

Project CPD2 - Report 16
LIFE ASSESSMENT AND PREDICTION

**Analytical Models for Assessing
Environmental Degradation of
Unidirectional and Cross-Ply Laminates**

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March 2001

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ABSTRACT

This report provides an assessment of analytical and semi-empirical models that can be used for evaluating the elastic and strength properties of unidirectional and cross-ply laminates exposed to heat and moisture. The models are shown to be applicable to both glass and carbon fibre-reinforced composite laminates. The study considers a number of different approaches; including micromechanics, classical laminate analysis, shear-lag theory, non-dimensional temperature function, Kitagawa power-law and Arrhenius temperature dependence relationships. These different approaches have been used to determine the degree and rate of degradation of stiffness and strength properties of glass and carbon fibre-reinforced composite laminates under tensile, shear and flexure loading conditions. Consideration is given to synergistic or superimposed effects between temperature and moisture.

The report presents results that demonstrate that classical laminate analysis combined with micromechanics can be used to predict the elastic and strength properties of moisture conditioned unidirectional and cross-ply laminates. It also shows that simple empirical models can be used to determine tensile, shear and flexural properties of hot/wet aged unidirectional laminates as a function of temperature and moisture. This assessment was carried out using durability data generated within the "Composite Performance and Design (CPD2) Project - Life Assessment and Prediction" and sourced from published literature.

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ISSN 1473 - 2734

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1 INTRODUCTION

This report provides an assessment of analytical and semi-empirical models that can be used for evaluating the elastic and strength properties of unidirectional and cross-ply laminates exposed to heat and moisture. The models are applicable to both glass and carbon fibre-reinforced composite laminates. A number of different approaches are considered; including micromechanics, classical laminate analysis, shear-lag theory, non-dimensional temperature function, Kitagawa power-law and Arrhenius temperature dependence relationships. The report presents case studies demonstrating the use of these models for determining the degree of mechanical degradation with the level of degrading agent (i.e. moisture content and temperature) for different loading conditions. Consideration is given to synergistic or superimposed effects between temperature and moisture.

The research presented in this report forms part of the DTI funded project “Composite Performance and Design (CPD2) Project – Life Assessment and Prediction”. The 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. Throughout this report comparisons are made between predictive analysis and experimental data. The assessment uses durability data generated within the programme, as well as data sourced from previous programmes and published literature. Parallel research has also been carried out within CPD2 to develop physics/mechanistic-based models for predicting stress corrosion failure of fibre bundles and impregnated strands, and progressive degradation of ply properties in composite laminates.

The report is divided into five sections (including the Introduction). Section 2 describes the materials used to develop and validate the predictive models and test methods in this programme. Material properties sourced from previous programmes and published literature has also been included in the report. Section 3 demonstrates the use of classical laminate analysis (combined with micromechanics) and shear-lag theory for predicting the elastic and strength properties of undamaged and damaged unidirectional and cross-ply laminates. Section 4 examines semi-empirical relationships (i.e. non-dimensional temperature function and Kitagawa power-law) that can be used for predicting strength and stiffness reduction due to hygrothermal ageing. This section also considers Arrhenius temperature dependence relationships, which can be used for determining half-life strength (i.e. time required for the strength to degrade to half its original value). Discussion and concluding remarks are presented in Section 5. Material properties used in the analyses are given in Appendix A (Tables A1 to A9).

2 MATERIALS CHARACTERISATION

2.1 MATERIALS DESCRIPTION

The materials used to develop and validate the predictive models and 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 ($0^\circ/90^\circ$) laminates were autoclave cured and 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. $[0^\circ/90^\circ]_{4S}$, $[0^\circ_2/90^\circ_2]_S$, $[0^\circ_2/90^\circ_4]_S$, $[0^\circ_2/90^\circ_6]_S$ and $[0^\circ_2/90^\circ_8]_S$) 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, V_f , fibre weight fraction, W_f , and composite density, ρ_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 (%)
<u>Aligned GRP</u>			
E-glass/F922	$2,122 \pm 53$	65.41 ± 4.46	78.84 ± 3.01
E-glass/913	$1,883 \pm 39$	50.95 ± 0.19	69.26 ± 0.26
<u>Aligned CFRP</u>			
HTA/F922	$1,562 \pm 17$	58.64 ± 2.21	66.41 ± 1.79
T300/924	$1,555 \pm 10$	61.49 ± 1.44	68.48 ± 1.24
<u>Cross-Ply GRP</u>			
E-glass/913 $[0^\circ/90^\circ]_{4S}$	$1,957 \pm 62$	56.47 ± 0.41	72.16 ± 0.48
E-glass/F922 $[0^\circ_2/90^\circ_2]_S$	$2,060 \pm 6$	60.73 ± 0.73	75.48 ± 0.62
E-glass/F922 $[0^\circ_2/90^\circ_4]_S$	$2,042 \pm 21$	59.70 ± 1.08	74.61 ± 0.58
E-glass/F922 $[0^\circ_2/90^\circ_8]_S$	$1,966 \pm 4$	53.32 ± 0.56	69.45 ± 0.49
<u>Cross-Ply CFRP</u>			
HTA/F922 $[0^\circ_2/90^\circ_2]_S$	$1,543 \pm 6$	57.52 ± 1.96	65.90 ± 2.00
HTA/F922 $[0^\circ_2/90^\circ_4]_S$	$1,548 \pm 8$	57.80 ± 0.86	65.94 ± 0.75
HTA/F922 $[0^\circ_2/90^\circ_6]_S$	$1,537 \pm 3$	56.02 ± 2.34	64.47 ± 2.69

3 CLASSICAL APPROACHES TO LAMINATE ANALYSIS

This section considers classical approaches, such as micromechanics, classical laminate analysis (combined with micromechanics) and shear-lag theory, to predict the elastic and strength properties of undamaged and environmentally degraded unidirectional and cross-ply laminates.

3.1 CLASSICAL LAMINATE ANALYSIS

A study was carried out to compare measured tensile elastic and strength properties with predictive analysis for dry and hot/wet conditioned unidirectional and cross-ply laminates (see Tables 2 to 4). The tensile tests were carried out under standard laboratory conditions (i.e. 23 °C and 50% relative humidity (RH)) on specimens that had been exposed to 70 °C and 85% RH for 6 weeks [4]. CoDA (Composite Design and Analysis) preliminary design software, developed by the NPL, was used for the predictive analysis. The Windows-based software can be used to synthesise material properties of continuous and discontinuous, random and aligned fibre-reinforced composite laminates from the properties and volume fractions of the constituents (i.e. fibre and matrix). Fibre and resin matrix (dry and conditioned) property data is presented in Appendix A (see also Tables A1 to A3).

CoDA can be used to determine initial elastic property data, laminate layer failure order and the failure stresses for each layer. In order to calculate the elastic properties after the first ply failure (FPF) in a cross-ply laminate, it was necessary to reduce the elastic properties of the damaged layers. The loss of layer integrity was modelled by setting all the elastic properties of the failed 90° plies to zero (with the exception of the longitudinal modulus). The analysis assumes that transverse matrix cracking of the 90° plies is the predominant failure mode prior to final failure. The elastic properties of the laminate were recalculated to determine the stiffness values of the damaged laminate. These values correspond to the elastic properties prior to the onset of final failure. The through-thickness moisture distribution in conditioned laminates is assumed to be uniform.

Table 2: Measured and Predicted Tensile Properties for Unidirectional Composites (Measured/Predicted)

Material	Tensile Strength (MPa)	Tensile Modulus (GPa)	Poisson's Ratio
<u>E-glass/913 (dry)</u>			
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
<u>E-glass/F922 (dry)</u>			
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
<u>E-glass/F922 (wet)</u>			
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
<u>T300/924 (dry)</u>			
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
<u>HTA/F922 (dry)</u>			
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 3: 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

**Table 4: 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)
<u>E-glass/F922</u>			
[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 ₆] _s	65/98	170/159	1.27/1.07
<u>HTA/F922</u>			
[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

The preliminary design analysis used in CoDA to predict the tensile properties of the dry and hot/wet conditioned unidirectional and cross-ply laminates was in good agreement with experimental data. 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 for the cross-ply laminates could be improved by taking into account hygrothermal residual stresses in the laminate analysis and non-uniform moisture distribution (see Table 3). 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.

3.2 SHEAR-LAG THEORY

The appearance of transverse cracks in the 90° plies is usually the first visible indication of damage in cross-ply laminates (Figures 1 and 2). 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 E-glass/F922 and HTA/F922 cross-ply laminates resulting from tensile loading. The laminate lay-ups used in this study were identical to those described in Section 2. This section compares measured and predicted values of longitudinal modulus at the onset of final failure with predictive values obtained using shear-lag theory and classical laminate analysis.

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 during the loading of the specimens. Optical techniques were used to monitor transverse crack formation after each loading step [4].



Figure 1: Transverse cracking of a cross-ply E-glass/F922 laminate.**Figure 2: Magnified image of transverse cracks along an edge of a cross-ply laminate.**

Multiple transverse cracking, which occurs as a result of increasing the applied load on the laminate, results in a reduction in the longitudinal stiffness of cross-ply laminates. Steif (see [5]) using shear-lag analysis derived a closed-form expression for determining stiffness reduction for $[0/90]_s$ laminates. The reduction in longitudinal stiffness as a function of average crack spacing, $2s$, is given by [5]:

$$\frac{E_{xx}}{E_{xx0}} = \frac{1}{1 + \frac{E_{xx0}}{E_{11}} \left(\frac{b+d}{b} - \frac{E_{11}}{E_{xx0}} \right) \frac{\tanh(\lambda s)}{\lambda s}} \quad (1)$$

where

$$\lambda^2 = \frac{3G_{12}(b+d)E_{xx0}}{d^2bE_{22}E_{11}} \quad (2)$$

E_{xx} , E_{xx0} , E_{11} and E_{22} are the longitudinal moduli of the cracked composite, uncracked composite, the longitudinal plies and the transverse plies, respectively. G_{12} is the longitudinal shear modulus of the transverse ply, and b and d are the thicknesses of individual longitudinal and transverse plies, respectively (Figure 3).

