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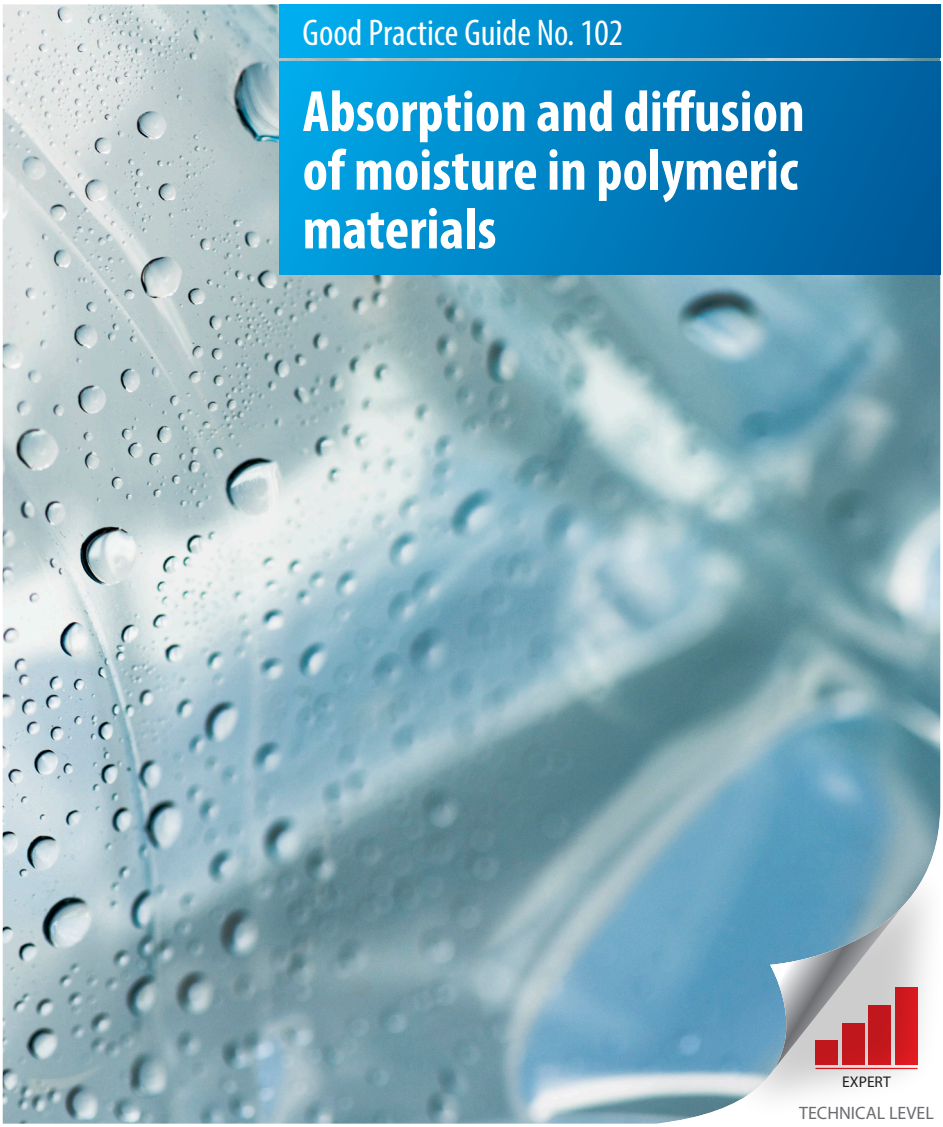
Good Practice Guide No. 102

Absorption and diffusion of moisture in polymeric materials



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Abstract

Accurate modelling of the absorption of moisture into engineering polymers is needed to design exposure procedures for durability assessment and carry out reliable lifetime predictions. This needs to be supported by good quality data obtained under representative conditions. This Guide describes methods for measuring the absorption and diffusion of moisture in polymeric materials, including plastics, adhesives, and composites. Factors that will affect moisture absorption, including service conditions (temperature, pressure, and stress) and the manufacture process (e.g., state of cure), are also covered.

NPL has made every effort to ensure all information contained in this Good Practice Guide was correct at the time of publication. NPL is not responsible for any errors, omissions, or obsolescence, and does not accept any liability arising from the use of this Good Practice Guide.

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Contents

Glossary of Terms (Based on BSI and ASTM Definitions)

Accelerated ageing test: Short-term test designed to simulate the effects of longer-term service conditions.
Adherend: Body that is or intended to be held to another body by an adhesive.
Adherend failure: Failure of a joint in the body of the adherend.
Adhesion (or adherence): State in which two surfaces are held together by interfacial bonds.
Adhesive: Non-metallic substance capable of joining materials by surface bonding (adhesion), the bonding possessing adequate internal strength (cohesion).
Adhesive failure: Failure of an adhesive bond, such that separation appears to be at the adhesive/adherend interface.
Ageing: Irreversible chemical and physical processes occurring in a material in the course of time.
Amorphous: Non-crystalline or devoid of crystalline structure.
Amorphous regions: Regions within a polymeric material that, on the basis of X-ray diffraction or other suitable techniques, do not show any evidence of crystalline structure.
ASTM: American Society for Testing and Materials.
Bond: The union of materials by adhesives.
Bond-line: The layer of adhesive, which attaches two adherends.
Bond strength: The unit of load applied to tension, compression, flexure, peel, impact, cleavage, or shear, required to break an adhesive assembly with failure occurring in or near the plane of the bond.
Breaking stress: Stress at the moment of rupture of a specimen.
Brittle failure: Failure in which the fracture surface exhibits no permanent material deformation to the naked eye (e.g., stretching, elongation and necking down).
BSI: British Standards Institute
Bulk adhesive: The adhesive unaltered by the adherend.
Cleavage: Mode of application of a force to a joint between rigid adherends, which is not uniform over the whole area, but results in a stress concentrated at one edge.
Cohesion: The ability of the adhesive to resist splitting or rupture.
Cohesive failure: Failure within the body of the adhesive (i.e., not at the interface).
Composite: Solid product consisting of two or more distinct phases, including a binding material (matrix) and a particulate or fibrous material.
Conditioning: A series of operations intended to bring a sample or specimen into a reference state with regard to temperature and humidity.
Contamination-free: Absence of foreign matter, both on a treated surface (i.e., cleanliness), or which could migrate through the bulk to a bonded interface with time.
Craze: Defect at or under the surface of a plastic, attributable to apparent cracks bridged by polymeric material of reduced (apparent) density.
Creep: The time-dependent increase in strain resulting from a sustained load.
Crystallinity: Presence of three-dimensional order at the level of molecular dimensions.
Cure: To set or harden by means of a chemical reaction.

Cure time: Time required to affect a cure at a given temperature.
Cure temperature: Temperature at which a polymeric system is exposed in order to achieve curing.
Degradation: Change in the chemical structure of a polymeric material involving a deleterious change in properties.
Delamination: Separation of layers (i.e., planar defect) in a laminate.
Deterioration: Permanent change in the physical properties of a material evident by impairment of these properties.
Diffusivity: The transport of chemical species, such as a liquid or gas, within a solid due to concentration differences. Diffusivity is generally temperature dependent.
Dimensional stability: Consistency of dimensions of a material part or specimen under environmental conditions.
Dissolution: Process of absorption of the chemical in the polymer and depends on the affinity (interaction energy) of the polymer for the chemical, the volume available for absorption and the concentration of chemical.
Durability: The endurance of joint strength relative to the required service conditions.
Environmental test: Test to assess the performance of an assembly under service conditions.
Fibre: Particle of relatively short length, characterised by a high ratio of length to thickness or diameter.
Filler: Relatively inert material (e.g., talc) added to a plastic or resin to modify its strength, fire resistance or other qualities, or to lower costs.
Fillet: Portion of an adhesive that bridges the adherends outside the bond-line.
Glass transition: A reversible change in an amorphous polymer or in amorphous regions of a partially crystalline polymer from (or to) a viscous or rubbery condition to (or from) a hard and relatively brittle one.
Hygroscopic: Material capable of absorbing and retaining environmental moisture.
Interface: The region where two materials are in intimate contact. Interfaces can be solid-solid (cured adhesive joint), solid-liquid (uncured adhesive joint), solid-gas (exposed adherend), liquid-gas (open adhesive) or liquid-liquid (insoluble liquids).
Interphase: The region near an interface where the properties of materials are altered from their bulk properties due to the presence of the interface.
ISO: International Standards Organisation.
Laminate: Product made by bonding together two or more layers (plies) of material or materials.
Permeability: Property of a material transmitting gases and liquids by passage through one surface and out at another surface by diffusion and sorption processes.
Plasticisation: Increase in softness, flexibility, and extensibility of an adhesive.
Polymeric material: A material whose continuous phase consists of long-chain organic molecules.
Porosity: A condition of trapped pockets of air, gas, or vacuum within a solid material.
Post-cure: Further treatment by time and/or temperature of an adhesive to obtain the required properties by curing.

Primer: A coating applied to a surface, prior to the application of an adhesive, to improve the performance of the bond.

Reinforced plastic: Polymer (plastic) with high-strength fibres embedded in the composition, resulting in some strength properties greatly superior to those of the base resin.

Sealant: An interlaminar layer of polymeric material applied for the purpose of filling gaps and insulating the interior of the joint from external environments. Sealants are not used to provide load bearing capacity although adhesives can also act as sealants.

Semi-crystalline: Polymer containing crystalline and amorphous phases.

Shelf life: The period for which the components of the adhesive may be stored, under the conditions specified by the manufacturer, without being degraded.

Soundness: Freedom from weak and loosely attached surface layers.

Stability: The stability of surface layers and oxides, towards water, organic compounds, and elevated temperatures, as a function of time following treatment.

Strain: Unit change due to force in size of body relative to its original size.

Stress: Force exerted per unit area at a point within a plane.

Stress-strain diagram (or curve): A diagram in which corresponding values of stress and strain are plotted against each other.

Structural bond: A bond, which is capable of sustaining in a structure a specified strength level under a combination of stresses for a specified time.

Substrate: An adherend, a material upon which an adhesive is applied.

Surface preparation (or treatment): Physical and/or chemical treatments applied to adherends to render them suitable or more suitable for adhesive bonding.

Swelling: Increase in volume of a test specimen immersed in a liquid or exposed to a vapour.

Thermoplastic: A material that can be repeatedly softened by heating.

Thermoset: A resin that is substantially infusible and insoluble after being cured.

Traveller: A test specimen used for example to measure moisture content because of environmental conditioning.

Uniformity: Visible or measurable consistency of the other characteristics, and of the regularity of a treated surface area.

Weathering: Effects on a material of exposure to outdoor conditions.

Yield strain: The strain, below which a material acts in an elastic manner, and above which it begins to exhibit permanent deformation.

Yield stress: The stress (either normal or shear) at which a marked increase in deformation occurs without an increase in load.

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Chapter 1

Introduction and scope

Introduction

Lifetime prediction is an important consideration in the selection of materials systems and the design of structures. The design approach for lifetime prediction of engineering polymers, such as composites or structural adhesives, is developing continuously but still relies on 'knockdown factors' or 'rules of thumb' generated from mechanical tests on conditioned samples.

Chemical exposure, in particular moisture exposure, is a key mechanism for degradation in polymer systems. An understanding of permeation of chemical species is essential for developing testing methodologies and accelerated ageing protocols for polymeric materials. The process of permeation of chemicals through polymers is a combination of two interrelated processes, dissolution in the polymer and diffusion through the polymer. Dissolution is the process of absorption of the chemical in the polymer and depends on the affinity (interaction energy) of the polymer for the absorbing molecules, the volume available for absorption and the concentration of absorbing chemical. There is a limit to the amount of the chemical that can be absorbed under any set of conditions – the solubility. Diffusion is the concentration gradient driven process whereby the absorbed molecules are transported within the polymer and diffusion properties are characterised via diffusion coefficients. A review [1] of the extensive body of literature on permeation and diffusion in polymers [e.g., 2-6] emphasised the strong need for reliable test methods to measure the diffusion of gases and liquids in polymers. Permeation properties are required under relevant service conditions, which may include transient and varying levels of chemical exposure, temperature, pressure, and stress.

Often, especially in thick sections, the time taken for deleterious species to diffuse in sufficient concentrations to critical regions is the rate-determining step in the ageing process. Accurate modelling of the absorption of moisture into engineering polymers is needed to design exposure procedures and carry out reliable lifetime predictions. This needs to be supported by good quality data obtained under representative conditions. The techniques described in this Guide focus on diffusion as part of a wider investigation of accelerated ageing of polymer materials [7].

