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Techniques for Monitoring Water Absorption in Fibre-Reinforced Polymer Composites

Prolonged, or even short term, exposure to aqueous environments can cause irreversible changes in the chemical and physical properties of fibre-reinforced polymer composites. These changes often compromise the load carrying properties of the material with the level of degradation increasing as moisture content increases. Reductions in stiffness and strength, and changes in thermo-mechanical behaviour can often be linked directly to the amount of moisture absorbed. The extent and rate of moisture absorbed by the composite material depends on a number of factors including temperature, relative humidity, moisture equilibrium levels, area of exposed surface, fibre content and diffusivity.

This Measurement Note considers the use of a number techniques, experimental and predictive analysis, suitable for determining through-thickness moisture distribution, moisture equilibrium content and diffusion coefficient for polymeric materials exposed to aqueous environments. It considers the effects of temperature and humidity on the moisture absorption characteristics and glass-transition temperature of neat resins and fibre-reinforced polymer composites. Experimental data are presented from tests conducted on glass and carbon fibre-reinforced epoxy, polyester and vinyl ester composites and their matrix resin systems for a variety of environments, including exposure to hot/humid environments, water immersion at elevated temperatures, or exposure to superheated pressurised steam. Effects of specimen geometry (i.e. thin rectangular plates and small diameter rods) and dimensions are also considered. The predictive analysis proved reliable and accurate for characterising moisture diffusion behaviour in these materials.

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Introduction

A review of test methodologies and standards [1] revealed that the general approach to accelerated ageing of fibre-reinforced polymer composites is to expose laminated structures to severe test conditions, often well in excess of actual service conditions. In hot/humid environments (e.g. 70°C and 85% relative humidity (RH)) it may take 10-15 years for a structure to reach a state of moisture equilibrium or saturation. This condition, however, is even more difficult to achieve under milder and more realistic conditions than those employed to accelerate moisture conditioning.

The extent and rate of moisture absorbed by the composite material depends on a number of factors, such as temperature, relative humidity, moisture equilibrium levels, areas of exposed surfaces, fibre content and diffusivity. This Measurement Note considers a number of methods that can be used to determine moisture distribution in polymeric materials. Experimental illustrations are provided to demonstrate the effects of key factors that influence moisture absorption. Moisture conditioning is also discussed.

Moisture Conditioning

The two main types of basic moisture conditioning are: (i) fixed conditioning, where a test specimen is exposed to a conditioning environment for a specified time; and (ii) equilibrium conditioning, where a specimen is exposed until the material reaches equilibrium with the conditioning environment.

The first technique is routinely employed for screening purposes. This approach results in non-uniform moisture distribution through the thickness of the test specimen. In principle, test data obtained from specimens conditioned in this manner are only considered suitable for comparing different batches of the same material or for quality control tests. This approach, however, is widely used for generating engineering data. **It is essential that test specimens used in this manner are identical in dimensions and have similar surface finishes.**

Ideally, comparative studies of water absorption properties of materials should be carried out only using the equilibrium moisture content of polymeric materials exposed to identical conditions. Comparisons between composite systems with different moisture absorption characteristics are possible if the materials are conditioned to equilibrium. **The thicker the material the longer the time required to reach equilibrium, hence the use of relatively thin specimens to determine the "through-the-thickness" moisture diffusion coefficient.** The large timescales involved, even under accelerated testing conditions, can make this approach impractical.

The International standard BS EN ISO 62 [2] describes a procedure for determining the moisture absorption properties and/or diffusion coefficients in the "through-the-thickness" direction of flat and curved solid plastics. BS EN ISO 62 is suitable for use with polymer and composite specimens. The method can be applied to vapour exposure and liquid immersion.

Conditioning usually consists of exposing pre-dried specimens to a steady-state environment (i.e. constant temperature and constant moisture level) and measuring the moisture gain (i.e. average moisture content) for a prescribed period of time or until the specimen reaches moisture equilibrium. The amount of water absorbed by the test specimen is determined by measuring its change in mass (i.e. difference between initial mass and the mass after exposure). All surfaces are in contact with the test environment. It is recommended that when determining moisture absorption properties that square shape specimens be used for homogeneous plastics. In this case, specimen dimensions and tolerances should comply with ISO 294-3 [3]. For reinforced plastics, it is recommended that square specimens also be used with a width $\mathbf{b} \leq 100$ x nominal thickness **h** (typically 2 mm).

It is recommended that specimens be pre-dried in an oven maintained at 50 ± 2°C until the specimen weight reaches a constant value. The temperature of the drying oven should not exceed the maximum operating temperature of the polymeric-matrix. Specimens are removed at fixed intervals (typically 24 hrs) and allowed to cool to room temperature in a desiccator before being weighed. After weighing, the specimen is returned to the oven and the process is repeated until the mass of the specimen is constant (zero datum level). Specimens should be free of voids in order to ensure accurate moisture absorption measurements. To minimise moisture uptake prior to conditioning, specimens are stored in a desiccator at room temperature. It should be noted that under standard laboratory conditions many polymers absorb significant levels of moisture.

Conditioned specimens need to be wiped with a clean cloth to ensure all surface water is removed prior to weighing. Damage may accumulate during long-term conditioning, and hence handling and monitoring of test specimens should be minimal. This is particularly pertinent to those specimens used for generating engineering data. Travellers are required to monitor specimen moisture content throughout the environmental history (i.e. manufacture, storage, conditioning and testing). Traveller specimens should have identical material properties, geometry and processing history as the test specimen.

Conditioning is often carried out at elevated temperatures or humidities to accelerate moisture uptake. Care should be taken to avoid exceeding the glass transition temperature $\mathbf{T_g}$ of the material. The recommended maximum conditioning temperatures are 45°C and 70°C for 120°C and 180°C cure systems, respectively [4].

The rate of moisture uptake is fairly rapid in the early stages of conditioning with the rate of moisture uptake decreasing with time (see Figure 1). It is therefore necessary to make frequent weight measurements in the early stages (3-4 measurements on day one) followed by at least two readings per day for the remainder of the first week. At least one reading per day is required per day for the second week, followed by a gradual decrease in frequency as the rate of weight gain diminishes. It is recommended that weighing be carried at approximately equal intervals of $(\text{time})^{1/2}$. The percentage uptake of water by weight, **M**, can be determined as follows:

$$M = \frac{(W_{WET} - W_{DRY})}{W_{DRY}} x100\%$$

where the wet and dry weights are denoted by $\mathbf{W_{WET}}$ and $\mathbf{W_{DRY}}$. A precision analytical balance capable of reading to within 0.0001 g is required. Accurate records need to be kept on the conditioning sequence including relative humidity, temperature and time, measured weights and derived moisture contents.

