

**CompTest 2004**

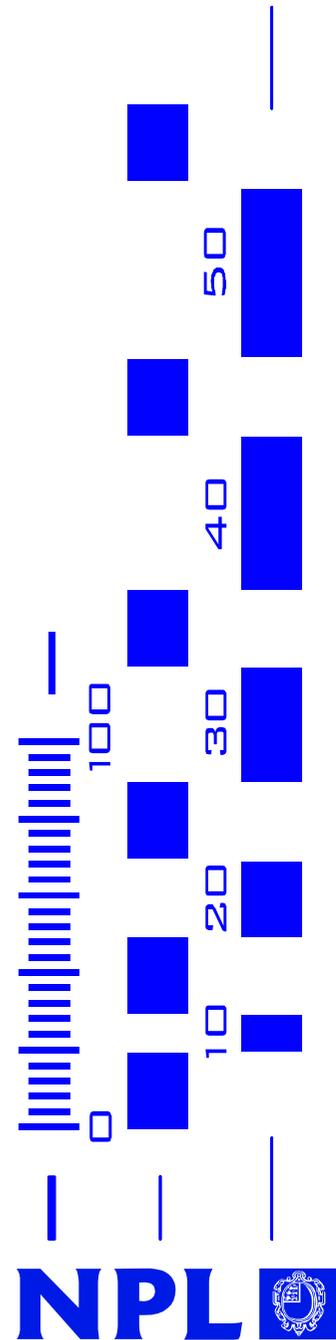
**Analytical Models for Assessing  
Environmental Degradation of  
Unidirectional and Cross-Ply Laminates**

**W R Broughton and M J Lodeiro**

**National Physical Laboratory**

**Teddington, UK**

**23 September 2004**



# Contents

- ◆ Introduction
- ◆ Materials
- ◆ Moisture Diffusion – Temperature Dependence
- ◆ Micromechanics + Classical Laminate Analysis
- ◆ Shear Lag Theory
- ◆ Empirical Relationships
  - ❖ Non-Dimensional Temperature
  - ❖ Kitagawa Power-Law Relationship
  - ❖ Arrhenius Model
- ◆ Concluding Remarks

# Introduction

- ◆ Mechanistic/physics based models are the preferred approach for determining the effect of environmental degradation on mechanical properties of PMCs
- ◆ Analytical and semi-empirical models can be used to determine the degree of degradation of elastic and strength properties with the level of degrading agent, typically:
  - ❖ Moisture
  - ❖ Temperature
  - ❖ Moisture + Temperature
- ◆ Experimental evaluation carried out on unidirectional and cross-ply GRP and CFRP laminates
- ◆ Models include input data obtained from conditioned resin samples

# Laminate Property Predictive Analysis

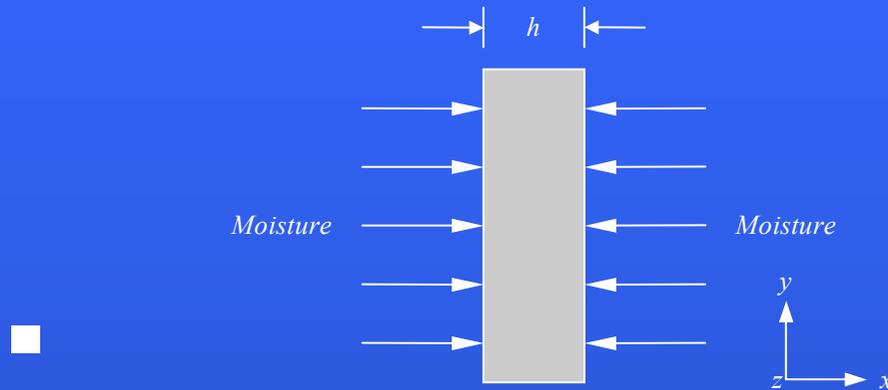
- ◆ Layer or ply properties - micro-mechanics
- ◆ Laminate properties - classical laminate analysis
- ◆ Thermo-elastic and strength properties
- ◆ Moisture diffusion (Fickian diffusion)
- ◆ CoDA (Composite Design and Analysis) and PREDICT\*
- ◆ Empirical relationships  $\Rightarrow$  predict moisture/temperature effects

\* NPL software packages

# Materials

- ◆ Unidirectional and cross-ply ( $0^\circ/90^\circ$ ) laminates
  - ❖ E-glass/913 and E-glass/F922
  - ❖ HTA/F922
  - ❖ T300/914, T300/924 and T300/976
  - ❖ APC-2 (carbon/peek)
  - ❖ T300B/R23
  - ❖ XAS/914
- ◆ Several cross-ply configurations were included in the assessment
  - ❖  $[0^\circ/90^\circ]_{4S}$
  - ❖  $[0^\circ_2/90^\circ_2]_S$
  - ❖  $[0^\circ_2/90^\circ_4]_S$
  - ❖  $[0^\circ_2/90^\circ_6]_S$
  - ❖  $[0^\circ_2/90^\circ_8]_S$

# Moisture Diffusion



Diffusion coefficient  $D$  can be calculated using:

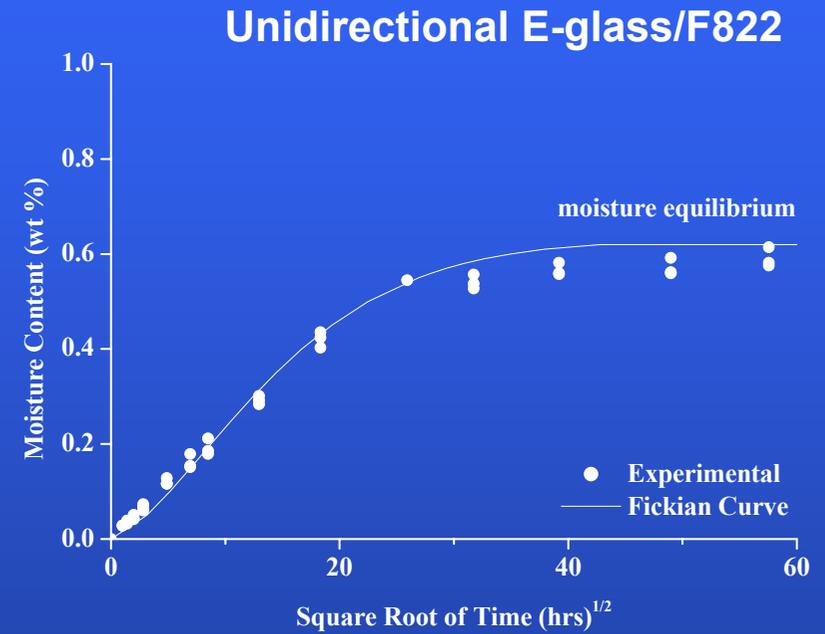
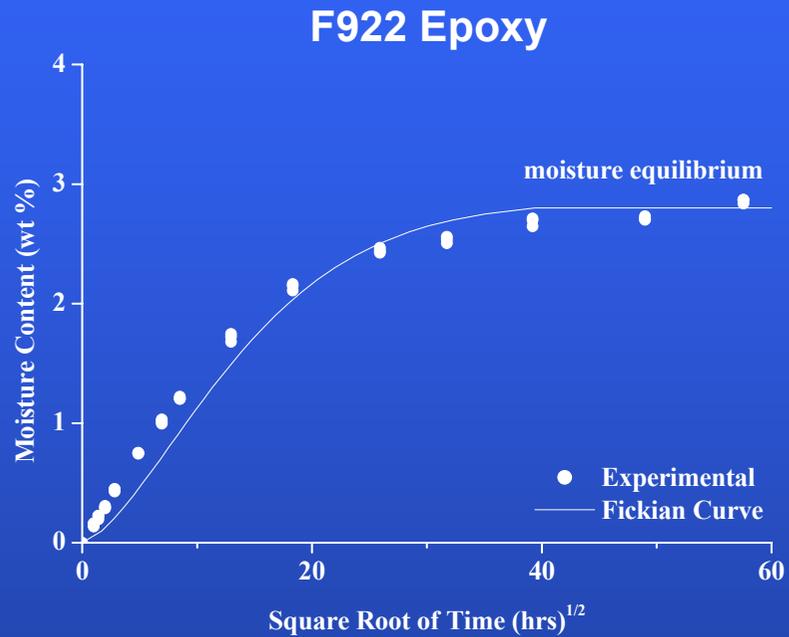
$$D = \frac{\pi}{16} \left( \frac{h(M_2 - M_1)}{M_\infty (\sqrt{t_2} - \sqrt{t_1})} \right)^2$$

$M$  Moisture content (wt%)

$M_\infty$  Equilibrium moisture concentration

$t$  Time

# Fickian Diffusion



# Diffusion Coefficients - Anisotropic Solids

Diffusion coefficients parallel and perpendicular to the fibres may be estimated using:

$$D_{11} = (1 - V_f) D_m \quad D_{22} = \left( 1 - 2\sqrt{\frac{V_f}{\pi}} \right) D_m$$

$D_m$  diffusivity of the matrix

$V_f$  fibre volume fraction

## Unidirectional E-glass/F922

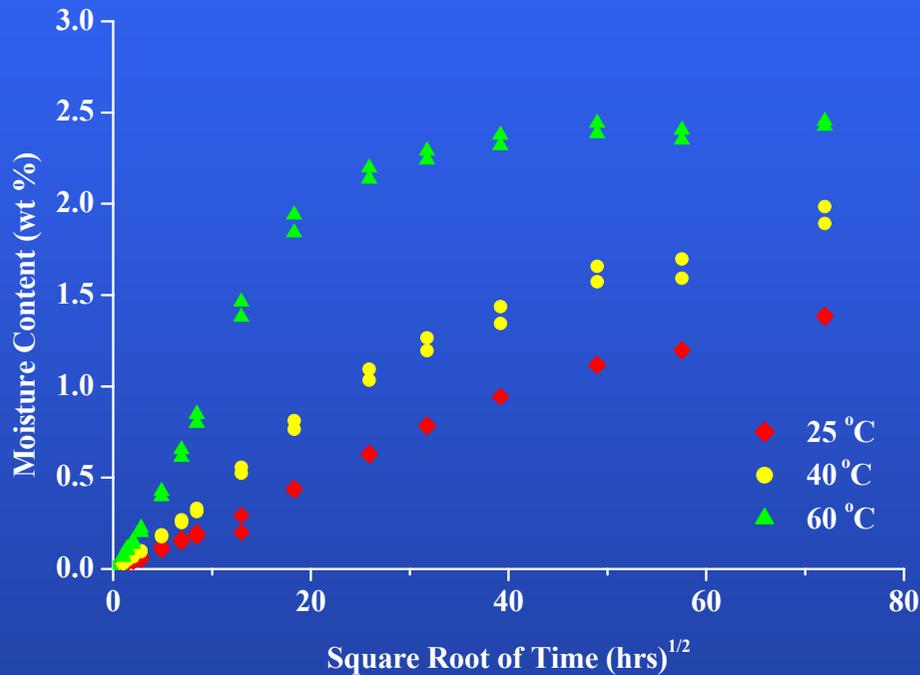
$$D_m = 8.3 \times 10^{-7} \text{ mm}^2 \text{ s}^{-1}$$

$$D_{22} = 6.3 \times 10^{-8} \text{ mm}^2 \text{ s}^{-1} \quad (\text{experimental})$$

