

# **Effects of Moisture Absorption on Polymer Composites and Adhesives**

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**National Physical Laboratory**

**TMAN Event**

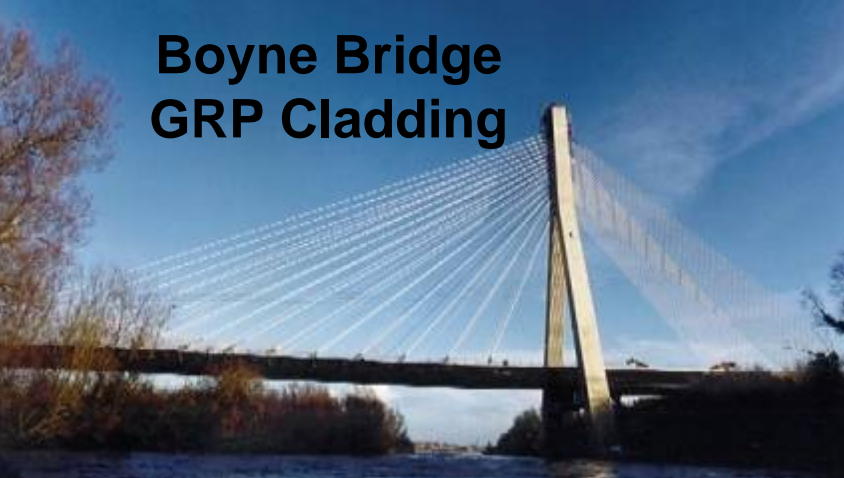
**Measurement & Control of Moisture in Materials**

**4th February 2009**

# Content

- ◆ **Background**
- ◆ **Composites**
- ◆ **Adhesive Joints**
- ◆ **Conclusions**

**Boyne Bridge  
GRP Cladding**



**Chemical Plant + Storage**



**Chemical + Water Treatment  
Over 30 year service**



# Applications

**Wind Turbine  
Off-shore**



*Courtesy of White Young Green*

# Applications



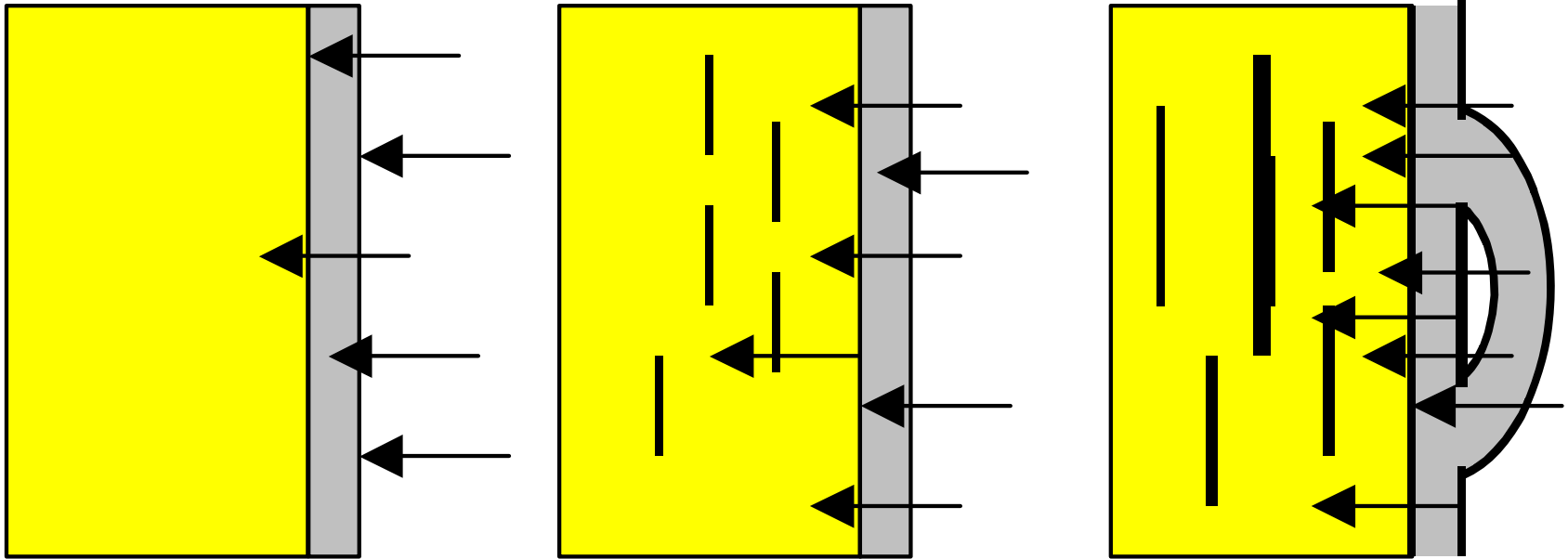
# Requirements

- ◆ **Growing demand for manufacturers to guarantee product life expectancy**
  - **Particularly where inspection and/or maintenance can be difficult or failure catastrophic**
- ◆ **Effective use of composites and adhesives for use in hostile (hot/wet) environments hinges on the availability of validated design data that is applicable for the entire structure service life (often 20-50 years, or longer)**
- ◆ **Reliable in-situ, real-time techniques for measuring moisture content and distribution in composite and bonded structures**

# Osmotic Blistering Glass Fibre-Reinforced Plastic (GRP)



# Osmotic Blistering Glass Fibre-Reinforced Plastic (GRP)



# Osmotic Blistering

## Glass Fibre-Reinforced Plastic (GRP)

- ◆ Water vapour permeates the structure
- ◆ As water diffuses into the composite it reacts with any hydrolysable components inside the laminate to form tiny cells of concentrated solution
- ◆ Under this osmotic process, more water is drawn through the semi-permeable membrane of the laminate in an attempt to dilute the solution
- ◆ The water can increase the fluid pressure of the cell substantially (up to 50 atmospheres), which eventually distorts or bursts the laminate and leads to a blistering of the surface
- ◆ Damage can be very extensive requiring major repair or the replacement of the structure

# BRE Study

**Deterioration of gel-coat**

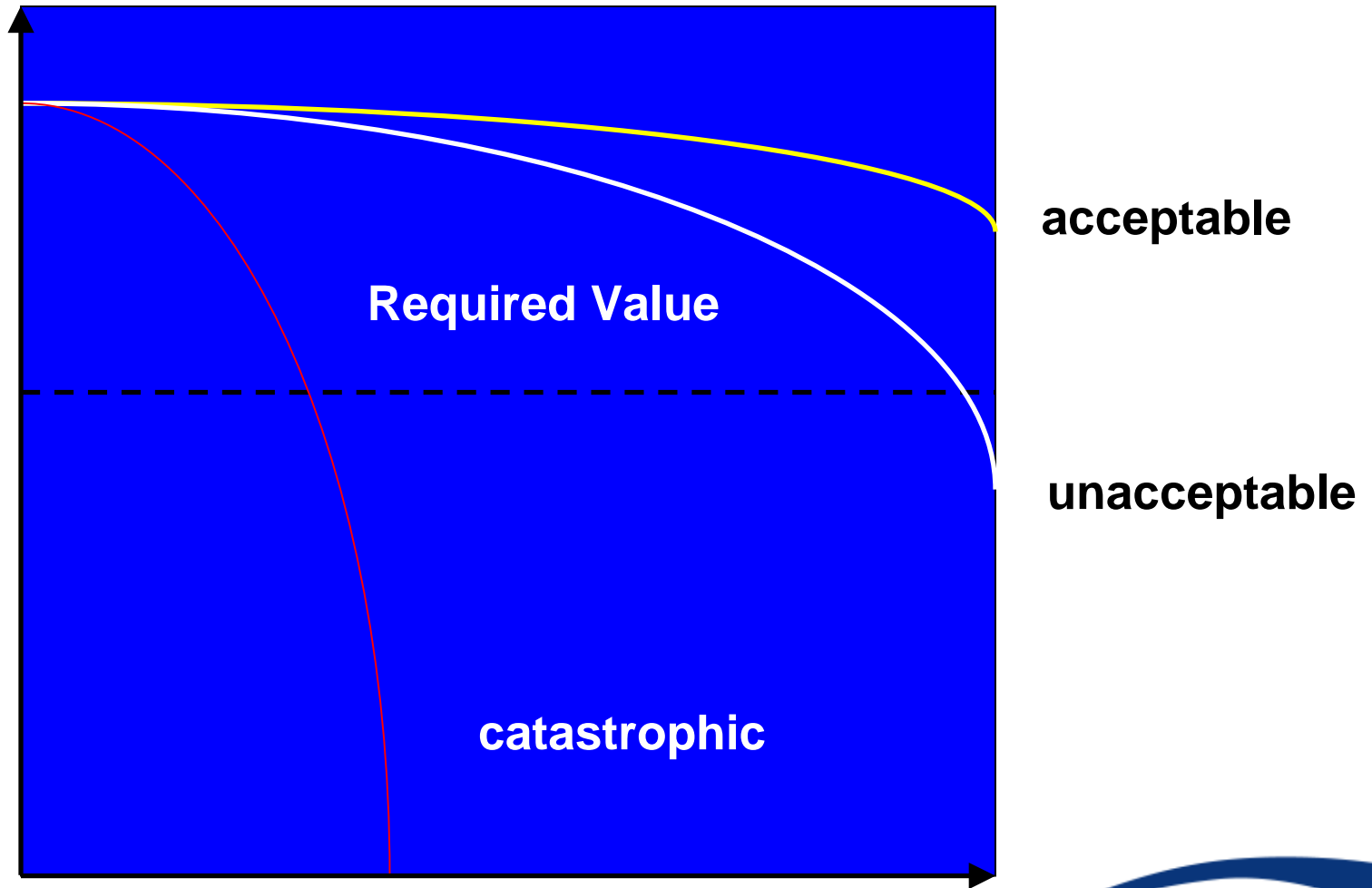


**Crazing of surface**



**Un-even discoloration**

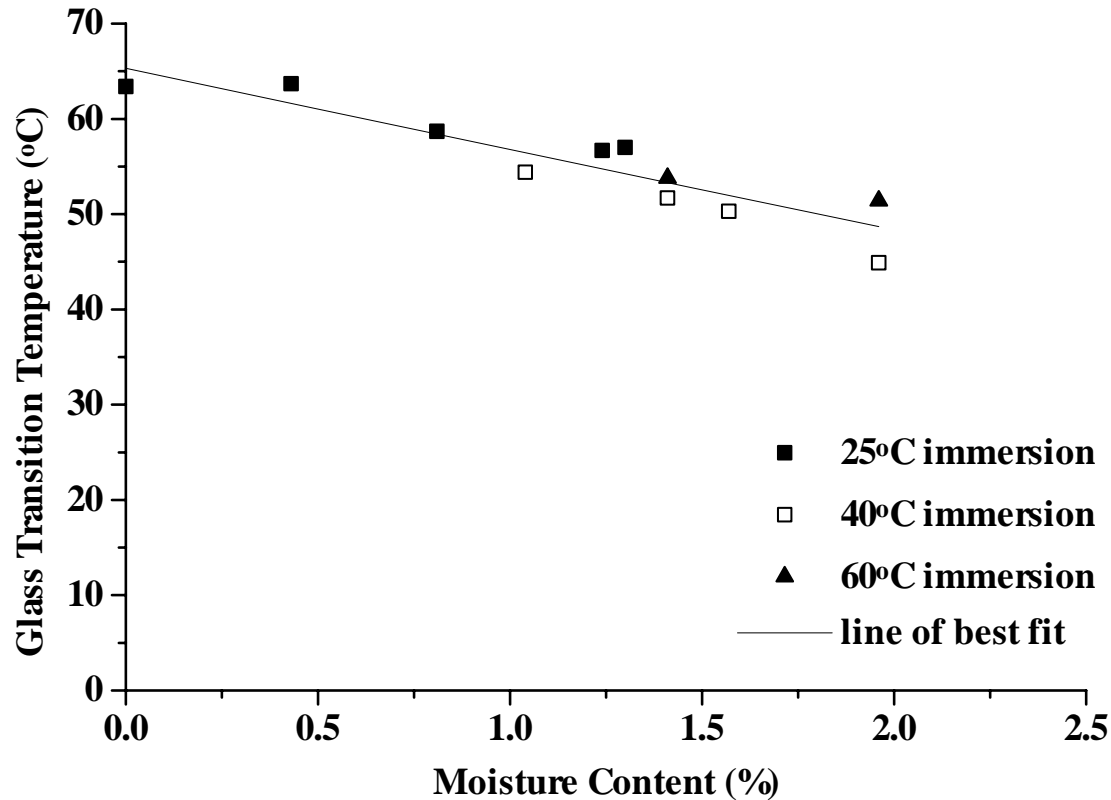
# Environmental Degradation Possible Outcomes



# 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**

# Glass Transition Temperature Moisture Conditioned Polyester Resin



# Fibre Types

## ◆ E-Glass (electrical)

- Relatively low cost (£1-2/kg)
- Most common form of fibre-reinforcement used for PMCs
- Sensitive to moisture and other chemicals

## ◆ C and E-CR Glass (chemical)

- Good chemical resistance to chemical attack

## ◆ Carbon Fibres

- High resistance to corrosion, moisture, creep and fatigue
- Low production volumes/relatively high price