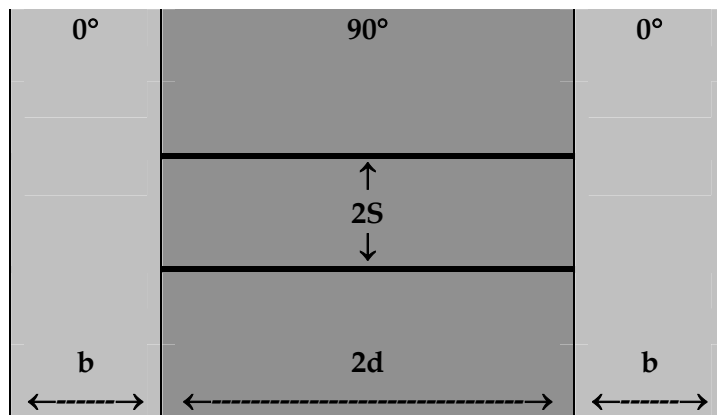
**Figure 3: Schematic diagram of a cracked $[0/90]_s$ laminate (edge view).**

Table 5 compares the measured and predicted values of longitudinal modulus at the onset of final (or last) ply failure (LPF) for unconditioned E-glass/F922 and HTA/F922 cross-ply laminates. The results show that shear-lag analysis provides a reasonable estimate of the laminate stiffness prior to LPF. It should be noted that the shear-lag analysis, presented above, assumes no limit on the size of average crack spacing, $2s$. In reality, there is a limit as

to the minimum spacing between transverse cracks. The calculated values presented in Table 5 are based on the assumption that s_{MIN} at saturation is approximately equal to d .

Table 5: LPF Longitudinal Modulus (GPa) of E-glass and HTA/F922 Cross-Ply Laminates

Material	Measured	Laminate Analysis	Shear Lag Theory
E-glass/F922			
$[0_2/90_2]_S$	23.5	22.1	23.1
$[0_2/90_4]_S$	16.1	14.5	16.1
$[0_2/90_8]_S$	9.4	8.5	11.5
HTA/F922			
$[0_2/90_2]_S$	60.7	66.3	67.2
$[0_2/90_4]_S$	41.9	44.4	45.6
$[0_2/90_6]_S$	31.8	32.3	34.2

The shear-lag model, presented above, tends to give a higher residual stiffness than the experimental results (see Figure 4). The stiffness data presented in Figure 4 has been normalised with respect to the stiffness of the undamaged laminate, E_{xx0} . The crack measurement data, shown in Figure 5, indicates that the average spacing between transverse cracks at final failure is distinctly different for the glass and carbon based systems. For the carbon/epoxy laminates and the thinner glass/epoxy laminates, it is reasonable to assume that s is equal to d .

Alternative shear-lag models tend to be more complicated and show marginal improvement on the analysis presented in this report. A number of researchers have opted to use models based on damage mechanics, statistical analysis or fracture mechanics in order to relate property reduction with accumulated damage. These approaches are generally complex and difficult to implement. Researchers, such as Dr L N McCartney at NPL, are also developing mechanistic/physics based models. Early indications are that predictions from the plain strain model developed by Dr L N McCartney are generally in good agreement with the experimental data.

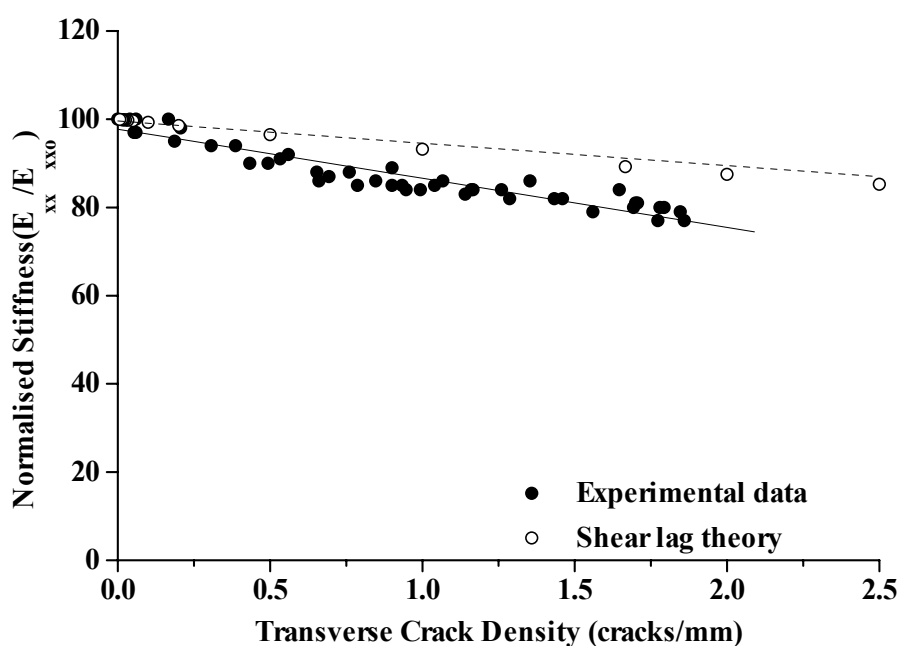


**Figure 4: Longitudinal modulus reduction in E-glass/F922 [0/90₂]_s laminate.
(lines added as visual aid to show trends)**

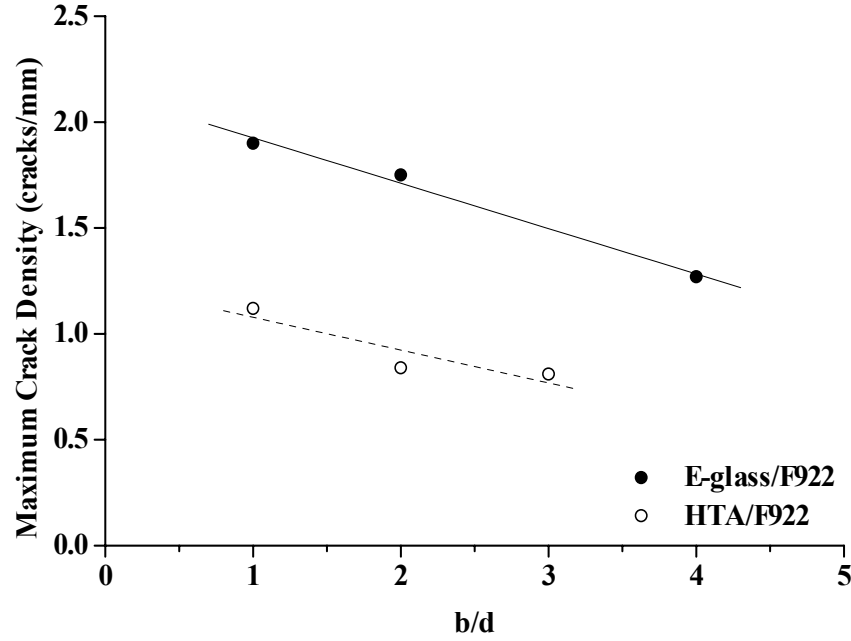


**Figure 5: Longitudinal modulus reduction in E-glass/F922 [0/90₂]_s laminate.
(lines added as visual aid to show trends)**

3.3 MICROMECHANICS ANALYSIS - NON-AMBIENT TEMPERATURES

This section examines the use of micromechanics formulations (incorporated into CoDA) to determine their applicability under non-ambient conditions, particularly at elevated temperatures. The data has been sourced from previous programmes and published literature.

3.3.1 Case Study 1

An experimental study [6] was carried out to evaluate the effects of temperature on the in-plane shear properties of unidirectional carbon fibre-reinforced composites. The V-notched beam (or Iosipescu) shear test [7] was used for measuring in-plane shear modulus and shear strength over the temperature range of -40 °C (233K) to 100 °C (373K). In-plane shear modulus, $G_{12'}$, was determined using the Halpin-Tsai equation [8]:

$$\frac{G_{12}}{G_m} = \frac{(1 + \xi \eta V_f)}{(1 - \eta V_f)} \quad (3)$$

where:

$$\eta = \frac{(G_{12f}/G_m) - 1}{(G_{12f}/G_m) + \xi} \quad (4)$$

G_m is the shear modulus of the unreinforced matrix, G_{12f} is the longitudinal shear modulus of the fibre and V_f is the fibre volume fraction. The reinforcement constant, ξ , which is

dependent on fibre geometry, packing geometry and loading conditions is assumed to be equal to unity.

Relating in-plane shear strength, S_{12} , of the composite to the mechanical properties of the constituents and simultaneously accounting for non-uniform fibre distribution, interfacial bonding, stress concentrators and residual thermal stresses can be exceedingly complex. However, it is possible to obtain reasonable agreement between the experimental data and the following empirical relationship [9-10]:

$$S_{12} = \left(1 - \left(\sqrt{V_f} - V_f\right)\left(1 - G_m / G_{12f}\right)\right) S_m \quad (5)$$

where S_m is the shear strength of the unreinforced matrix.

