditions. Conservative strength and stiffness values are obtained using this approach.

- Moisture conditioned carbon/epoxy and glass/epoxy can be stored in a refrigerator for at least 6 weeks at 5 °C with minimal effect on the composite's tensile properties.

Flexure

- Transverse flexural properties are particularly sensitive to the combined effect of moisture and elevated temperature. Transverse flexure tests offer a rapid and economic method of assessing environmental degradation.

Environmental Effects

- The tensile properties of the T300/924 and HTA/F922 carbon/epoxy laminates were insensitive to environmental attack from water immersion, steam, and sulphuric acid and sodium hydroxide solutions.

- Glass/epoxy laminates undergo irreversible degradation in hostile environments. Longitudinal tensile strength is substantially reduced when exposed to steam, sulphuric acid or sodium hydroxide solutions.

- Generally, moderate levels of moisture (i.e. 0.6 –1.0 wt %) had a minimal effect on the elastic properties of the glass/epoxy and carbon/epoxy laminates.

Progressive Transverse Cracking in Cross-Ply Laminates

- The transmission optical technique proved the most reliable method for monitoring progressive transverse cracking in cross-ply glass/epoxy. The number of transverse cracks observed using the edge crack measurement technique was 5-10% less than that observed using the transmission technique. X-ray diffraction techniques may prove more suitable for measuring transverse cracks in carbon/epoxy laminates.

- Acoustic emission (AE) proved unsatisfactory for counting transverse cracks, particularly for glass/epoxy laminates. In most cases, it proved impossible to differentiate the cause of the AE events. Limited success was achieved with $[0_2/90_2]_S$ glass/epoxy laminate.

- Increasing the number of 90° plies reduces the stress level at which the first ply failure occurs and the maximum crack density.

- Elastic properties (particularly Poisson's ratio) of cross-ply laminates were sensitive to progressive transverse cracking with the reduction in elastic properties appearing to be directly related to the transverse crack density. The large uncertainty associated with Poisson's ratio measurements make it difficult to accurately monitor progressive damage using this parameter.

- Transverse cracking had a greater effect on the elastic properties of cross-ply glass/epoxy laminates. The combined effect of increased damage (see Figure 26) and the larger contribution made by 90° plies to the overall laminate stiffness for these materials, compared with equivalent carbon/epoxy laminates, results in a more severe reduction in stiffness for glass/epoxy.

- Transverse cracking in the cross-ply laminates occurred at higher stress levels following hot/wet conditioning at 70 °C and 85% RH. Absorbed moisture produces hygroscopic residual stresses. These stresses partially counteract the deleterious effects

that thermal residual stresses (induced during processing) have on the tensile strength properties of the individual layers.

Predictive Modelling

- The preliminary design analysis used proved satisfactory for predicting tensile strength and stiffness properties of unidirectional and cross-ply glass/epoxy and carbon/epoxy laminates. It was possible to predict the stiffness before and after transverse cracking in the cross-ply laminates.

- Simplistic empirical models can be used to determine the flexural properties as a function of temperature and moisture content of hot/wet aged composite materials.

- The normalised stress rupture curves for unidirectional and cross-ply glass/epoxy laminates were essentially "S" shaped (i.e. sigmoidal). A best-fit straight line could be used as a first "approximation".

- Due to edge effects, the results from the 3 mm wide E-glass/F922 strips cannot be extrapolated to larger coupon specimens. The normalised stress rupture curve for this specimen type when plotted on a linear-log plot can be approximated by a straight line (Equation (5)):