The time dependent concentration of chemical species in a component can be predicted using diffusion modelling approaches [2-6]. A common assumption used in interpreting diffusion measurements is Fickian diffusion - the steady state flux of diffusant per unit area (J) per unit time (t) is a function of the concentration gradient (concentration, ϕ, per unit length, x) and Fick's first law is expressed:

$$\frac{dJ}{dt} = -D\frac{d\phi}{dx} \qquad (1)$$

Where the diffusion coefficient *D* does not depend on concentration then Fick's second law (Equation 2) can be used to determine the time dependence of the concentration of the diffusant in the sample.

$$\frac{dJ}{dt} = -D\frac{d^2\phi}{dx^2} \quad (2)$$

The diffusion coefficient *D*(*T*) is temperature dependent, increasing the temperature (*T*) should increase the rate of diffusion and accelerate the ageing of the system.

Scope

This Good Practice Guide covers techniques for measuring the absorption and diffusion of moisture in polymeric materials, which include plastics, polymer matrix composites (PMCs) and adhesives.

The applicable standards for these measurements is ISO 62 (Plastics - Determination of Water Absorption) [8] and ASTM D570 (Standard Test Method for Water Absorption of Plastics) [9]. The ISO Standard includes an Appendix for determining the diffusion coefficient that is absent from the ASTM Standard. Chapter 2 of this guide describes these methods and explores the factors that influence the accuracy of the results obtained. Chapter 3 outlines a method for analysing the results of measurements and the calculation of Fickian diffusion properties. Environmental factors, such as stress and temperature, will affect diffusion and methods for assessing these effects are covered in Chapter 4.

Chapter 5 describes factors that affect measurements in non-homogenous and non-isotropic materials systems, such as polymeric composites and adhesive joints. Sources of uncertainties are described in Chapter 6. Chapter 7 provides a summary of key points. Chapter 8 lists standards for assessing permeation and diffusion in polymers. These standards enable the measurement of properties for comparison or specification. However, the standards do not cover all the aspects of measurement required to provide data for design.

Measurements of moisture absorption in a rubber-toughened epoxy adhesive and in a film, adhesive are described to illustrate some of the techniques employed.

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Chapter 2

Experimental procedures

- Introduction
- Specimens
- Exposure conditions and times
- Weighing and balance requirements
- Specimen preparation before testing
- Immersion and mass measurement
- Completion of tests

Introduction

ISO 62 [8] and ASTM D 570 [9] are standard measurement methods for water absorption by immersion. The absorption of liquids into polymers is followed through mass uptake (or gravimetric) measurements. Since liquid densities are comparable with polymer densities the mass changes should be measurable. Mass increases of the order of a few percent of the original mass of the polymer are typical in systems with an affinity for the liquid [2-5].

This approach can also be applied to study diffusion of vapours (e.g., water vapour) in polymers; pre-conditioned samples are exposed to a controlled atmosphere (vapour concentration and temperature) and periodically weighed [10-13]. The analysis approach described in Chapter 3 can be used to calculate solubility and diffusion coefficients. Direct contact with a liquid rather than its vapour normally leads to greater levels of absorption (higher saturation concentrations) and, therefore, condensation of vapour on the surface will affect results.

Specimens

The standards recommend a series of preferred sample geometries for flat sheets (either directly moulded or cut from larger sections), rod and tubes to enable comparison of water absorption properties. The procedures for assessing flat sheets are described in this guide but the processes and items to consider are common for all of sample types.

For example, the geometries for flat sheets are specified as:

- The ISO 62 standard specimen is a square 60 mm × 60 mm × 1 mm thick.
- The preferred test specimen for ASTM D 570 is a 50.8 mm diameter disk with a thickness of 3.2 mm.

Standards	Geometric Parameter	Dimension (mm)	Manufacture Tolerance (mm)	Measurement Tolerance (mm)
ISO 62 [8]	Length	60	± 2	± 0.1
	Width	60	± 2	± 0.1
	Thickness	1	± 0.05	± 0.1
ASTM D570 [9]	Radius	25.4	Not stated	± 0.0252
	Thickness	3.2	± 0.15	± 0.025

Table 1. Standard specimen dimensions for flat sheets

Dimensions and tolerances allowed are shown in Table 1. The tolerances on length, width and radius are wide as these dimensions have little significant effect on the results. The thickness (and accuracy of the measured thickness) is much more critical for comparing materials (and samples tested at different labs) and for the calculation of diffusion coefficients. It is good practice to measure the thickness to an accuracy of 1% or better, regardless of the tolerances specified in the standards.

Deviations from the standard dimensions are allowed for but must be recorded. Examples where samples may need to deviate from the standard dimensions include:

- Laminates, where the lay-up needs to be representative of the material.
- Highly absorbing plastics where saturation may be approached very rapidly may be better measured using thicker samples.
- Where the material properties are known or suspected to be thickness or manufacturing process dependent and the sample needs to be prepared to be representative.

Changing the thickness of the test specimen may result in the need to use different values for the other dimensions (i.e., length and width or radius). Factors than need to be considered in selecting new specimen dimensions include:

- Maintaining a similar ratio of edge to face area to the standard specimen (e.g., for the ISO square a length to thickness ratio of 60).
- Ensuring the mass of the sample is such that the change in mass on absorption can be measured with sufficient accuracy.
- Ensuring the sample fits on the balance.
- Ensuring the sample fits in the exposure system.
- Controlling and measuring the dimensions to sufficient accuracy, in particular the level of uncertainty in the thickness can increase significantly with reducing thickness.
- The time taken to reach saturation – this increases with the square of thickness.

Exposure conditions and times

The standards specify a set of standard exposure conditions (temperature and time) that allow for comparing different materials. These are:

Room temperature immersion (23 ± 2 °C) (ISO and ASTM)	Immerse for 24 ± 1 hours then weigh. Re-immerse and repeat for increasing intervals (e.g., 24h, 48h, 96h, 192h, then weekly etc.) until saturation. ASTM specifies a 2-hour (120 ± 4 minute) exposure for materials having a high rate of absorption or for thin samples. Samples can be re-immersed for measurement at 24 hours (and subsequent intervals).
Boiling water immersion (ISO and ASTM)	Immerse for 30 ± 2 minutes in boiling water remove and place in water at room temperature to cool for 15 ± 1 minute, then weigh. After weighing the procedure is repeated until saturation is reached. ASTM also specifies a 2-hour (120 ± 4 minute) boiling water exposure.

Immersion at 50 °C (ASTM)	Immersion period is specified as 48 ± 1 hours.
Exposure under standard laboratory conditions of 23 ± 2 °C and 50 ± 5% RH (ISO)	Follows the intervals from room temperature immersion.

Note 1: Appropriate safety precautions should be taken when working with boiling water.

Other exposure conditions may also be specified [14, 15]. For example, the military consider the worst worldwide environment to be represented by 70 °C and 85% RH (relative humidity). The standard exposures and intervals may not be appropriate for obtaining diffusion data for design and alternative procedures more clearly reflecting the service conditions may need to be considered.

- Time to reach saturation depends on the square of thickness and therefore exposure timescales will need to be considered in light of the sample dimensions. A maximum sample thickness of 1 mm is recommended by ISO [8] to ensure that test durations do not exceed one week for typical D values for polymers (ca. 10-12 m^2s^{-1}).
- The exposure temperature should reflect the application temperature.
- Multiple temperature exposures may be needed to build up a picture of the full behaviour of the material.
- High temperatures may cause chemical or phase changes in the polymer, which could limit the possibility of extrapolating behaviour from one temperature to another.
- Where possible, the exposure intervals should match these in the standards to enable comparability with standard data.
- If multiple specimens are to be exposed in a study then the exposure intervals for each of the specimens should be consistent. The start of the exposures may need to be staggered to allow mass measurements to be carried out efficiently.

Weighing and balance requirements

The ISO and ASTM standards require the use of a balance capable of reading to 0.1 mg. Typically, the dry masses of the specimens referred to in the standards will be in the range 2 g – 10 g. Thus, the sensitivity of the concentration measurement will be at least 0.005%, which is more than adequate if absorption levels are greater than 1%. If specimens with lower masses (< 1 g) are used, e.g., using very thin samples, or saturation concentrations are low (< 1%) then a higher resolution balance (e.g., with a resolution of 0.01 mg) may be necessary.

Procedures for weighing good practice [16] should be followed. The balance used should have a capacity such that the mass of the specimen is neither at the lower or upper end of the balance range (i.e., the sample mass is within 10%-90% of the full scale of the balance). The total mass of sample expected at saturation should also be considered. The balance should be calibrated over the expected range of masses. An enclosure around the balance pan to eliminate drafts is recommended.

To minimise reproducibility problems, it is recommended that the same balance be used throughout the test programme. The samples should be placed in the same position on the balance each time a measurement is made.

Specimen preparation before testing

If test specimens are machined then care should be taken to avoid damage to the surfaces (e.g., cracking). Rough surfaces should be smoothed, for example by polishing with fine glass paper.

In materials with anisotropic diffusion properties (e.g., fibre reinforced plastics where faces cut normal to the fibre direction in composites may have significantly higher diffusion properties) erroneous results can be obtained if absorption through exposed edges is significantly different to absorption through surfaces. For this reason, the ratio of edge area to surface area of samples should be minimised.

Where edge effects are of concern then edges can be sealed (e.g., by bonding aluminium foil to the edges or applying a barrier coating). The additional mass of the sealing material needs to be accounted for when analysing results. Any coating/foil used for sealing the edges must:

- Be applied as a thin layer to avoid becoming a significant component of the mass of the system.
- Have a significantly lower permeability than the sample; if it does not then the thin layer will not act as a barrier to diffusion.
- Be applied carefully so as to not overlap the main faces of the sample.

The second requirement usually means that sealing coatings are not commonly used for isotropic materials. However, for systems where diffusion is directionally dependent and diffusion through the edges may be high (e.g., composites) sealing may be necessary.

The samples should be dried to constant mass, M0, before testing. Standards recommend drying at 110 °C for 1 hour or at 50 °C for 24 hours then cooling in a desiccator prior to measuring mass (and testing). Drying cycles should be repeated until constant mass (i.e., change in mass between successive measurements is less than 0.1 mg). The lower temperature should be used if there are worries about thermal stability or changing the state of cure of the material.

Immersion and mass measurement

Samples should be immersed in a sufficient volume of liquid such that the samples are fully immersed and any species leaching from the samples are sufficiently diluted. ISO 62 specifies at least 300 ml per test specimen and a minimum of 8 ml of fluid per square cm of surface area. The fluid should be topped up or replaced regularly to ensure that the correct immersion conditions are maintained.

Samples of the same composition can be placed in the same container provided that the minimum volume of fluid per sample is maintained. Samples should not make any significant contact with each other or the container. A 'rack' manufactured from a material that does not degrade in the fluid (e.g., stainless steel) can be used to maintain separation. Where the samples have densities less than the fluid, a means of weighting the samples needs to be used. A stainless-steel mesh cage is recommended in IS0 62.

After immersion for the fixed period (at constant temperature), the sample is removed from the medium and surface liquid wiped off using a dry cloth or paper before immediately weighing (in a weighing bottle for very thin samples). Assessing the total removal of liquid from the surface of the sample is judged by the appearance of the surface and from the appearance of the drying cloth. Therefore, it is subjective and a potential source of uncertainty in the measurements. It is much easier to dry and to judge dryness of smooth surfaces than textured surfaces.

Samples removed from the exposure medium will lose absorbed moisture continuously during the period that they are out from the medium. The loss of absorbed moisture is a diffusion driven process depending on the difference between the surface moisture concentration and the equilibrium moisture concentration for the material in the laboratory environment (generally 23 ± 2°C and 50 ± 5% relative humidity). If this loss of absorbed material is low, then samples can then be returned to the medium for continuing exposure. This requires that the time out of the medium be minimised. Acceptable periods of time that the samples can be out of the exposure medium will be sample and material specific. The periods out of exposure should be insignificant compared to exposure periods between each weighing.

The date, time and mass readings should be recorded. Any changes to the samples (e.g., discolouration, blistering, cracking) should be noted.

It is recommended that the shape of the uptake curve be monitored by plotting the increase in mass divided by the initial mass, measured at each time intervals, against time (see Chapter 3).

Completion of tests

Saturation mass, M_∞, is defined when the weight gains from three successive measurements differ by less than 1% of the overall weight gain. The saturation moisture content C_s is simply:

$$C_s = \frac{(M_\infty - M_0)}{M_0} \quad (3)$$

Loss of water-soluble matter from test samples may also affect results. This can be checked by reconditioning (drying) the sample back to constant mass M_c and comparing against the original mass M_0.