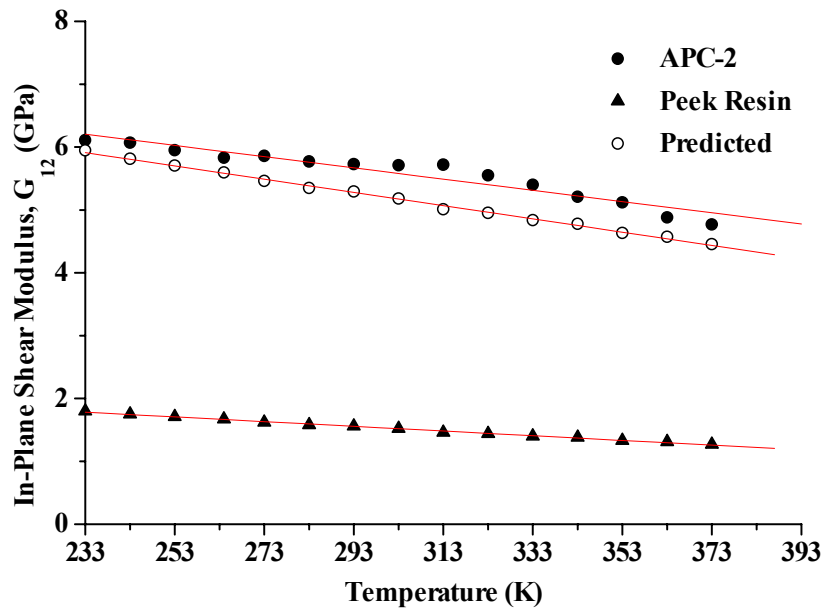


Figure 6: Shear modulus versus temperature for continuous aligned APC-2.

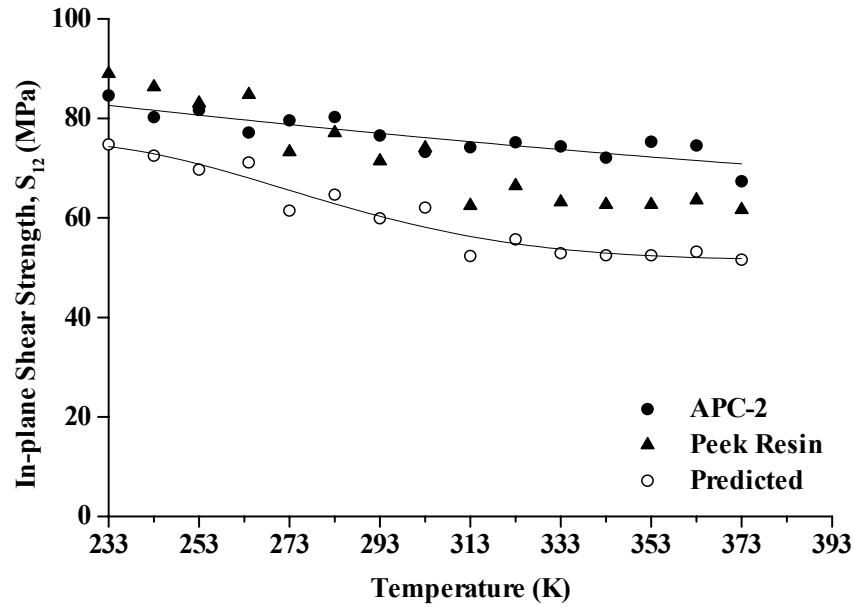


Figure 7: Shear strength versus temperature for continuous aligned APC-2.

Figure 6 compares experimental and predicted shear modulus values for APC-2 carbon/PEEK (polyetheretherketone). The results indicate that there is good correlation between the two sets of data over the temperature range $-40\text{ }^{\circ}\text{C}$ (233K) to $100\text{ }^{\circ}\text{C}$ (373K). The degree of correlation between the predicted (see Equation (5)) and actual stiffness values is better than that for the shear strength (see Figure 7). The results presented in Figure 7 show that fibre-reinforcement had minimal effect on the shear strength of the composite. Thermoplastic matrices, such as PEEK, are able to relieve stress concentrations through local deformation processes and therefore it is not surprising to observe that $S_{12} \approx S_m$.

3.3.2 Case Study 2

This section compares experimental and predicted longitudinal and transverse tensile data for continuous aligned T300/914 carbon/epoxy. The composite and unreinforced 914 epoxy data was extracted from the European Space Agency (ESA) Composites Design Handbook for Space Structure Applications (Volume 1). The predictive analysis was carried out using the CoDA software. The results for three test temperatures are shown in Table 6.

Table 6: Measured and Predicted Tensile Properties for T300/914 Carbon/Epoxy

Property	Temperature ($^{\circ}\text{C}$)		
	-40	20	120
Longitudinal tensile modulus, E_{11}^T (GPa)			
Measured	133	135	139
Predicted	144	143	142
Transverse tensile modulus, E_{22}^T (GPa)			
Measured	10.8	10.5	8.2
Predicted	13.3	10.5	8.4
Longitudinal shear modulus, G_{12} (GPa)			
Measured	5.9	5.1	3.5
Predicted	7.7	5.1	4.5

<u>Longitudinal Poisson's ratio, ν_{12}</u>			
Measured	0.37	0.40	0.39
Predicted	0.40	0.40	0.39
<u>Longitudinal tensile strength, S_{11}^T (MPa)</u>			
Measured	1,750	1,683	1,550
Predicted	2,211	2,195	2,186
<u>Transverse tensile strength, S_{22}^T (MPa)</u>			
Measured	63.6	60.8	56.1
Predicted	48.9	44.1	24.7

Considerable scatter in tensile strength data for unreinforced (bulk) resin specimens is common, with premature failure often occurring due to the presence of voids which act as stress concentrators. This can result in large differences between measured and predicted transverse tensile strength, S_{22}^T , values (see Table 6).

3.3.3 Case Study 3

Hua and Springer [11] evaluated the effect of elevated temperature on the mechanical properties of Fiberite 976 epoxy resin and Fiberite T300/976 carbon/epoxy ($V_f = 66\%$) in the range 75 °F to 350 °F (24 °C to 178 °C). Tensile, compressive and shear tests were conducted at four different temperatures (see Tables 7 and 8). Table 8 compares experimental data with CoDA predictions. The measured values presented in Tables 7 and 8 have been converted to SI units and rounded-off.

Table 7: Measured Mechanical Properties for 976 Epoxy Resin [11]

Property	Temperature (°F)			
	75	250	300	350
Tensile modulus, E_m^T (GPa)	3.78	2.71	2.48	2.17
Compressive modulus, E_m^C (GPa)	4.69	3.31	2.83	2.39
Shear modulus, G_m (GPa)	1.49	1.08	0.98	0.84
Poisson's ratio, ν_m	0.270	0.258	0.260	0.286
Tensile strength, S_m^T (MPa)	54.4	35.0	31.4	30.2
Compressive strength, S_m^C (MPa)	361	270	254	227

Table 8: Measured and Predicted Mechanical Properties for Fiberite T300/976 [11]

Property	Temperature (°F)			
	75	250	300	350
<u>Longitudinal tensile modulus, E_{11}^T (GPa)</u>				
Measured	157	154	156	-
Predicted	153	153	153	153
<u>Longitudinal tensile modulus, E_{22}^T (GPa)</u>				
Measured	9.1	7.9	8.2	7.7
Predicted	8.9	7.7	7.4	6.9
<u>Longitudinal compressive modulus, E_{11}^C (GPa)</u>				
Measured	167	160	165	159
Predicted	153	153	153	153
<u>Transverse compressive modulus, E_{22}^C (GPa)</u>				
Measured	13.0	10.4	9.7	9.3
Predicted	9.6	8.4	7.9	7.3
<u>Longitudinal shear modulus, G_m (GPa)</u>				
Measured	7.0	6.0	5.4	4.3
Predicted (based on $G_m = E_m^T / (1 + \nu_m)$)	5.8	4.4	4.1	3.6
	6.9	5.2	4.6	4.0

Predicted (based on $G_m = E_m^C / (1 + \nu_m)$)				
<u>Longitudinal Poisson's ratio, ν_{12}</u>				
Measured	0.228	0.232	0.216	-
Predicted	0.224	0.220	0.220	0.229
<u>Transverse Poisson's ratio, ν_{21}</u>				
Measured	0.013	0.012	0.011	-
Predicted	0.017	0.011	0.011	0.010
<u>Longitudinal tensile strength, S_{11}^T (MPa)</u>				
Measured	1,517	1,531	1,386	-
Predicted	1,606	1,602	1,601	1,600
<u>Transverse tensile strength, S_{22}^T (MPa)</u>				
Measured	49.0	29.2	25.6	24.1
Predicted	48.4	30.7	27.5	26.3
<u>Longitudinal compressive strength, S_{11}^C (MPa)</u>				
Measured	1,593	1,434	1,310	1,179
Predicted	851	714	658	668
Predicted ($S_{11}^C = S_m^C (1 - V_f) + S_{11f}^T V_f$)	1,715	1,684	1,679	1,670
<u>Transverse compressive strength, S_{22}^C (MPa)</u>				
Measured	253	221	181	175
Predicted	137	87	78	74

The experimental results and CoDA predictions (with the exception of S_{11}^C and S_{22}^C) are generally in reasonable agreement for the entire temperature range of 75 °F to 350 °F. In this case, a rule of mixture approach (see Table 8) provides a far better estimate of the longitudinal compressive strength than the micromechanics formulation used in CoDA.