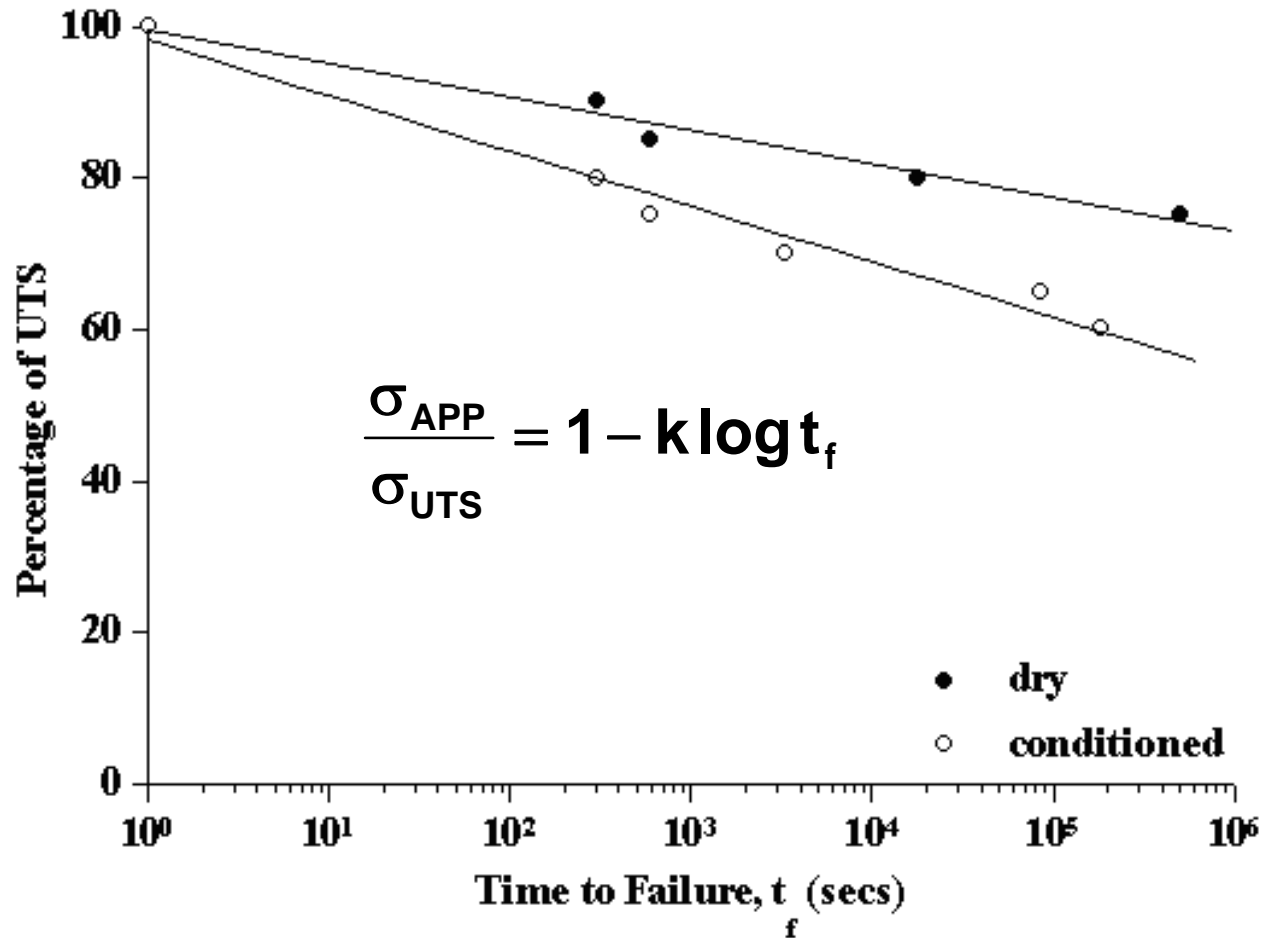
## ◆ Aramid Fibres

- Sensitive to moisture

# Moisture Effects on E-glass Fibres

- ◆ Leaching of alkali oxides (sodium and potassium oxide) from the fibre surface
- ◆ Formation of surface micro-cracks ⇒ stress concentrators
- ◆ Glass fibres slowly decompose/dissolve
- ◆ Permanent loss of strength (even after drying)
  - **Strength reduces by 20% in de-ionised water at room temperature after 3 weeks exposure**
- ◆ Degradation accelerates as temperature and stress increase
- ◆ De-ionised water more aggressive than tap water and saltwater

# Stress Rupture of E-glass Fibres



# Moisture Effects on PMCs

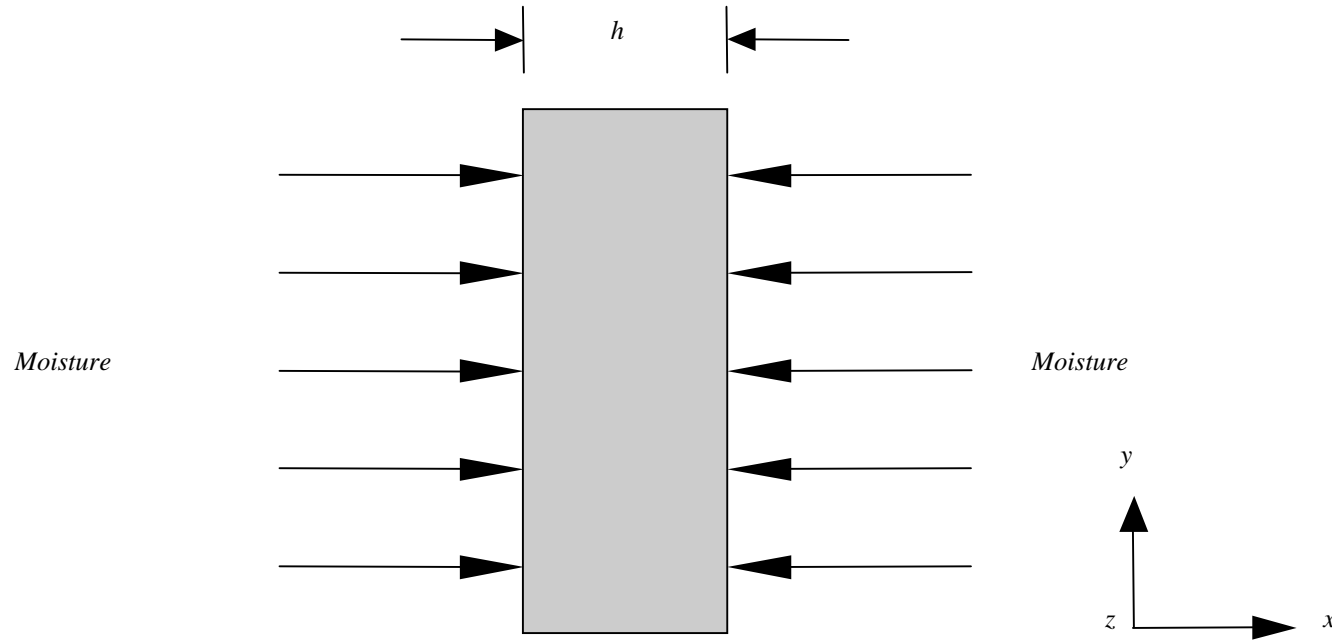
## ◆ Physical Effects

- Capillarity effects on fluid uptake
- Fibre/matrix interfacial breakdown
- Swelling and weight gain
- Micro-cracking
- Fibre/matrix interfacial breakdown
- Loss of fillers, catalysts, hardeners, pigments or fire retardants
- Osmotic blistering/cavity formation

## ◆ Mechanical/Physical Property Effects

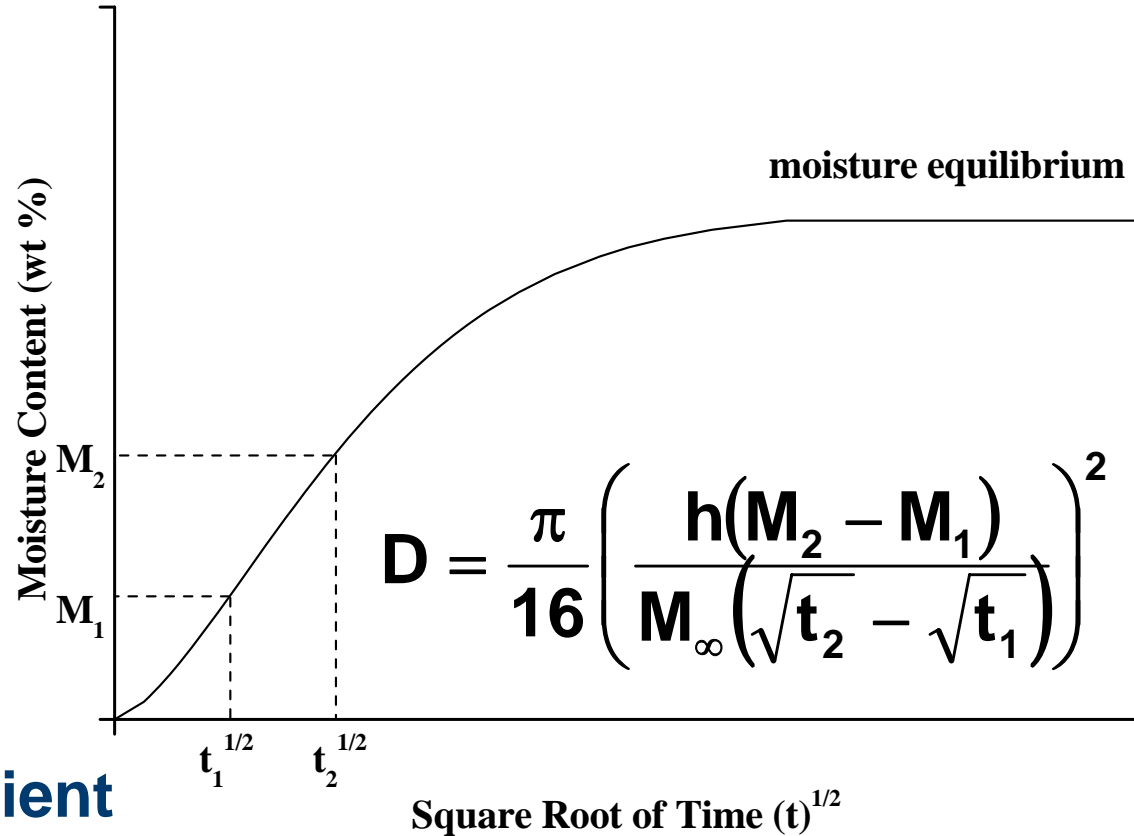
- Reduction in glass transition + operating temperatures
- Reduction in stiffness and strength properties
- Reduction in fatigue performance
- Shortened life expectancy

# Moisture Diffusion



$$M = \frac{(W_{\text{WET}} - W_{\text{DRY}})}{W_{\text{DRY}}} \times 100\%$$

# Fickian Diffusion



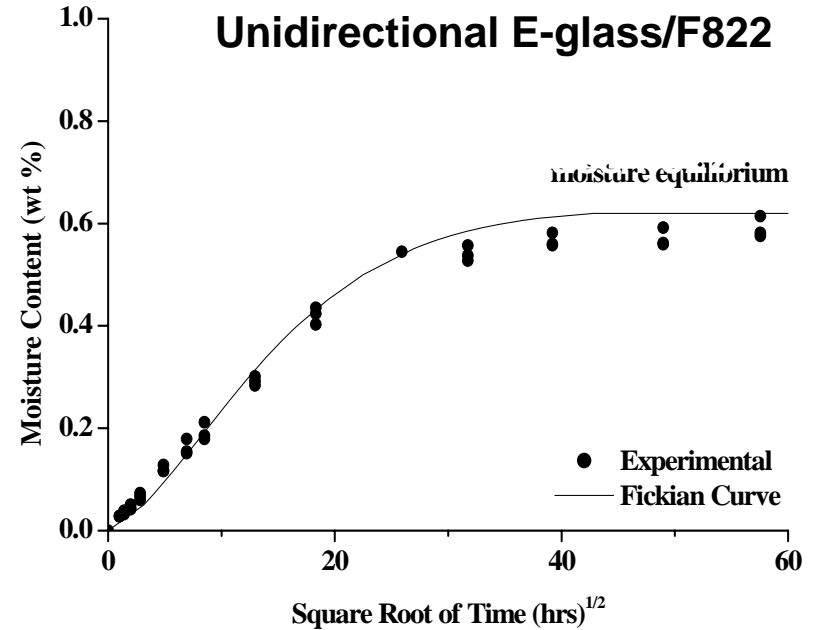
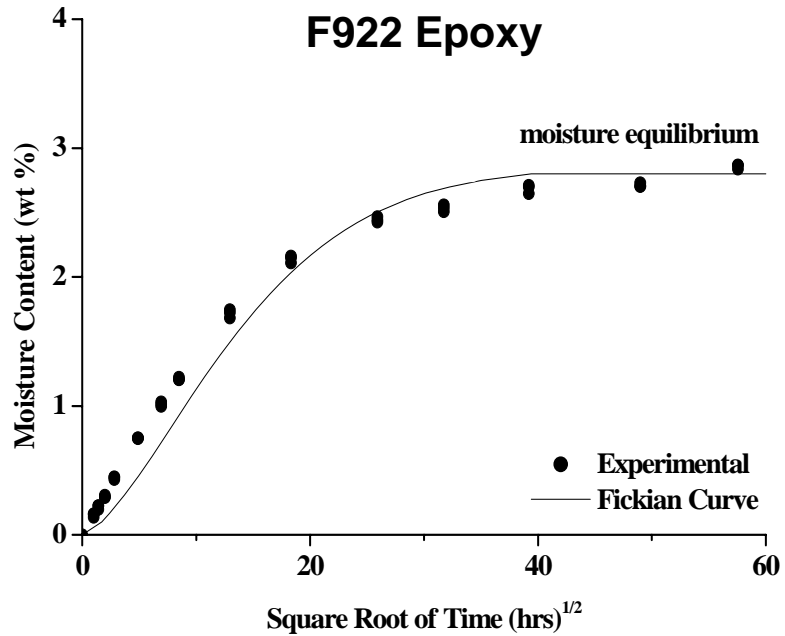
**D is Diffusion coefficient**