$$\sigma_{APP} / \sigma_{UTS} = 1 - k \log t_f$$

ACKNOWLEDGEMENTS

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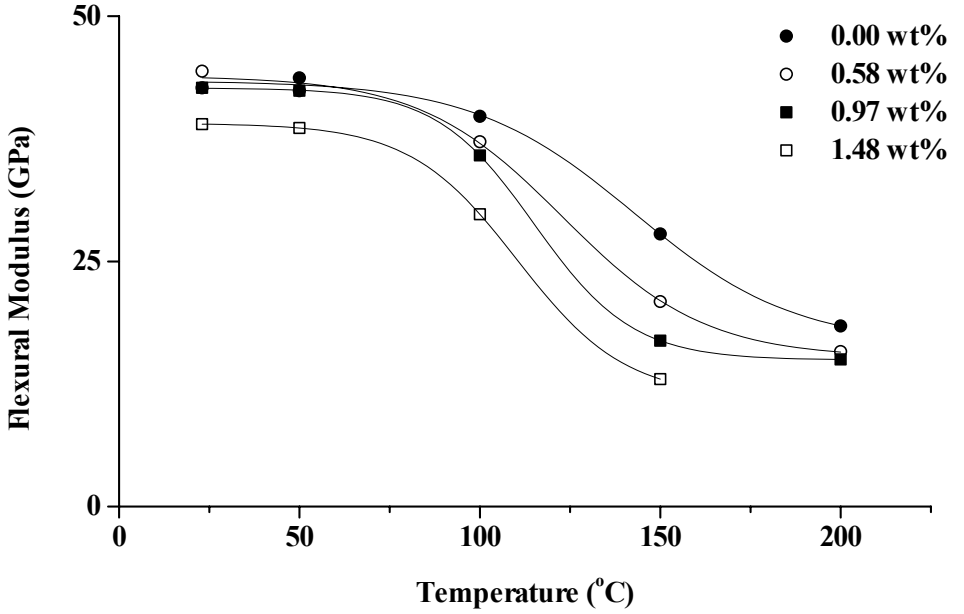
APPENDIX

HYGROTHERMAL EFFECTS ON FLEXURE PROPERTIES OF UNIDIRECTIONAL E-GLASS/913 AND T300/924



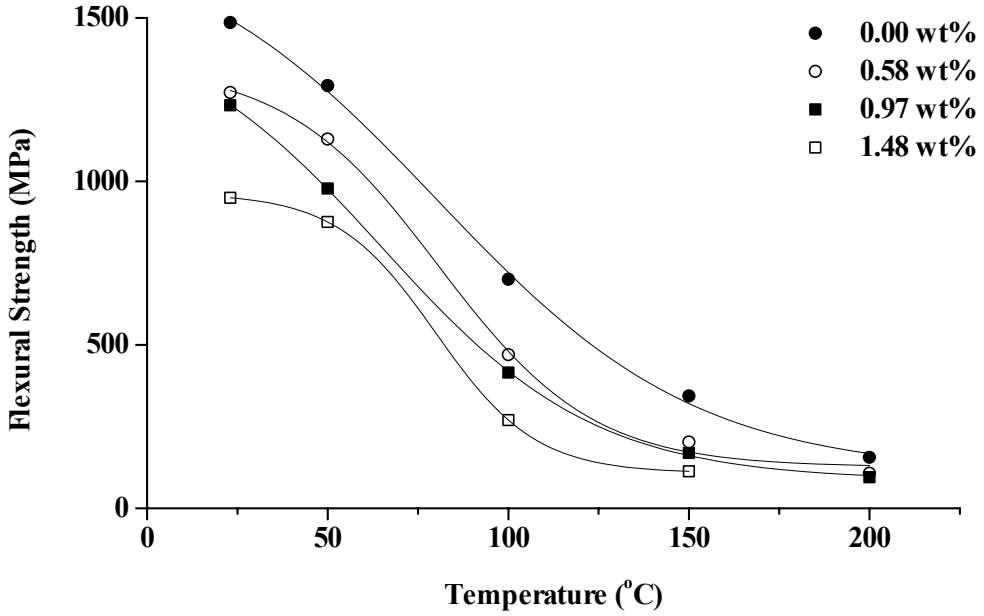
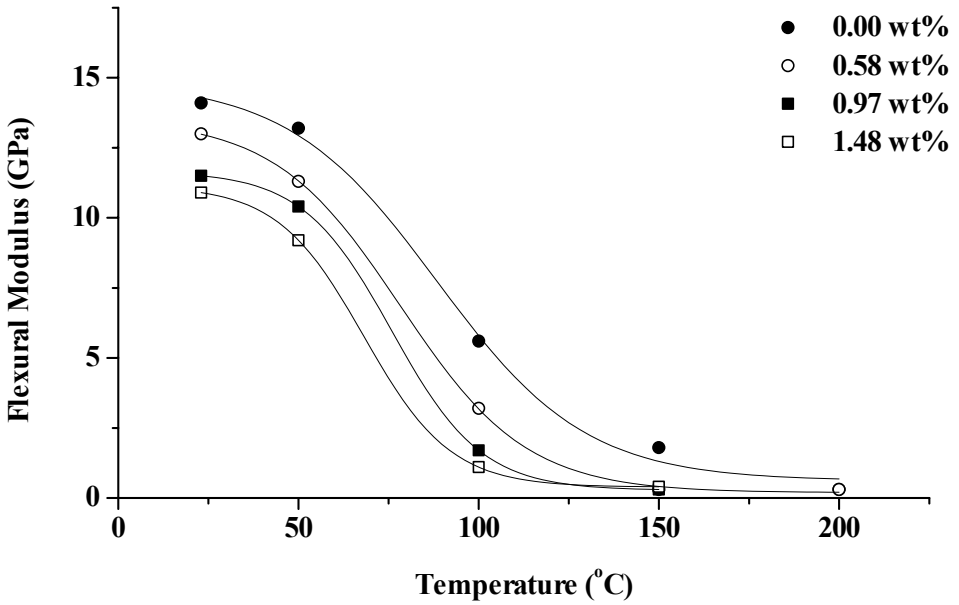