4 EMPIRICAL RELATIONSHIPS

As previously indicated, 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 [6, 13-15]. 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 both strength and strength reduction due to hygrothermal ageing: (i) non-dimensional temperature function [12]; and (ii) Kitagawa power-law relationship [6, 14, 15]. The two relationships will be used to estimate the mechanical properties of unidirectional glass and carbon fibre-reinforced systems for a range of temperatures and moisture contents.

4.1 NON-DIMENSIONAL TEMPERATURE, T^*

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

$$\frac{P}{P_o} = \left(\frac{T_g - T}{T_g - T_o} \right)^n \quad (6)$$

P denotes a material property (e.g. longitudinal tensile strength) at the test temperature T (in K), P_o is the initial property value of the dry material measured at room or reference temperature T_o (296 K), and T_g is the glass transition temperature of the material (dry or conditioned). The relationship will only provide a rational solution when $T_g > T$ and $T_g > T_o$. The exponent n is a constant, which is empirically derived from experimental data. The bracketed term in Equation (6) is the non-dimensional temperature function, T^* .

Chamis et al [12] suggested a similar relationship for hot/wet conditioned resin systems to that given in Equation (6). 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]:

$$\frac{P}{P_o} = \left(\frac{T_{gw} - T}{T_{gd} - T_o} \right)^n \quad (7)$$

T_{gd} and 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 $T_{gw} > T$ and $T_{gd} > T_o$.

The matrix and fibre strength and stiffness properties determined using Equations (6) or (7) 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 generally causes mechanical properties to decrease, although mechanical properties have been known to increase with moisture uptake. In these cases, residual stresses that have been produced in the laminate during the curing process are relieved through moisture plasticisation of the resin matrix.

4.1.1 Case Study 1

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 Table 1 in Section 2.2). The flexural properties were measured at five temperatures (23 °C, 50 °C, 100 °C, 150 °C and 200 °C). The flexure specimens were immersed in deionised water at a temperature of 60 °C and removed 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 traveller specimens (see NPL Report CMMT(A) 251 [4]). DMA (dynamic mechanical analysis) measurements were carried out on dry and conditioned specimens to determine the change in T_g as a function of moisture content.

The results, presented in Figure 8, show that moisture reduces T_g with the shift in temperature being related to moisture content by the following linear relationship [16]:

$$T_{gw} = T_{gd} - gM \quad (8)$$

T_{gd} is the glass transition temperature of the dry material, 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 temperature shift, g , was 36.8 K and 28.9 K for T300/924 and E-glass/913, respectively. The corresponding T_g for the unconditioned materials was 430 K (157 °C) and 482 K (209 °C).

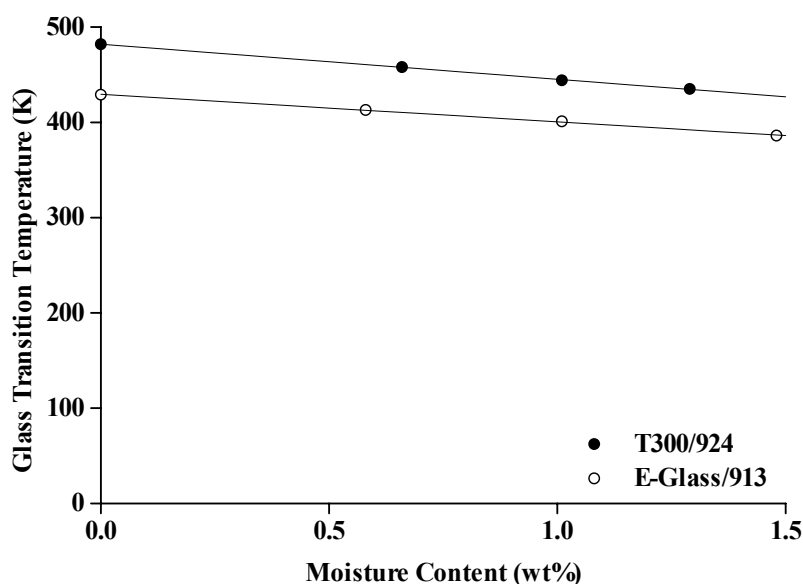


Figure 8: Glass transition temperature for hot/wet conditioned E-glass/913 and T300/924.

Equation (7) 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 9 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 9 is a linear regression best fit to all the modulus and strength data, which was obtained at four moisture levels ranging from 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 (8).

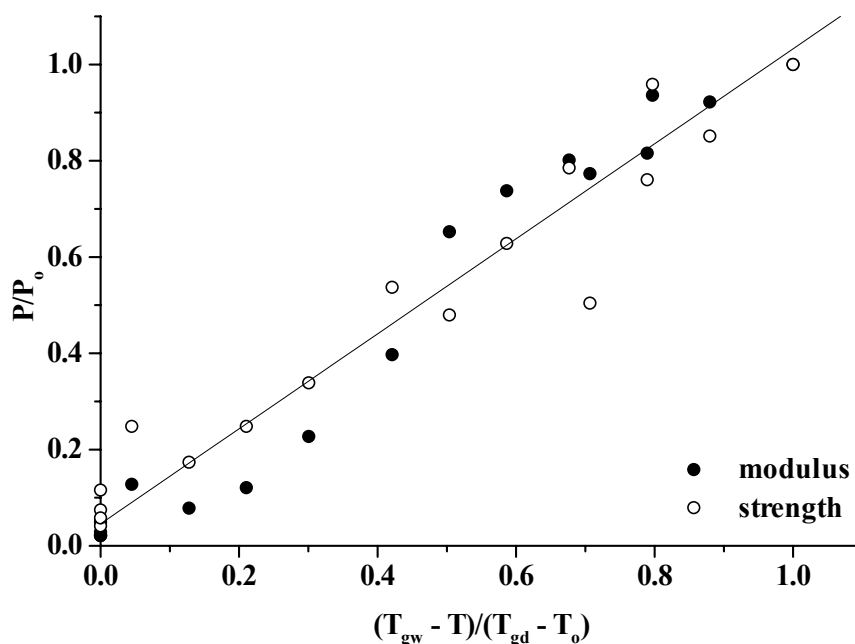


Figure 9: Transverse flexure properties of unidirectional E-glass/913.

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.**

4.1.2 Case Study 2

An experimental study [6] was carried out to evaluate the effects of temperature on the in-plane shear properties of unidirectional carbon fibre-reinforced composites. The V-notched beam (or Iosipescu) shear test [7] was used for measuring in-plane shear modulus and shear strength over the temperature range of -40 °C (233K) to 100 °C (373K). The experimental study focused on three carbon/epoxy systems (Hercules AS4/3501-6, Hexcel Composites XAS/914 and Hyfil T300B/R23) and ICI APC-2 carbon/PEEK.

The results for the four materials, shown in Figures 10 and 11, indicate that the normalised strength and stiffness values (i.e. P/P_o) form a tight band with respect to the non-dimensional temperature ($T^* = (T_{gw} - T)/(T_{gd} - T_o)$). Shear modulus and shear strength data presented in Tables A4 to A6 in Appendix A can be represented by master curves. The exponent n of the master curves was estimated to have a value of 0.15 and 0.11 for shear modulus and shear strength, respectively. For unconditioned materials T_{gw} is equal to T_{gd} . The glass transition temperatures, which were determined by DMTA, are shown in Table A7 in Appendix A.

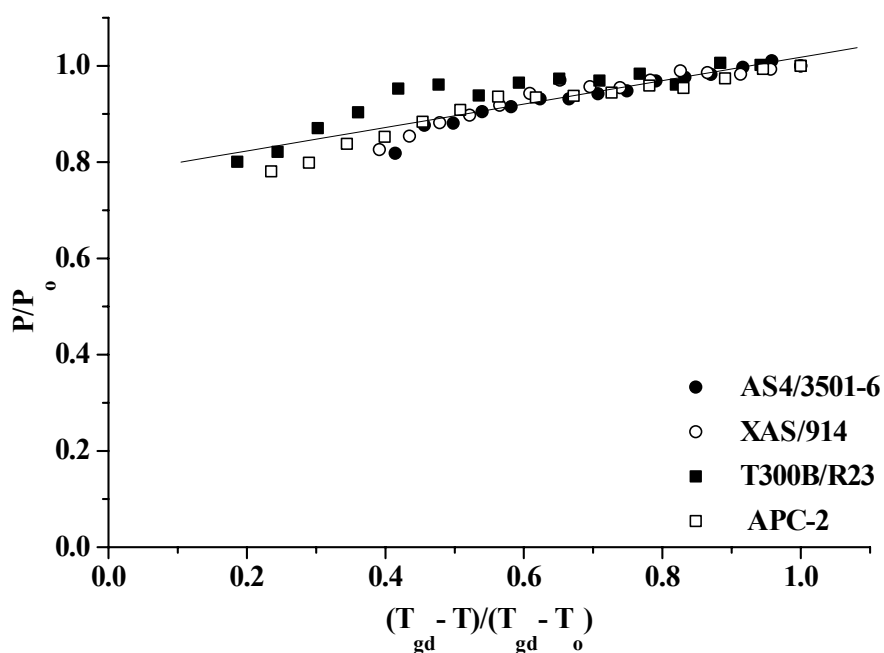


Figure 10: Shear modulus of unidirectional carbon fibre-reinforced laminates.