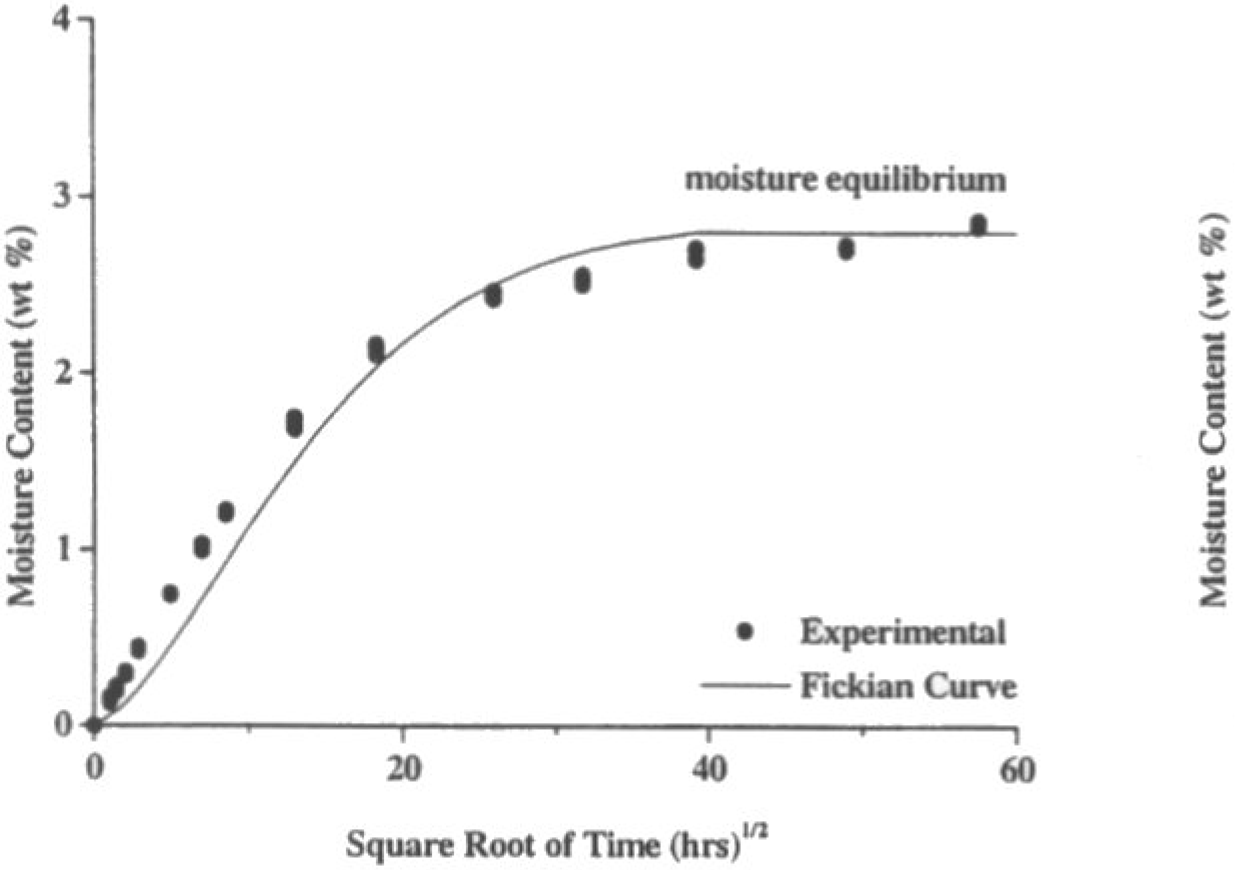


Figure 1: Fickian diffusion curves for F922 epoxy (left) and E-glass/F922 (right).

Fickian Diffusion

At temperatures well below the **T_g** of the conditioned material, water absorption of most polymers correlates well with Fick's laws (see Annex A of BS EN ISO 62 [2]). The diffusion coefficient, independent of time and moisture concentration (i.e. humidity level) can be calculated from the Fickian diffusion curve (Figure 1). The diffusion coefficient **D** is determined from the initial linear region of the Fickian diffusion curve using the following relationship [4]:

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

where **M_∞** is the equilibrium moisture concentration (or content), **M_1** is the moisture uptake after time **t_1**, **M_2** is the moisture uptake after time **t_2** and **h** is the thickness. The moisture equilibrium concentration corresponds to the final asymptotic value on the diffusion curve.

The fractional moisture content gain **G** can be approximated by [5-7]:

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

where **M_i** is the initial moisture content of the sample and **M = M(t)** the percent moisture content of the composite at any time **t.** When only one side of the sample is exposed, the thickness **h** is replaced by **2h.**

The analysis used to derive **D** assumes that the specimen is an infinite rectangular plate with no moisture diffusion from the specimen edges. In practice, moisture diffusion occurs from all six surfaces. Shen and Springer [5] derived a correction factor to account, which enables the true one-dimensional diffusion coefficient $\mathbf{D_x}$ to be determined as follows:

$$D_x = D\left(1 + \frac{h}{l} + \frac{h}{b}\right)^{-2}$$

where **l** and **b** are the sample length and width, respectively.

If the moisture entering through the specimen edges is neglected then $\mathbf{D_x}$ the diffusivity of the material in the direction normal to the surface is:

$$D_x = D$$

For anisotropic materials, the diffusion coefficients vary with direction. The diffusion coefficients parallel and perpendicular to the fibres ($\mathbf{D_{11}}$ and $\mathbf{D_{22}}$) for aligned glass and carbon fibre-reinforced systems may be estimated by the following relationships [6]:

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

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

where $\mathbf{D_m}$ is the diffusivity of the resin and $\mathbf{V_f}$ is the fibre volume fraction.

Absorption measurements for hot/wet conditioned (70 °C/85% RH) F922 epoxy and continuous aligned E-glass/F922 (see Figure 1) indicate that the predicted value and measured value of diffusion coefficient $\mathbf{D_{22}}$ are in reasonable agreement (see below).