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Chapter 3

Data analysis

- Moisture absorption curves
- Calculation of diffusion coefficients
- Correcting for edge effects

Moisture absorption curves

The absorbed moisture concentration $C(t)$ is calculated from the mass $M(t)$, initial mass M_0 and the reconditioned mass M_c. If there is no loss of water-soluble matter (or reconditioned mass data are not available) then use $M_c = M_0$.

$$C(t) = \frac{M(t) - M_c}{M_0} \tag{4}$$

$C(t)$ is often expressed as a percentage of the specimen dry mass. The plot of $C(t)$ against time has a decreasing slope that asymptotically approaches a saturation concentration at large time. There is a limit to the amount of the moisture that can be absorbed under any set of conditions (i.e., solubility).

A common approach is to plot $C(t)$ against square root of time since a linear section at the start of the curve is indicative of Fickian diffusion. The "apparent" diffusion coefficient D_a (uncorrected for edge effects) for a polymer specimen can be determined from the initial linear region of the Fickian diffusion curve. Figure 1 shows absorption curves measured for the example epoxy at different temperatures. Reducing the sample thickness and/or increasing the exposure temperature decrease the time required to reach saturation (i.e., initial gradient of the diffusion curves increases with temperature). The saturation concentration does not appear to depend on the sample thickness but seems to decrease with increasing temperature.

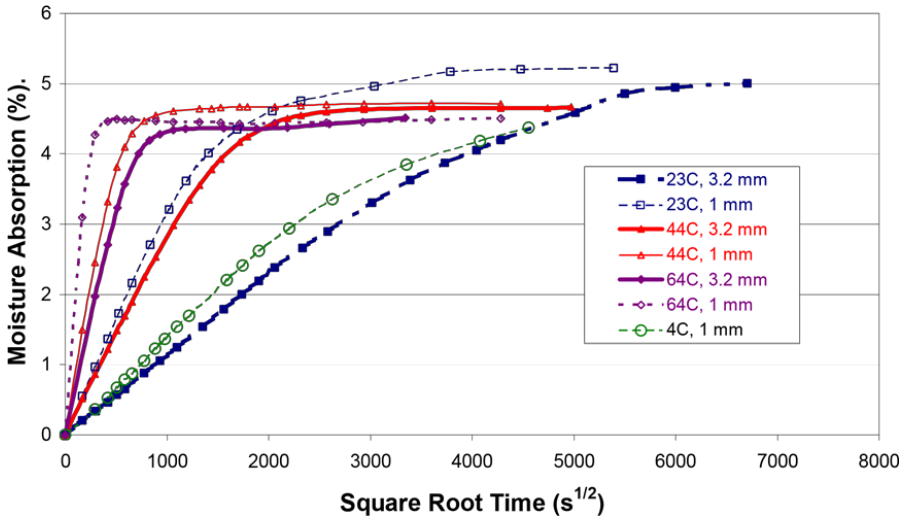

Figure 1. Moisture absorption curves measured by mass uptake

Calculation of diffusion coefficients

Through consideration of the 1-D diffusion case, analytical solutions for the temporal and spatial distribution of moisture concentration $C(t)$ at a distance x from the mid-plane can be derived [17, 18]:

$$\frac{C(t)}{C_s} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)}exp\left[\frac{-(2n+1)^2\pi^2 Dt}{4l^2}\right]cos\left[\frac{(2n+1)\pi x}{2l}\right] \quad (5)$$

Here, l is the half thickness of the film and D is the Fickian diffusion constant. However, as experimental determination of point moisture concentrations is difficult to measure experimentally, this expression is integrated with respect to x to generate an expression in terms of mass gain as a function of time:

$$\frac{C(t)}{C_s} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)}exp\left[\frac{-(2n+1)^2\pi^2 Dt}{4l^2}\right] \quad (6)$$

By assuming a one-dimensional Fickian process a method has been derived [4,5,17] for calculating the "apparent" diffusion coefficient D_a, which is not corrected for edge effects, is calculated from the moisture concentration versus time measurements, $C(t)$, and the sample thickness, h:

$$D_a = \frac{\pi}{16}\left[\frac{h(C(t_2) - C(t_1))}{C_s(\sqrt{t_2} - \sqrt{t_1})}\right]^2 \quad (7)$$

where C_s is the saturation concentration (or percentage) of moisture. If the starting point is a dry sample at time zero, then t_1 and $C(t_1)$ can be eliminated, and the fractional mass uptake $C(t_2)/C_s$ plotted as a function of $\sqrt{t_2}$ has a slope proportional to ${D_a}^{1/2}$.

$$\frac{C(t_2)}{C_s} = {D_a}^{1/2}\frac{4\sqrt{t_2}}{h\sqrt{\pi}} \quad (8)$$

For Fickian diffusion, this plot is approximately linear (e.g., Figure 2, until $C(t_2)$ approaches $0.7C_s$). D_a can be calculated from the square of the slope. Alternatively, if a full diffusion curve is not available then D_a can be evaluated from single point values of $C(t_2)$ and t_2 if a value for C_s is known or can be estimated with reasonable accuracy.

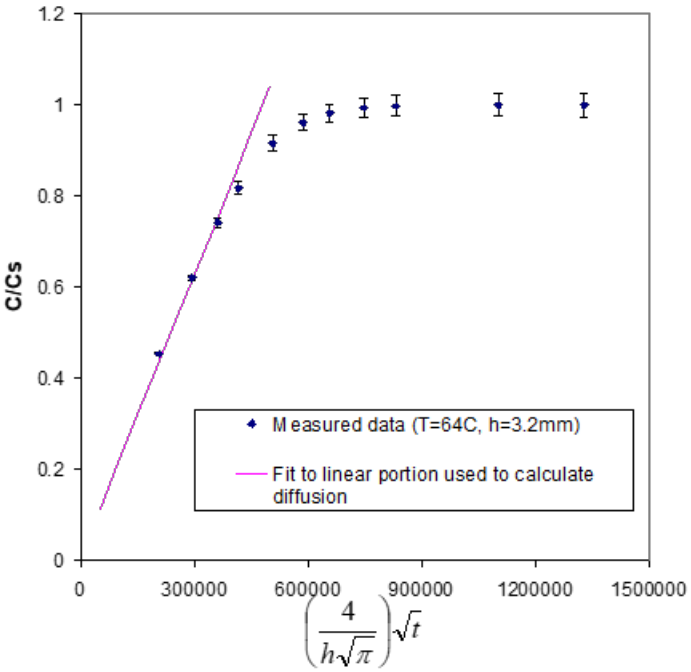

Figure 2. A linear fit to the absorption data up to C/Cs = 0.7 used to calculate D_a (See Equation 8)

Figure 2 shows mean absorption values obtained from three 3.2mm thick epoxy samples exposed simultaneously at 64 °C. The error bars represent one standard deviation and are ~2% - 4% of the mean. A straight line was fitted to the data up to an approximate value of C/C_s of 0.7 (72 hours exposure). Only three absorption measurements lie in this range.

Equation 6 can be expanded and approximated to calculate moisture concentration as a function of time. Where $Dt/h^2 > 0.05$, Equation 5 reduces to:

$$C(t_2) = C_s\left[1 - \frac{8}{\pi} exp\left[-\pi^2\left(\frac{D_a t_2}{h^2}\right)\right]\right] \quad (9)$$

The following approximation is also commonly used [17]:

$$C(t_2) = C_s\left[1 - exp\left[-7.3\left(\frac{D_a t_2}{h^2}\right)\right]\right]^{3/4} \quad (10)$$

Table 2 shows the calculate slopes and apparent diffusion coefficients for each of the three specimens. These were averaged and standard deviations calculated. The coefficients of variation for C_s and Da are 2.7% and 4.8%, respectively.

Sample	Saturation C_s (%)	Slope ($ms^{-1/2}$)	Apparent Diffusion Coefficient D_a (m^2s^{-1})
1	4.28	2.00×10^{-6}	4.20×10^{-12}
2	4.33	2.06×10^{-6}	4.24×10^{-12}
3	4.52	2.14×10^{-6}	4.57×10^{-12}
Mean	4.37	2.08×10^{-6}	4.33×10^{-12}
SD	± 0.12	$\pm 0.05 \times 10^{-6}$	$\pm 0.21 \times 10^{-12}$
CoV	2.7%	2.4%	4.8%

Table 2. Diffusion properties determined from Figure 2
(SD = standard deviation and CoV = coefficient of variation)

Correcting for edge effects

The one-dimensional approximation ignores additional diffusion of moisture through the edges of the sample. Edge effects are minimised by ensuring the samples have a large ratio of face area to edge area. Edge effects can also be minimised by sealing the edges.

A correction was derived by Shen and Springer [17] to account for edge effects. The true one-dimensional diffusion coefficient D_x can be calculated from the apparent diffusion coefficient Da and the length l, width b and thickness h of the plaques using a correction factor E.

$$D_x = ED_a = D_a\left(1 + \frac{h}{l} + \frac{h}{b}\right)^{-2} \tag{11}$$

For example, the correction factors for 1 mm and 3.2 mm thick squares with 50 mm sides are 0.925 and 0.786, respectively. As Table 3 shows, applying the correction factor narrows the differences between D_x values obtained from the two different thicknesses. However, the values obtained from the thicker specimens are still greater than those obtained from the thinner samples, suggesting that in this case there may be a greater flux through the edges than the faces.

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Chapter 4

Effect of temperature and stress

- Representing relevant service conditions
- Effect of temperature
- Effect of tensile stress
- Determining the effect of hydrostatic pressure

Representing relevant service conditions

In many applications, materials will be simultaneously exposed to moisture and stress. Many degradation processes are known to accelerate under the combination of load and exposure. For example, the residual strength of composite samples that are immersed in water under constant load decreases much more rapidly than specimens loaded in air or specimens immersed but not loaded [7]. The degradation of the material strength may have been accelerated by enhanced moisture diffusion in stressed materials.

Effect of temperature

Diffusion coefficients depend on temperature. The diffusion coefficient $D(T)$ is temperature dependent and for ideal systems follows an Arrhenius relationship, with an energy barrier to diffusion E_D.

$$D(T) = D_0 \, exp\left(-\frac{E_D}{kT}\right) \tag{12}$$

Therefore, increasing the temperature T should increase the rate of diffusion and accelerate the ageing of the system. k is Boltzmann's constant and the material parameters D_0 and E_D can be determined by plotting log $D(T)$ against $1/T$. Table 3 shows diffusion coefficients determined for an epoxy adhesive at different temperatures. Figure 3 shows a plot of logarithm of diffusion coefficient plotted against $1/T$ determined for an epoxy adhesive. This is linear suggesting that the Arrhenius coefficients holds for this range of temperatures.

Sample Thickness (mm)	Temperature (°C)	Apparent D_a (m^2s^{-1})	Saturation Concentration (%)	Corrected D_x (m^2s^{-1})
1	4	1.28×10^{-14}	5.2*	1.19×10^{-14}
1	23	6.89×10^{-14}	5.2	6.38×10^{-14}
1	44	5.69×10^{-13}	4.7	5.24×10^{-13}
1	64	3.23×10^{-12}	4.5	2.99×10^{-12}
3.2	23	9.02×10^{-14}	5.2	7.09×10^{-14}
3.2	44	7.23×10^{-13}	4.7	5.80×10^{-13}
3.2	64	4.02×10^{-12}	4.5	3.16×10^{-12}

Table 3. Diffusion properties determined from bulk sample
(Saturation not reached, value for 23 °C used to calculate the diffusion coefficient)*

Using this relationship and the data in Figure 3, the effect of changing the exposure temperature on diffusion coefficient can be calculated. Standard room temperature for materials testing is defined as 23 ± 2 °C. Calculated values for D at 21 °C and 25 °C are approximately 20% different to the value at 23 °C.

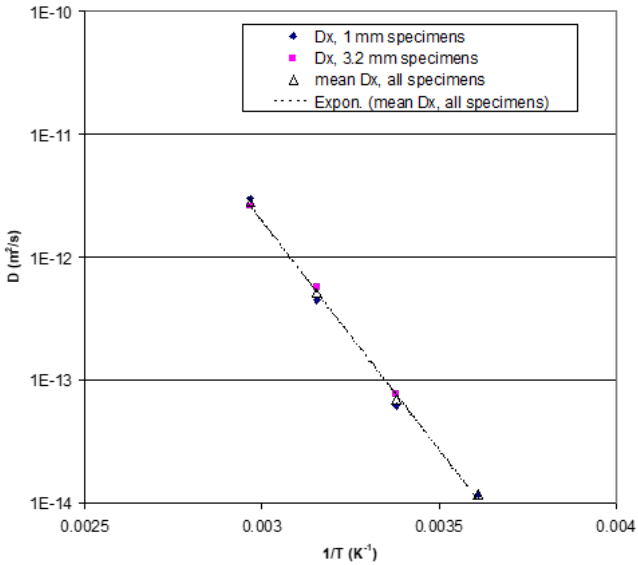

Figure 3. Temperature dependence of the diffusion coefficient

Effect of tensile stress

Specimens can be tested in liquid cells and deadweight loading frames that are used for environmental stress cracking tests for polymers or self-stressing fixtures, Figure 4. In the deadweight loading frames stress is applied using calibrated weights and in the self stressing fixtures through calibrated springs.