**M is moisture content (wt%)**

**$M_\infty$  is equilibrium moisture concentration**

**t is exposure time**

# Fickian Diffusion



# Diffusion Coefficients- Anisotropic Solids

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

$$D_{11} = (1 - V_f)D_m$$

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

$D_m$  = diffusivity of the matrix,  $V_f$  = fibre volume fraction

## Unidirectional E-glass/F922

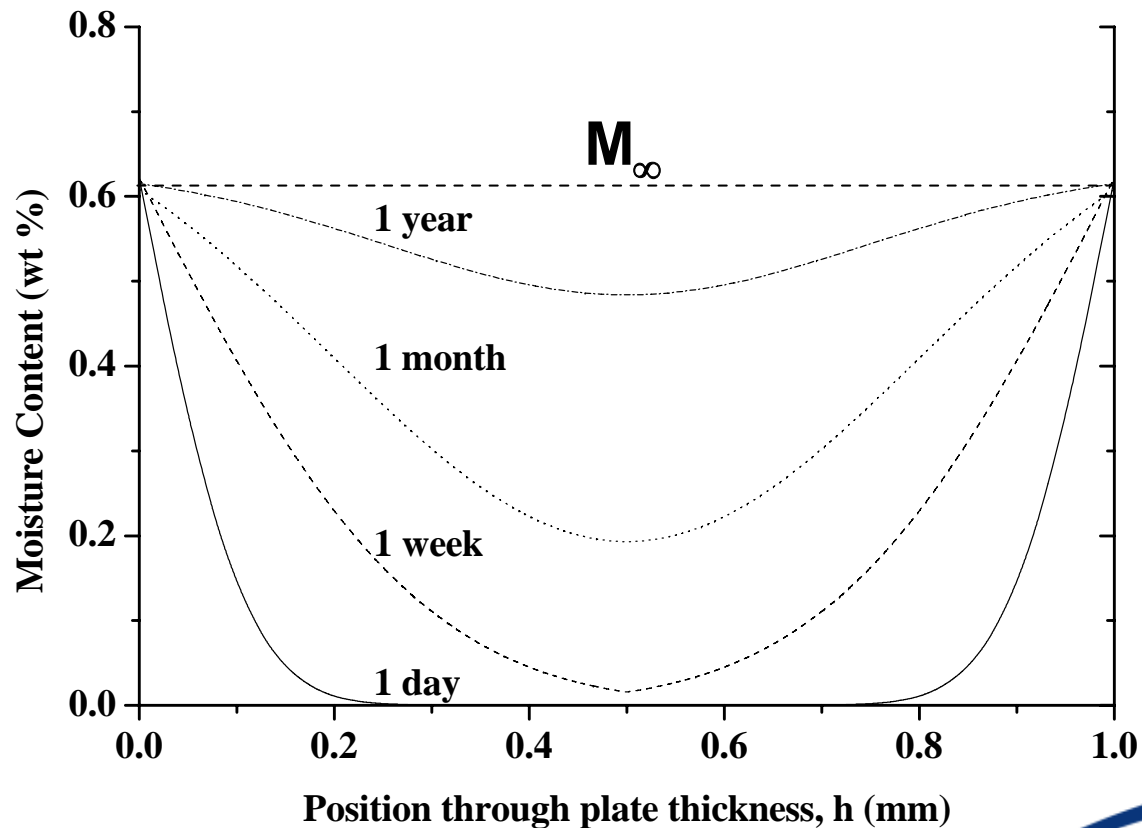
$$D_m = 8.3 \times 10^{-1} \text{ m}^2/\text{s}$$

$$D_{22} = 6.3 \times 10^{-2} \text{ m}^2/\text{s (experimental)}$$

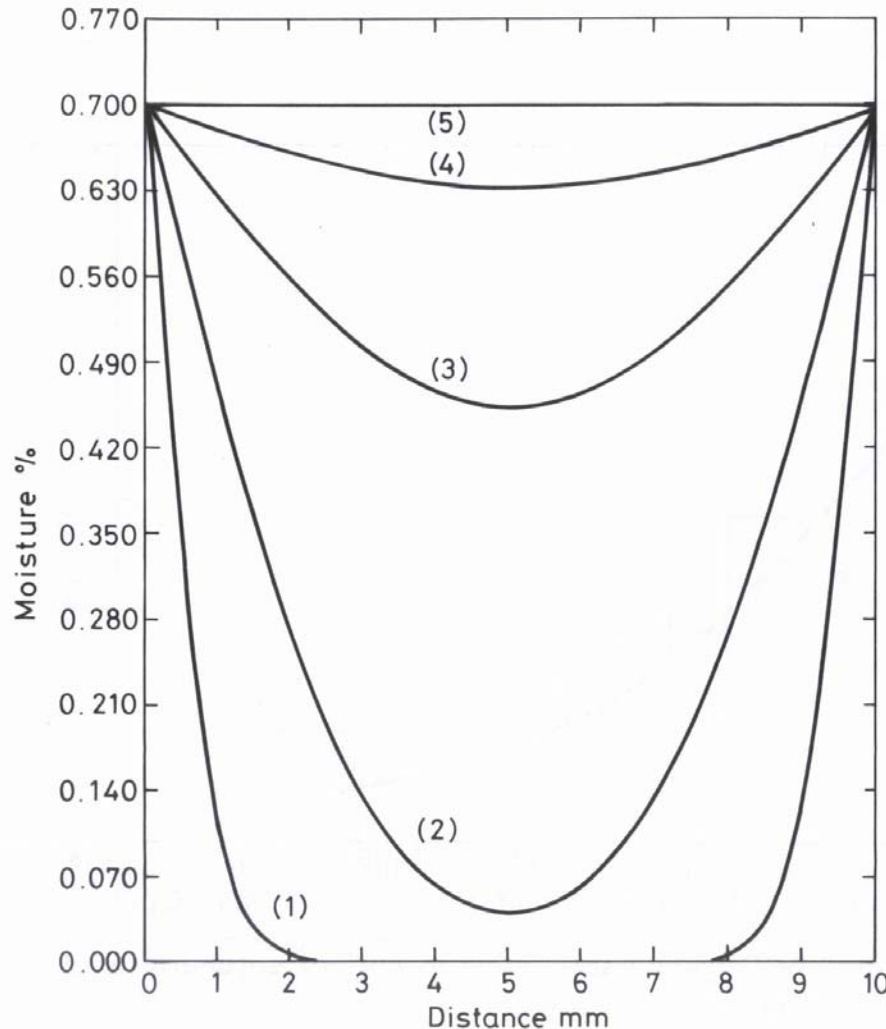
$$D_{22} = 7.3 \times 10^{-2} \text{ m}^2/\text{s (predicted)}$$

# Moisture Distribution

$$G = \frac{M - M_i}{M_\infty - M_i} = 1 - \exp\left[-7.3\left(\frac{Dt}{h^2}\right)^{0.75}\right]$$

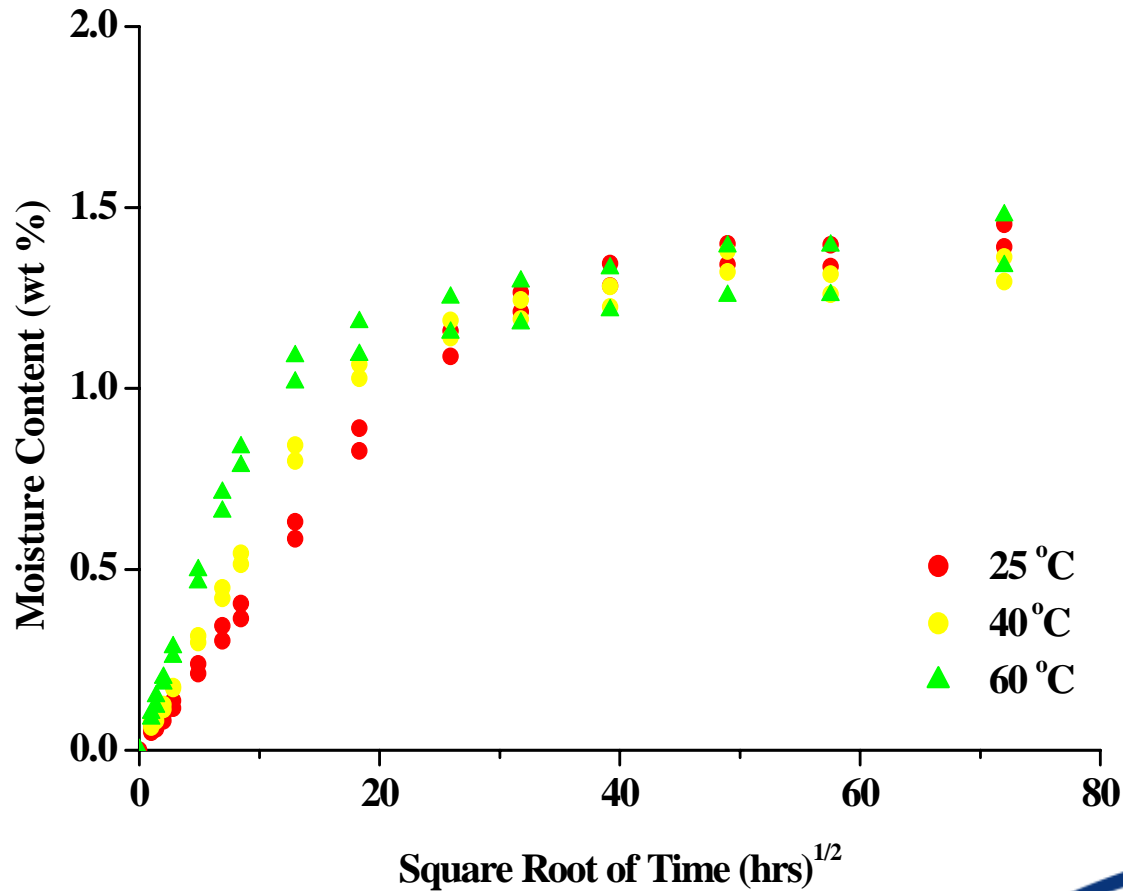


# Moisture Distribution - GRP Laminate (10 mm) Water Immersion @ 23°C



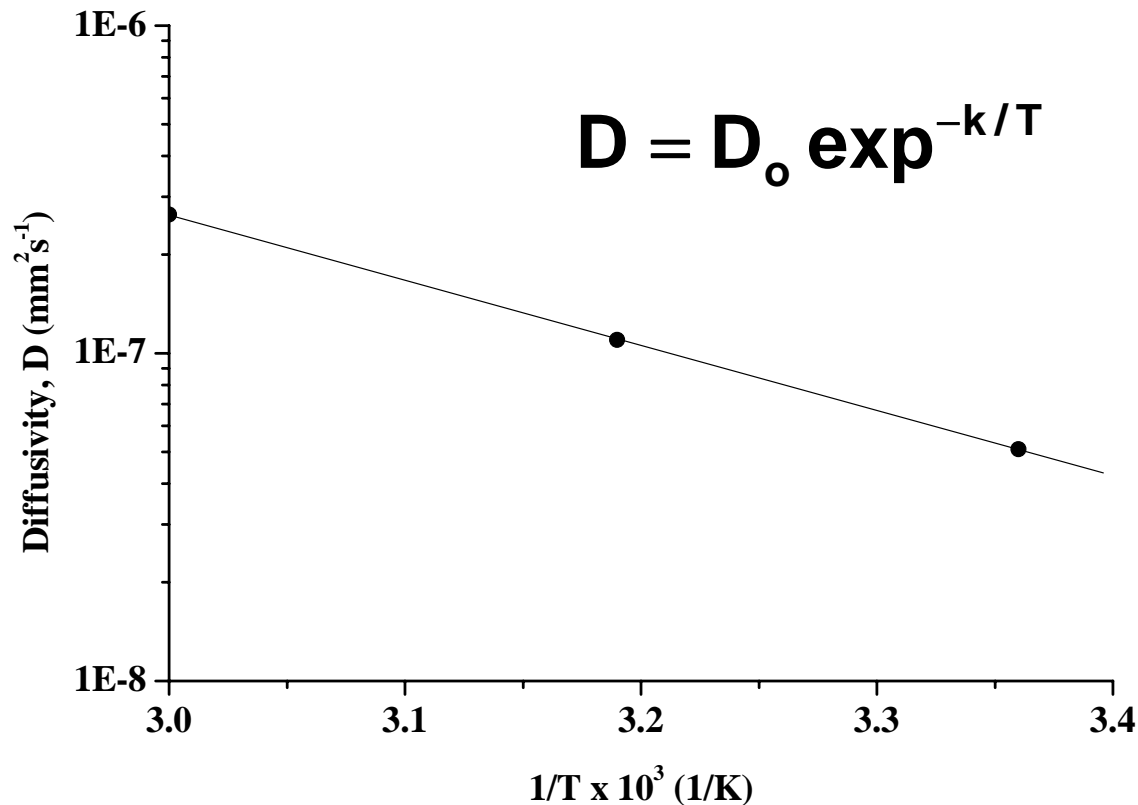
- (1) 10 days**
- (2) 100 days**
- (3) 500 days**
- (4) 1000 days**
- (5) 2500 days**