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

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

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

Correction for edge effects

$$D_m = 4.7 \times 10^{-7}\ \mathrm{mm^2 s^{-1}}$$

$$D_{22} = 5.8 \times 10^{-8}\ \mathrm{mm^2 s^{-1}} \quad \text{(experimental)}$$

$$D_{22} = 4.1 \times 10^{-8}\ \mathrm{mm^2 s^{-1}} \quad \text{(predicted)}$$

The diffusion coefficient for a composite laminate is given by the following relationship [6]:

$$D = D_x\left(1 + \frac{h}{l}\sqrt{\frac{D_y}{D_x}} + \frac{h}{b}\sqrt{\frac{D_z}{D_x}}\right)^2$$

where $\mathbf{D_x}$, $\mathbf{D_y}$ and $\mathbf{D_z}$ are diffusivities through the thickness, along the length and across the width of the material.

The 3-D diffusivities with respect to the orientation of the fibres are [6]:

$$D_x = D_{11}\cos^2\alpha + D_{22}\sin^2\alpha$$

$$D_y = D_{11}\cos^2\beta + D_{22}\sin^2\beta$$

$$D_z = D_{11}\cos^2\gamma + D_{22}\sin^2\gamma$$

where α, β and γ are fibre orientations with respect to the **x, y** and **z** axes of the laminate. For homogeneous materials, $\mathbf{D_x}$ $\mathbf{D_y}$ and $\mathbf{D_z}$ are equal.

Effects of Temperature and Humidity

The rate of moisture uptake by a composite laminate is dependent on the temperature and relative humidity of the environment. The equilibrium moisture concentration $\mathbf{M_\infty}$ is assumed to be independent of temperature, depending only on the moisture content or relative humidity of the environment [6].

For a material immersed in water, $\mathbf{M_\infty}$ is a constant [5]:

$$M_\infty = \text{constant} \quad (\text{liquid})$$

For material exposed to humid air, $\mathbf{M_\infty}$ increases with increasing relative humidity ϕ according to the relationship [5]:

$$M_\infty = a\phi^b \quad (\text{humid})$$

where **a** and **b** are constants derived from a linear regression fit to the data.

Water immersion results for continuous aligned T300/924 carbon/epoxy (Figure 2) show that Ficks law applies over the temperature range 25°C to 60°C. Equilibrium moisture content was constant with temperature ($\mathbf{M_\infty}$ approximatley equal to 1.5 wt %). The specimens were immersed in deionised water for up to 216 days.

Although moisture diffusion behaviour for most resin systems can be modelled using Fickian diffusion theory, there are temperatures and humidities where Fickian behaviour is not applicable. For Ciba 913 epoxy, Ficks law only applies for temperature up to 45°C and for humidities up to 75% RH [7].

Water immersion results for continuous aligned E-glass/913 (Figure 2) show that for the temperature range 25°C to 60°C, both maximum moisture content $\mathbf{M_\infty}$ and diffusivity **D** increase with increasing temperature.

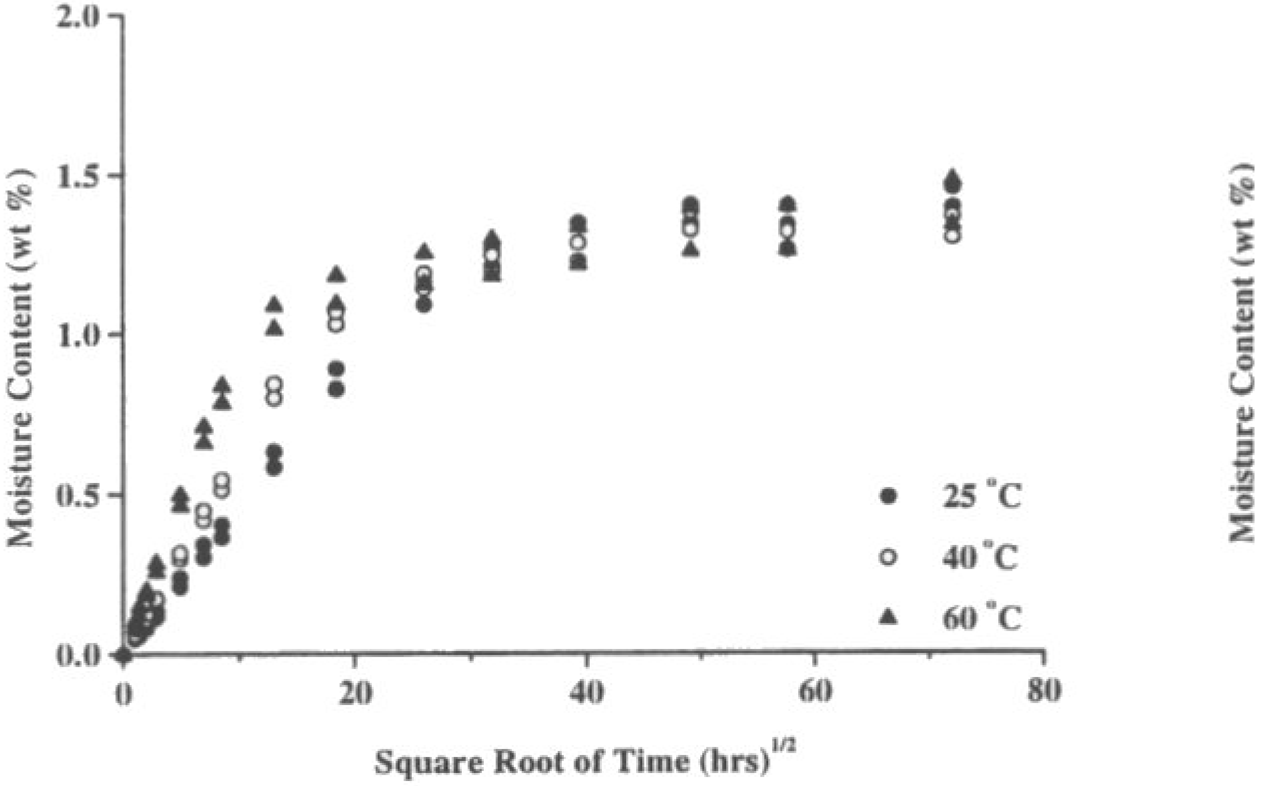


Figure 2: Moisture absorption in continuous aligned T300/924 (left) and E-glass/913 (right).