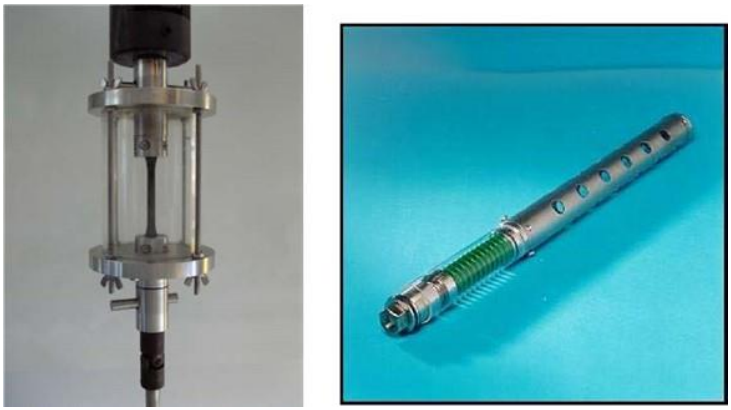

Figure 4. Liquid cell (left) and self-stressing fixture (right) for assessing properties of polymers under combined stress and chemical exposure

The square plaque used for standard moisture diffusion measurements is unsuitable for the controlled application of load in a test. Therefore, measurements of moisture uptake under tensile stress should be carried out using either dog-bone specimens [19] or parallel strips. Although the shape of the dog-bone specimen is not suitable for accurate calculation of diffusion coefficients, the uptake results can be readily compared to determine 'acceleration' factors.

Experiments should be undertaken to assess whether variability of clamping samples in the grips has a significant effect on uptake. Specimens clamped but with no applied stress should be compared with control unclamped specimens exposed at the same time. The difference between measured uptakes in unloaded specimens was found to be negligible, suggesting that the serrated grip faces did not significantly restrict absorption of moisture in the tabs in the series of tests reported.

Figure 5 shows the uptake curves measured with the example epoxy at 23 °C under different levels of tensile stress plotted against square root of time. The absorption increases with increasing stress, with very significant increases and non-linear absorption observed at high stress levels around the yield stress (i.e., between 20 MPa and 25 MPa). The epoxy adhesive is known to yield in tension through a cavitation process initiating around 20 MPa. This level of stress also corresponds with increasing creep rate in the material.

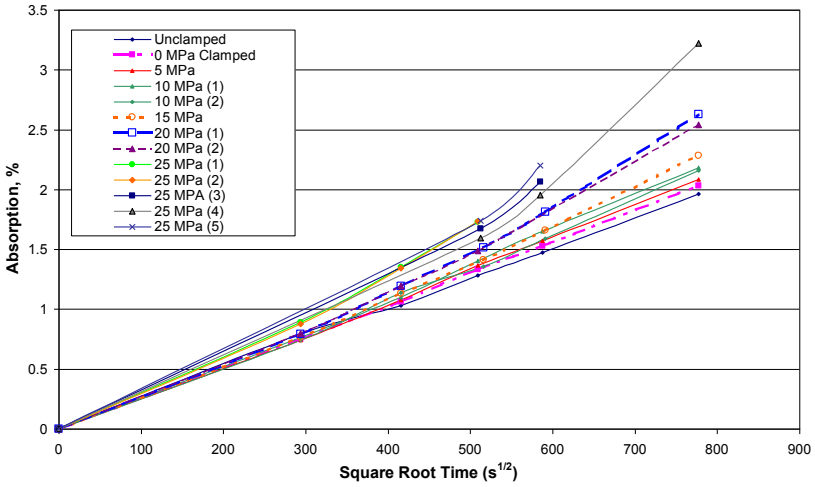

Figure 5: Effect of tensile stress on moisture absorption of epoxy at 23 °C

For the samples under load, part of the increase in absorption with stress may be due to changes in the geometry of the sample, i.e., an increase exposed area from the increase in length due to creep and shorter diffusion paths resulting from decreased width and thickness due to Poisson's contraction.

The geometrical effect can be checked by approximating the tensile specimen as a rectangular bar (60 mm × 10 mm × 1 mm) and using Equation 9 to calculate an 'apparent' diffusion coefficient from the dimensions. Mechanical tests may need to be conducted to provide an indication how dimensions change with strain and creep tests may be required.

For the epoxy evaluated in Figure 5, creep measurements made in air using standard specimens (exposed at 50% relative humidity and containing 2.5% moisture) indicated a tensile strain of 5.4% after 72 hours under 26.2 MPa stress. This strain was taken as a good approximation for the strain under 25 MPa stress and was used with an assumed Poisson's ratio of 0.4 to calculate the dimensions of the strained bar (length 1.05 × unstressed length, width, and thickness 0.98 × original values). Equation 9 was used to predict apparent diffusion coefficients for samples with the stressed ($0.804D_x$) and unstressed dimensions ($0.802D_x$) – the difference was less than 1%.

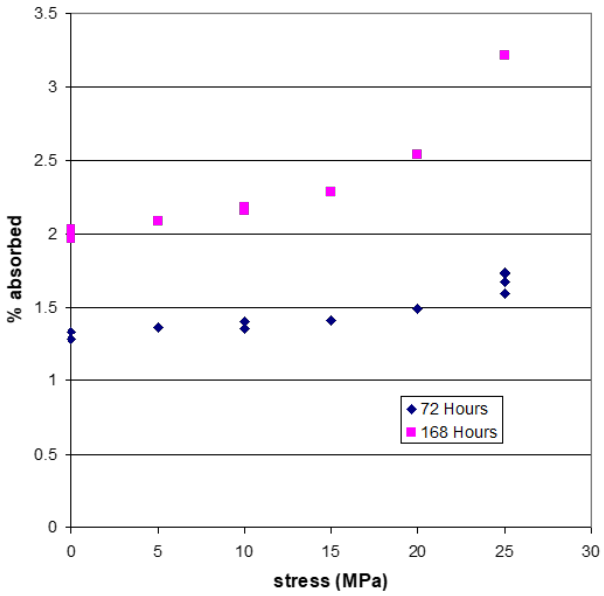

Figure 6. Effect of stress on moisture absorption

The calculated apparent diffusion coefficients and sample dimensions were used with Equation 10 to compare predicted moisture concentrations after 72 hours for 25 MPa and unstressed systems. Although there were significant discrepancies between the measured and predicted moisture uptakes, due to the assumptions made in simplifying the shape of the specimen, comparing the two sets of predictions provides further insight into changes in the diffusion behaviour under stress.

The 25 MPa system was predicted to have a moisture concentration only 1.02 times the concentration predicted for the 0 MPa system whereas the measured 72-hour moisture concentrations under stress were 1.2-1.3 times greater than those measured in the unstressed samples. The difference between the moisture concentrations measured in low stress and high stress samples increases with time, Figure 6, as diffusion in high stress samples becomes non-Fickian, as shown by the non-linearity of the high stress absorption curves in Figure 5.

Determining the effect of stress on saturation concentration would require exposing samples until saturation is reached. However, removing the sample from the apparatus for mass measurements and then reloading may lead to failure of the specimens, particularly at high stresses. Measuring the full absorption curve may require that some samples are designated for long-term exposure, and these are not removed for mass measurements, until the required exposure time has been achieved. Samples would only be used for one mass measurement; thus, fresh specimens would be needed to obtain other points on the absorption curve. This approach could potentially require a high number of specimens (particularly as repeatability between specimens may need to be established), tie up apparatus for prolonged periods and take a long time to complete.

Although very few structures would be designed to operate continuously close to the yield stress of their constituent materials there may be non-uniform stress distributions in components. Regions of high stress could be more permeable to moisture then regions of low stress, leading to preferential absorption in these areas and faster degradation.

Determining the effect of hydrostatic pressure

Diffusion properties are normally obtained at ambient pressure. However, materials may be used in applications (e.g., sub sea structures) where they are exposed to fluids under pressure. Pressure may be a further means of accelerating moisture uptake in some materials.

A system for exposing materials under pressure is shown in Figure 7. A custom-made heating jacket wrapped around the exterior of each autoclave vessel supplies any required heating. A thermostat and thermocouple probe attached to the vessel control the temperature. The accuracy of the temperature control should be confirmed by setting the thermostat to the test temperature and measuring the temperature of liquid within the unsealed vessel. A high-pressure pump is used to pressurise each vessel with air. The readings on the pump gauge and the pressure gauge of each vessel should be checked against a calibrated pressure gauge. Specimens are exposed in pressure vessels filled with water by sealing the vessels and then pressurising them to required pressure at the test temperature. In operation the pressure should be checked regularly (e.g., daily) and re-pressurised as required. It is recommended that pressure and temperature be logged automatically during tests.

Figure 7. Autoclave vessels used for conditioning specimens at elevated pressure

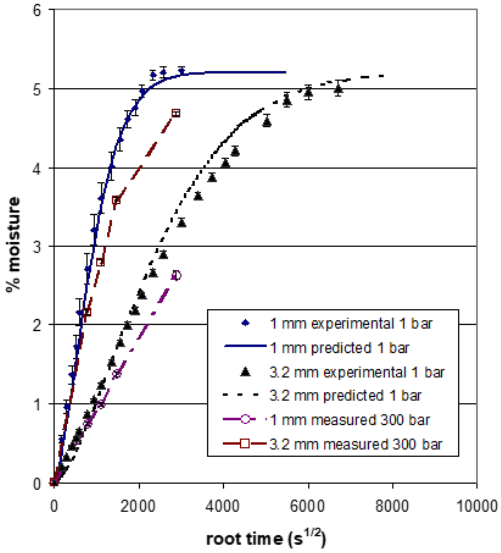

Figure 8. Measured and predicted (using Equation 10) moisture uptake at 23 °C, ambient pressure (1 bar) compared with measured moisture uptake at 23° C and 300 bar pressure

Measurements on pultruded glass-fibre reinforced polyester composite bars suggested that equilibrium moisture content could be achieved in a shorter time than at ambient pressure. Samples of the epoxy were immersed in deionised water within the autoclave. Pressure of 300 bar was applied and three 1mm and 3.2 mm thick specimens were conditioned at ambient temperature (23 °C). Owing to the time-consuming nature of the pressure and the repressurising process, samples were weighed on a weekly basis.

Figure 8 shows that moisture diffusion into the samples exposed at 300 bar is slower than for samples exposed at ambient pressure. It can be conjectured that the hydrostatic pressure may close micro voids in the sample and reduce sites and pathways for diffusion.

From these observations, it is evident that pressure may affect the diffusion of moisture into different materials in different ways. If diffusion rates under pressure are important then specific tests may need to be carried out in preference to assuming the same properties as at atmospheric pressure.

Chapter 5

Diffusion in multi-component systems

- Fibre-reinforced polymer composites
- Adhesive joints and coatings
- Multi-layer systems

Fibre-reinforced polymer composites

Diffusion in PMCs, particularly of water, has been studied extensively, with comprehensive coverage given by Springer [4, 5]. The mass transport properties will depend on the fibre material, the volume fraction of fibres and the fibre orientation. Glass and carbon fibres are normally considered to be impermeable. Transport in the direction of the fibres may be very different to that normal to the fibres. Capillary action along the fibres or the fibre resin interfaces can account for a significant proportion of initial moisture uptake. Shrinkage of the resin away from the fibres during curing could be a contributing factor to the capillary effect. Composite laminates, particularly multi-directional laminates may have a complex structure with permeation behaviour defined by a complex mixture of properties.

Diffusion in orientated fibre composite layers can be treated by a rule of mixtures approach. For a volume fraction of fibres V_f and a reasonable assumption that diffusion coefficients D_f in fibres are much less than the molecular diffusion coefficient in the polymer matrix D_m then the directional diffusion coefficients D_{11} (longitudinal) and D_{22} (transverse) can be expressed [4-5]:

$$D_{11} = (1 - V_f)D_m \tag{13}$$

$$D_{22} = \left(1 - 2\sqrt{\frac{V_f}{\pi}}\right)D_m \tag{14}$$

The diffusion coefficient for a composite is given by the following relationship [4-5]:

$$D = D_x\left(1 + \frac{h}{l}\sqrt{\frac{D_y}{D_x}} + \frac{h}{b}\sqrt{\frac{D_z}{D_x}}\right)^2 \tag{15}$$

D_x, D_y and D_z are diffusivities through the thickness, along the length and across the width of the material.

In most assessments of moisture distributions in composites, the fibres are assumed to be impermeable to moisture. Therefore, all of the water must be contained either within the matrix or bound at the fibre-matrix interface [5]. This may be applicable for glass or carbon fibres but is very unlikely to apply to natural fibres or polymer fibre reinforcements.