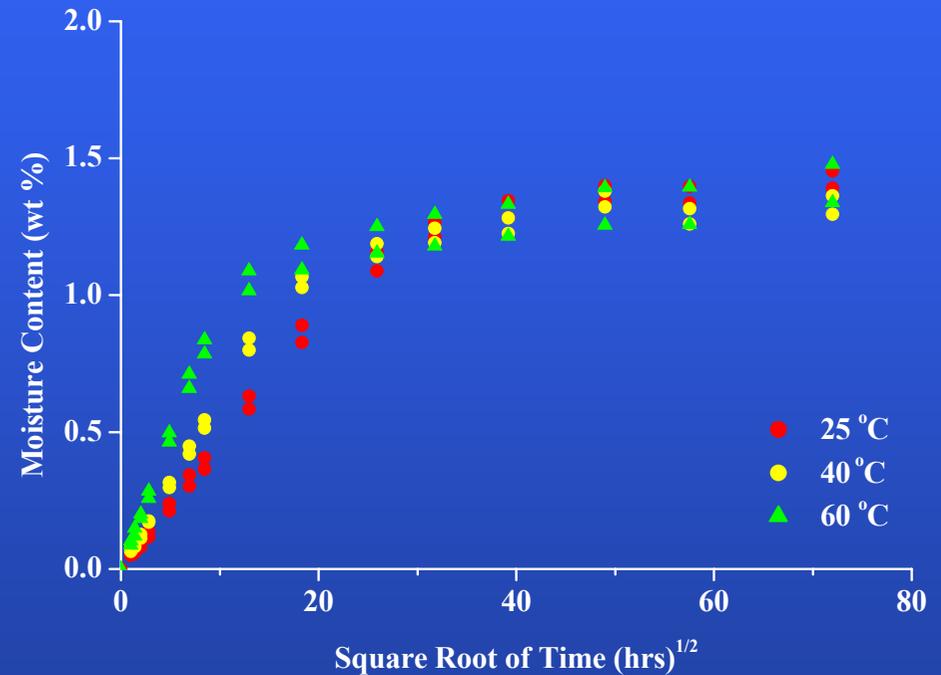
$$D_{22} = 7.3 \times 10^{-8} \text{ mm}^2 \text{ s}^{-1} \quad (\text{predicted})$$

# Diffusivity - Temperature Dependence

## Unidirectional E-glass/913



## Unidirectional T300/924



# Diffusivity - Temperature Dependence

## Arrhenius Relationship

$$D = D_0 \exp^{-E/RT}$$

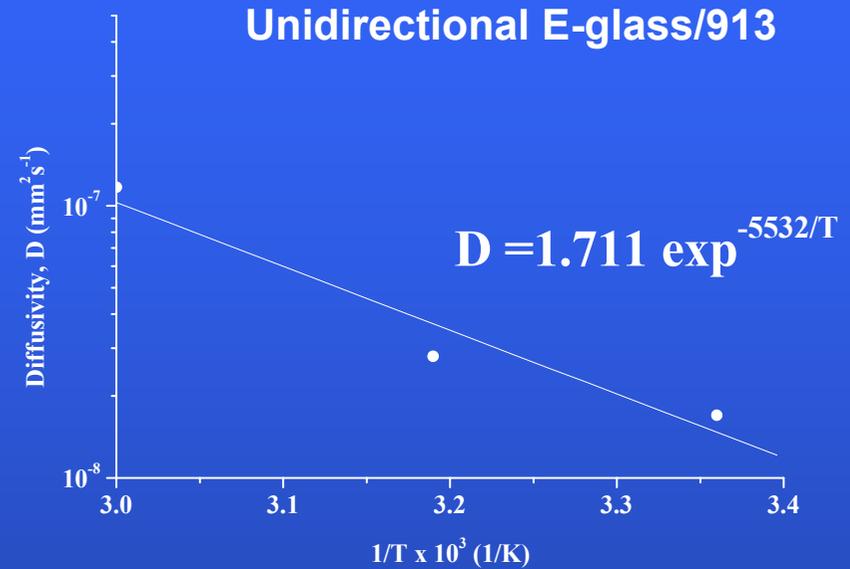
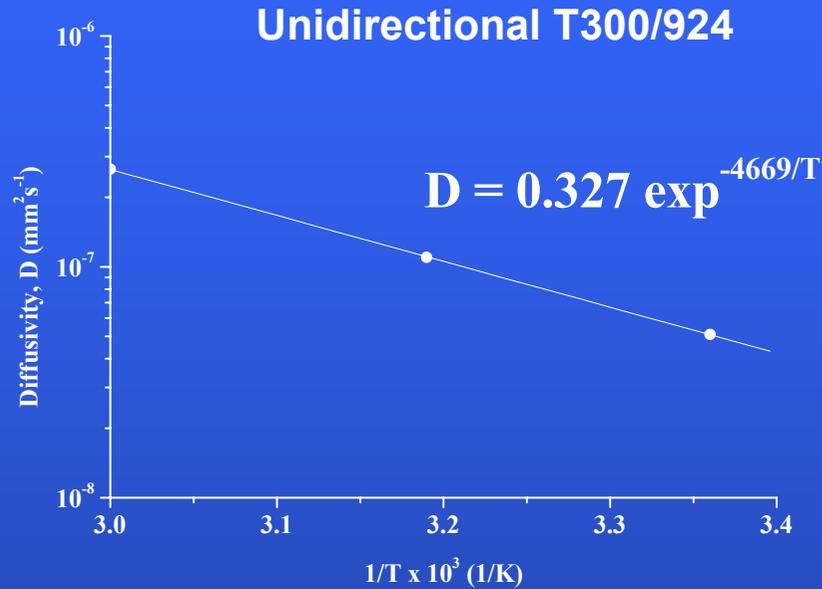
$D_0$  - constant

$E$  - activation energy

$R$  - ideal gas constant

$T$  - absolute temperature

# Transverse Diffusivity - Temperature Dependence



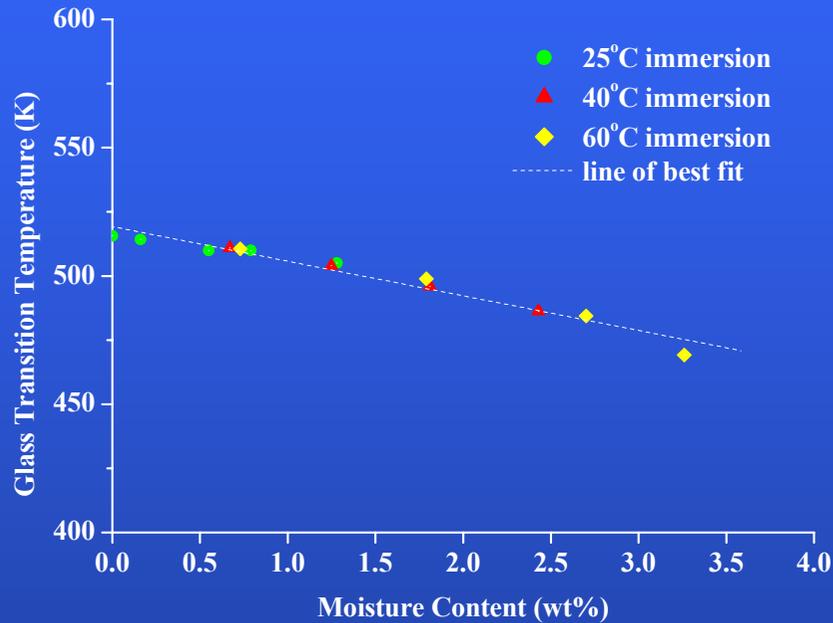
Arrhenius relationship:

$$D = D_0 \exp^{-k/T}$$

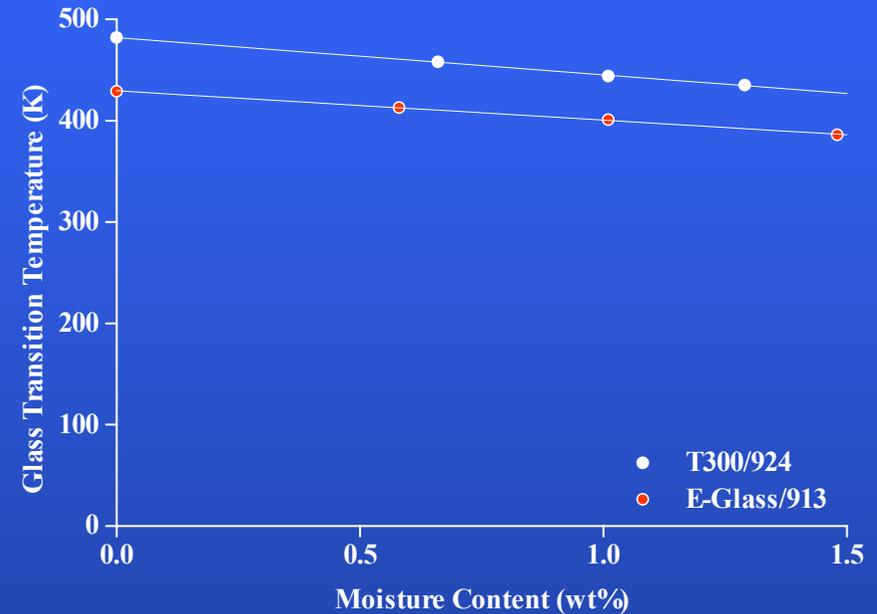
Note:  $D_0$  and  $k$  are experimentally determined constants

# Glass Transition Temperature vs Moisture Content

## F922 Epoxy



## Unidirectional E-glass/913



$$T_{\text{gwet}} = T_{\text{gdry}} - gM$$

**g** temperature shift (in K) per unit moisture absorbed

**M** moisture content (wt %)

# Moisture Effects on Thermoset Resins

- ◆ Swelling, weight gain and cavity formation
- ◆ Plasticisation
  - ❖ Reduction in glass transition temperature
  - ❖ Lower operating temperatures
  - ❖ Reduction in stiffness and strength properties
- ◆ Chemical leaching
  - ❖ Loss of fillers, catalysts, hardeners, pigments or fire retardants

# Moisture Effects on E-Glass Fibres

- ◆ Leaching of alkali oxides (sodium + potassium) from the fibre surface
- ◆ Formation of surface micro-cracks  $\Rightarrow$  stress concentrators
- ◆ Glass fibres slowly decompose/dissolve
- ◆ Permanent loss of strength (even after drying)
- ◆ Process accelerated with increasing temperature and stress

# Moisture +Temperature Effects Unidirectional and Cross-Ply Laminates

- ◆ Conditioned at 70°C/85% RH (1,000 hrs)
- ◆ Micromechanics  $\Rightarrow$  lamina (layer) elastic and strength properties
  - ❖ Rule of mixtures, Halpin-Tsai, etc.
- ◆ Classical analysis  $\Rightarrow$  laminate elastic and strength property predictions
  - ❖ Loss of integrity (i.e. ply failure) - ply discount theory
  - ❖ All elastic properties (except  $E_{11}$ ) of failed 90° plies set to zero
- ◆ CoDA  $\Rightarrow$  synthesise lamina and laminate properties

# Tensile Properties for UD Laminates at Ambient (Measured/Predicted)

Material	Tensile Strength (MPa)	Tensile Modulus (GPa)	Poisson's Ratio
<b><u>E-glass/913 (dry)</u></b>			
Longitudinal	1215/ 1178	43.0/ 36.6	0.30/ 0.33
Transverse	73.1/ 56.5	12.5/ 10.7	0.094/ 0.091
<b><u>E-glass/F922 (dry)</u></b>			
Longitudinal	1087/ 1479	43.0/ 46.0	0.31/ 0.33
Transverse	58.6/ 52.9	13.9/ 15.4	0.098/ 0.102
<b><u>E-glass/F922 (wet)</u></b>			
Longitudinal	797/ 1475	37.2/ 45.9	0.31/ 0.33
Transverse	64.1/ 36.5	14.3/ 14.5	0.108/ 0.096
<b><u>T300/924 (dry)</u></b>			
Longitudinal	1723/ 2193	133 ± 2/ 136	0.34/ 0.29
Transverse	92.7/ 56.1	8.5/ 8.7	0.020/ 0.021
<b><u>HTA/F922 (dry)</u></b>			
Longitudinal	1684/ 2016	126/ 134	0.32/ 0.34
Transverse	46.2/ 53.0	9.9/ 8.3	0.023/ 0.020
<b><u>HTA/F922 (wet)</u></b>			
Longitudinal	1728/ 2014	130/ 134	0.33/ 0.34
Transverse	48.6/ 36.4	8.9/ 7.9	0.022/ 0.022