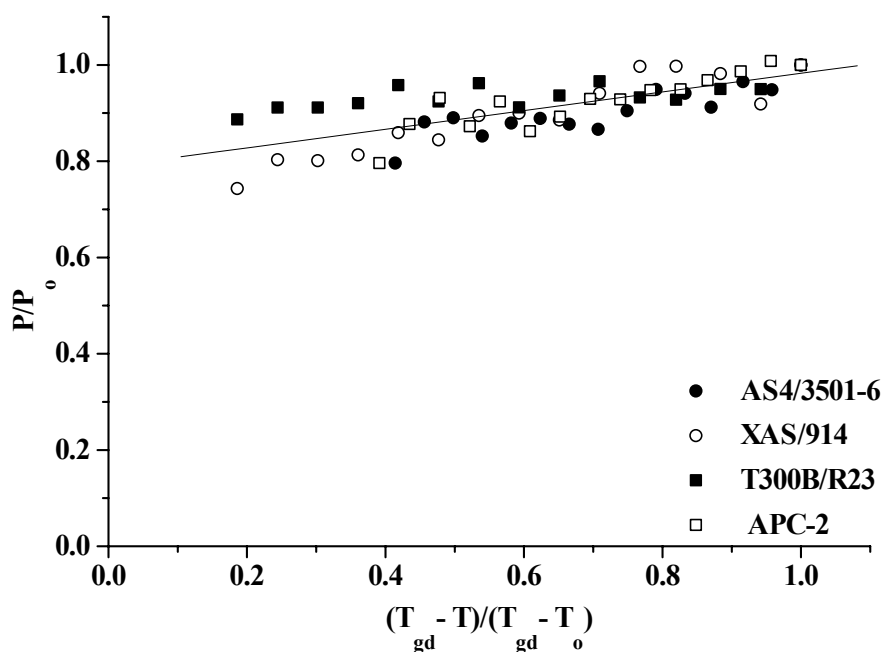


Figure 11: Shear strength of unidirectional carbon fibre-reinforced laminates.

4.1.3 Case Study 3

The natural process of moisture absorption in composite materials is normally slow, and hence it is difficult to obtain saturation conditions or even realistic levels of moisture within a

practical timescale. Collings et.al [17] postulated that an increase in test temperature, equivalent to the change in the glass transition temperature δT_g (i.e. $T_{gd} - T_{gw}$) due to hot/wet exposure, could be used to represent the degradation of PMCs due to moisture.

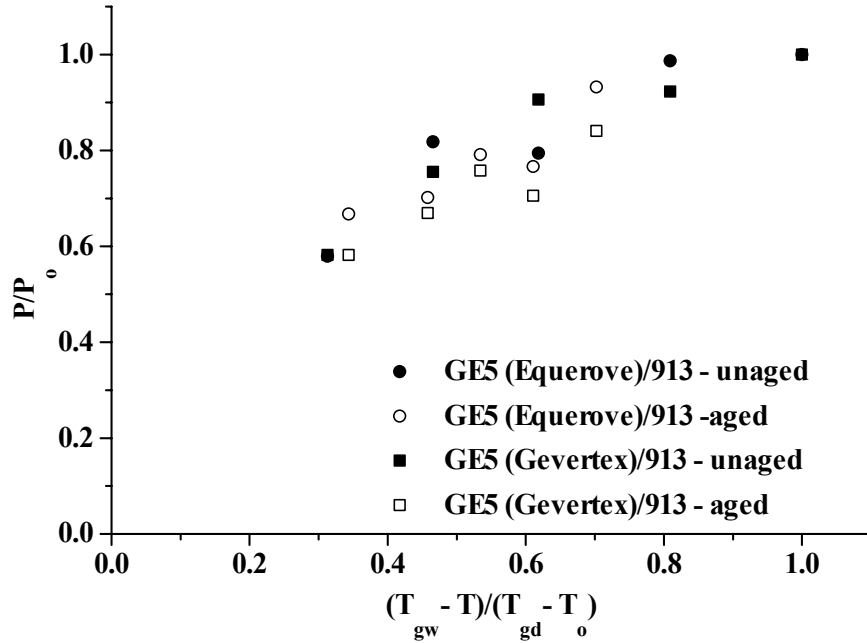


Figure 12: Longitudinal compression strength of E-glass/913 laminates (see [17]).

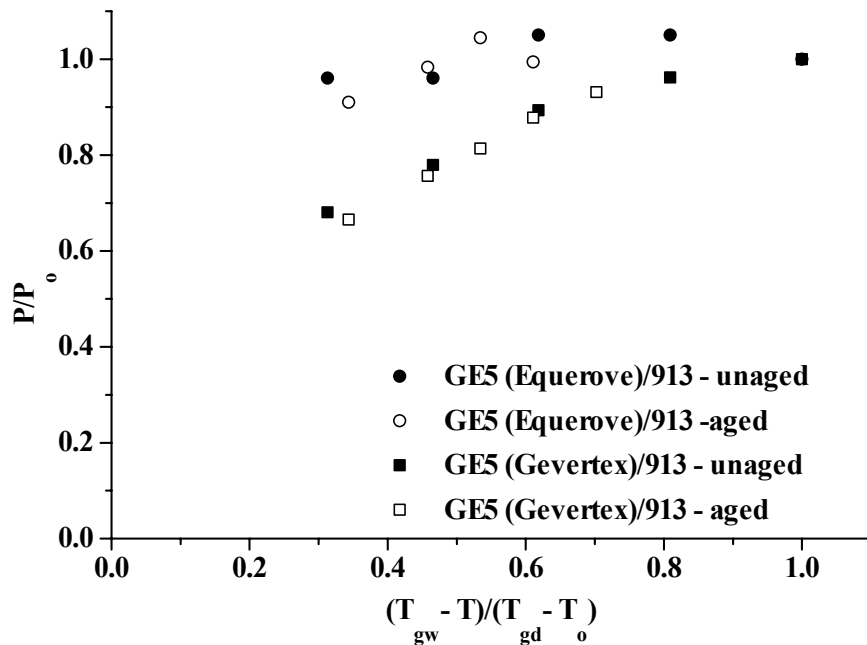


Figure 13: $\pm 45^\circ$ tensile strength of unidirectional E-glass/913 laminates.

An attempt has been made to apply the non-dimensional relationship given by Equation (7) to longitudinal compression and $\pm 45^\circ$ tension (i.e. shear) strength data [17] for unidirectional GE5 (Equerove)/913 and GE5 (Gevertex)/913 glass fibre-reinforced laminates. The strength data was extracted from Tables 2, 3, 7 and 8 of reference [17]. Mechanical tests had been

carried out on unaged and aged tensile specimens at five different temperatures within the temperature range of 20 °C to 110°C. Specimens were conditioned at 45 °C and 84% RH using a humidity chamber with a saturated salt solution to maintain a constant environment. Conditioning ceased when moisture equilibrium was reached in the traveller specimens that accompanied the test specimens. The glass transition temperatures of the two materials, determined by DMTA, are shown in Table 9.

Table 9: Glass Transition Temperatures of Glass Fibre-Reinforced Laminates [17]

Material	Condition	T _g (°C)
GE5 (Equerove)/913	Unaged	151
	Aged	115
GE5 (Gevertex)/913	Unaged	147
	Aged	116

The results for the two materials, shown in Figures 12 and 13, show the normalised longitudinal compression and tensile shear strength values as a function of non-dimensional temperature, T^* . A master curve was fitted to the compression data for the two materials (wet and dry). The exponent n of the master curve was approximately 0.46. It was estimated that value of n for the shear strength data was 0.11 for GE5 (Equerove)/913 (wet and dry) and 0.38 for GE5 (Gevertex)/913 (wet and dry).

There was insufficient data available at different moisture levels to have confidence in the n values for these materials, however, the results presented in this section and Section 4.1.1 provide experimental support for the hypothesis postulated by Collings et al [17] where the strength properties of a conditioned material tested at a temperature T would be equivalent to the strength properties of the dry material tested at a temperature of $T + \delta T_g$.

4.2 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:

$$\frac{T_0 \tau}{T \tau_0} = \left(\frac{T_0 G}{T G_0} \right)^n \quad (9)$$

where T_0 is the reference temperature (in K), τ_0 , and G_0 are the shear yield stress and the shear modulus at T_0 respectively, and the exponent n is a constant. The reference temperature T_0 is frequently taken as room temperature. The values of $\log (T_0 \tau / T \tau_0)$ are plotted against those of $\log (T_0 G / T G_0)$, such that the exponent n is the gradient of the linear regression fit through the log-log data. Broughton [6] and Padmanabhan [15] demonstrated that the power-law relationship given by Equation (9) could also be applied to unidirectional carbon/epoxy and glass/epoxy composites.

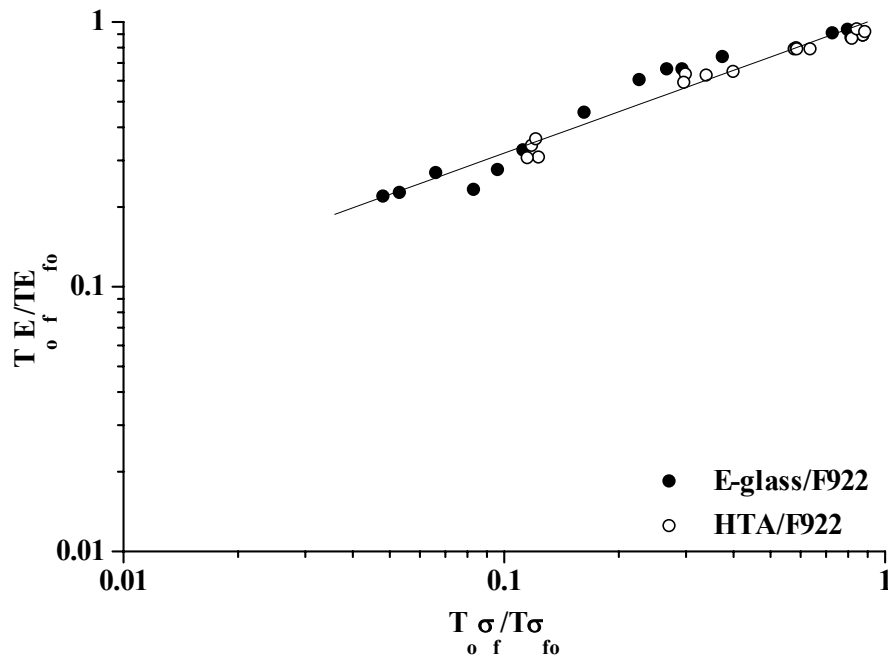


Figure 14: Kitagawa's power-law relationship for longitudinal flexure data.