# Temperature Effects on Moisture Diffusivity Unidirectional T300/924 Carbon/Epoxy



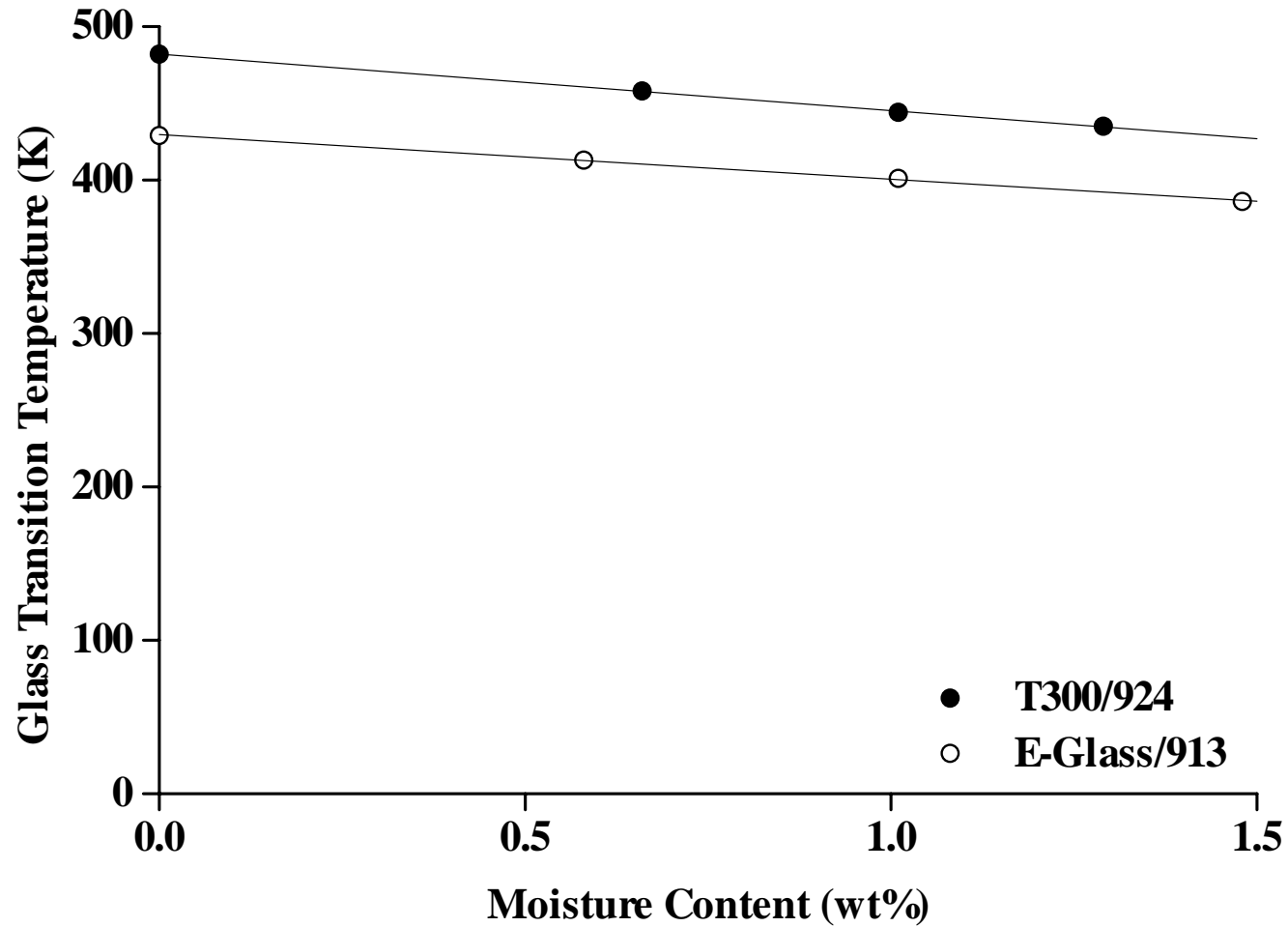
# Temperature Effects on Moisture Diffusivity

## Unidirectional T300/924 Carbon/Epoxy



- ◆ Moisture diffusivity increases with temperature
- ◆  $D_0 = 0.327 \text{ mm}^2\text{s}^{-1}$  and  $k = 4,669 \text{ K}$

# Moisture Effects on $T_g$

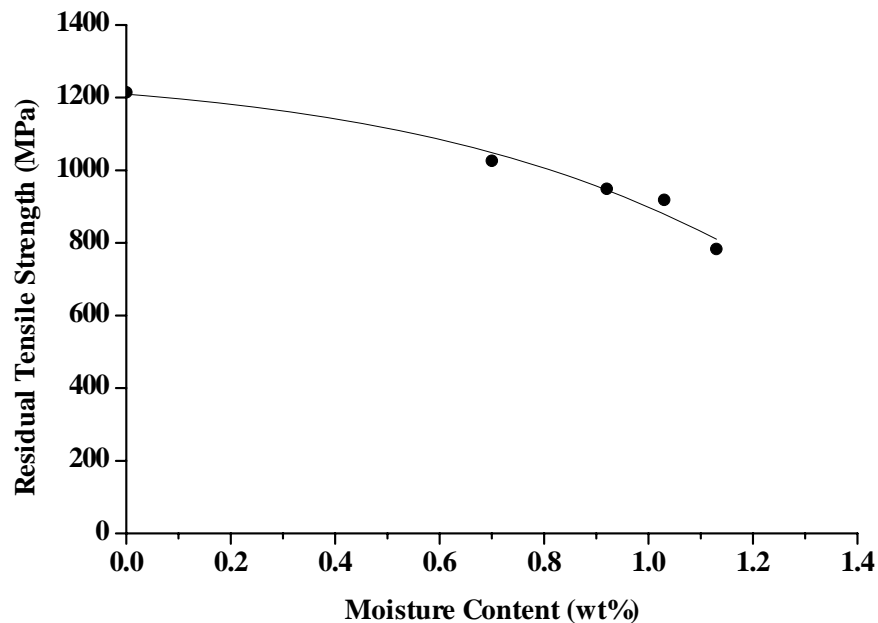
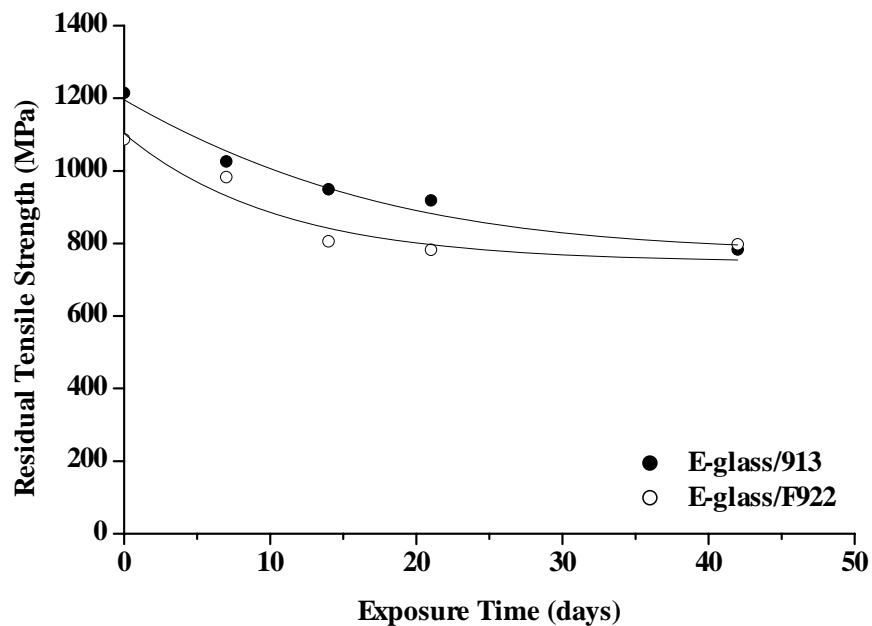


# Moisture Effects on $T_g$

$$T_{gw} = T_{gd} - gM$$

- ◆  $T_{gd}$  is the  $T_g$  of the dry material
- ◆  $T_{gw}$  is the  $T_g$  of conditioned (or wet) material
- ◆  $M$  is the amount of moisture absorbed (wt %)
- ◆  $g$  is the temperature shift (in K) per unit moisture absorbed
  - $g$  is 28.9 K for E-glass/913 and 36.8 K for T300/924
  - Corresponding values of  $T_{gd}$  are 430 K and 482 K

# Moisture Effects on Tensile Strength Unidirectional E-glass/913 and E-glass/F922



# Temperature Effects on Transverse Flexure Properties

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

- ◆  $P$  is material property at the test temperature  $T$
- ◆  $P_o$  is the initial property (un-aged) value of the dry material at room or reference temperature  $T_o$
- ◆  $n$  is an empirical constant experimentally derived
- ◆  $n$  is 1 for E-glass/913 and 0.3 for T300/924
- ◆  $T_{gd} > T_o$  and  $T_{gw} > T$

# Temperature Effects on Tensile Strength

$$\ln t_{1/2} = k + A/T$$

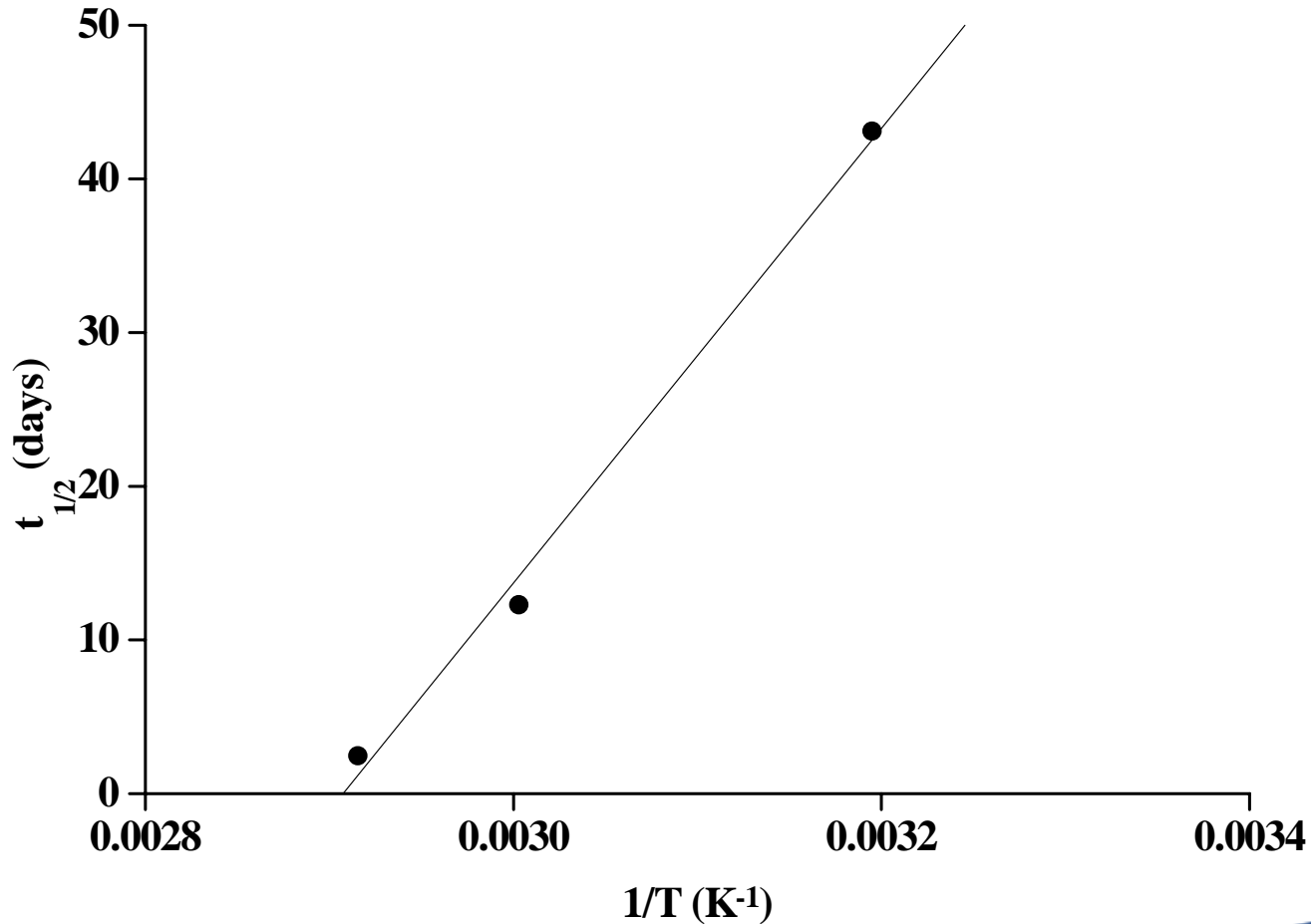
- ◆  $t_{1/2}$  is time required for the tensile strength to degrade to half its original value (half-life) at each temperature
- ◆ A and k are material constants determined experimentally
- ◆ T is the ageing (or conditioning) temperature