Adhesive joints and coatings

Diffusion in adhesive joints is often done by casting bulk sheets of adhesive and determining the diffusion properties of the bulk adhesive. These values are then used with a model [e.g., 1, 18] to predict moisture uptake into the joint. If the adherends are also permeable (e.g., composites) then their diffusion properties should be obtained and included in the model. This approach relies on:

- The bulk adhesive having the same properties as the adhesive in the joint; and
- The adhesive-adherend interface playing no role in moisture absorption and transport.

It is well established that the properties of materials near the interface, the so-called interphase, differ from those of the bulk material. Therefore, the diffusion properties in the interfacial region may not be the same as the bulk material. Few studies comparing bulk adhesive and adhesive joint diffusion have been reported. Bond et al. [20] determined diffusion coefficients for an epoxy adhesive as being 6.4 × 10-13 m^2s^{-1} when obtained from mass measurements on bulk adhesive specimens and 6.7 × 10-12 m^2s^{-1} when determined from measurements of weight gain in lap joints (1 mm thick grit blasted stainless steel adherends). These results suggest a significant contribution from the interface to diffusion. It is well recognised that diffusion of chemicals to the interface in a bond degrades bond performance [18, 20-24].

In the assessment of moisture absorption into adhesive joints the following points should be considered:

- The mass of the adherends needs to be subtracted to determine the mass of the adhesive layer - this will introduce additional uncertainties in the mass results.
- Metal adherends are likely to have significantly higher masses than the adhesive layer of interest. The total mass of the system may require that a larger capacity balance, possibly with lower resolution, be used.
- Any absorption of moisture into the adherends will contribute to measured mass gains. Traveller adherend specimens can be exposed to assess this and corrections made to calculate the moisture concentration in the adhesive layer. However, this correction will increase the uncertainty in the mass gain in the adhesive. Uncertainties can become very significant if the mass of moisture absorbed in the adherends is greater than the mass absorbed in the adhesives.
- Metallic adherends may corrode when exposed to moisture. Traveller samples can be used to determine corrections for any resulting gain in mass (or better to confirm the absence of corrosion). Uncertainties will increase due to these corrections. Traveller specimens may not detect all of the corrosion occurring in an adhesive joint. Corrosion has been observed located under adhesive bonds but not on the exposed surfaces of the same metallic adhesives [24], suggesting that chemical or stress conditions at the

interface promote corrosion. It is recommended that exposed specimens used for uptake measurements should be separated and their surfaces examined.

- Adsorption in joints is mainly through the edges and the resulting long diffusion path lengths to the centre of the joint mean that the time to reach saturation may be extremely high.
- If all edges are available for absorption then there is a two-dimensional diffusion situation. The analysis approach outlined in Chapter 3 is not appropriate and a much more complex analysis procedure is needed to calculate diffusion coefficients. A simpler approach might be to seal off two (opposite) edges leaving a one-dimensional diffusion situation.

Multi-layer systems

Overall absorption into multi-layer systems can be measured using the same methods that are used for homogeneous, isotropic systems. The measurements will produce an average saturation value and diffusion coefficient. Obtaining data on individual layers in a multi-layer system is difficult. Each layer will have a different saturation concentration and diffusion coefficient. Layer thickness may be extremely difficult to measure, particularly in very thin films.

In steady state moisture permeation measurements [1,10-13], where there is a high concentration on one side of the film and low concentration on the other (e.g., liquid and air), a constant flux per unit concentration gradient across the film occurs when boundary conditions are fixed and the moisture concentration within the membrane is in equilibrium.

Figure 9 shows, schematically, one-dimensional diffusion in a multi-layer system.

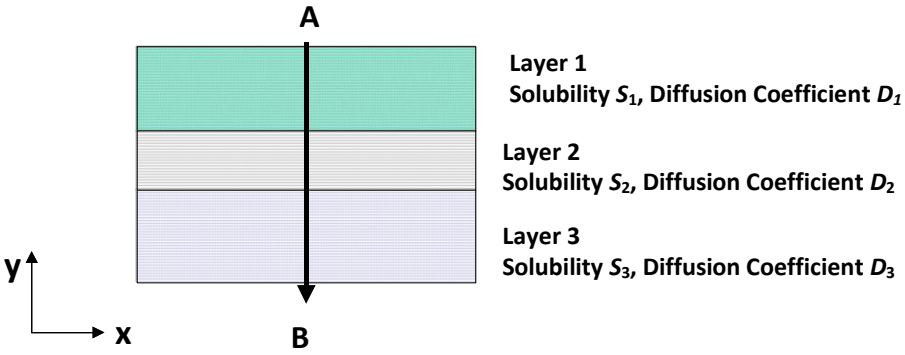

Figure 9. One-dimensional diffusion through a multi-layer system

For a layer of total thickness *L*, at constant temperature and gas concentrations ϕ_1 and ϕ_2 at *A* and *B*, respectively (assuming $\phi_1 > \phi_2$) then Equation 1 can be integrated across the thickness using an average diffusion coefficient D to give permeation rate or permeability:

$$\frac{dQ}{dt} = D\frac{\phi_1 - \phi_2}{L} \tag{16}$$

When one side is in contact with liquid then ϕ_1 is the saturation concentration of the material in contact with the liquid.

In laminated systems, the total permeability of a multi-layer system Q_L with *n* layers can be calculated from the series permeation 'resistance' of each layer and expressed as a sum of the diffusion coefficients D_i and thickness x_i of all of the layers.

$$\frac{1}{Q_L} = \frac{1}{L}\sum_{j=1}^{n}\frac{x_i}{D_i} \tag{17}$$

In cases where the diffusion coefficients of only one of the layers is unknown, then Equation 17 can be used to calculate the diffusion coefficient of the unknown layer.

Determining saturation concentrations of internal layers presents a problem. In the onedimensional diffusion situation illustrated in Figure 9 the moisture concentration in any layer can never exceed the saturation concentration of the preceding layer(s), since diffusion requires a concentration gradient. If both surfaces are exposed then the concentration in internal layers can never exceed those of the layers outside of them.

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Chapter 6

Estimating uncertainties in diffusion coefficients

- Estimating uncertainties
- Uncertainty in specimen dimensions
- Uncertainty in elapsed time
- Uncertainty in moisture concentration
- Exposure temperature
- Material variability
- Changes occurring post material manufacture
- Example uncertainty calculations

Estimating uncertainties

Uncertainties in measurements should be combined according to the methods described in UKAS M3003 [25]. The significance of uncertainties ΔV in the different measured values V used to calculate the diffusion coefficient can be examined by using the expanded uncertainties from Equation 7 and the simplifying assumption that t_1 is zero:

$$\left(\frac{\Delta D}{D}\right)^2 = 2x\left[\left(\frac{\Delta h}{h}\right)^2 + \left(\frac{\Delta C_s}{C_s}\right)^2 + \left(\frac{\Delta(C(t_2) - C(t_1))}{(C(t_2) - C(t_1))}\right)^2 + 0.5x\left(\frac{\Delta t_2}{t_2}\right)^2\right] \qquad (18)$$

Uncertainties will arise from:

- Calibration and resolution uncertainties of the measurement instruments;
- Variations in test procedure (repeatability and reproducibility); and
- Sample variability

Normal distributions are assumed in these calculations, implying a coverage factor of 2 should be used.

Uncertainty in specimen dimensions

The accuracy of the thickness measurement is the most important of the dimensions in determining diffusion coefficients. Uncertainty in sample thickness h arises from two sources.

Resolution and calibration of thickness measuring device:- measurements should be made using instruments such as callipers and micrometers with sufficient accuracy so that this uncertainty is low relative to the measurement. Devices with a resolution of 0.01 mm contribute a relative uncertainty of ± 0.5% for a 1 mm thick specimen, likely to be acceptable for most measurements. Higher resolution instruments are recommended for thinner specimens.

Variations of sample thickness:- samples should have uniform thickness for accurate determination of diffusion coefficients. Thickness should be measured and recorded at several locations on the sample (both at the edges and centre). A minimum of five locations is recommended but if the maximum and minimum readings differ significantly (e.g., by more than 3-5%) then additional measurements should be made. The mean and standard deviation of the thickness should be determined. If the standard deviation in the measurements is high then this will have a significant effect on the overall uncertainty and further preparation (including polishing) should be considered to reduce the thickness variations.

Uncertainties in the other dimensions contribute to the overall uncertainty budget through the correction for edges (Equation 11). The uncertainty in the edge correction factor E can be calculated as:

$$\Delta E^2 = 2x\left(\left[\left(\frac{\Delta h}{h}\right)^2 + \left(\frac{\Delta l}{l}\right)^2\right]\left(\frac{h}{l}\right)^2 + \left[\left(\frac{\Delta h}{h}\right)^2 + \left(\frac{\Delta b}{b}\right)^2\right]\left(\frac{h}{b}\right)^2\right) \quad (19)$$

For example, for square plaques (with sides l = b = 50 ± 1 mm) with thicknesses of 1 ± 0.05 mm and 3.2 ± 0.1 mm the correction factors are 0.925 ± 0.003 and 0.786 ± 0.007, respectively.

Uncertainty in elapsed time

Since the samples are typically exposed over periods of days or weeks the accuracy and resolution required of time measurement is not critical. Recording the date and time of the start of the exposure and each measurement should be sufficient. There will be some uncertainty due to the periods when the sample is removed from exposure for the purposes of mass measurements. Since this period is unlikely to be more than 15 minutes and measurements are unlikely to be made more often than daily then the relative uncertainty in elapsed time is unlikely to exceed 1%. Records should be made of the time at which the sample is measured and returned to the exposure and elapsed time can be calculated to omit these periods.

Where measurements are made with less than 24 hours of exposure the uncertainty in time measurement may become more significant. In such measurements, it is advisable to use a stopwatch for time measurements and to ensure that the time that the sample is taken out of exposure for measurement is minimised (e.g., a minute or less). A 15 minute uncertainty in an 8 hour exposure leads to a relative uncertainty of 3%.

For most exposures, the uncertainty in the time measurement is negligible and can be ignored in the uncertainty estimation.

Uncertainty in moisture concentration

Uncertainties in the mass measurement lead to uncertainties in the concentration gain, $C(t_2)C(t_1)$, and the saturation concentration, C_s, terms. In most cases $C(t_1)$ is zero and $M(t_1)$ is the dry mass of the sample. Concentration $C(t)$ is defined in Equation 4 from the measured mass gain divided by the dry mass. The uncertainties in concentrations (both $C(t)$ and C_s) are defined from the uncertainties in the mass measurements. The uncertainty in the mass gain is expressed:

$$\Delta(M(t_2) - M(t_1))^2 = \Delta\big(M(t_1)\big)^2 + \Delta\big(M(t_2)\big)^2 \quad (20)$$

Resolution of the weighing balance: Provided a sufficiently sensitive balance is used then the uncertainty in concentration due to the resolution of the balance is only likely to be significant for very small changes in concentration.

For example if the balance has a resolution of 0.1mg then the resolution uncertainty in mass ΔM is taken as 0.05 mg. Equation 20 then produces an uncertainty of 0.071 mg in the mass gain. If a sample with an initial dry mass of 2.5 g gains 0.1% moisture then the relative uncertainty in the 2.5 mg mass change is 2.8%. At 1% moisture absorption this reduces to 0.28% uncertainty in the 25 mg mass gain. The uncertainty in the dry mass measurement is negligible in this case (0.05 mg in 2500 mg) and can be ignored in determining the uncertainty in concentration.

The significance of the resolution uncertainties is minimised if:

- The resolution of the balance is much smaller than the mass changes.
- A specimen with a large area is used to increase the mass of polymer and, thence, the size of the mass gain for a given concentration.
- Specimens are sufficiently thick - reducing the thickness will reduce the mass of material and hence the mass of moisture absorbed.
- Moisture absorption is high.

Measurement repeatability: Since the moisture content in the samples are continually changing whether in or out of the exposure medium, assessing repeatability of mass measurement of the samples is not recommended. Replicate specimens should be exposed under the same conditions and measured after the same exposure durations to assess repeatability in measured concentrations. The standard deviation in the measurements should be included in the uncertainty budget.

If the repeatability (or reproducibility between operators) of the weighing process is considered to be a concern then this should be assessed through repeat measurements using an unchanging specimen with similar mass and dimensions to the exposed specimens. A sample that has been left to achieve equilibrium in the weighing laboratory is ideal for this purpose.

Procedural variations: Factors such as the drying of specimen surfaces and time between removing the sample from exposure and weighing will lead to reproducibility uncertainties in the results. All surface moisture must be removed prior to weighing since it would lead to an overestimate of absorbed moisture concentration. Moisture will desorb from dried surfaces into the atmosphere, leading to diffusion of moisture from the sample. The rate of moisture loss will depend on the concentration of moisture in the sample and the diffusion properties of the material. Therefore, the procedure used for each weighing should be as consistent as possible. The importance of the procedure and procedural variations may differ appreciably between materials.