The diffusion coefficient **D** is assumed to be a function of absolute temperature **T** only and is given by the Arrhenius relation:

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

where **D_o** is a constant, **E** is the activation energy of diffusion and **R** is the ideal gas constant. **D_o** and **E/R** are determined from a linear regression fit to log **D** versus **1/T** graph.

The values of **D_o** and **E/R** determined for continuous aligned T300/924 and E-glass/913 continuous aligned laminates immersed in deionised water at temperatures ranging from 25°C to 60°C are shown below (see Figure 3).

T300/924

$$D_o = 0.327 \mathrm{mm}^2 \mathrm{s}^{-1}; \qquad E/R = 4669 \mathrm{K}$$

E-glass/913

$$D_o = 1.711 \mathrm{mm}^2 \mathrm{s}^{-1}; \qquad E/R = 5532 \mathrm{K}$$

Diffusivity of the material increased by a factor of 5 for T300/924 and by a factor of 7 for E-glass/913 over the temperature range 25°C to 60°C.

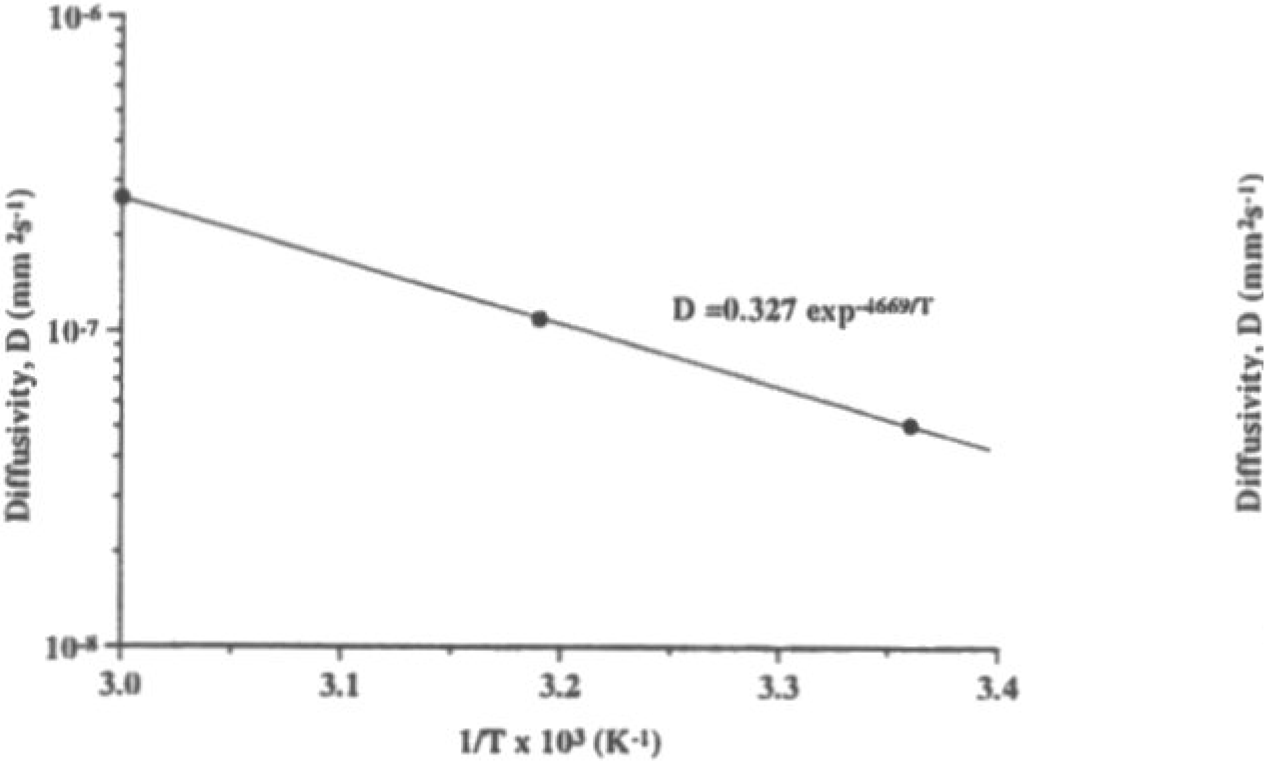


Figure 3: Transverse diffusivity vs temperature for T300/924 (left) and E-glass/913 (right).

Thickness Effects

Absorption measurements were carried out on 1 and 2 mm thick continuous aligned T300/924 carbon/epoxy laminates exposed to 70°C and 85 % RH. As expected, the diffusion coefficient D_x for the two laminates were in close agreement when corrections were made for "edge effects".

$$D_x = 3.11 \times 10^{-7}\ \mathrm{mm^2 s^{-1}} \quad \text{(1mm thick)}$$
$$D_x = 3.47 \times 10^{-7}\ \mathrm{mm^2 s^{-1}} \quad \text{(2mm thick)}$$

The diffusivity in the hot/humid environment was 6 times that for water immersion at room temperature and almost the same for water immersion at 60°C.

Laminate Stacking Effects

Absorption measurements for 1 mm thick unidirectional and cross-ply E-glass/F922 laminates indicated that the corrected diffusivity for the two stacking sequences were almost the same.

$$D_x = 3.11 \times 10^{-7}\ \mathrm{mm^2 s^{-1}} \quad \text{(unidirectional)}$$
$$D_x = 2.90 \times 10^{-7}\ \mathrm{mm^2 s^{-1}} \quad \text{(cross-ply)}$$

Differences in diffusivity can be expected as the laminate thickness is increased. A more comprehensive analysis to take into account complex stacking sequences is presented in reference [6].

Accelerated Conditioning

A number of techniques may be used to accelerate moisture uptake by a composite. Exposure to superheated pressurised steam can induce levels of moisture of between 2 and 3 wt % within 48 hours exposure. Tests conducted using a Midas 40 bench top autoclave (Prior Clave Ltd) at a temperature of 136°C and a pressure of 2.2 bar were able to produce these levels of moisture in E-glass/F922 and HTA/F922 carbon/epoxy laminates. The rate of moisture uptake is increased by a factor of 100, or more.