## Unidirectional E-glass/Polyester

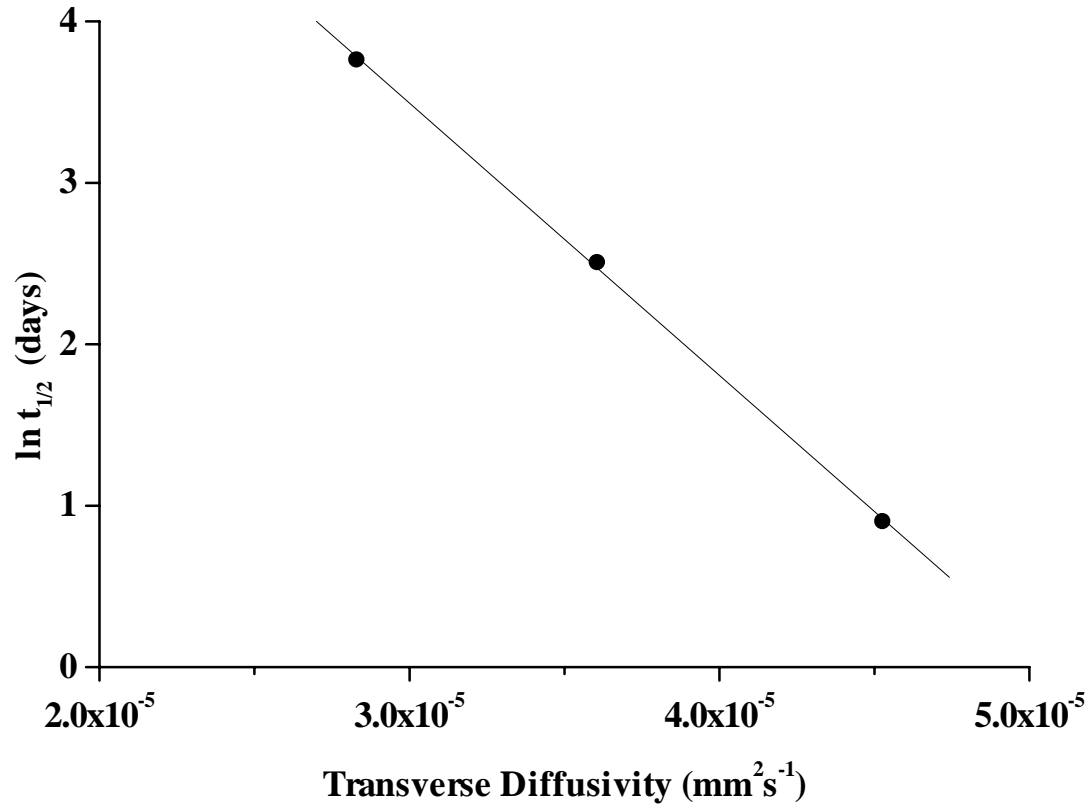
$$A = -430 \text{ and } k = 1.48 \times 10^5$$

# Tensile Strength Half-Life vs. Temperature

## E-glass/Polyester



# Tensile Strength Half-Life vs. Diffusivity E-glass/Polyester



# Empirical Approach

## Non-Dimensional Temperature

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

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

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

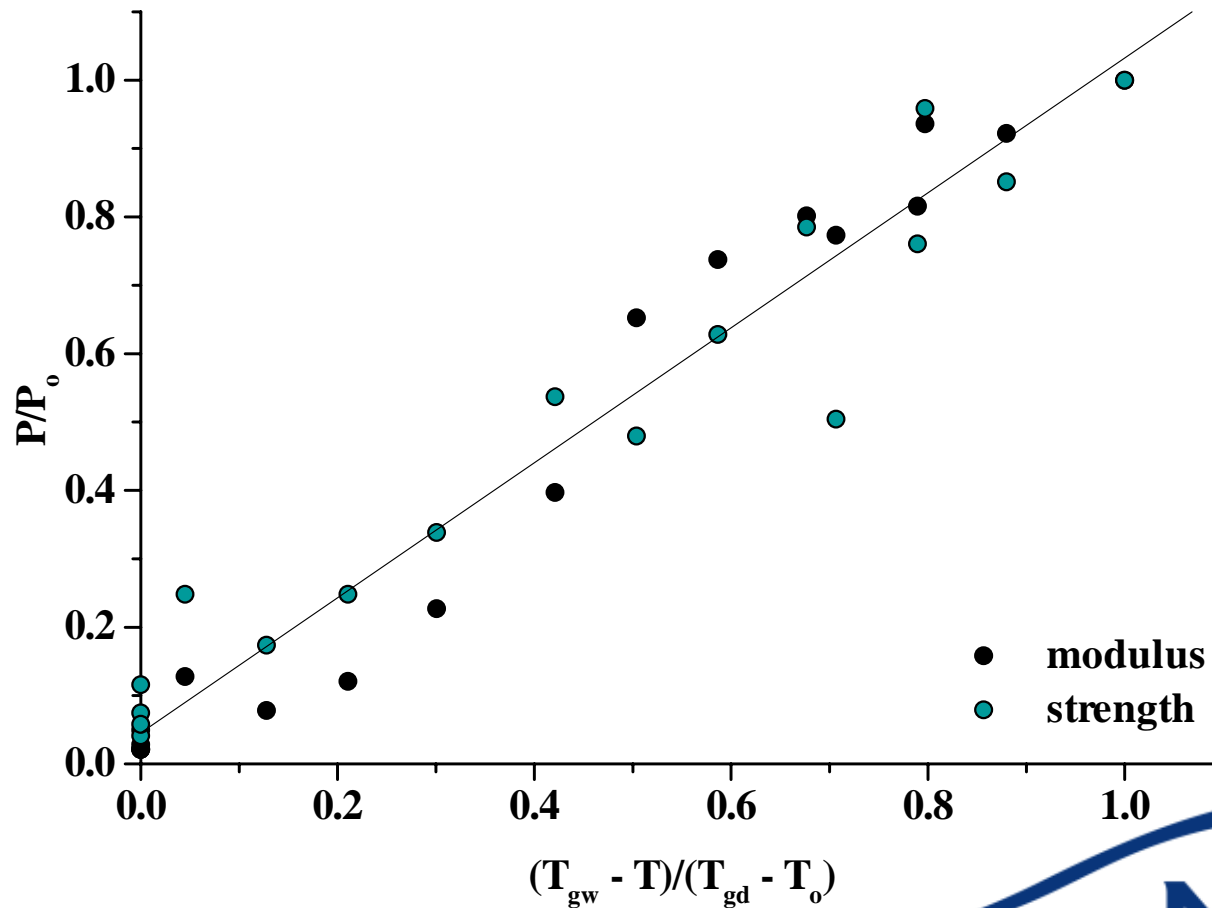
**T** Test temperature (K)

**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 UD E-glass/913 Epoxy



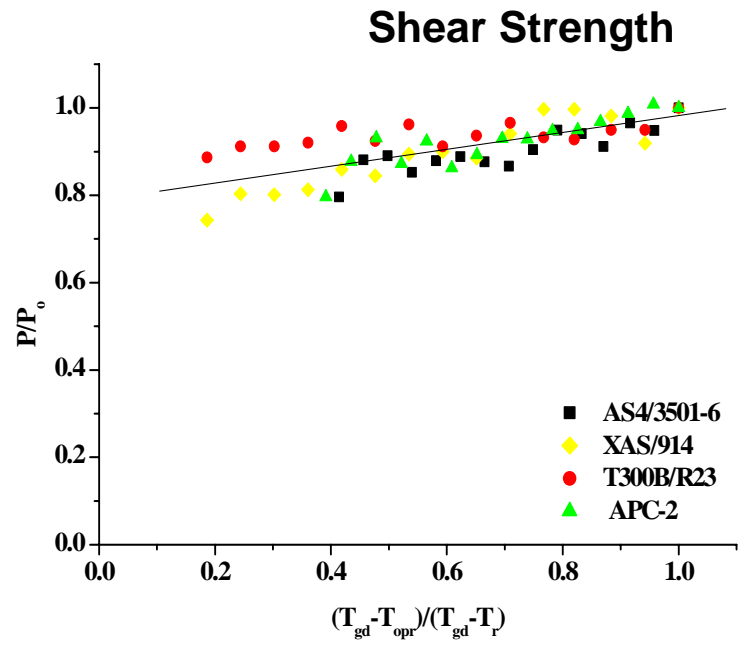
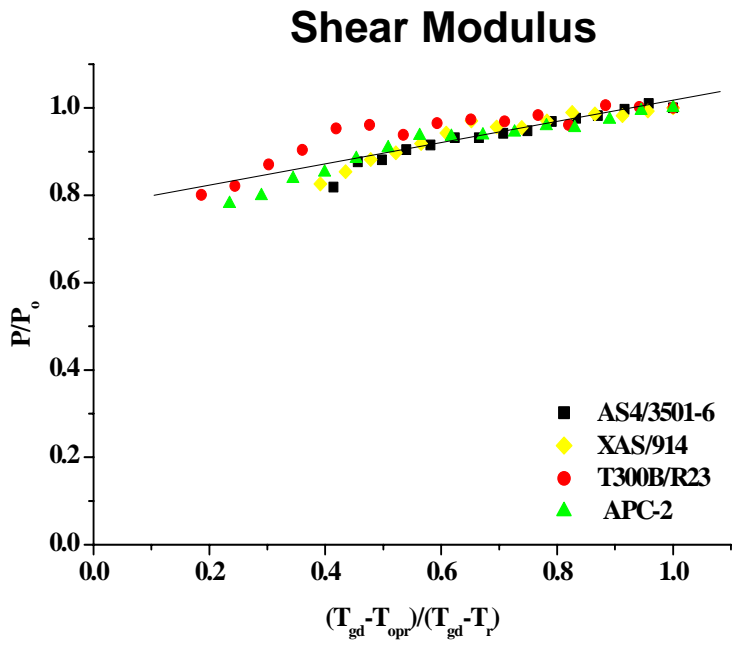
# Kitagawa Power-Law Relationship Shear Properties

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

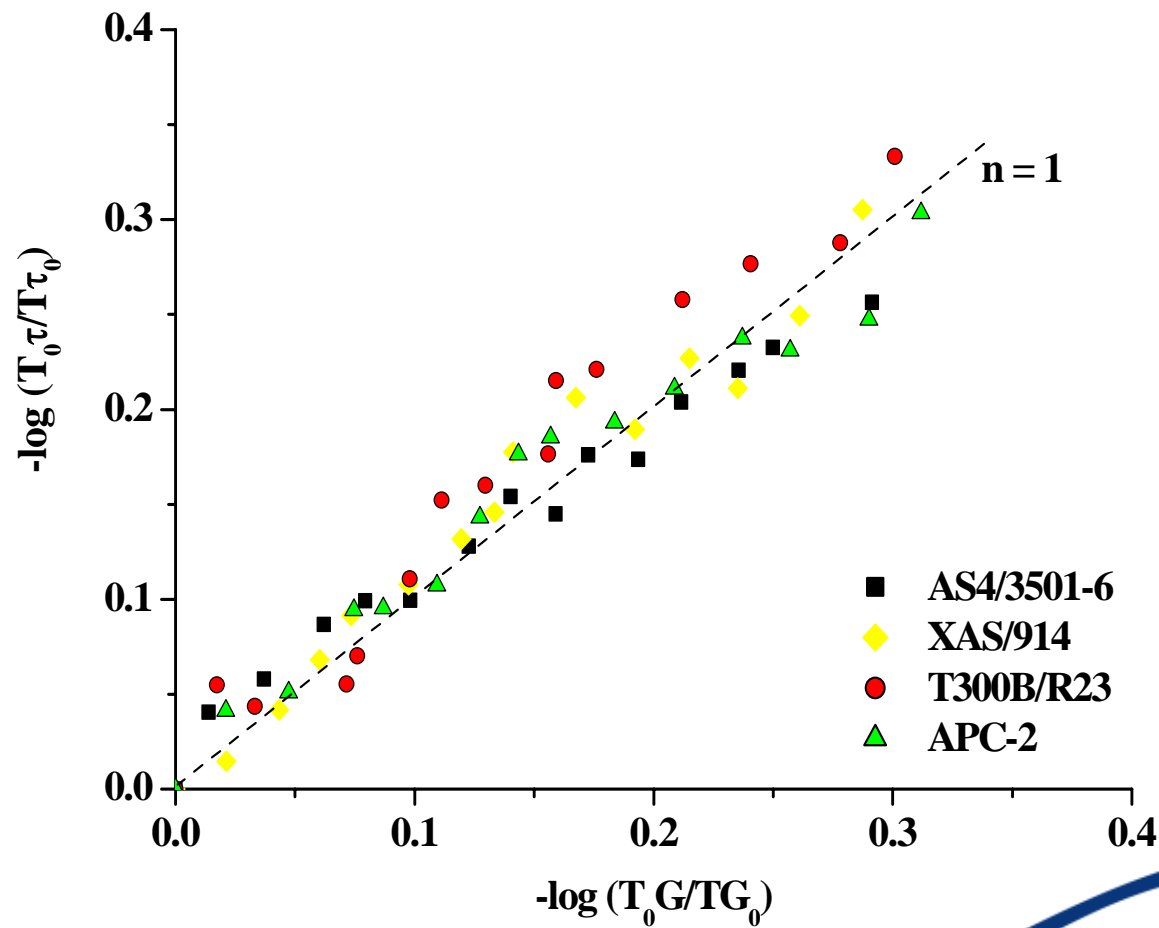
$$\frac{T_o \tau}{T \tau_o} = \left( \frac{T_o G}{T G_o} \right)^n$$

- ◆  $T_o$  is the reference temperature (K) – (e.g. 23°C or 296K)
- ◆  $\tau_o$  is the shear yield stress at  $T_o$
- ◆  $G$  is shear modulus
- ◆  $n$  is an empirical constant experimentally derived