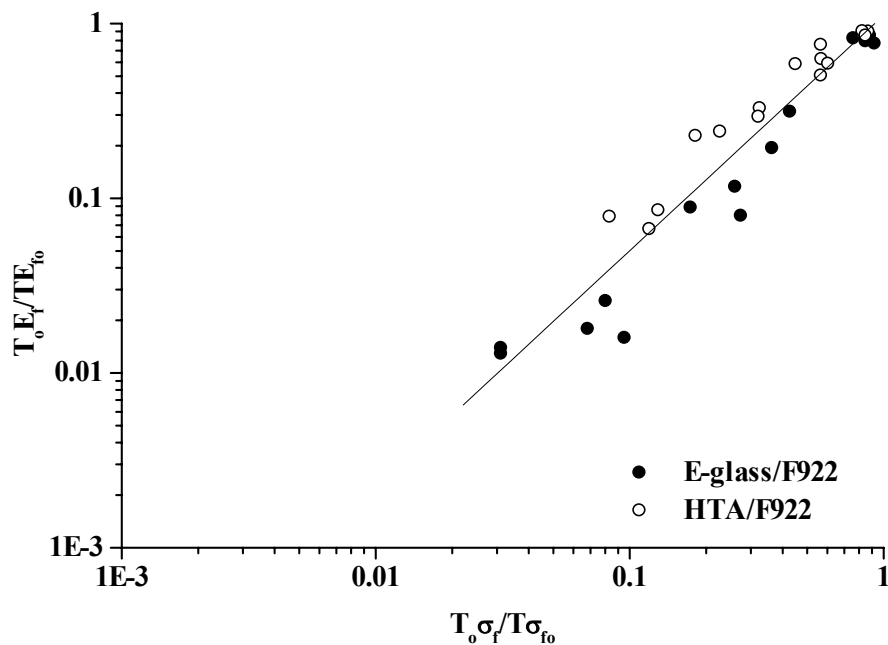


Figure 15: Kitagawa's power-law relationship for transverse flexure data.

Figures 14 and 15 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. Details on the flexure

tests are presented Section 4.1.1 and NPL Report CMMT(A) 251 [4]. The relationship can be rewritten in the form:

$$\frac{T_o \sigma_f}{T \sigma_{fo}} = \left(\frac{T_o E_f}{T E_{fo}} \right)^n \quad (10)$$

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.

The power-law relationship has also been applied to the shear modulus and shear strengths of four carbon fibre-reinforced systems (AS4/3501-6, XAS/914, T300B/R23 and APC-2 carbon/PEEK) and a thermoplastic resin (Vitrex PEEK) [6] (see Section 4.1.2). The values of n (see Table 10) were determined for each composite using the experimental data presented in Tables A5 and A6 in Appendix A

Table 10: Value of n for Unidirectional Carbon-Fibre Composites and Vitrex PEEK

AS4/3501-6	XAS/914	T300B/R23	APC-2	Vitrex PEEK
0.85	1.00	1.10	0.89	1.07

The shear data for the carbon fibre-reinforced systems can be represented by a master curve with a slope n of approximately unity. As expected, the results indicate that shear deformation of the composite materials is matrix dominated. Further tests would be required to isolate the effect of factors, such as surface treatment of fibres, fibre volume fraction and fibre and matrix stiffness, which can be expected to contribute to differences in n for the different composite systems.

4.3 ARRHENIUS MODEL

4.3.1 Introduction

Modelling any degradation process requires information on the change in material properties with time, and the rate of change of those properties with the level of degrading agent(s). A number of semi-empirical relations (both linear and non-linear) for property degradation have been suggested [16-19]. These are usually of the form:

$$P(t, T) = P(\infty, T) + [P(0, T) - P(\infty, T)]e^{[-k(T)t^n]} \quad (11)$$

k is the reaction rate (or degradation rate), P is the material property (e.g. strength or stiffness), T is the ageing temperature (K), t is the ageing time and n is an experimentally determined constant. The strength decays exponentially with time to an asymptotic value (usually zero). This process assumes only one time-dependent process is occurring; when in reality there can be several processes occurring simultaneously.

An alternative approach is to plot material property data against time for one temperature-moisture level with the data being represented by one of the following empirical relations:

$$\log P(t, T) = A(T) - B(T)t \quad (11)$$

$$P(t, T) = P(0, T)e^{[-k(T)t]^n} \Rightarrow P(\infty, T) = 0 \quad (12)$$

B is the degradation rate and **A** is a constant. Similar data are generated at different temperatures. The time required for the strength to degrade to a pre-determined or limit value (usually half its original value (half-life)) at each temperature is calculated from the fitted equations. The next step is to plot the limit value as a function of the reciprocal of the ageing temperature (i.e. $1/T$). The half-life $t_{1/2}$ is related to the ageing temperature **T** as follows:

$$\ln t_{1/2} = C + \frac{D}{T} \quad (13)$$

C and **D** are material constants. The half-life at service temperature can be estimated by extrapolation from the plot of $\ln t_{1/2}$ versus $1/T$ (a straight line fit) or by fitting the data to Equation (13). It is important that the test temperatures are kept moderate to ensure the chemical reactions (e.g. thermal oxidation) that occur at higher temperatures are avoided and that the dominant mode of failure is identical at all the temperatures and stress levels.

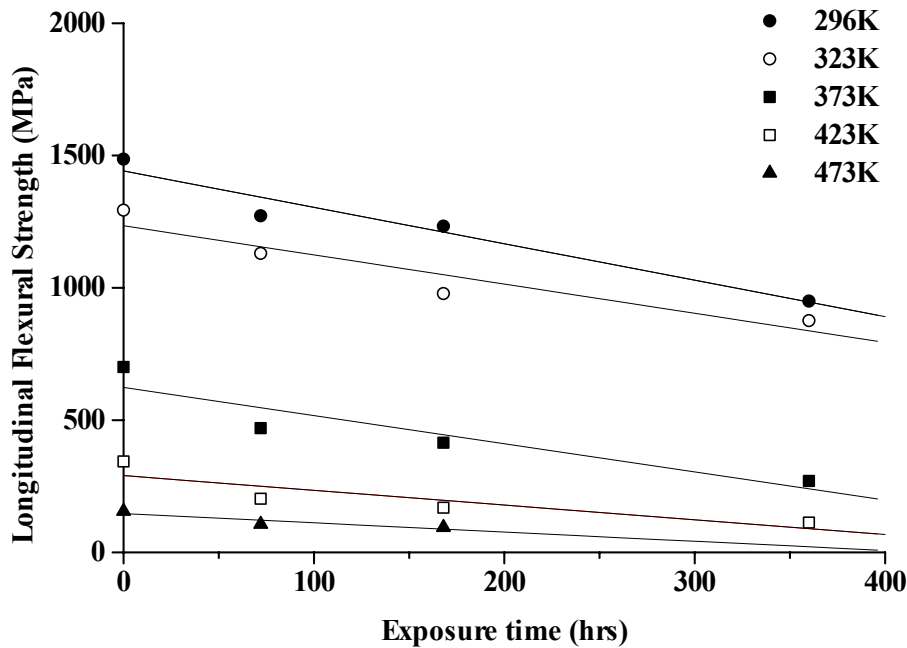


Figure 16: Longitudinal flexure strength versus time for unidirectional E-glass/913.

The above analysis has been used to evaluate the combined effects of moisture content and elevated temperature on the flexural properties of unidirectional glass and carbon fibre-reinforced composite materials. Four-point flexure tests were carried out on unconditioned and moisture conditioned longitudinal and transverse flexure specimens that were sectioned from 2 mm thick unidirectional (UD) E-glass/913 and T300/924 laminates [4]. The flexural properties were measured at five temperatures (23 °C, 50 °C, 100 °C, 150 °C and 200 °C).

The 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 and tested. Five specimens were tested at each temperature after 0, 3, 7 and 15 days exposure. The moisture content (wt.%) was monitored using traveller specimens. DMA measurements were carried

out on dry and conditioned specimens to determine the change in T_g as a function of moisture content (further details are given in Section 4.1.1 and reference [4]). The flexural strength and modulus data are presented in Tables A8 and A9 in Appendix A. Figure 16 shows the longitudinal flexural strength of unidirectional E-glass/913 as a function of test temperature following immersion in water at 60 °C.