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

Composite Rods

The use of small diameter composite rods (1.5 to 5 mm) enables rapid environmental conditioning under more moderate and realistic temperatures and moisture levels compared with those used to accelerate ageing in laminates. **Degradation effects on the composite rod by the environment are quickly manifested (within 7 days) in terms of strength reduction.**

A series of tests were carried out on axially aligned continuous E-glass/polyester and Graphil 34-700/vinyl ester composite rods with diameters ranging from 1.5 to 5.0 mm. The composite rods were immersed in deionised water for periods up to 6 weeks at temperatures ranging from 25°C to 60°C. Specimens were withdrawn at selected intervals and the moisture content determined. Tests were conducted on composite rods of various lengths (i.e. 25, 50, 100 and 200 mm) with or without sealed ends. The specimen ends were sealed with a two-part silicone rubber compound to prevent water diffusion from the specimen ends to enable direct measurement of the transverse diffusion coefficient.

The results indicate that the moisture diffusion behaviour was almost identical for the sealed and unsealed (i.e. open) rods, and independent of rod length (see Figure 4). The degree of uncertainty in the weight gain measurements was observed to decrease as the rod length and diameter were increased. Tests conducted on 1.5 mm rods conditioned at room temperature show that moisture equilibrium content was reached within 4 days for the glass/polyester and 14 days for the carbon/vinylester rods. The rate of moisture uptake tends to increase with increasing temperature (Figure 5) and decreasing rod diameter.

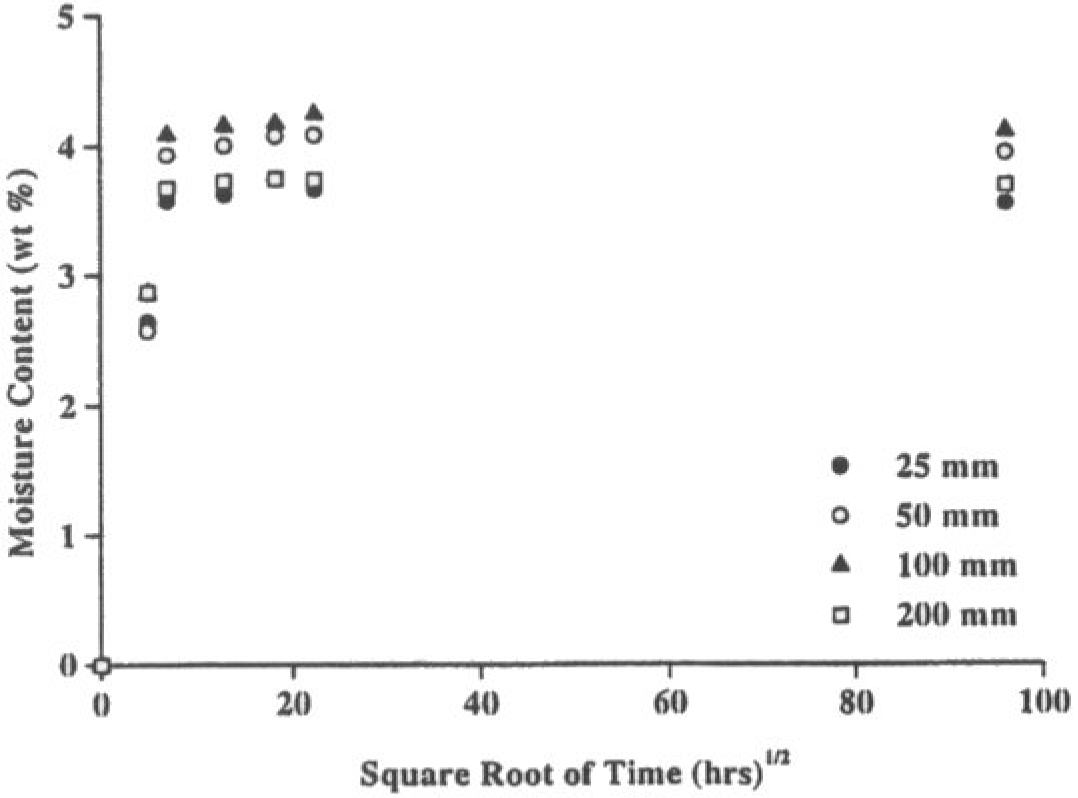


Figure 4: Moisture absorption of 1.5 mm diameter glass/polyester rods in deionised water length dependence (left) and temperature dependence (right).

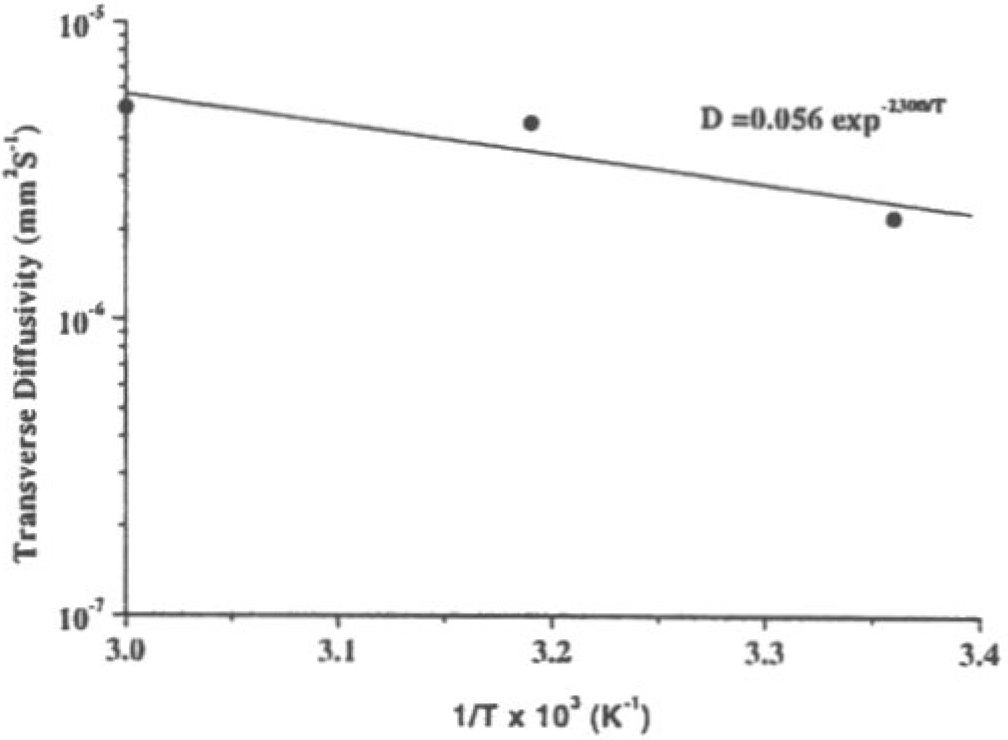


Figure 5: Transverse diffusivity vs temperature for E-glass/polyester.