# Strength of E-glass/F922 and HTA/F922 Cross-Ply Laminates (Ambient Test Conditions)

Material	First Ply Failure Stress (MPa)		Tensile Strength (MPa)	
	Measured	Predicted	Measured	Predicted
<b><u>E-glass/F922 (dry)</u></b>				
[0 <sub>2</sub> / 90 <sub>2</sub> ] <sub>s</sub>	150	110	486	431
[0 <sub>2</sub> / 90 <sub>4</sub> ] <sub>s</sub>	99	91	316	253
[0 <sub>2</sub> / 90 <sub>8</sub> ] <sub>s</sub>	65	76	170	135
<b><u>E-glass/F922 (wet)</u></b>				
[0 <sub>2</sub> / 90 <sub>2</sub> ] <sub>s</sub>	178	80	340	312
[0 <sub>2</sub> / 90 <sub>4</sub> ] <sub>s</sub>	134	65	282	181
[0 <sub>2</sub> / 90 <sub>8</sub> ] <sub>s</sub>	98	54	159	98
<b><u>HTA/F922 (dry)</u></b>				
[0 <sub>2</sub> / 90 <sub>2</sub> ] <sub>s</sub>	360	455	814	972
[0 <sub>2</sub> / 90 <sub>4</sub> ] <sub>s</sub>	135	322	516	649
[0 <sub>2</sub> / 90 <sub>6</sub> ] <sub>s</sub>	149	255	407	484
<b><u>HTA/F922 (wet)</u></b>				
[0 <sub>2</sub> / 90 <sub>2</sub> ] <sub>s</sub>	399	455	864	972
[0 <sub>2</sub> / 90 <sub>4</sub> ] <sub>s</sub>	267	322	569	649
[0 <sub>2</sub> / 90 <sub>6</sub> ] <sub>s</sub>	189	182	413	454

# Longitudinal Moduli of E-glass/F922 and HTA/F922 Cross-Ply Laminates (Ambient Test Conditions)

Material	Initial Modulus (GPa)		Final Modulus (GPa)	
	Measured	Predicted	Measured	Predicted
<b><u>E-glass/F922 (dry)</u></b>				
[0 <sub>2</sub> / 90 <sub>2</sub> ] <sub>s</sub>	29.4	28.6	23.5	22.1
[0 <sub>2</sub> / 90 <sub>4</sub> ] <sub>s</sub>	26.2	23.1	16.1	14.5
[0 <sub>2</sub> / 90 <sub>8</sub> ] <sub>s</sub>	20.2	16.8	9.4	8.5
<b><u>E-glass/F922 (wet)</u></b>				
[0 <sub>2</sub> / 90 <sub>2</sub> ] <sub>s</sub>	25.3	28.1	21.4	22.0
[0 <sub>2</sub> / 90 <sub>4</sub> ] <sub>s</sub>	26.8	22.5	16.7	14.5
[0 <sub>2</sub> / 90 <sub>8</sub> ] <sub>s</sub>	19.2	16.1	9.5	8.5
<b><u>HTA/F922 (dry)</u></b>				
[0 <sub>2</sub> / 90 <sub>2</sub> ] <sub>s</sub>	64.4	70.2	60.7	66.3
[0 <sub>2</sub> / 90 <sub>4</sub> ] <sub>s</sub>	46.7	49.8	41.9	44.4
[0 <sub>2</sub> / 90 <sub>6</sub> ] <sub>s</sub>	37.6	39.1	31.8	32.3
<b><u>HTA/F922 (wet)</u></b>				
[0 <sub>2</sub> / 90 <sub>2</sub> ] <sub>s</sub>	66.4	70.0	61.0	66.2
[0 <sub>2</sub> / 90 <sub>4</sub> ] <sub>s</sub>	47.0	49.8	42.1	44.4
[0 <sub>2</sub> / 90 <sub>6</sub> ] <sub>s</sub>	38.1	38.9	31.7	31.8

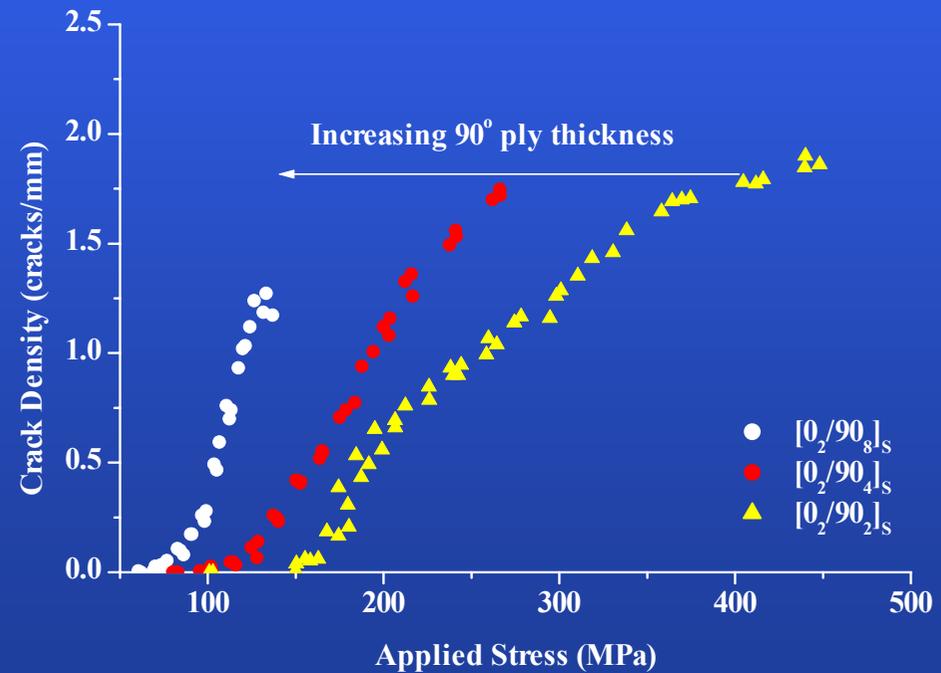
## Poisson's Ratios of E-glass/F922 and HTA/F922 Cross-Ply Laminates (Ambient Test Conditions)

Material	Initial Poisson's Ratio		Final Poisson's Ratio	
	Measured	Predicted	Measured	Predicted
<b><u>E-glass/F922 (dry)</u></b>				
$[0_2/90_2]_s$	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
<b><u>E-glass/F922 (wet)</u></b>				
$[0_2/90_2]_s$	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
<b><u>HTA/F922 (dry)</u></b>				
$[0_2/90_2]_s$	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
<b><u>HTA/F922 (wet)</u></b>				
$[0_2/90_2]_s$	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