Figure A1: Longitudinal flexural properties of conditioned E-glass/913 with temperature.

APPENDIX (CONT.)

HYGROTHERMAL EFFECTS ON FLEXURE PROPERTIES OF UNIDIRECTIONAL E-GLASS/913 AND T300/924



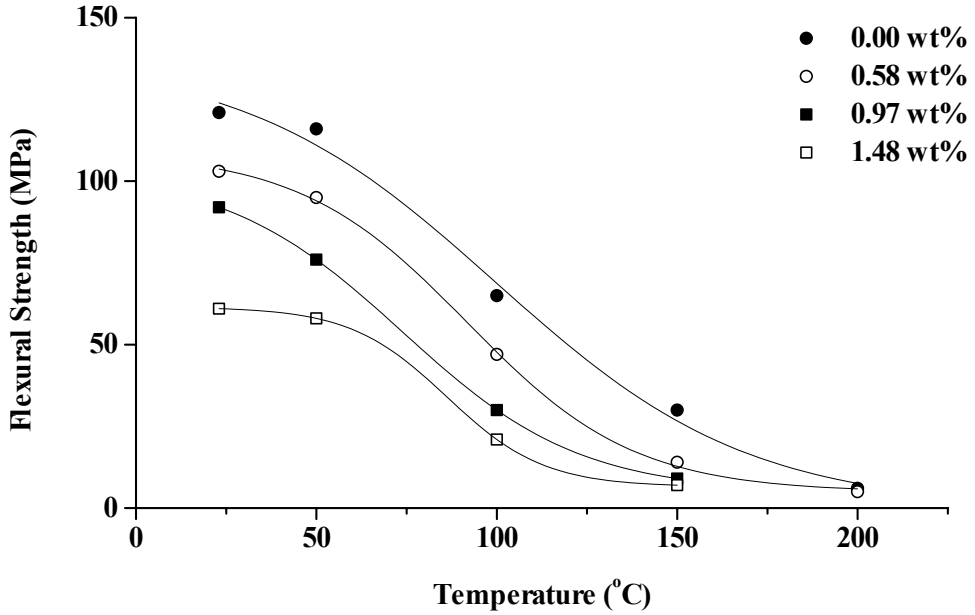
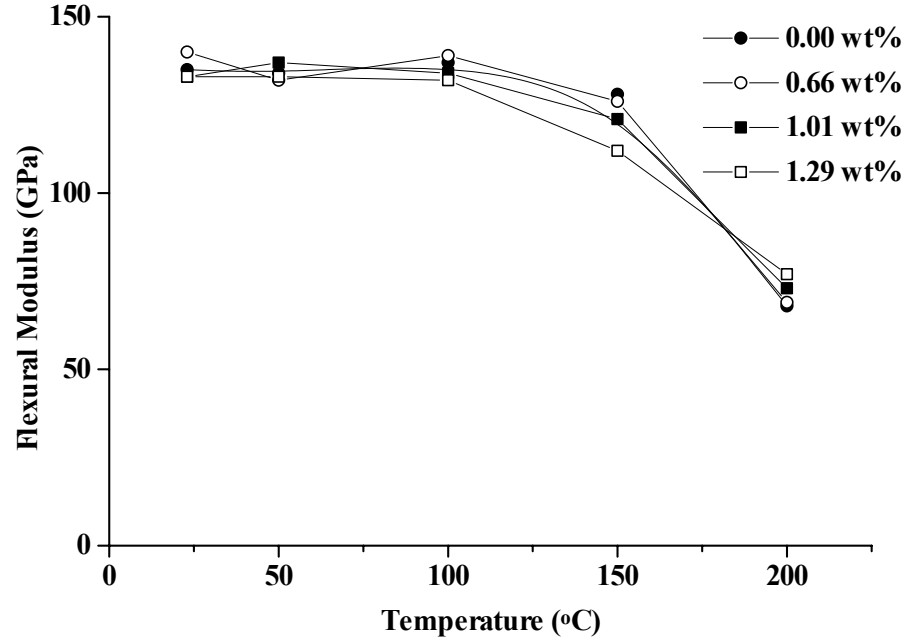