Prolonged exposure to water at elevated temperatures (i.e. 40 to 60°C) resulted in weight reduction in the glass/polyester rods (Figure 4). This weight loss can be attributed to leaching of uncured monomer and additives from the polyester resin. Material loss to the surrounding environment during conditioning makes reliable diffusion measurements virtually impossible. There was no weight loss observed for the carbon/vinyl ester rods, however the maximum moisture content increased as the conditioning temperature was increased.

Moisture Distribution in a Solid

Assuming a rectangular plate is taken to be infinitely long in the y- and z- directions (Figure 6), the moisture content inside the plate varies only in the x-direction (i.e. the problem is one-dimensional). Initially the moisture concentration $\mathbf{c_i}$ inside the plate is uniform. The plate is suddenly exposed to a moist environment and the exposed faces instantaneously reach the equilibrium moisture concentration $\mathbf{c_a}$, which remains constant. The moisture uptake through the thickness of an infinite plate is given by the following relationship [11]:

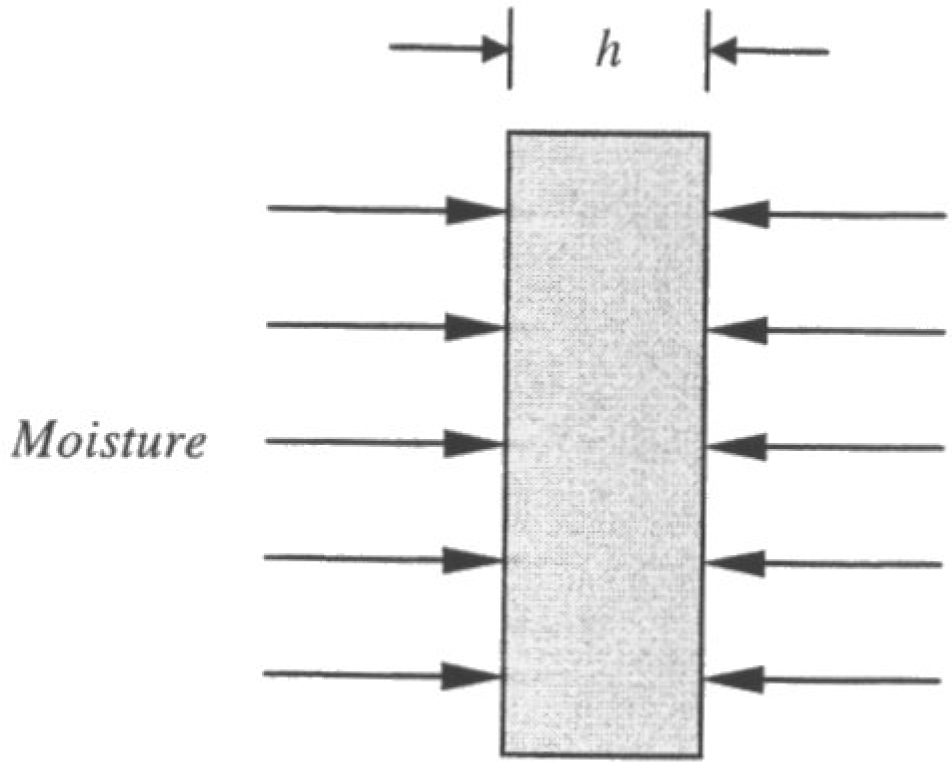
$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2}$$

Where **c** is the moisture concentration, **x** is the thickness coordinate, $\mathbf{D_x}$ is the diffusivity of the material, **t** is time and the boundary conditions are:

$c = c_i \qquad 0 < x < h \qquad t \leq 0$

$c = c_a \qquad x = 0; x = h \qquad t > 0$

The diffusivity changes very little with moisture content and thus the solution to the above equations is given by the equation shown in Figure 6 [12]. **N** is the number of summation terms and **c(t)** is the instantaneous concentration.



$$\frac{c(t)-c_i}{c_a-c_i} = 1-\frac{4}{\pi}\sum_{j=0}^{N}\frac{1}{(2j+1)}\sin\frac{(2j+1)\pi x}{h}\exp\Bigg[-$$

Figure 6: Graphical representation of one-dimensional diffusion.

Theoretical plots of moisture distribution through the thickness of a 1 mm thick continuous aligned E-glass/F922 composite plate, following exposure to a hot/humid environment (i.e. 70°C and 85% RH) for a period of up to 1 year, is shown in Figure 7.

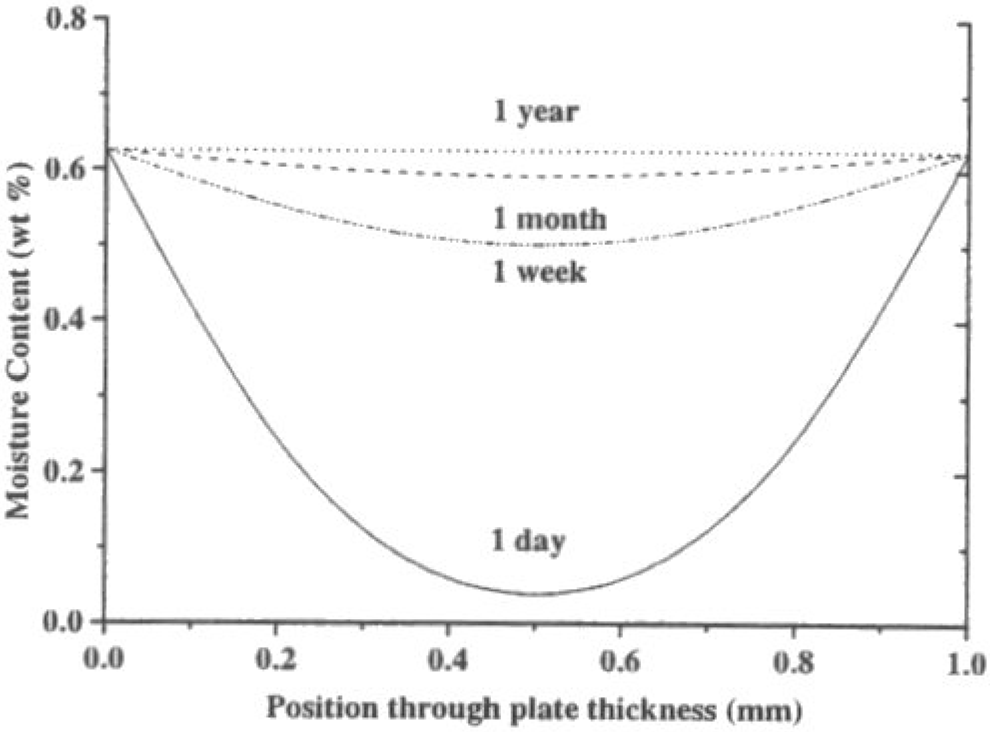


Figure 7: Moisture distribution in a 1 mm thick E-glass/F922 composite specimen following exposure at 70°C and 85% RH.