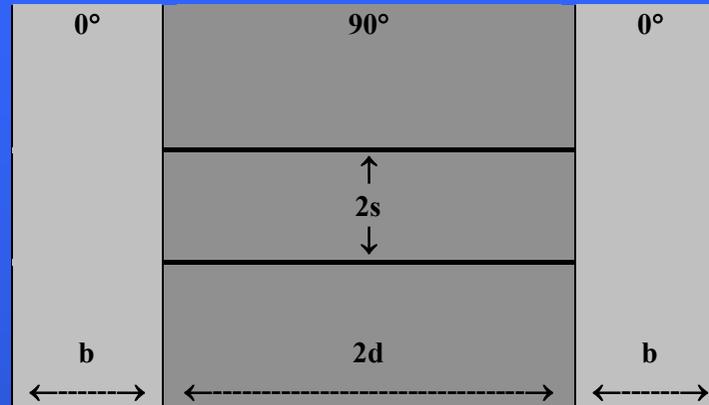
# Temperature Dependence - Unidirectional T300/924

Property	Temperature (°C)		
	-40	20	120
<b><u>Longitudinal tensile modulus, <math>E_{11}^T</math> (GPa)</u></b>			
Measured	133	135	139
Predicted	144	143	142
<b><u>Transverse tensile modulus, <math>E_{22}^T</math> (GPa)</u></b>			
Measured	10.8	10.5	8.2
Predicted	13.3	10.5	8.4
<b><u>Longitudinal shear modulus, <math>G_{12}</math> (GPa)</u></b>			
Measured	5.9	5.1	3.5
Predicted	7.7	5.1	4.5
<b><u>Longitudinal Poisson's ratio, <math>\nu_{12}</math></u></b>			
Measured	0.37	0.40	0.39
Predicted	0.40	0.40	0.39
<b><u>Longitudinal tensile strength, <math>S_{11}^T</math> (MPa)</u></b>			
Measured	1,750	1,683	1,550
Predicted	2,211	2,195	2,186
<b><u>Transverse tensile strength, <math>S_{22}^T</math> (MPa)</u></b>			
Measured	63.6	60.8	56.1
Predicted	48.9	44.1	24.7

# Transverse Cracking E-glass/F922 Cross-Ply Laminates



# Shear Lag Theory



- ◆ Reduction in  $E_{xx}$  as a function of average crack spacing,  $2s$ , is given by:

$$\frac{E_{xx}}{E_{xx0}} = \frac{1}{1 + \frac{E_{xx0}}{E_{11}} \left( \frac{b+d}{b} - \frac{E_{11}}{E_{xx0}} \right) \frac{\tanh(\lambda s)}{\lambda s}}; \quad \lambda^2 = \frac{3G_{12}(b+d)E_{xx0}}{d^3 b E_{22} E_{11}}$$

- ◆  $E_{xx}$ ,  $E_{xx0}$ ,  $E_{11}$  and  $E_{22}$  are the longitudinal moduli of the cracked composite, uncracked composite, the longitudinal plies and the transverse plies, respectively.

# Longitudinal Moduli at Onset of Failure for Cross-Ply Laminates E-glass/F922 and HTA/F922 (Ambient Test Conditions)

Material	Measured	Laminate Analysis	Shear Lag Theory
<b><u>E-glass/F922</u></b>			
$[0_2/90_2]_s$	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
<b><u>HTA/F922</u></b>			
$[0_2/90_2]_s$	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

# Empirical Approach - Non-Dimensional Temperature Laminate Property Predictions

$$\frac{P}{P_0} = \left( \frac{T_{\text{gwet}} - T}{T_{\text{gdry}} - T_0} \right)^n \quad \text{where} \quad T_{\text{gwet}} = T_{\text{gdry}} - gM$$

■

**P** Material property (e.g. longitudinal tensile strength)

**P<sub>0</sub>** Initial property value of the dry material at room or reference temperature **T<sub>0</sub>** (296 K)

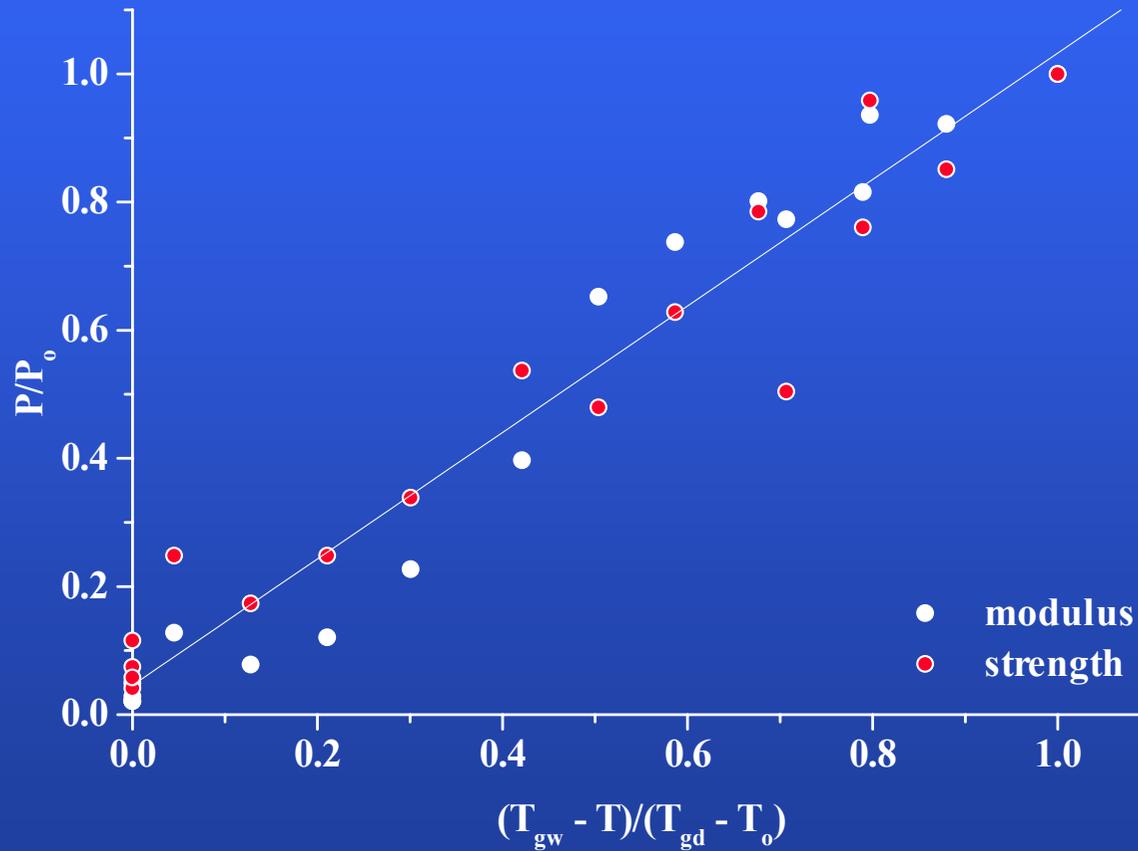
**T** Test temperature (K)