For example, the epoxy adhesive studied had a smooth, flat and poorly wetted surface that became dry to the touch (with no noticeable residual moisture transfer to the cloth) after brief wiping. Consequently, the weighings could be carried out within a controllable, short period of time and the resulting scatter in absorption between different samples were small (typically less than ±3% of the measurement).

However, in another example, it proved very difficult to obtain reliable uptake measurements for bulk plaque samples prepared with different numbers of plies of a film adhesive, Figure 10. These samples had rough textured surfaces and appeared to be well wetted by water. It took considerably longer to dry the surfaces of the samples (i.e. until no transfer to the drying cloth was observed). Figure 11 illustrates possible variations in 'moisture concentration' that could occur from the drying and weighing process. Two samples were weighed at variable time intervals after removal from the water. A point is indicated on each of the two curves when it was considered that all surface moisture had been removed – this is the value used as the concentration in the moisture absorption measurement. However, it is clear that the mass of the sample is changing rapidly during this period and there must be a large uncertainty in this value.

As a result of this, the moisture uptake curves were noisy and there was considerable scatter between specimens, as shown in Figure 10. The standard deviations in the concentration measurements were typically between 10-20%. The diffusion coefficients calculated differed considerably, with a factor of 10 between the values for 1 ply and 4 ply samples, Table 4. Some of that difference may reflect real differences between the samples.

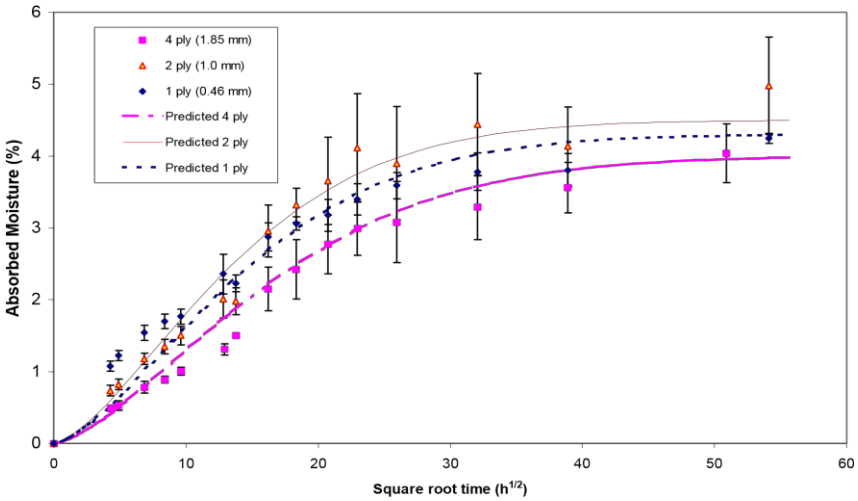

Figure 10. Moisture absorption curves obtained for film adhesive samples
(predicted curves were generated using Equation 10 and the data in Table 4)

Number of Plies	Thickness (mm)	C_s (%)	D_a (m^2s^{-1})
1	0.46	4.3	1.5×10^{-14}
2	1.00	4.5	8.1×10^{-14}
4	1.85	4.0	1.9×10^{-13}
Average	-	4.3 ± 0.3	$1.0 \pm 0.9 \times 10^{-13}$

Table 4. Diffusion parameters determined from Figure 10

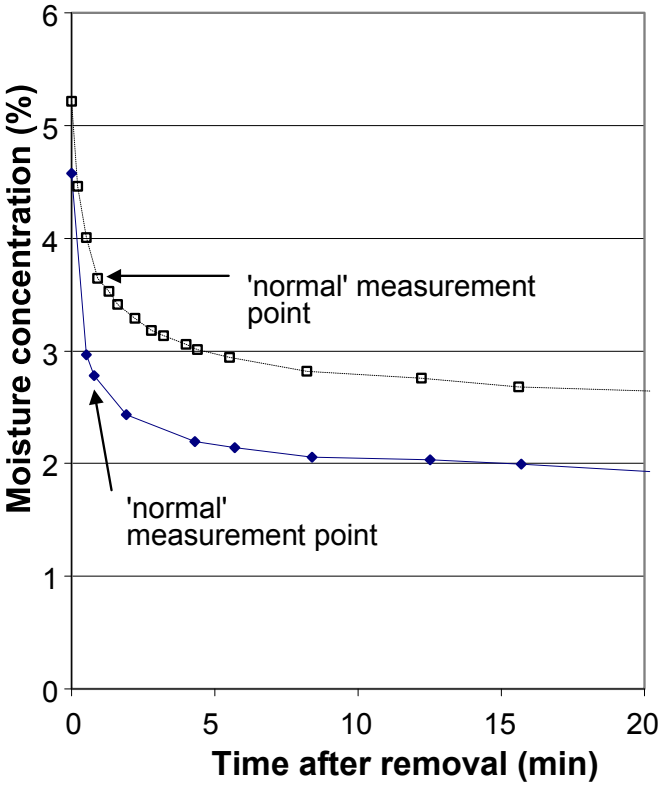

Figure 11. Effect of time out of exposure and drying on measured moisture concentrations

Exposure temperature

The saturation concentrations and diffusion coefficients of polymeric materials are sensitive to temperature. Table 3 shows that the diffusion coefficient of the example epoxy studied increases by a factor of ca. 40 on increasing the temperature from 23 °C to 64 °C. Therefore, as Table 5 shows, even relatively small differences between exposure temperatures can have a significant effect on the diffusion coefficient.

Therefore, it is good practice to maintain and monitor the exposure temperature, using accurate and calibrated instruments, throughout the measurements.

Temperature (°C)	Predicted D_x (m^2s^{-1})	Variation of D_x (% of 23° C Value)
21	6.33×10^{-12}	81.9
22	7.22×10^{-14}	90.5
22.5	7.59×10^{-14}	95.1
23	7.98×10^{-14}	100
23.5	8.38×10^{-14}	105
24	8.81×10^{-14}	110
25	9.72×10^{-14}	122

Table 5. Variation of predicted diffusion coefficient with small temperature changes (D_x predicted from Figure 3)

Material variability

In order to produce relevant information the samples used to assess diffusion behaviour should have the same properties as the materials in the components and structures for which the data will be used. The properties of polymeric materials are affected by the way they have been processed. When the samples are taken from directly from the component of interest and tested, then there should be little concern about the reliability of the results. However, many samples will be manufactured specifically for testing, often using a different process than the components of ultimate interest.

Factors that should be taken into consideration when deciding whether a sample is representative of a component or structure include:

- Composition – same material (including grade of polymer, type and proportion of filler/fibre, toughening agents, processing agents, etc.);
- Lay-up (e.g., for composite laminates or multi-layer films);
- State of cure;
- Degree of crystallinity;
- Processing conditions; and
- Extent of defects including delaminations and voids.

One example where processing conditions could have a significant effect on properties is in the state of cure of thermosetting polymers (including composites). The state of cure can vary within materials (particularly in thick sections where the centre may not reach as high a temperature as the exterior, or may exceed the exterior temperature if large amounts of heat are generated by exothermic reactions) or between samples, particularly if thicknesses differ.

Thin specimens are often preferred for diffusion studies as saturation will be reached much sooner than in thick sections, but there is a danger that the cure state in the thin sections may not match those of the thick sections leading to results of dubious relevance.

For example, Figure 12 shows moisture absorption in two samples of 2-ply film adhesive that were cured under different conditions. One sample (Sample 1) was cured for 20 minutes in an oven preheated at 165 °C. This sample reached 165 °C, as measured by a thermocouple embedded in the mould, towards the end of the sure period. The other sample (Sample 2) was left to continue curing for a further 20 minutes, giving a total of 40 minutes in the oven at 165 °C. The manufacturer's data sheet specified curing for 15 minutes at 165 °C, which is unclear whether the time refers to total time (including heating) or the time that the specimen is actually at the cure temperature (excluding heating). Glass transition temperature T_g for samples cured under both conditions were determined using DSC (differential scanning calorimetry [26]). T_g was 84 °C for sample 1 cured for the shorter time period and 90 °C for sample 2 cured for the longer period. Second and third DSC runs on the samples were carried out and Tg for each sample reached 96 °C, suggesting that neither sample was fully cured.

At equivalent exposure times, there is approximately twice as much moisture absorbed into the sample 1 than into sample 2. It is also apparent that the two samples will have significantly different saturation levels. These major differences exist despite what could be seen as fairly minor differences in cure state.

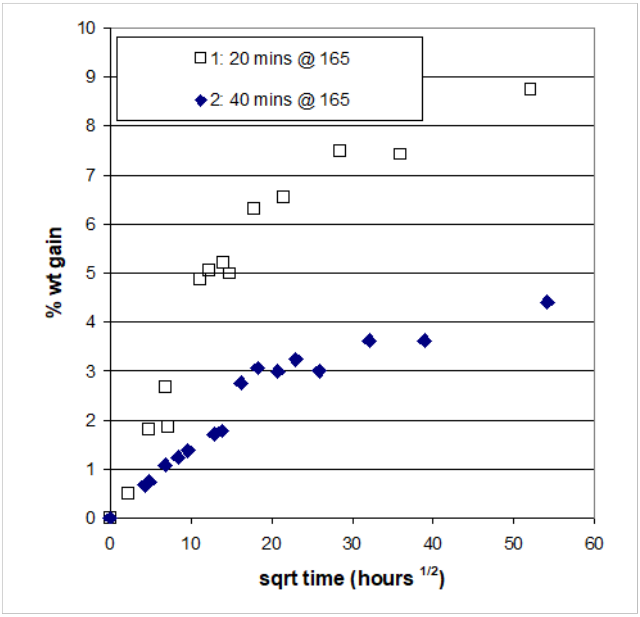

Figure 12. Effect of cure conditions on moisture absorption

Changes occurring post material manufacture

Post-curing: The curing process that occurs when manufacturing components from polymers that cross-link through cure reactions (e.g., thermosets, may not fully cure the materials). Therefore, polymers may continue to cure post manufacture, changing their moisture absorption properties, potentially very significantly (e.g., as indicated in Figure 12). This is more likely to occur where the material is kept or exposed at temperatures at or above its glass transition temperature (where higher molecular mobility makes interaction of unreacted groups more likely). For example:

- Room temperature cured systems, e.g., adhesives, will continue to cure slowly after the material is nominally 'cured' (in practice having reached a sufficient state of mechanical performance).
- Elevated temperature cured systems exposed to elevated temperatures.

Curing can be completed through a deliberate post cure, e.g., heating the material significantly above T_g for sufficient time to ensure completion of reactions. Completeness of cure can be checked by thermal analysis methods [26].

Physical ageing: The structure of polymers continues to evolve through molecular relaxation and realignments after completion of the component 'manufacture' in a process known as physical ageing. Thus, the mobility of polymer chains decreases with time after high temperature processing until an equilibrium structure is obtained. These structural changes are influenced by many factors, including stress and temperature. The moisture absorption kinetics of polymer systems will change with physical ageing and, therefore, it is advisable to compare results from samples having the same physical age. Materials can be 'de-aged' by heating them above their glass transition temperature for a short period of time, typically an hour.

Glass transition temperature (T_g): The properties of the polymeric material will also change with chemical ageing. For example, the T_g for a typical polyester resin will decrease by ~15-20 °C for a 2% moisture weight gain and reduced for the example epoxy by ~5 °C for a similar moisture gain. Figure 13 shows the effect of moisture content on T_g for a glass reinforced epoxy that was immersed in distilled/deionised water for prolonged periods of time at three different temperatures [27]. This reduction in T_g is induced by plasticisation (softening) of the polymer matrix and in some cases by loss of organic additives through leaching to the surrounding media.

Long periods of exposure to moisture at elevated temperatures could lead to phase changes in the polymer (e.g., a glass to rubber transition) and moisture absorption and/or transport processes not relevant to lower temperature exposure may occur. Physical ageing and stress may increase the potential for phase changes occurring during exposure. Therefore, it is advisable, when using elevated temperatures to accelerate moisture uptake, to ensure that the maximum operating temperature is below the T_g of the material (e.g., at least 30-40 °C, taking into account moisture effects).