It is possible to measure the through-thickness spatial and temporal distribution of moisture for a conditioned laminate. The method involves exposing a number of specimens for different periods of time and then slitting the specimens through the thickness to produce a number of slices. Each slice is weighed, dried and then reweighed. The results are plotted as a function of position and time to give spatial and temporal moisture distributions.

Techniques For Chemical And Physical Characterisation

This section briefly examines a number of thermo-mechanical and physico-chemical techniques that can be used for characterising physical and chemical changes in polymeric materials through exposure to aqueous environments.

Dynamic Mechanical Analysis (DMA)

This technique enables the determination of transition temperatures, storage and loss moduli of the sample over a wide range of temperatures (-150°C to 800°C), frequencies (0.01 to 200 Hz) or time, by free vibration, and resonant or non-resonant forced vibration techniques (ISO 6721 [9]) -see also [10]. Flexural samples are popular, the sample is mounted on a clamp and then subjected to sinusoidal changes in strain (or stress) while undergoing a change in temperature. DMA is suitable for polymers and laminated composites with stiffnesses ranging from 1 kPa to 1,000 GPa. Tension, compression and flexure loading configurations can be employed. Three-point flexure specimens can be up to 50 mm in length, 15 mm wide and 7 mm thick.

DMA has many advantages, including:

- Fast analysis time (typically 30 minutes)
- Easy sample preparation
- Wide range of temperature applicability

DMA measurements were carried out on hot/wet conditioned F922 epoxy, and continuous aligned E-glass/F922 and HTA/F922 specimens to determine the change in the glass transition temperature, $\mathbf{T_g}$, as a function of moisture content. Each specimen was immersed in deionised water at elevated temperatures (25, 40 or 60°C) for a select period (either 1, 2, 3 or 6 weeks). The results, presented in Figure 8, show that moisture reduces $\mathbf{T_g}$ with the shift in temperature being related to moisture content by the following linear relationship:

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

where $\mathbf{T_{gd}}$ is the glass transition temperature of the dry material, $\mathbf{T_{gw}}$ is the glass transition temperature of the conditioned (or wet) material, **g** is the temperature shift (in K) per unit moisture absorbed and **M** is the amount of moisture absorbed (wt %).

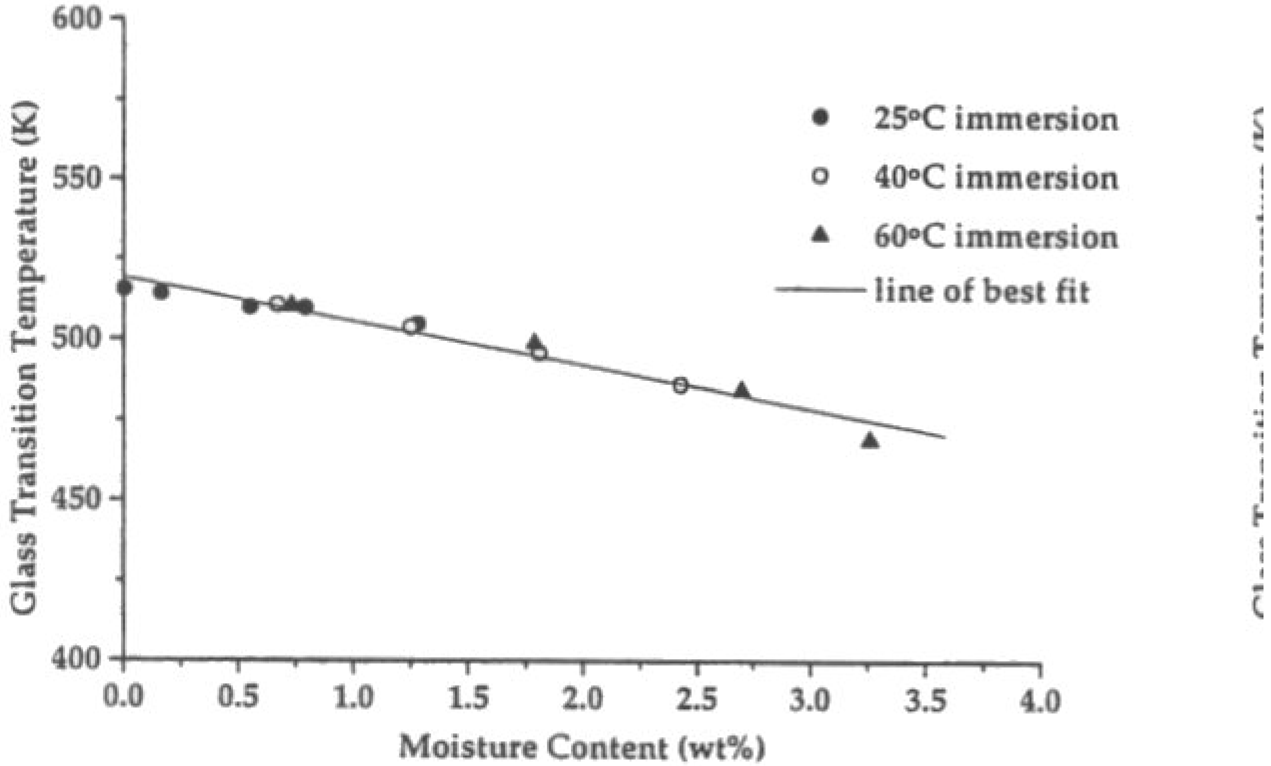


Figure 8: Glass transition temperature as a function of moisture content. F922 epoxy (left) and T300/924 and E-glass/913 (right).