**T<sub>g</sub>** Glass transition temperature of the material

**g** Temperature shift (in K) per unit moisture absorbed

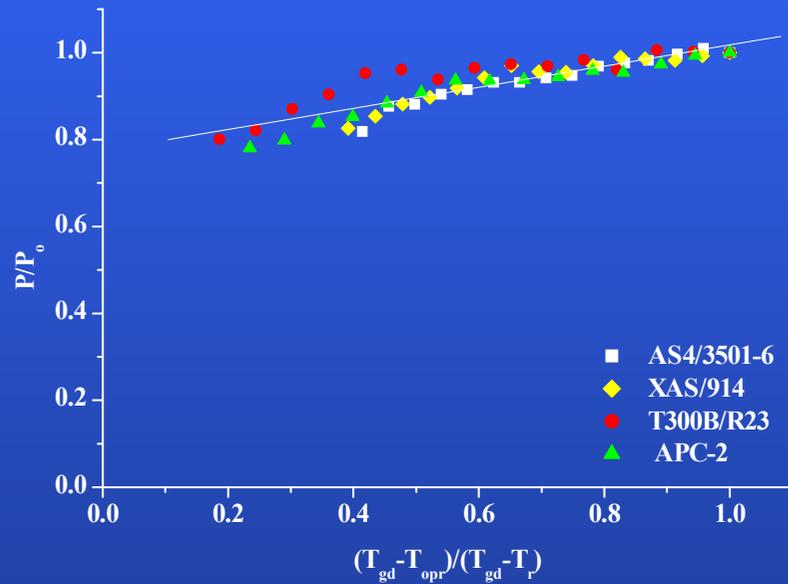
**M** amount of moisture absorbed (wt %)

# Transverse Properties Unidirectional E-glass/913 Epoxy

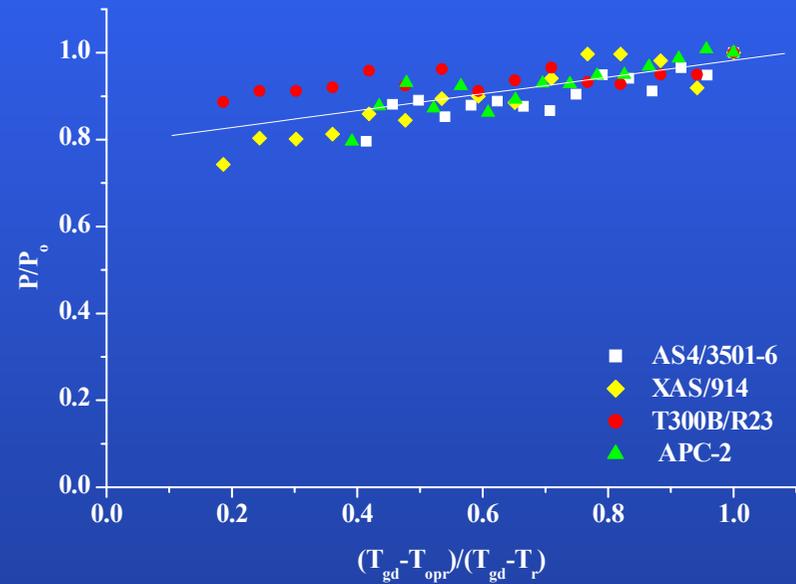


# In-Plane Shear Properties Unidirectional Laminates

## Shear Modulus



## Shear Strength



# Kitagawa Power-Law Relationship Shear Properties

Kitagawa power-law relationship between shear yield stress,  $\tau$ , and shear modulus,  $G$ , for glassy polymers is:

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

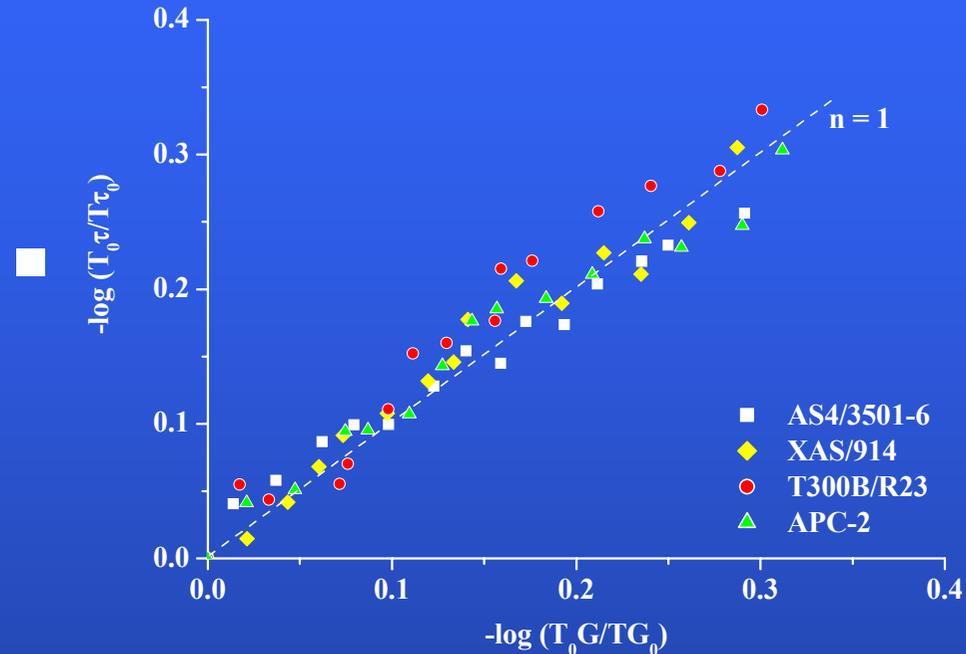
$T_0$  Reference temperature (K) - generally room temperature (296K)