# In-Plane Shear Properties Unidirectional Laminates



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



# GRP Pultruded Rods

- ◆ **Fibre Volume Fraction ( $V_f$ )**
  - ❖ **Well bonded:  $56.2 \pm 0.7$**
  - ❖ **Poorly bonded:  $55.8 \pm 0.8$**
- ◆ **Glass Transition Temperature ( $T_{gdry}$ )**
  - ❖ **Well bonded:  $118.2 \text{ }^\circ\text{C}$**
  - ❖ **Poorly bonded:  $122.2 \text{ }^\circ\text{C}$**

# GRP Pultruded Rods – Flexure Properties

Material	Moisture Content (%)	Flexural Modulus (GPa)	Flexural Strength (MPa)
<b><u>Dried at 50 °C</u></b>			
Well Bonded	0.00	33.8 ± 0.8	853 ± 39
Poorly Bonded	0.00	30.1 ± 1.1	371 ± 56
<b><u>1 Month</u></b>			
Well Bonded	0.16 ± 0.07	36.0 ± 1.1	871 ± 61
Poorly Bonded	0.27 ± 0.15	29.2 ± 0.8	281 ± 6
<b><u>3 Months</u></b>			
Well Bonded	0.27 ± 0.04	36.1 ± 1.4	866 ± 52
Poorly Bonded	0.83 ± 0.22	28.3 ± 1.9	298 ± 31

- ◆ Flexural stiffness and strength reduced due to poor fibre/matrix interfacial strength
- ◆ Poorly bonded systems tend to absorb higher levels of moisture – deionised water at 23°C

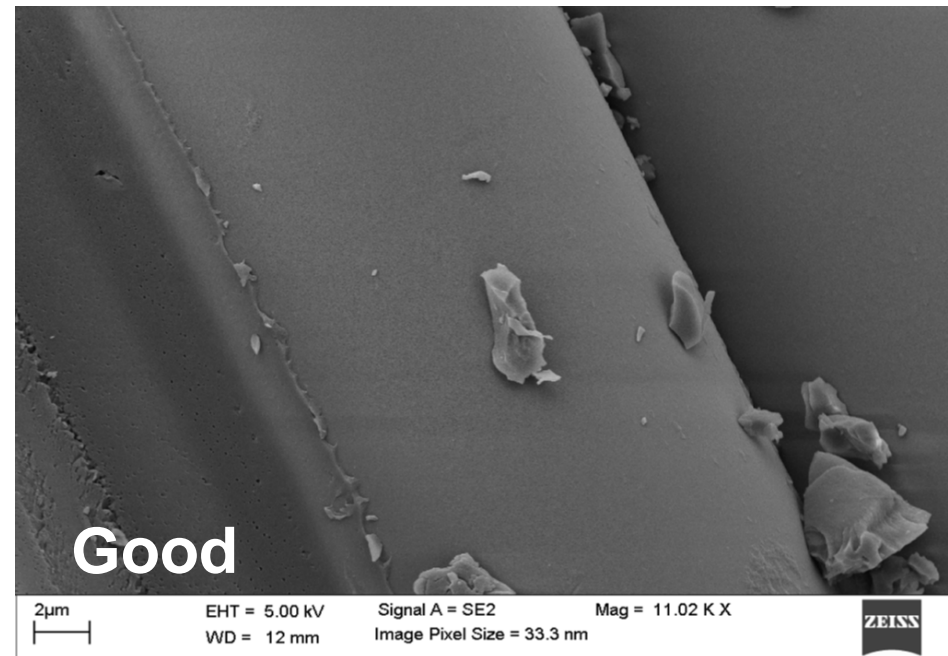
# GRP Pultruded Rods – Test Data

- ◆ **Fibre Volume Fraction (%)**
  - Well bonded:  $56.2 \pm 0.7$
  - Poorly bonded:  $55.8 \pm 0.8$
- ◆ **Flexural Modulus (GPa)**
  - Well bonded:  $33.8 \pm 0.8$
  - Poorly bonded:  $30.1 \pm 1.1$
- ◆ **Flexural Strength (MPa)**
  - Well bonded:  $853 \pm 39$
  - Poorly bonded:  $371 \pm 56$
- ◆ **Interlaminar Shear Strength (MPa) – core material**
  - Well bonded:  $54.6 \pm 3.1$
  - Poorly bonded:  $20.0 \pm 1.4$
- ◆ **Moisture Content (%) – 3 months in deionised water at 23°C**
  - Well bonded:  $0.27 \pm 0.04$
  - Poorly bonded:  $0.83 \pm 0.22$

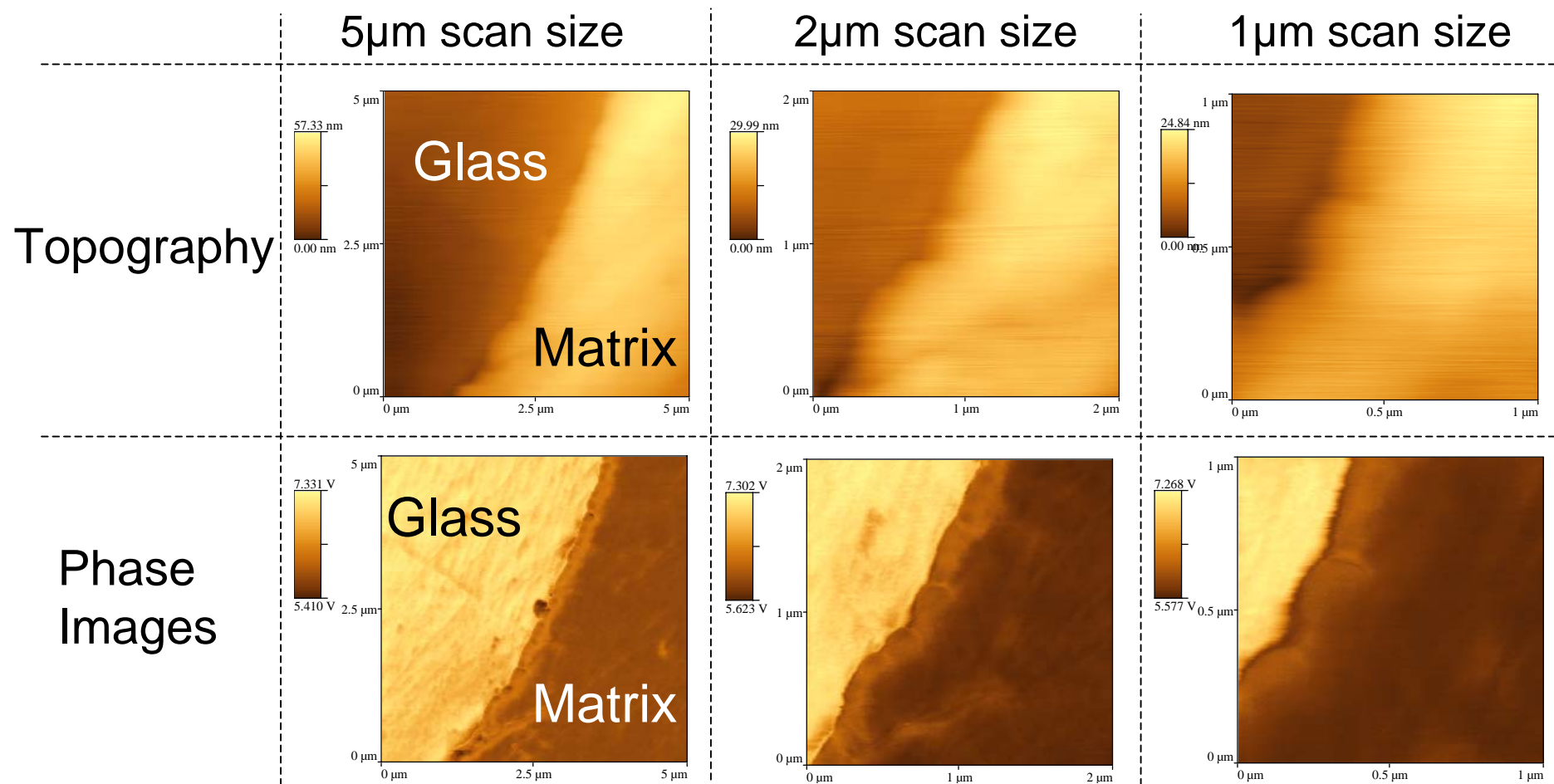
# GRP Pultruded Rods

## ◆ Interphase region

- ❖ < 50 nm (well bonded)
- ❖ 100-350 nm (poorly bonded)



# Phase Image of interface region for poorly bonded sample



5,2 and 1 $\mu\text{m}$  Phase Images of a portion of a unidirectional GFRP specimen with poor interfacial bonding

# Property Predictions - E-glass/Vinylester

## ◆ Undamaged – core material

- $E_{11c} = 48.1 \pm 1.3 \text{ GPa}^M / 41.90 \text{ GPa}^P$
- $S_{11c}(T) = 1216 \pm 83 \text{ GPa}^M$
- $G_{12} = 3.88 \text{ GPa}^P$
- $S_{13} = 54.6 \pm 3.1 \text{ MPa}^M$
- $S_{11c}(F) = 1216 \pm 83 \text{ GPa}^M$

## ◆ Degraded by 100% – core material

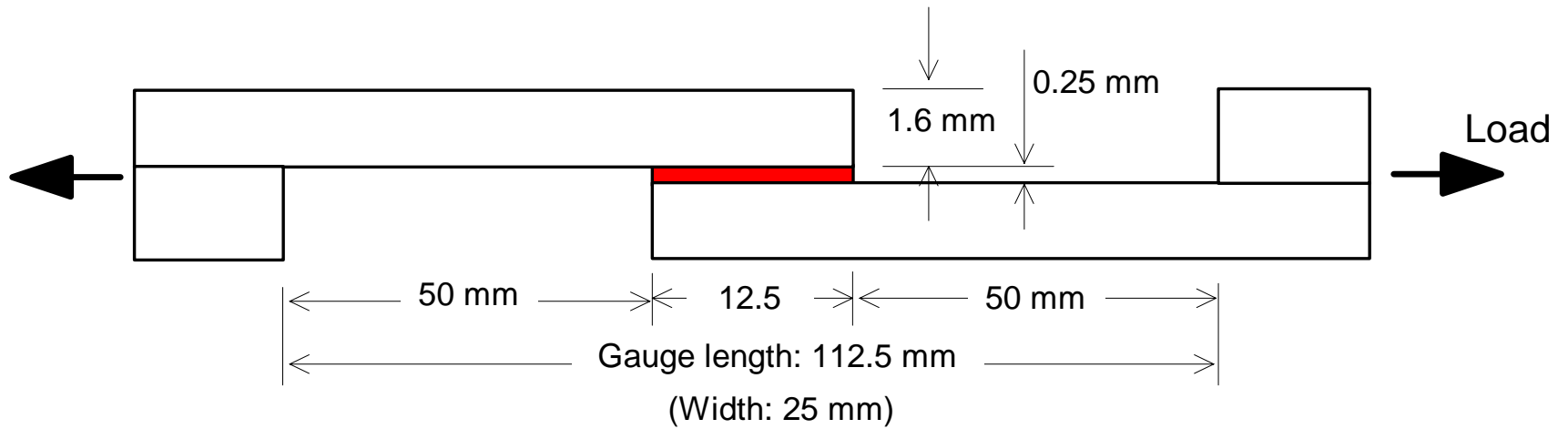
- $E_{11c} = 43.5 \pm 1.3 \text{ GPa}^M / 41.87 \text{ GPa}^P$
- $S_{11c}(T) = 540 \pm 52 \text{ GPa}^M (0.44S_{11c}(T))$
- $G_{12} = 1.44 \text{ GPa}^P (0.37G_{12}^P)$
- $S_{13} = 20.0 \pm 1.4 \text{ MPa}^M (0.37S_{13})$