F922 epoxy resin: The value of **g** for F922 was 13.5 K and the measured and projected (i.e. Y-intercept of linear regression fit) values of $\mathbf{T_{gd}}$ for F922 epoxy were 515.6 K (243.6°C) and 519.2 K (246.2°C), respectively.

Continuous aligned E-glass/913 and T300/924: The temperature shift, g, was 36.8 K and 28.9 K for T300/924 and E-glass/913, respectively. The corresponding transition temperatures for the unconditioned composite materials were 430 K (157°C) and 482 K (209°C).

Differential Scanning Calorimetry (DSC)

DSC is used to determine the heat flow associated with material transitions as a function of time and temperature or changes in heat capacity using minimal amounts of material. The technique provides quantitative and qualitative data on endothermic (heat absorption) and exothermic (heat evolution) processes of materials during physical transitions caused by phase changes, melting, oxidation and environmental degradation. The technique involves slowly heating a small sample of material and measuring the heat absorbed or emitted by the sample as a function of temperature compared to a reference material. DSC can be used to measure changes in $\mathbf{T_g}$ with increasing moisture content for neat resins and fibre-reinforced composite materials.

The technique has many advantages, including:

- Fast analysis time (30 minutes)
- Easy sample preparation
- Small test specimens

- Wide range of temperature applicability

ISO 11357 [13] specifies methods for the thermal analysis of polymeric materials, including composite materials using DSC.

Thermal Mechanical Analysis (TMA)

This technique is used in conjunction with DSC to study thermal transition behaviour (e.g. $\mathbf{T_g}$) of polymeric materials. TMA can be used to measure heat distortion temperature, and thermal expansion and contraction (i.e. coefficient of thermal expansion) under dynamic or isothermal heating conditions.

Thermal Gravimetric Analysis (TGA)

TGA can be used to monitor weight changes in a sample as a function of temperature. The technique is primarily used for studying degradation processes, providing information on thermal oxidative degradation rates and thermal degradation temperatures of polymeric materials. This information is useful for determining the life expectancy of composites at elevated temperatures and for comparing degradation rates.

Dielectric Analysis (DEA)

DEA measures the capacitive and conductive properties of materials as a function of temperature, time and frequency under controlled environments. It provides information on rheology (flow) and molecular mobility (relaxation) of materials, and can measure permitivity, loss factor and ionic conductivity of solids. Ionic conductivity is a useful measure of moisture ingression and leaching of chemicals, such as uncured monomer and additives from composite materials.

Ultrasonic Spectroscopy

Ultrasonic spectroscopy can be used to detect the damage caused to fibre-reinforced polymer materials due to hygrothermal ageing. Acoustic parameters, such as velocity and attenuation, are linked to the viscoelasticity and microstructure of the propagation medium. The acoustic parameters can be measured by means of pulsed ultrasonic spectroscopy. It is possible to relate changes in these properties to moisture content and the level of material degradation, and also identify damage mechanisms. Changes in frequency dependency of velocity and attenuation have been related to matrix cracking.

Nuclear Reaction Analysis

Nuclear reaction analysis can be used to directly measure localised moisture content through the thickness of polymeric materials. Specimens are conditioned in D_2O instead of H_2O and the resultant deuterium concentrations in the specimen are measured. The surface is bombarded with a finely collimated ^{3}He beam, which reacts with the deuterium in the sample, releasing high energy protons. The proton yield is directly proportional to deuterium in the reaction volume. Moisture profiles with a resolution of 12 μm have been measured [6].

Electron Dispersive X-ray Analysis (EDX)

Detection and analysis of characteristic X-ray lines of various elements can be obtained using an EDX system attached to a scanning electron microscope (SEM). The maximum operational depth of EDX is typically 3 to 10 μm. The actual penetration depth depends on the type of material being analysed and the acceleration potential used in the SEM. The technique can be used to generate elemental distribution maps of the area of interest, enabling both qualitative (boron to uranium) and quantitative (sodium to uranium) elemental analysis. Although the technique cannot provide information on chemical bonds, it could provide information on element depletion and migration.

Infrared Spectroscopy (IRS)

IRS provides both qualitative and quantitative chemical analysis data and can be used to observe environmental effects on polymer chemistry. The technique provides a fingerprint of the polymer composition and can be used to analyse gases, liquids and solids. Computerised databases of spectra for common polymeric materials are available to enable characterisation of molecular structure by observing spectral differences between known materials and the test sample. Fourier transform infrared spectroscopy (FTIR) can be used to assess the state of cure of thermoset resins.

X-ray Photoelectron Spectroscopy (XPS)

XPS is frequently used for quantitative elemental analysis of fracture surfaces and for monitoring chemical changes in composite samples. The technique, which is capable of detecting all elements with the exception of hydrogen, can provide information of chemical groups present on the surface of polymeric materials. The technique can be used to determine the effect of elevated temperature and surface preparation on surface chemistry and is used to examine the cause of adhesion problems. The maximum operational depth of XPS is 3 nanometres.

Auger Electron Spectroscopy (AES)

AES is a non-destructive technique for identifying the elements in the first few atomic layers (~2 nanometres) on a specimen surface and is able to provide quantitative data on the detected elements. Combined with inert gas ion sputtering, AES can be used to obtain depth composition profiles. The technique can be used to map the distribution of elements present on a specimen surface and is capable of detecting all elements with the exception of hydrogen. Spectrometers can be fitted with a facility for in-situ testing of specimens enabling rapid analysis of fracture surfaces under high vacuum conditions (1×10^{-10} Pa), thus preventing contamination and oxidation of the fracture surfaces. The technique is not particularly suited to examination of polymers (i.e. insulating materials) due to the possibility of beam damage and electrical charging of the sample, which can complicate data interpretation.

Concluding Remarks

This Measurement Note has presented a number of methods, experimental and predictive analysis, suitable for determining through-thickness moisture distribution, moisture equilibrium content and diffusion coefficient for neat resin and composite specimens. **The predictive analysis proved reliable and accurate for characterising moisture diffusion behaviour in these materials.** These methods allow for the effects of fibre orientation, temperature, humidity and specimen geometry (e.g. thickness) on moisture diffusion behaviour.

It was also observed that Ficks diffusion equation could be used to determine moisture diffusion curves for all the materials studied. The equation applied equally to hot/humid and water immersion data. It was also possible to directly relate changes in glass transition temperature with moisture content. In a number of cases, long-term exposure resulted in chemical and microstructure damage of the material and material loss to the surrounding environment.

References

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