Figure A2: Transverse flexural properties of conditioned E-glass/913 with temperature.

APPENDIX (CONT.)

HYGROTHERMAL EFFECTS ON FLEXURE PROPERTIES OF UNIDIRECTIONAL E-GLASS/913 AND T300/924



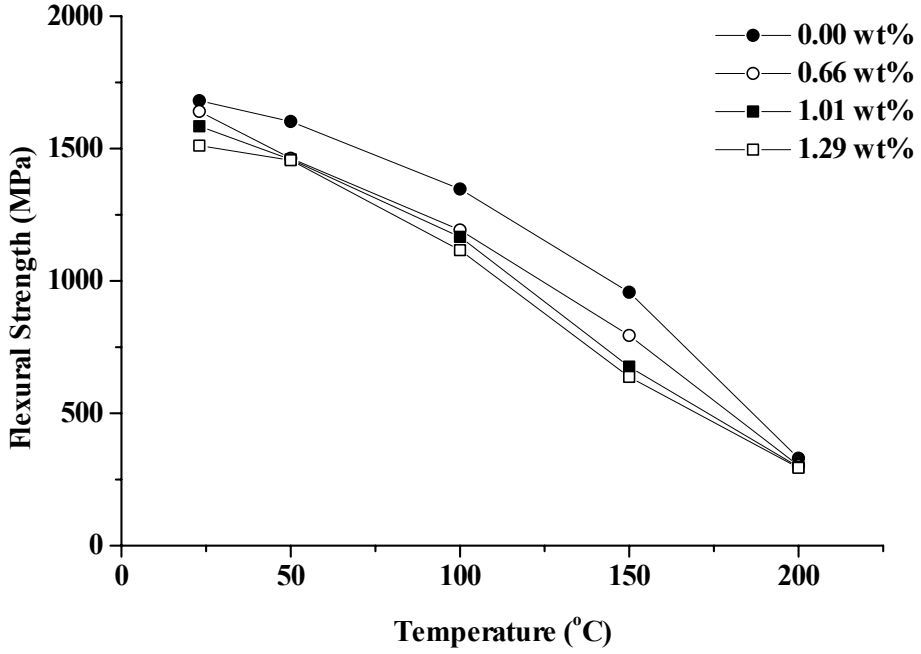


Figure A3: Longitudinal flexural properties of conditioned T300/924 with temperature.

APPENDIX (CONT.)

HYGROTHERMAL EFFECTS ON FLEXURE PROPERTIES OF UNIDIRECTIONAL E-GLASS/913 AND T300/924