## ◆ Measured – m, predicted - p

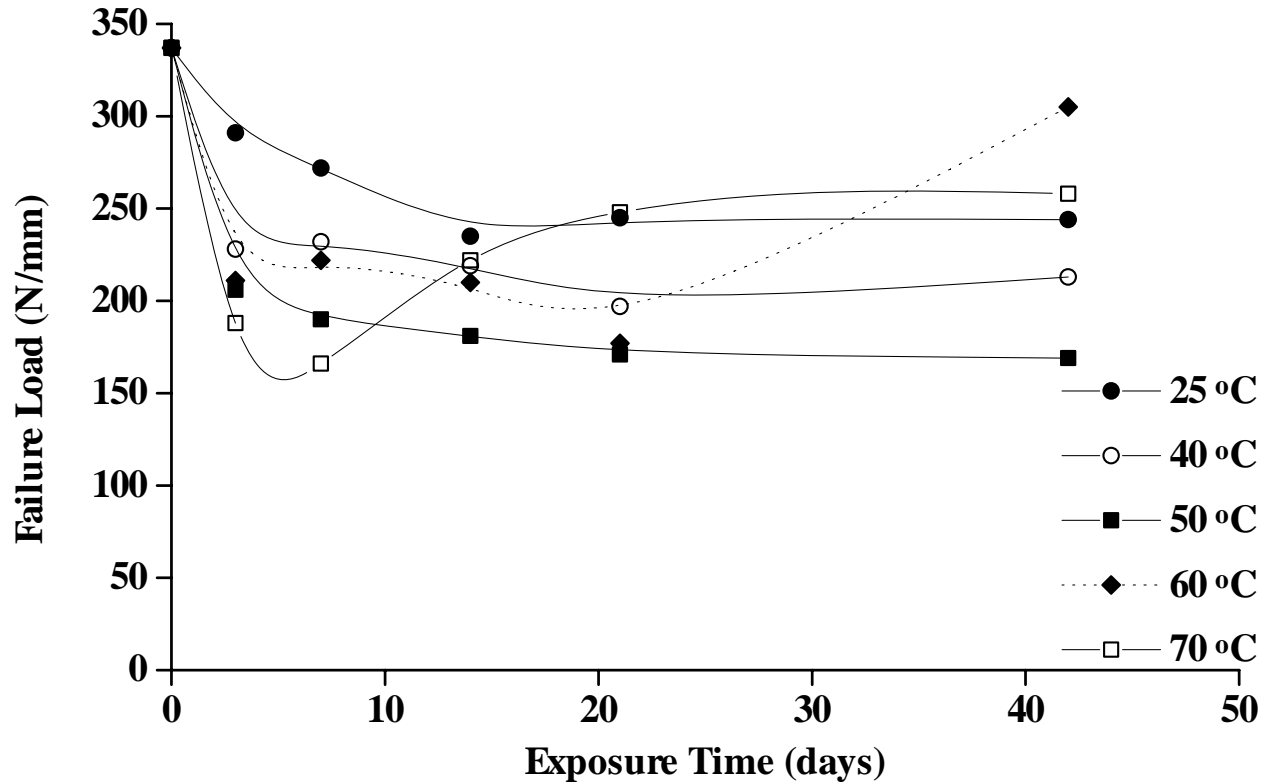
# Steam Autoclave - 2.2 bar/136 °C

Material	Moisture Content (wt %)	Tensile Strength (MPa)
<u>E-glass/F922</u>		
Dry	0.00	1087 ± 29
70 °C/85% RH (6 weeks)	1.00	763 ± 42
Steam autoclave (24 hrs)	2.09	654 ± 22
Steam autoclave (48 hrs)	2.94	579 ± 47
Steam autoclave (72 hrs)	2.83	585 ± 50
<u>HTA/F922</u>		
Dry	0.00	1684 ± 132
70 °C/85% RH (6 weeks)	1.06	1728 ± 132
Steam autoclave (24 hrs)	2.12	1691 ± 91
Steam autoclave (48 hrs)	1.90	1725 ± 42
Steam autoclave (72 hrs)	2.20	1784 ± 94

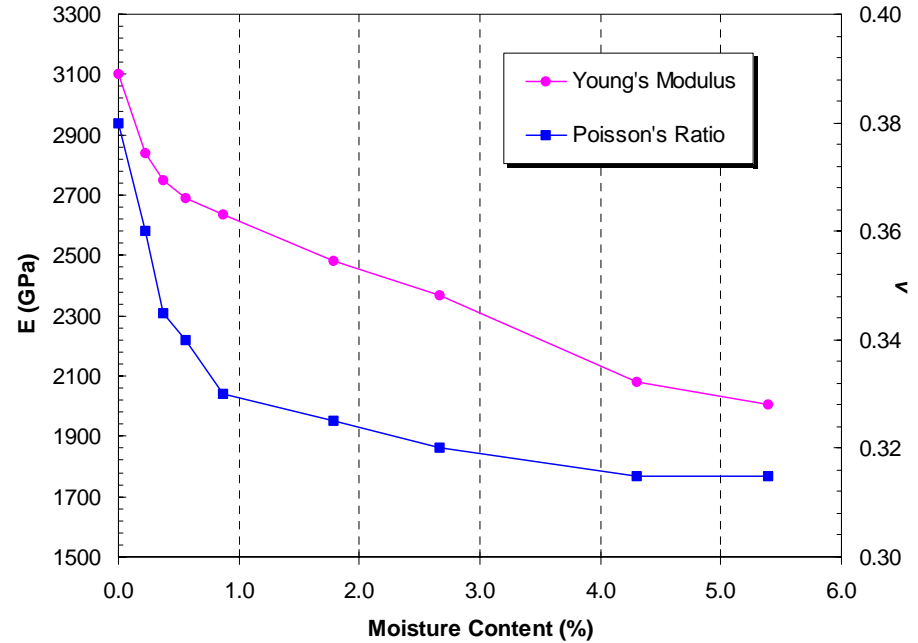
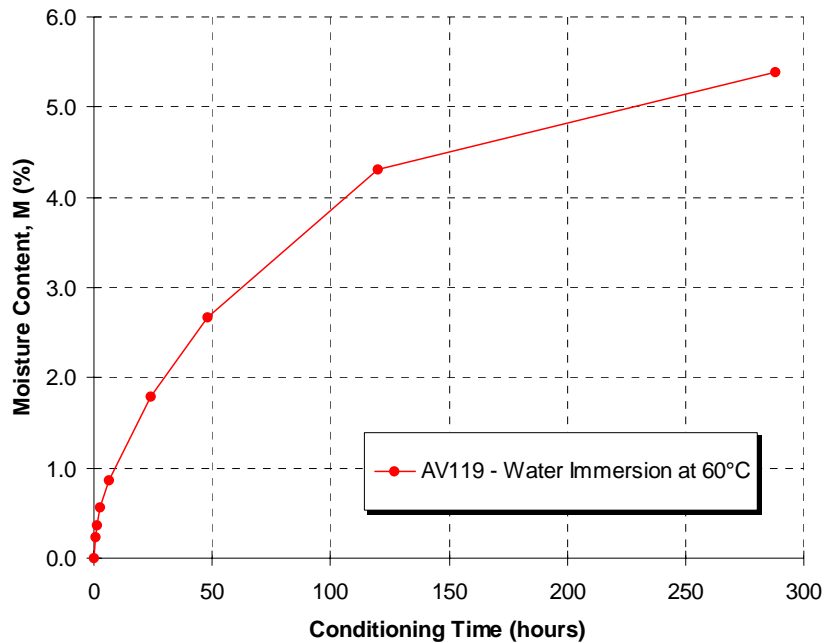
# Single-Lap Joint Aluminium/Epoxy



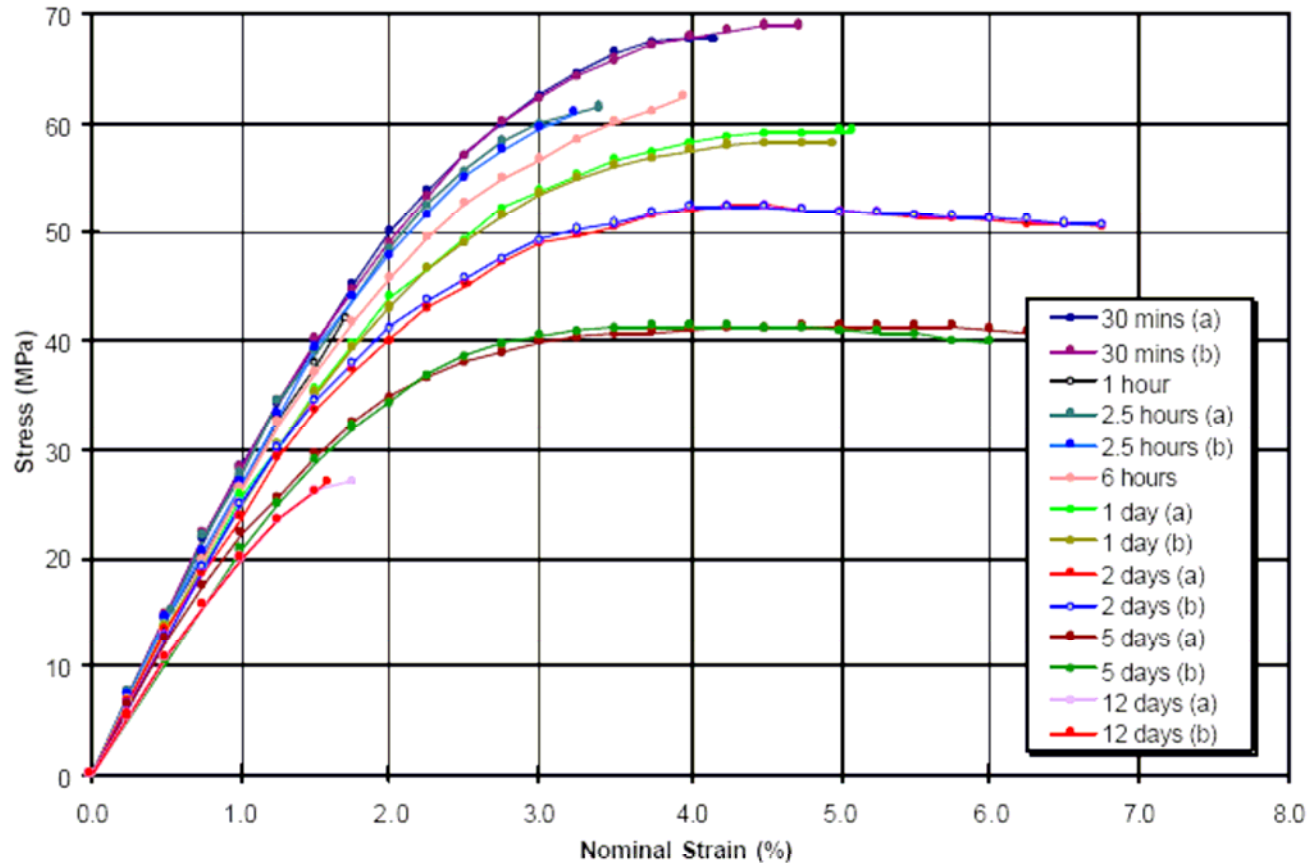
# Moisture Effects on Joint Strength Aluminium/Epoxy Single-Lap Joint



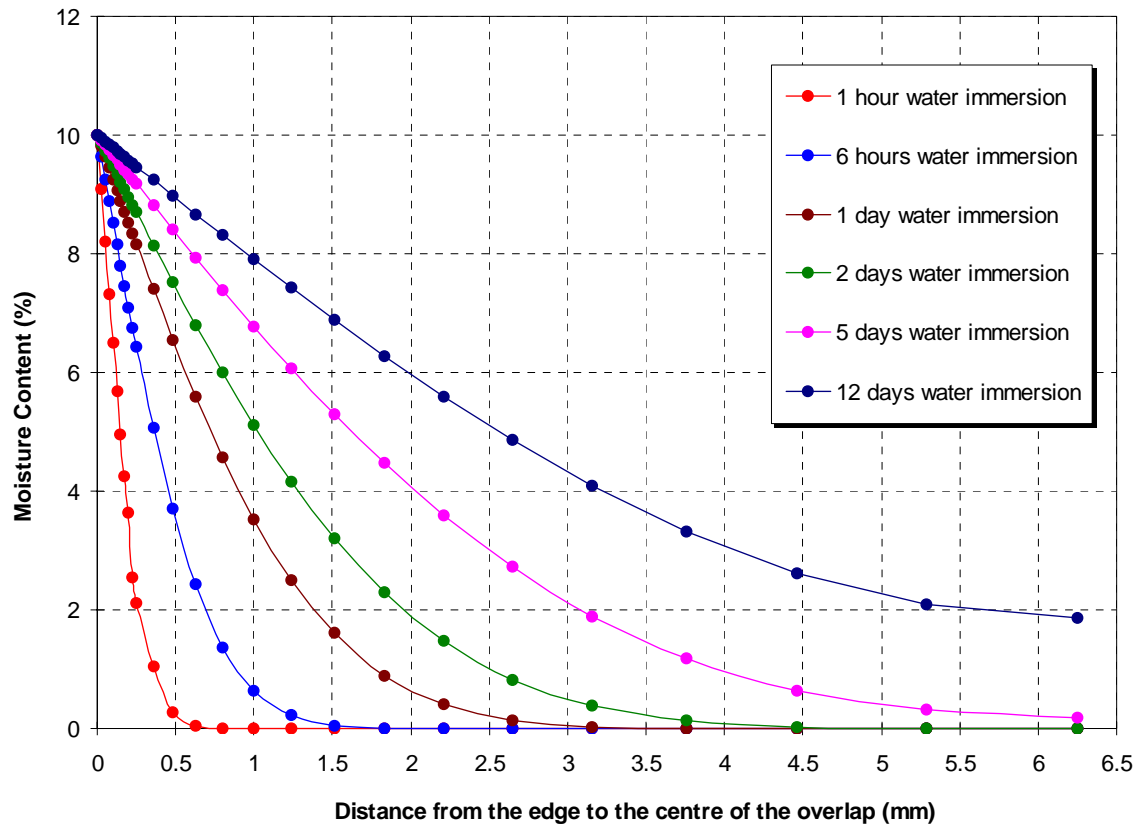
# Effects of Moisture on Elastic Properties Epoxy Adhesive (Water Immersion)