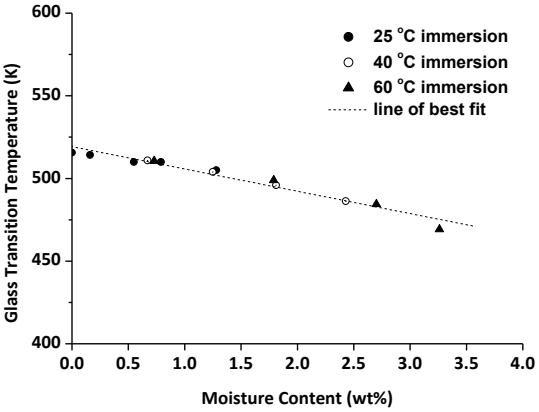

Figure 13. Glass transition temperature of F922 epoxy as a function of moisture content

Combined effects: Exposure of polymeric materials to moisture, elevated temperature, physical ageing and stress may lead to behaviour that cannot be predicted from less complex situations. In Chapter 5, samples exposed at room temperature and elevated pressure absorbed moisture more slowly than materials exposed at atmospheric pressure. However, when the temperature was increased to 64 °C (Figure 14), moisture concentrations under high pressures were found to be considerably higher than the saturation concentrations obtained at atmospheric pressure. The predicted curves in Figure 14 were calculated from Equation 10 and data in Table 3.

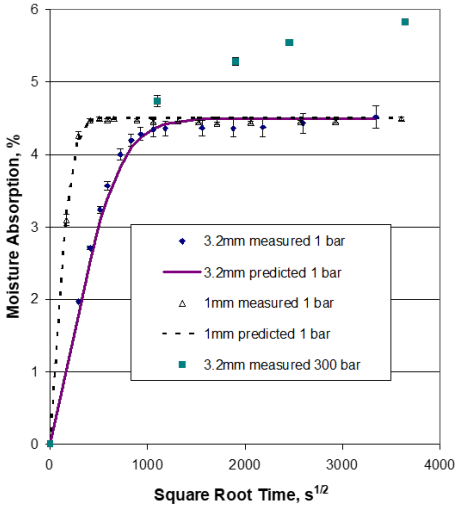

Figure 14. Measured and predicted moisture uptake at 64 °C, ambient pressure (1 bar) compared with measured moisture uptake at 64° C and 300 bar pressure

In addition to the high pressure the test specimens were several months older than the atmospheric test specimens, having been prepared at the same time but not tested until significantly later. It is possible that the moisture and elevated temperature combined with the physical ageing and high pressure to cause phase changes not occurring in younger and unstressed materials.

Example uncertainty calculations

As an example, the calculation of the diffusion coefficient for a 1 mm thick sample of the rubber toughened epoxy exposed at 23 ± 2 °C is used in conjunction with Equation 18 (see below).

$$\left(\frac{\Delta D}{D}\right)^2 = 2x\left[\left(\frac{\Delta h}{h}\right)^2 + \left(\frac{\Delta C_s}{C_s}\right)^2 + \left(\frac{\Delta(C(t_2) - C(t_1))}{(C(t_2) - C(t_1))}\right)^2 + 0.5x\left(\frac{\Delta t_2}{t_2}\right)^2\right]$$

Calculated D_a = 6.89 × 10^{-14} m^2s^{-1} (Table 3)

Sample plaque (dimensions): l = b = 50 ± 1 mm; h = 1.0 ± 0.05 mm

Dimensions measured using digital callipers with resolution 0.01 mm, which is insignificant compared with the variability in dimensions, i.e.:

$$\Delta l = \Delta b = \pm\sqrt{1^2 + 0.005^2} \approx \pm\ 1.0$$

$$\Delta h = \pm\sqrt{0.05^2 + 0.005^2} \approx \pm\ 0.05$$

$$\frac{\Delta h}{h} = 0.05$$

C_s was 5.20% with a standard deviation of ± 0.07%; t_2 was 393 ± 3 hours; $C(t_2)$ was 3.61% with a standard deviation of ± 0.19%

M_0 was 3.055 g; mass gain at t_2 was 0.110 ± 0.005 g, and mass gain at saturation was 0.1595 ± 0.0008 g.

Balance resolution = 0.1 mg which, when used in Equation 20 to calculate uncertainties in the mass gain, is insignificant compared with the variability in mass gain measurements and ignored.

Although $C(t_1)$ was taken to be zero, a standard deviation in $C(t_1)$ of ± 0.07% was assumed, the same as the standard deviation in the saturation value. This was included to account for possible variability in the 'dry' state (which may arise from the drying time being insignificant to ensure complete drying and the possible the pick up of moisture from the atmosphere before the first weighing).

Thus:

$$\Delta\big(C(t_2) - C(t_1)\big) = \sqrt{0.19^2 + 0.07^2} = 0.20, \quad \frac{\Delta\big(C(t_2) - C(t_1)\big)}{\big(C(t_2) - C(t_1)\big)} = 0.055$$

$$\frac{\Delta D_a}{D_a} = \sqrt{2x[(0.05)^2 + (0.019)^2 + (0.055)^2 + 0.5x(0.0076)^2]} = 0.109$$

$$\frac{\Delta t_2}{t_2} = 0.0076$$

Therefore, excluding temperature uncertainty, the uncertainty in Da can be calculated from Equation 17:

$$\frac{\Delta D_a}{D_a} = \sqrt{2x[(0.05)^2 + (0.019)^2 + (0.055)^2 + 0.5x(0.0076)^2]} = 0.109$$

Assuming a coverage factor of 2 then the uncertainty in the value of D_a is 21.8%, thus the value of D_a (taking the uncertainty into account) is **6.9 ± 1 .5x10^{-14} m^{2}s^{-1}**.

The uncertainty in D_x is of a similar order, as the uncertainty in the correction factor is negligible.

The uncertainty due to temperature can be included using the data presented in Table 5. A ± 2 °C difference in temperature causes a maximum of 22% in the value for *D* at a temperature of 23 °C. This can be combined with the calculated uncertainty in D_a (10.9%) using the squaring and adding process (and applying a coverage factor of 2) to yield an estimated uncertainty in the value of D at 23 °C of:

$$\frac{\Delta D(T = 23)}{D(T = 23)} = 2x\sqrt{0.109^2 + 0.22^2} = 0.49$$

Therefore, the value of D_a at 23 °C is **6.9 ± 3.4 ×1 0^{-14} m^{2}s^{-1}**.

In this case the uncertainty could be considerably reduced by tighter control of the exposure temperature. A temperature tolerance of ± 1 °C reduces the relative uncertainty to 0.3, i.e., D_a = 6.9 ± 2.1 × 10^{-14} m^{2}s^{-1} and a temperature tolerance of ± 0.5 °C reduces the relative uncertainty to 0.24 (Da = 6.9 ± 1.7 × 10^{-14} m^{2}s^{-1}), which is little more than the uncertainty due to the non-temperature factors.

Chapter 7

Conclusions

- Key points
- Concluding remarks

Key points

The measurement of moisture absorption and diffusion is, in principle, straightforward to carry out. It requires only the capability to manufacture representative specimens to the required tolerances, measure their dimensions to the required accuracy and make mass measurements at the required time intervals. However, there are several key points to recognise when making measurements.

- **Variations in sample processing** can cause large differences in moisture absorption and diffusion behaviour.
- **Replicate samples** should be tested to improve the reliability of the results and provide some indication of the effects of procedural and material variations.
- The **sample thickness** is the specimen dimension that should be controlled most carefully to minimise uncertainties.
- The **weighing procedure**, and in particular the period the sample is dried for after being taken from exposure, can lead to significant variability in results.
- It is much more difficult to remove all the surface moisture from samples with textured surfaces than from smooth samples. Thus **surface texture** of samples should be controlled.
- Diffusion in polymers depends on **temperature** and any variation in temperature is likely to have significant influence on the accuracy of the results. Temperatures should be controlled and monitored within appropriate tolerances to ensure accuracy: within ± 0.5 °C is recommended.
- The molecular structure of polymers reorganises following processing and the properties will be **time-dependent** to some extent. Ageing of polymers, especially when combined with elevated temperature and/or stress, may lead to unexpected changes in behaviour.

Concluding remarks

The use of simple gravimetric techniques and a one-dimensional Fickian analysis for determining moisture and diffusion have been described. Reasonable accuracy can be obtained provided that good quality samples are available and the procedures outlined in this guide are followed.

Standards

ISO Standards

Plastics

Permeation

ISO 2528	Sheet Materials — Determination of Water Vapour Transmission Rate (WVTR) - Gravimetric (Dish) Method.
ISO 7783-1	Paints and Varnishes - Determination of Water-Vapour Transmission Rate - Part 1: Dish Method for Free Films.

Effects of liquids

ISO 62	Plastics – Determination of Water Absorption.
ISO 175	Plastics - Determining the Effect of Liquid Chemical Including Water.
ISO 483	Plastics - Small Enclosures for Conditioning and Testing Using aqueous Solutions to Maintain Relative Humidity at Constant Value.
ISO 4611	Plastics - Determination of the Effect of Exposure to Damp Heat, Water Spray and Salt.

Thermal degradation

ISO 176	Plastics - Determination of Loss of Plasticizers — Activated Carbon Method.
ISO 177	Plastics - Determination of Migration of Plasticizers.
ISO 291	Plastics - Standard Atmospheres for Conditioning and Testing.
ISO 305	Determination of Thermal Stability of Polyvinyl Chloride Related Chlorine Containing Polymers, and their Compounds - Discoloration Method.
ISO 554	Standard Atmospheres for Conditioning and/or Testing - Specification.
ISO 1137	Plastics: Determination of Behaviour in a Ventilated Tubular Oven.
ISO 2578	Plastics: Determination of Time/Temperature Limits after Exposure to Prolonged Action of Heat.

Environmental stress cracking (ESC)

ISO 4599	Plastics: Determination of Time/Temperature Limits after Exposure to Prolonged Action of Heat Plastics - Determination of Resistance to Environmental Stress Cracking (ESC) - Bent Strip Method.
ISO 4600	Plastics - Determination of Environmental Stress Cracking (ESC) - Ball and Pin.

ISO 6252 Plastics - Determination of Resistance to Environmental Stress Cracking (ESC) - Constant Tensile Stress Method.

ISO 16770 Plastics - Determination of Environmental Stress Cracking (ESC) of Polyethylene - Full-Notch Creep Test (FNCT).

ISO 22088-5 Plastics - Determination of Resistance to Environmental Stress Cracking (ESC) - Part 5: Constant Tensile Deformation Method.

ISO 22088-6 Plastics - Determination of Resistance to Environmental Stress Cracking (ESC) - Part 6: Slow Strain Rate Method.

Weathering

ISO 877 Plastics - Determination of Resistance to Change upon Exposure under Glass to Daylight.

ISO 2579 Plastics - Instrumental Evaluation of Colour Differences.

ISO 3577 Plastics - Recommended Practice for Spectrophotometry and Calculation of Colour in CIE Systems.

ISO 3558 Plastics - Assessment of the Colour of Near-White or Near-Colourless Materials.

ISO 4582 Plastics - Determination of Changes in Colour and Variations in Properties and Exposure to Daylight under Glass, Natural Weathering or Laboratory Light Sources.

ISO 4607 Plastics - Methods of Exposure to Natural Weathering.

ISO 4892 Plastics - Methods of Exposure to Laboratory Light Sources.

ISO 9370 Guide for the Iinstrumental Determination of Radiant Exposure in Weathering Tests.

ISO TR 9673 Solar Radiation and Its Measurements for Determining Outdoor Weather Exposure Levels.

ISO 11403-3 Plastics - Acquisition and Presentation of Comparable Multipoint Data - Part 3: Environmental Influences on Properties.

Biological attack

ISO 846 Plastics — Evaluation of the Action of Microorganisms.

Mechanical (Creep)

ISO 899-1 Plastics - Determination of Creep Behaviour - Part 1: Tensile Creep.

ISO 899-2 Plastics - Determination of Creep Behaviour - Part 2: Flexural Creep by Three-Point Loading.

Rubbers

Thermal degradation

ISO 188 Rubber, Vulcanized or Thermoplastic - Accelerated Ageing and Heat Resistance Tests.

ISO 6914 Rubber, Vulcanized or Thermoplastic - Determination of Ageing Characteristics by Measurement of Stress Relaxation in Tension.

Effect of liquids

ISO 1817 Rubber, Vulcanized or Thermoplastic - Determination of the Effect of Liquids.

Weathering

ISO 4665-1 Assessment of Change in Properties after Exposure to Natural Weathering or Artificial Light.

ISO 4665-2 Methods of Exposure to Natural Weathering.

ISO 4665-3 Methods of Exposure to Artificial Weathering.

Effect of ozone

ISO 1431-1 Resistance of Ozone Cracking - Static Strain Test

ISO 1431-2 Resistance to Ozone Cracking - Dynamic Strain Test.

ISO 1431 -3 Determination of Ozone Concentration.

Biological degradation

ISO 846 Determination of Behaviour under the Action of Fungi and Bacteria - Evaluation by Visual Examination or Measurement of Change in Mass or Physical Properties.

Mechanical (stress relaxation in compression)

ISO 3384 Determination of Stress Relaxation in Compression at Normal and High Temperatures.