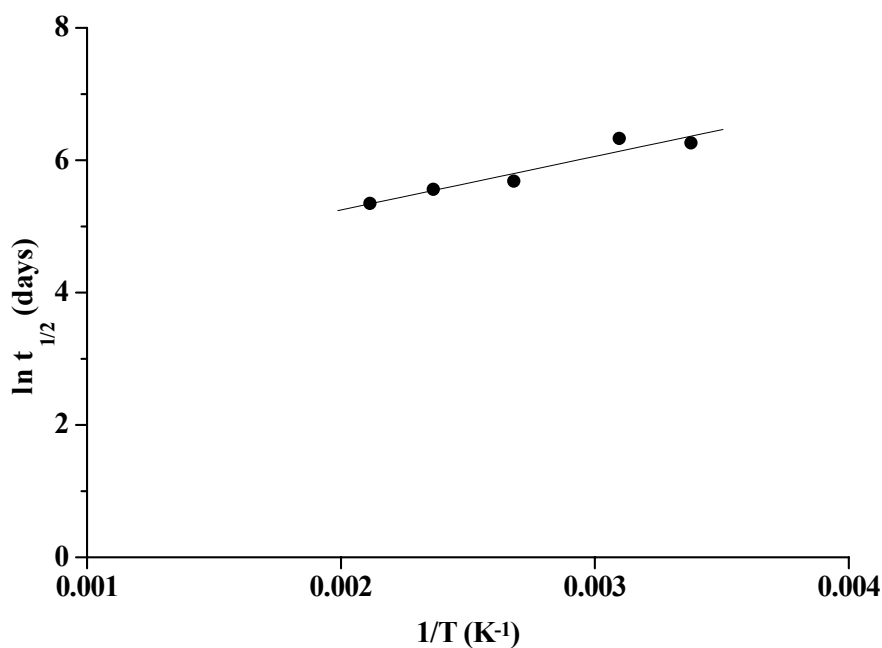


Figure 17: Longitudinal flexural strength half-life versus temperature for E-glass/913.

Figure 17 shows a plot of the time required for the longitudinal flexural strength of unidirectional E-glass/913 to degrade to half its original value as a function of reciprocal of the test temperature, $1/T$. For this material, the constants C and D were 3.63 and 808. This exercise was repeated for the various flexural properties of the two materials. The variations between the different sets of data raised a number of concerns with this approach:

- Constants C and D are significantly different for each property
- Constants C and D for a given property are significantly different for the two materials
- Only applicable when there is a significant reduction in material property with time and temperature

Analysis has also been carried out on the tensile strength data obtained for hot/wet conditioned unidirectional E-glass/polyester rod specimens. Tensile tests were conducted on 1.5 mm diameter E-glass/polyester rods that had been immersed in deionised water at 23°C, 40 °C, 60 °C or 70 °C [20]. Specimens were withdrawn at selected intervals over a period of 42 days (or 6 weeks) and tested. Five specimens were tested at each temperature after 0, 7, 14, 21 and 42 days exposure. The tensile tests were conducted according to BS ISO 9163 [21].

The results, shown in Table 11 and Figure 18, indicate that the rate of reduction in tensile strength of the glass/polyester rods increases with ageing (i.e. conditioning) temperature. The tensile strength, as shown in Figure 18, has been normalised with respect to the ultimate tensile strength of unconditioned (i.e. dry) composite rod specimens measured at the same

strain rate (i.e. 1057 ± 16 MPa). The tensile modulus was found to be constant with temperature and exposure time.

Table 11: Tensile Strength (MPa) for Hot/Wet Aged E-glass/Polyester Rods

Exposure Time (days)	Ageing Temperature (°C)			
	23	40	60	70
0	1057 ± 16	-	-	-
7	958 ± 10	914 ± 21	629 ± 9	574 ± 79
14	869 ± 9	722 ± 82	524 ± 25	523 ± 12
21	798 ± 51	656 ± 24	460 ± 12	496 ± 24
42	751 ± 26	538 ± 19	468 ± 27	478 ± 27

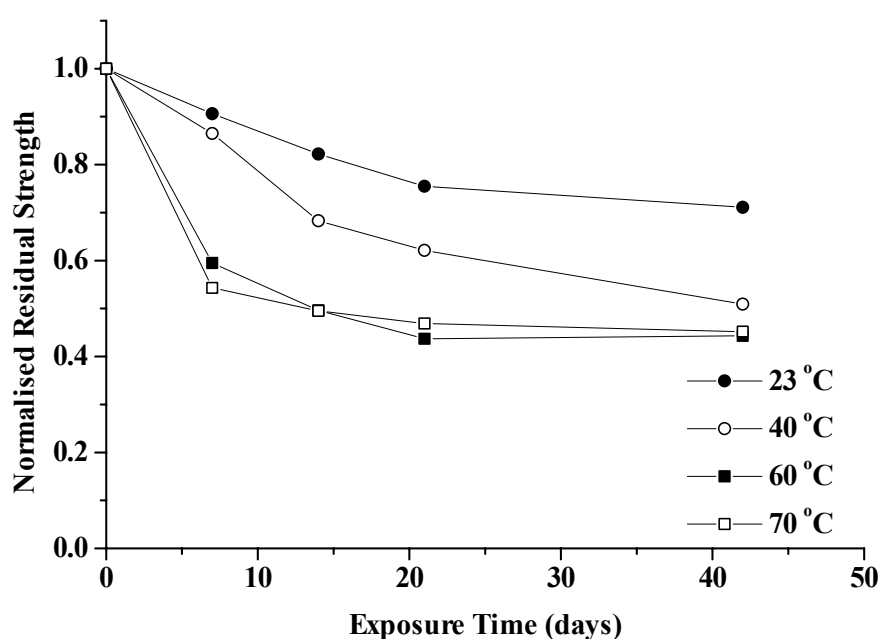


Figure 18: Residual strength versus exposure time for hot/wet aged E-glass/polyester.

The results indicate that tensile strength decreases exponentially to a non-zero equilibrium value. This value, with the exception of room temperature conditioning, was less than 50% of the original strength of the unconditioned material. The relationship between half-life $t_{1/2}$ and ageing temperature T ($40\text{ °C} \leq T \leq 70\text{ °C}$) can be represented by the following equation:

$$t_{1/2} = A + \frac{B}{T} \quad (14)$$

A and **B** are material constants determined by fitting the data to Equation (14). For the material under investigation, **A** is equal to -430 and **B** is equal to $147,915$. The values of $t_{1/2}$ for the different ageing temperatures were determined from curves fitted to the strength versus exposure plots.

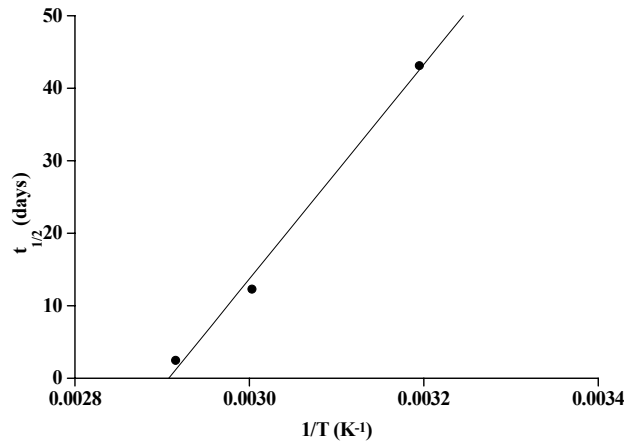


Figure 19: Tensile strength half-life versus temperature for E-glass/polyester.

It is possible to relate the rate of degradation of tensile strength with the rate of moisture uptake (i.e. diffusivity D), as shown in Figure 19. The diffusivity D is a function of absolute temperature T and is given by the Arrhenius relation:

$$D = D_0 \exp^{-E/RT} \quad (15)$$

D_0 is a constant, E is the activation energy of diffusion and R is the ideal gas constant. For the case of the unidirectional E-glass polyester material:

$$D = 0.056 \exp^{-2,300/T} \quad (16)$$

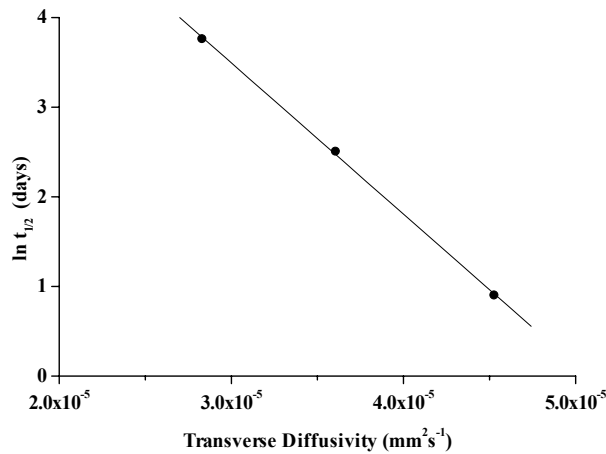


Figure 20: Tensile strength half-life as a function of diffusivity for E-glass/polyester.

The relationship between tensile strength half-life, $t_{1/2}$, and diffusivity, D , can be approximated by the following empirical relationship (see Figure 20):

$$\ln t_{1/2} = A - BD \quad (17)$$

Here, constants A and B have values of 9 and 168,662, respectively.

5 DISCUSSION AND CONCLUDING REMARKS

It was apparent when assessing the validity of the predictive models that the constituent property information was often unavailable or the manufacturers data was incomplete. This highlighted a need for the development of test procedures for measuring the mechanical and physical properties of the fibre, matrix and fibre-matrix interface. The fibre properties are often back calculated from experimental data. In the analysis, several assumptions were made about the fibre-matrix interface:

- (i) The fibre and matrix were perfectly bonded (i.e. no strain discontinuity across the boundary); and
- (ii) The matrix in the vicinity of the fibres has identical thermoelastic and strength properties as the unreinforced matrix material

The micromechanics formulations and laminate analysis used in the CoDA software proved satisfactory for predicting tensile strength and stiffness properties of dry and moisture conditioned unidirectional and cross-ply laminates. The analysis is applicable to both glass and carbon fibre-reinforced composite laminates.