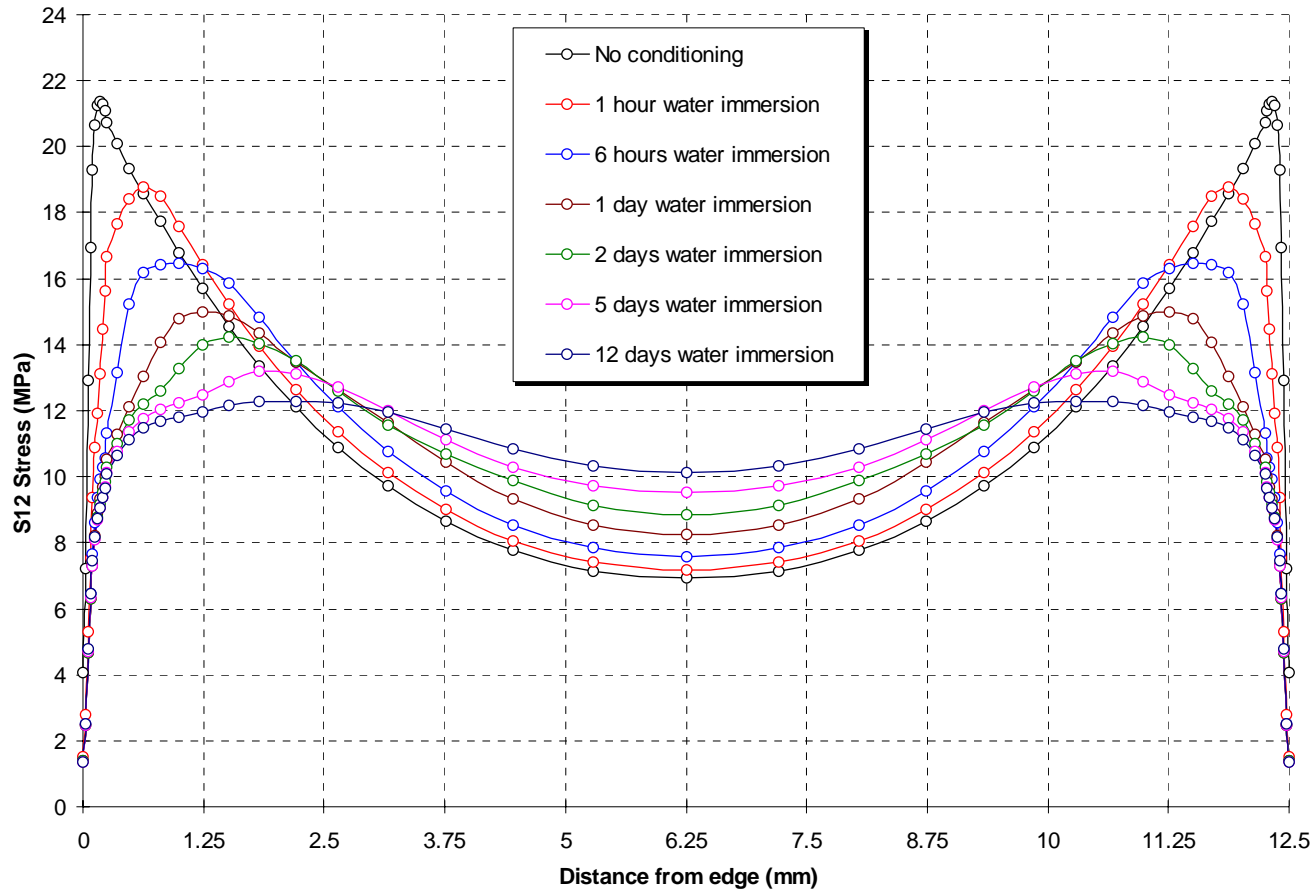
# Effects of Moisture on Tensile Strength Epoxy Adhesive (water Immersion)



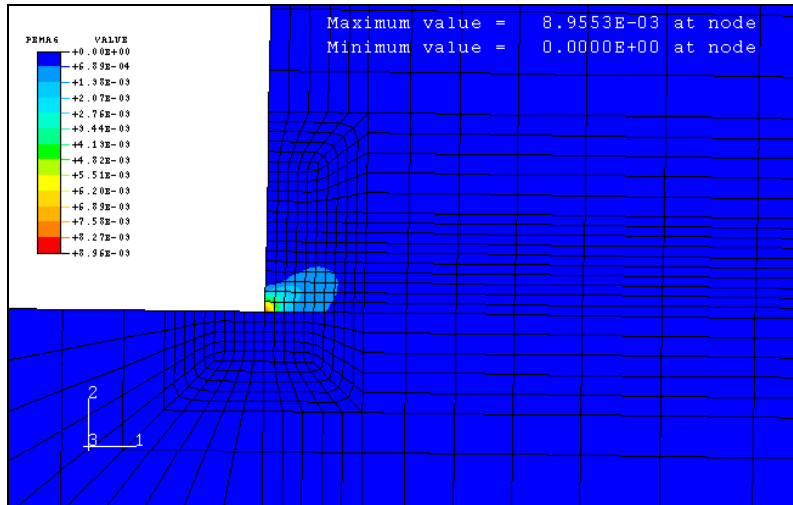
# Predicted Moisture Concentration Distributions Aluminium/Epoxy Single-Lap Joint



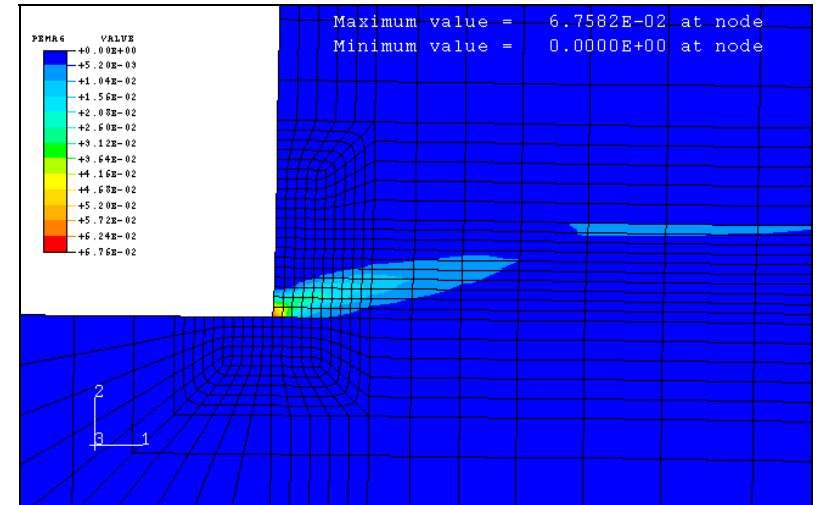
# Predicted Shear Stress Distributions Aluminium/Epoxy Single-Lap Joint



# Predicted Plastic Strain Distributions Aluminium/Epoxy Single-Lap Joint Immersed in Deionised Water @ 60°C

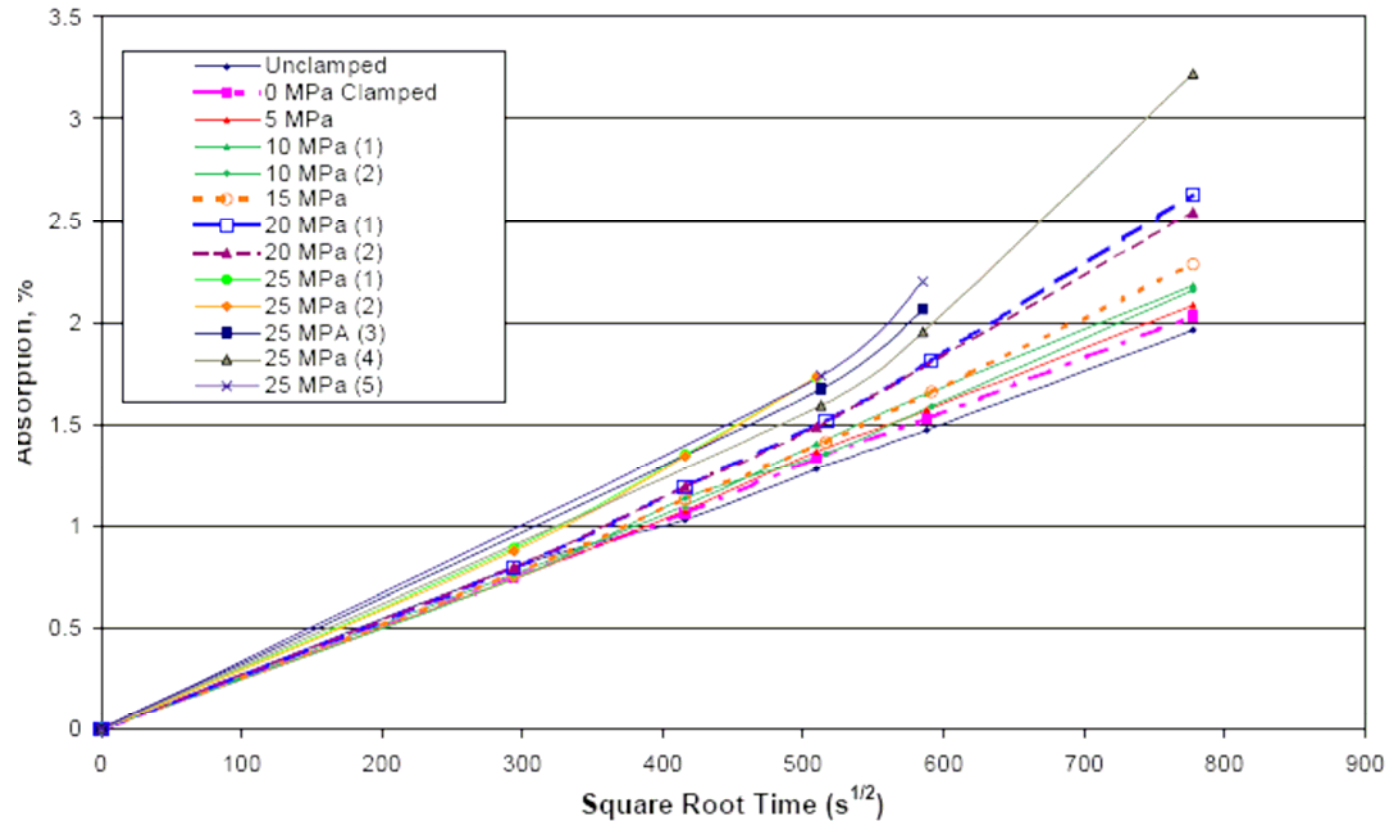


**Unconditioned**

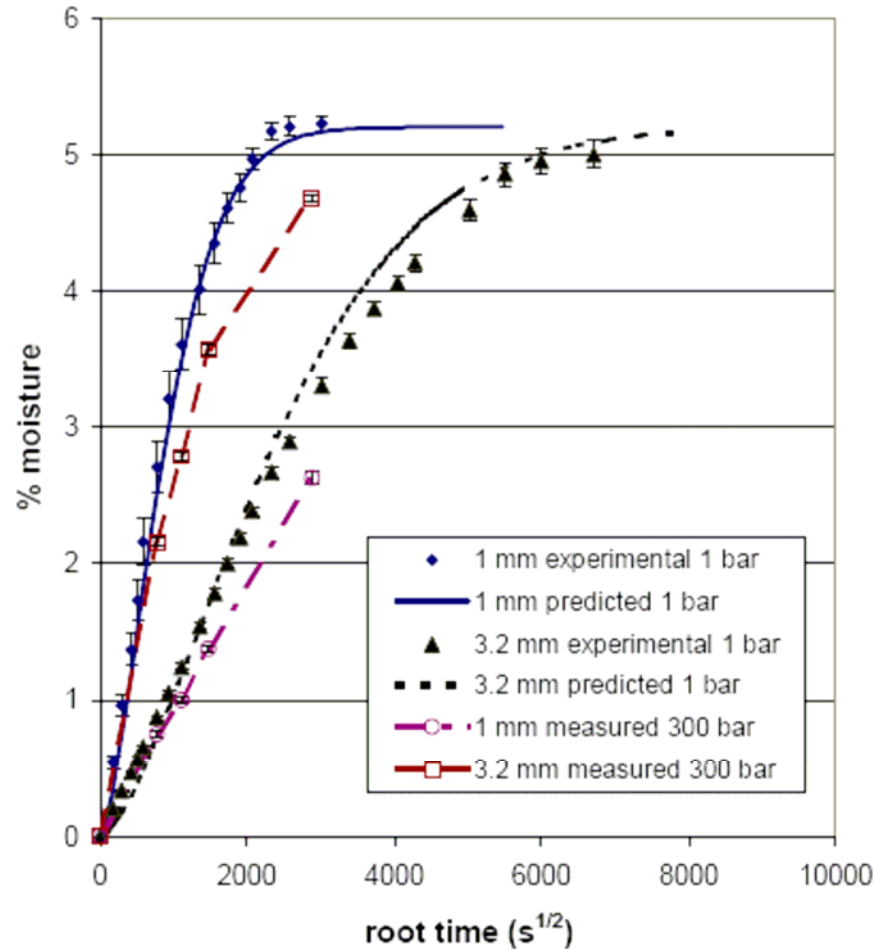


**12 days immersion**

# Effects of Stress on Moisture Absorption Epoxy Adhesive



# Effects of Pressure on Moisture Absorption Epoxy Adhesive



# Future Trends

- ◆ **Dielectric measurements to monitor water content in adhesive joints**
- ◆ **Optic fibre systems – Embedded Fibre Bragg Gratings for in-situ sensing of chemical species (including water) – composites and adhesive joints**
- ◆ **Improved predictive analysis – fracture mechanics based FE modelling incorporating interfacial degradation**

# Conclusions

- ◆ Fibre/matrix interfacial bond strength is critical to structural and long-term performance
- ◆ Tests exist that can be used differentiate between well and poorly bonded composite systems
- ◆ Continuous Immersion in Deionised Water
  - Analytical/semi-empirical relationships - relate degree of material property degradation with level of degrading agent
  - Enabling extrapolation for longer exposure times under more benign (realistic) conditions
- ◆ Embedded sensors, such as Fibre Bragg gratings are now being used to determine expansion or swelling due to moisture and chemical species concentrations

# Conclusions

- ◆ Concern regarding the relationship of the results of accelerated ageing tests for polymeric materials and the actual service performance
- ◆ Few test methods or standards exist that predict life expectancy with confidence
- ◆ A major challenge is to ensure that performance testing for determination of chemical resistance (level of degradation) is based upon a set of “quantitatively” measurable criteria

# Acknowledgements

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**Neil McCartney Gordon Pilkington Graham Sims**

**Tim Young**

# Thank You

Questions?

Comments