$\tau_0$  Shear yield stress at  $T_0$

$G_0$  Shear modulus at  $T_0$

$n$  Constant

# Kitagawa Power-Law – In-Plane Shear Properties Unidirectional CFRP Laminates



Value of Exponent n

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

# Kitagawa Power-Law Relationship Flexural Properties

Kitagawa power-law relationship between flexural strength,  $\sigma_f$ , and flexural modulus,  $E_f$ , for glassy polymers is:

$$\frac{T_0 \sigma_f}{T \sigma_{f_0}} = \left( \frac{T_0 E_f}{T E_{f_0}} \right)^n$$

$T_0$  Reference temperature (K)

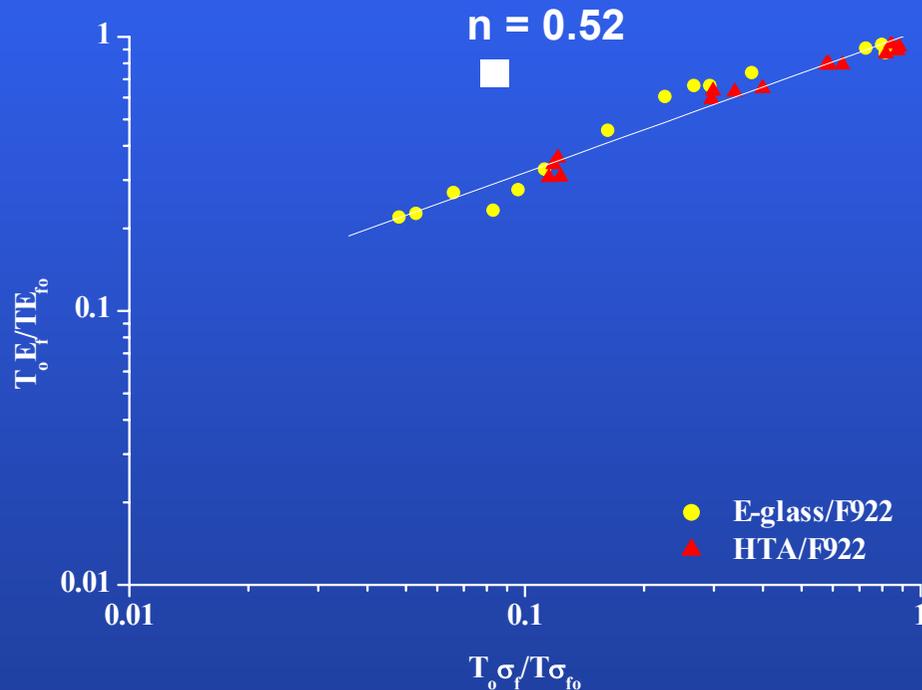
$\sigma_{f_0}$  Flexural strength at  $T_0$

$E_{f_0}$  Flexural modulus at  $T_0$

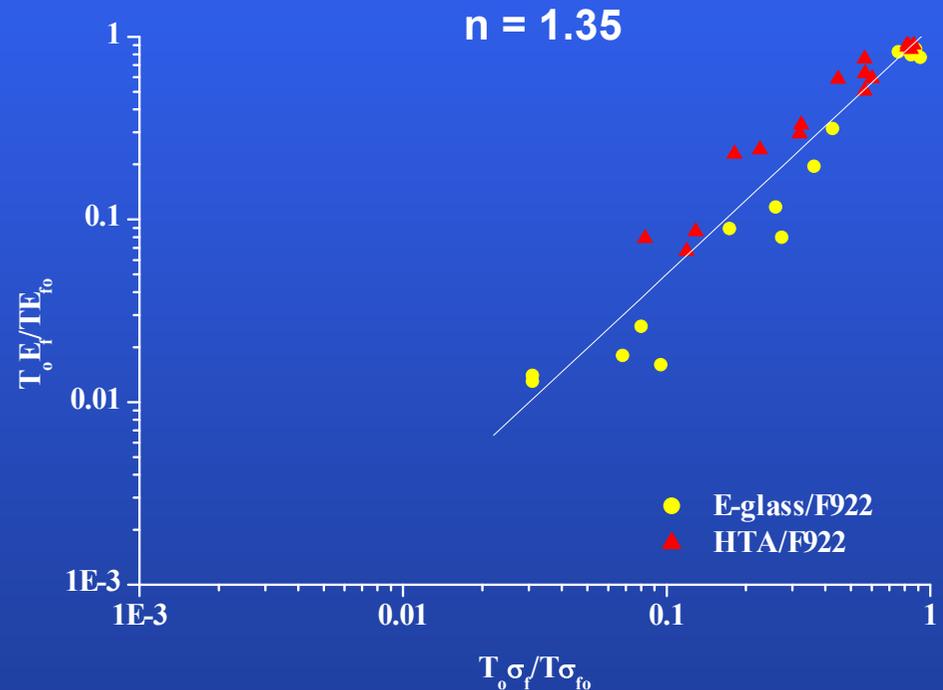
$n$  Constant

# Kitagawa Power-Law – Flexural Properties Unidirectional E-glass/F922 and HTA/F922

## Longitudinal Flexure



## Transverse Flexure



# Concluding Remarks

- ◆ Micromechanics combined with laminate analysis proved satisfactory for predicting tensile properties of dry and moisture conditioned unidirectional and cross-ply laminates.
- ◆ Using ply discount theory, it was possible to determine the elastic properties of damaged cross-ply laminates prior to final ply failure.
- ◆ Shear-lag theory can be used to determine changes in laminate stiffness with transverse cracking – mechanistic/physics based models offer improved accuracy.
- ◆ Kitagawa power-law + non-dimensional temperature analysis can be used to determine shear and flexural properties of unidirectional laminates as a function of temperature and moisture content.

# ACKNOWLEDGEMENTS

This work forms part of the Measurements for Materials Systems (MMS) Programme funded by the United Kingdom Department of Trade and Industry (National Measurement System Directorate).

The authors would like to express their gratitude to the Industrial Advisory Group, and NPL colleagues Dr S Maudgal, Dr D Mulligan, Mr R Shaw, Mr S Gnaniah and Mr G Nunn, whose contributions and advice have made the work possible.