The results show that micromechanics formulations (e.g. Halpin-Tsai) can be applied with reasonable confidence at elevated and sub-zero temperatures. The use of these equations, however, is limited to temperatures below the glass-transition temperature of the composite. As expected, the degree of correlation between the predicted and actual elastic constants was far better than that for the strength properties. The elastic properties of the resin systems can be reliably measured, whereas there is often considerable scatter in tensile strength data for unreinforced (bulk) resin specimens. Premature failure often occurs due to the presence of voids, which act as stress concentrators. This can result in large differences between measured and predicted transverse tensile strength for unidirectional laminates.

Using ply discount theory, it was possible to determine the elastic properties of damaged cross-ply laminates prior to final ply failure. The predicted and measured stiffness properties for the damaged laminate were in good agreement. The degree of correlation between predicted and actual first ply failure (FPF) stress for the cross-ply laminates could be improved by taking into account hygrothermal residual stresses in the laminate analysis and non-uniform moisture distribution. As previously mentioned, 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.

The shear-lag theory evaluated in Section 3.2 tended to underestimate the change in laminate stiffness with increasing transverse crack density for the cross-ply laminates. A number of alternative shear-lag models are available, but these tend to be more complicated and show only marginal improvement on the analysis presented in this report. A number of researchers have opted to use models based on damage mechanics, statistical analysis or fracture mechanics in order to relate property reduction with accumulated damage. These approaches are generally complex and difficult to implement. Indications are that mechanistic/physics based models, such as the plain strain model developed by Dr L N McCartney at NPL, provide better agreement with experimental data.

Semi-empirical models, such as the Kitagawa power-law and the non-dimensional temperature analysis can be used to determine the shear and flexural properties of hot/wet aged unidirectional laminates as a function of temperature and moisture content. Nevertheless, it proved difficult to apply the two modelling approaches to woven fabric materials, although this does not preclude the use of these methods for other systems and conditions.

The Arrhenius modelling approach proved useful for evaluating the rate of degradation and the residual strength with temperature for hot/wet conditioned unidirectional laminates at elevated temperatures. This approach can be used to determine the time required for the strength to degrade to a pre-determined or limit value (usually half its original value (half-life)). As with all the methods investigated, the method is not universally applicable to all materials, loading and environmental conditions. It was also possible to relate the rate of moisture uptake (i.e. diffusivity) with the rate of strength reduction.

ACKNOWLEDGEMENTS

This work forms part of the programme "Composites Performance and Design" funded by the Engineering Industries Directorate of the UK Department of Trade and Industry, as part of its support of the technological competitiveness of UK industry. The author would like to express his gratitude to all members of the Industrial Advisory Group (IAG) and to colleagues at the National Physical Laboratory, particularly to Ms M Lodeiro, Dr S Maudgal, Dr D Mulligan, Mr R Shaw, Mr S Gnaniyah and Mr G Nunn whose contributions have made this work possible.

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APPENDIX A
Material Properties

Table A1: Elastic and Strength Properties for AS4, XAS, T300B and T300 Carbon Fibres (Ambient Conditions)

Property	AS4	XAS	T300B	T300
Longitudinal modulus, E_{11} (GPa)	235	225	230	230
Transverse modulus, E_{22} (GPa)	20.9	14	15.9	20
Longitudinal shear modulus, G_{12} (GPa)	27.6	35.0	24.0	29.7
Longitudinal Poisson's ratio, ν_{12}	0.20	0.25	0.29	0.20
Longitudinal tensile strength, S_{11}^T (MPa)	3,587	3,200	3,500	3,530

Table A2: Elastic and Strength Properties of E-glass and HTA Carbon Fibres (Ambient Conditions)

Property	E-glass	HTA
Longitudinal modulus, E_{11} (GPa)	72	238
Transverse modulus, E_{22} (GPa)	72	20
Longitudinal shear modulus, G_{12} (GPa)	30	30
Longitudinal Poisson's ratio, ν_{12}	0.2	0.2
Longitudinal tensile strength, S_{11}^T (MPa)	2,200	3,400

Table A3: Epoxy Resin Elastic and Strength Properties (Ambient Conditions)

Property	F922		913	924
	Dry	Wet		
Young's modulus, E (GPa)	3.75	3.54	3.80	3.90
Shear modulus, G (GPa)	0.41	0.40	1.40	1.38
Poisson's ratio, ν	1.33	1.26	0.36	0.41
Tensile strength, S^T (MPa)	62	55	70	65
Compressive strength, S^C (MPa)	203	-	140	175
Shear strength, S (MPa)	117	-	70	175

Table A4: Shear Moduli of Unidirectional Carbon Fibre-Reinforced Laminates [6]

Temperature (K)	Composite System			
	AS4/3501-6	XAS/914	T300B/R23	APC-2
233	6.72	5.75	4.87	6.11
243	6.79	5.71	4.88	6.07
253	6.70	5.65	4.90	5.95
264	6.60	5.67	4.68	5.83
273	6.56	5.69	4.79	5.86
283	6.51	5.58	4.72	5.77
293	6.37	5.49	4.74	5.73
303	6.33	5.50	4.70	5.71
313	6.26	5.58	4.57	5.72
323	6.26	5.42	4.68	5.55
333	6.15	5.28	4.64	5.40
343	6.08	5.16	4.40	5.21
353	5.92	5.07	4.24	5.12
363	5.89	4.91	4.00	4.88

373	5.50	4.75	3.90	4.77
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Table A5: Shear Strength of Unidirectional Carbon Fibre-Reinforced Laminates [6]

Temperature (K)	Composite System			
	AS4/3501-6	XAS/914	T300B/R23	APC-2
233	80.30	88.18	85.86	84.59
243	76.27	88.91	78.89	80.22
253	76.28	87.00	84.31	81.67
264	74.51	85.39	85.62	77.15
273	74.86	83.72	85.59	79.60
283	77.56	83.57	80.81	80.27
293	75.19	81.87	76.02	76.53
303	73.21	81.96	77.25	73.28
313	77.26	78.71	76.82	74.17
323	74.21	76.04	72.50	75.18
333	76.94	81.48	73.77	74.38
343	73.92	76.95	69.80	72.10
353	73.19	82.13	68.79	75.30
363	73.20	77.36	68.96	74.56
373	71.21	69.91	63.80	67.34

Table A6: Shear Properties of Victrex Peek and R23 Epoxy [6]

Temperature (K)	Resin System			
	Victrex PEEK		R23 Epoxy	
	Modulus	Strength	Modulus	Strength
233	1.80	88.98	1.89	54.71
243	1.75	86.32	1.85	52.79
253	1.71	83.03	1.81	56.25
264	1.67	84.75	1.77	61.10
273	1.62	73.25	1.71	52.36
283	1.58	77.09	1.59	54.97
293	1.56	71.43	1.55	61.39
303	1.52	74.02	1.53	61.10
313	1.46	62.44	1.49	61.52
323	1.44	66.45	1.44	56.58
333	1.40	63.17	1.38	56.99
343	1.38	62.67	1.34	60.69
353	1.33	62.68	1.25	50.81
363	1.31	63.56	1.13	48.08
373	1.27	61.65	1.01	15.25

Table A7: Glass Transition (°C) Temperatures of Carbon Fibre-Reinforced Laminates [6]

AS4/3501-6	XAS/914	T300B/R23	APC-2
199	190	132	143

**Table A8: Flexure Properties of Unidirectional E-Glass/913 as a Function of Temperature
(Moisture content wt.%/Glass Transition Temperature)**

Test Temperature (K)	0 hrs (0.00%/429 K)	72 hrs (0.49%/413 K)	168 hrs (0.86%/401 K)	360 hrs (1.48%/386 K)
<u>Longitudinal modulus (GPa)</u>				
296	42.7	44.4	42.7	39.0
323	43.7	42.4	42.4	38.6
373	39.8	37.2	35.8	29.8
423	27.8	20.9	16.9	13.0
473	18.4	15.8	15.0	-
<u>Transverse modulus (GPa)</u>				
296	14.1	13.0	11.5	10.9
323	13.2	11.3	10.4	9.2
373	5.6	3.2	1.7	1.1
423	1.8	0.3	0.3	0.4
473	0.3	0.3	-	-
<u>Longitudinal strength (MPa)</u>				
296	1,486	1,272	1,233	950
323	1,293	1,130	978	876
373	701	470	415	270
423	344	203	169	113
473	156	107	95	-
<u>Transverse strength (MPa)</u>				
296	121	103	92	61
323	116	95	76	58
373	65	47	30	21
423	30	14	9	7
473	6	5	-	-

**Table A9: Flexure Properties of Unidirectional T300/924 as a Function of Temperature
(Moisture Content wt.%/Glass Transition Temperature)**

Test Temperature (K)	0 hrs (0.00%/429 K)	72 hrs (0.49%/413 K)	168 hrs (0.86%/401 K)	360 hrs (1.48%/390 K)
<u>Longitudinal modulus (GPa)</u>				
296	139	141	134	134
323	135	146	137	134
373	138	140	134	132
423	127	123	115	104
473	71	69	73	77
<u>Transverse modulus (GPa)</u>				
296	9.10	9.10	9.00	9.47
323	9.00	8.78	8.95	8.87
373	8.71	7.24	6.72	6.05
423	7.66	4.92	3.79	3.27
473	3.33	1.25	0.97	1.19
<u>Longitudinal strength (MPa)</u>				
296	1,681	1,640	1,584	1,511
323	1,602	1,463	1,459	1,456
373	1,347	1,192	1,166	1,116
423	957	794	676	637
473	330	302	297	294
<u>Transverse strength (MPa)</u>				
296	128	136	116	97
323	121	122	104	94
373	91	97	88	69
423	82	63	53	38
473	37	28	22	19