ISO 6056 Determination of Compression Stress Relaxation (Rings).

Composites

ISO 75-3 Plastics - Determination of Temperature of Deflection Under Load. Part 3: High-Strength Thermosetting Laminates and Long-Fibre-Reinforced plastics.

ISO 13003 Fibre-Reinforced Plastics - Determination of Fatigue Properties under Cyclic Loading Conditions.

ISO 21746 Composites and Metal Assemblies - Galvanic Corrosion Tests of Carbon Fibre Reinforced Plastics (CFRPs) Related Bonded or Fastened Structures in Artificial Atmospheres - Salt Spray Tests.

ISO 22836 Fibre-Reinforced Composites - Method for Accelerated Moisture Absorption and Supersaturated Conditioning by Moisture Using Sealed Pressure Vessel.

Note: *The standards listed in this section refer specifically to fibre-reinforced composites. More general standards covering both plastics and composites are given in the section on ISO plastic related standards.*

Adhesives

ISO 9142 Adhesives - Guide to the Selection of Standard Laboratory Ageing Conditions for Testing Bonded Joints.

ISO 9664 Test Methods for Fatigue Properties of Structural Adhesives in Tensile Shear.

ISO 10354 Adhesives - Characterisation of Durability of Structural Adhesive Assemblies - Wedge Rupture Test.

ISO 10363 Hot Melt adhesives - Determination of Thermal Stability.

ISO 14615 Adhesives - Durability of Structural Adhesive Joints - Exposure to Humidity and Temperature under Load.

BSI and EN Standards

Composites

BS EN 2378 Fibre Reinforced Plastics - Determination of Water Absorption by Immersion in Demineralised Water.

BS EN 2489 Fibre reinforced Plastics - Determination of the Action of Liquid Chemicals.

BS EN 2823 Fibre Reinforced Plastics - Determination of the Effect of Exposure to Humid Atmosphere on Physical and Mechanical Characteristics.

ASTM Standards

Plastics

Permeation

ASTM E96 Water Vapor Transmission Standard Test Methods.

ASTM D1653 Standard Test Methods for Water Vapor Transmission of Organic Coating Films.

Thermal degradation

ASTM D1203 Standard Test Methods for Volatile Loss From Plastics Using Activated Carbon Methods.

ASTM D2115 Standard Practice for Oven Heat Stability of Poly (Vinyl Chloride) Compositions.

ASTM D3045 Standard Practice for Heat Aging of Plastics Without Load.

Effects of liquids

ASTM D543 Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents.

ASTM D570 Standard Test Method for Water Absorption of Plastics.

ASTM D1712 Standard Practice for Resistance of Plastics to Sulfide Staining.

Environmental stress cracking (ESC)

ASTM D1693 Standard Test Method for Environmental Stress-Cracking of Ethylene Plastics.

ASTM F1248 Standard Test Method for Determination of Environmental Stress Crack Resistance (ESCR) of Polyethylene Pipe.

Weathering

ASTM D1435 Standard Practice for Outdoor Weathering of Plastics.

ASTM D1499 Standard Practice Filtered Open-Flame Carbon-Arc Type Exposures of Plastics.

ASTM D2565 Standard Practice for Xenon Arc Exposure of Plastics Intended for Outdoor Applications.

ASTM D4329 Standard Practice for Fluorescent UV Exposure of Plastics.

ASTM D4364 Standard Practice for Performing Outdoor Accelerated Weathering Tests of Plastics Using Concentrated Sunlight.

ASTM G24 Standard Practice for Conducting Exposures to Daylight Filtered Through Glass.

ASTM G156 Standard Practice for Selecting and Characterizing Weathering Reference Materials Used to Monitor Consistency of Conditions in an Exposure Test.

ASTM G178 Standard Practice for Determining the Activation Spectrum of a Material (Wavelength Sensitivity to an Exposure Source) Using the Sharp Cut-On Filter or Spectrographic Technique.

Biological attack

ASTM G21 Standard Practice for Determining Resistance of Synthetic Polymeric Materials to Fungi.

Creep

ASTM D2990 Standard Test Methods for Tensile, Compressive, and Flexural Creep and Creep-Rupture of Plastics.

Rubber

Thermal degradation

ASTM D454 Standard Test Method for Rubber Deterioration by Heat and Air Pressure.

ASTM D572 Standard Test Method for Rubber—Deterioration by Heat and Oxygen.

ASTM D573 Standard Test Method for Rubber—Deterioration in an Air Oven.

ASTM D865 Standard Test Method for Rubber-Deterioration by Heating in Air (Test Tube Enclosure).

Effects of liquids

ASTM D471 Standard Test Method for Rubber Property-Effect of Liquids.

ASTM D1460 Standard Test Method for Rubber Property-Change in Length During Liquid Immersion.

ASTM D3137 Standard Test Method for Rubber Property-Hydrolytic Stability.

Weathering

ASTM D518 Standard Test Method for Rubber Deterioration Surface Cracking.

Effect of ozone

ASTM D1149 Standard Test Method for Rubber DeteriorationSurface Ozone Cracking in a Chamber.

ASTM D1171 Standard Test Method for Rubber DeteriorationSurface Ozone Cracking Outdoors or Chamber (Triangular Specimens).

Mechanical stress relaxation in compression

ASTM F38 Standard Test Methods for Creep Relaxation of a Gasket Material.

Composites

ASTM C480 Standard Test Method for Flexure Creep of Sandwich Constructions.

ASTM D1151 Standard Practice for Effect of Moisture and Temperature on Adhesive Bonds.

ASTM D1828 Standard Practice for Atmospheric Exposure of Adhesive Joints Stressed in Peel.

ASTM D2295 Standard Test Method for Strength Properties of Adhesives in Shear by Tension Loading at Elevated Temperatures (Metal-to-Metal).

ASTM D2918 Standard Test Method for Durability Assessment of Adhesive Joints Stressed in Peel.

ASTM D2919 Standard Test Method for Determining Durability of Adhesive Joints Stressed in Shear by Tension Loading.

ASTM D5229 Standard Test Method for Moisture Absorption Properties and Equilibrium Conditioning of Polymer Matrix Composite Materials.

ASTM D7792 Standard Practice for Freeze/Thaw Conditioning of Pultruded Fiber Reinforced Polymer (FRP) Composites Used in Structural Designs.

Adhesives

BS EN 1465 Adhesives – Determination of Tensile Lap-Shear Strength of Rigid-to-Rigid Bonded Assemblies.

BS 5350-A1 Methods of Test for Adhesives - Part A1: Adherend Preparation.

BS 7079 General Introduction to Standards for Preparation of Steel Substrates Before Application of Paints and Related Products.

BS EN 2243-5 Non-Metallic Materials Structural Adhesives Test Method Part 5: Ageing Tests.

BS EN 13887 Structural Adhesives. Guidelines for Surface Preparation of Metal and Plastics Prior to Adhesive Bonding.

BS EN 26922 Adhesives - Determination of Tensile Strength of Butt Joints.

ASTM Standards

Plastics

Mechanical

ASTM D695 Standard Test Method for Compressive Properties of Rigid Plastics.

ASTM D2990 Standard Test Methods for Tensile, Compressive, and Flexural Creep and Creep-Rupture of Plastics.

Environmental conditioning and testing

ASTM D543 Standard Practices for Evaluating the resistance of Plastics for Chemical Reagents.

ASTM D570 Standard Test Method for Water Absorption of Plastics.

ASTM D618 Standard Practice for Conditioning Plastics for Testing.

Environmental stress cracking (ESC)

ASTM D1693 Standard Test Method for Environmental Stress-Cracking of Ethylene Plastics.

ASTM F1248 Standard Test Method for Determination of Environmental Stress Crack Resistance (ESCR) of Polyethylene Pipe.

Adhesives

Thermal degradation

ASTM D1151 Standard Practice for Effect of Moisture and Temperature on Adhesive Bonds.

ASTM D2295 Standard Test Method for Strength Properties of Adhesives in Shear by Tension Loading at Elevated Temperatures (Metal-to-Metal).

ASTM D4498 Standard Test Method for Heat-Fail Temperature in Shear of Hot Melt Adhesives.

ASTM 4502 Standard Test Method for Heat and Moisture Resistance of Wood-Adhesive Joints.

Chemical resistance

ASTM D896 Standard Practice for Resistance of Adhesive Bonds to Chemical Reagents.

Environmental conditioning and testing

ASTM D1151 Standard Practice for Effect of Moisture and Temperature on Adhesive Bonds.

ASTM D1183 Standard Practices for Resistance of Adhesives to Cyclic Laboratory Aging Conditions.

ASTM D1828 Standard Practice for Atmospheric Exposure of Adhesive Joints Stressed in Peel.

ASTM D2295 Standard Test Method for Strength Properties of Adhesives in Shear by Tension Loading at Elevated Temperatures (Metal-to-Metal).

ASTM D2918 Standard Test Method for Durability Assessment of Adhesive Joints Stressed in Peel.

ASTM D2919 Standard Test Method for Determining Durability of Adhesive Joints Stressed in Shear by Tension Loading.

ASTM D3434 Standard Test Method for Multiple-Cycle Accelerated Aging Test (Automatic Boil Test) for Exterior Wet Use Wood Adhesives.

ASTM D3632 Standard Test Method for Accelerated Aging of Adhesive Joints by the Oxygen-Pressure Method.

ASTM D3762 Standard Test Method for Adhesive-Bonded Surface Durability of Aluminium (Wedge Test).

ASTM D4498 Standard Test Method for Heat-Fail Temperature in Shear of Hot Melt Adhesives.

Creep

ASTM D1780 Standard Practice for Conducting Creep Tests of Metal-to-Metal Adhesives.

ASTM D2293 Standard Test Method for Creep Properties of Adhesives in Shear by Compression Loading (Metal-to-Metal).

ASTM D2294 Standard Test Method for Creep Properties of Adhesives in Shear by Tension Loading (Metal-to-Metal).

Surface treatment

ASTM D2093 Standard Practice for Preparation of Surfaces of Plastics Prior to Adhesive Bonding.

ASTM D2651 Standard Guide for Preparation of Metal Surfaces for Adhesive Bonding.

Useful contacts

Useful contacts

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BSI
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ISO
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Website: www.istructe.org

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Abstract

Accurate modelling of the absorption of moisture into engineering polymers is needed to design exposure procedures for durability assessment and carry out reliable lifetime predictions. This needs to be supported by good quality data obtained under representative conditions. This Guide describes methods for measuring the absorption and diffusion of moisture in polymeric materials, including plastics, adhesives, and composites. Factors that will affect moisture absorption, including service conditions (temperature, pressure, and stress) and the manufacture process (e.g., state of cure), are also covered.

NPL has made every effort to ensure all information contained in this Good Practice Guide was correct at the time of publication. NPL is not responsible for any errors, omissions, or obsolescence, and does not accept any liability arising from the use of this Good Practice Guide.

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Contents

Glossary of Terms (Based on BSI and ASTM Definitions)

Accelerated ageing test: Short-term test designed to simulate the effects of longer-term service conditions.
Adherend: Body that is or intended to be held to another body by an adhesive.
Adherend failure: Failure of a joint in the body of the adherend.
Adhesion (or adherence): State in which two surfaces are held together by interfacial bonds.
Adhesive: Non-metallic substance capable of joining materials by surface bonding (adhesion), the bonding possessing adequate internal strength (cohesion).
Adhesive failure: Failure of an adhesive bond, such that separation appears to be at the adhesive/adherend interface.
Ageing: Irreversible chemical and physical processes occurring in a material in the course of time.
Amorphous: Non-crystalline or devoid of crystalline structure.
Amorphous regions: Regions within a polymeric material that, on the basis of X-ray diffraction or other suitable techniques, do not show any evidence of crystalline structure.
ASTM: American Society for Testing and Materials.
Bond: The union of materials by adhesives.
Bond-line: The layer of adhesive, which attaches two adherends.
Bond strength: The unit of load applied to tension, compression, flexure, peel, impact, cleavage, or shear, required to break an adhesive assembly with failure occurring in or near the plane of the bond.
Breaking stress: Stress at the moment of rupture of a specimen.
Brittle failure: Failure in which the fracture surface exhibits no permanent material deformation to the naked eye (e.g., stretching, elongation and necking down).
BSI: British Standards Institute
Bulk adhesive: The adhesive unaltered by the adherend.
Cleavage: Mode of application of a force to a joint between rigid adherends, which is not uniform over the whole area, but results in a stress concentrated at one edge.
Cohesion: The ability of the adhesive to resist splitting or rupture.
Cohesive failure: Failure within the body of the adhesive (i.e., not at the interface).
Composite: Solid product consisting of two or more distinct phases, including a binding material (matrix) and a particulate or fibrous material.
Conditioning: A series of operations intended to bring a sample or specimen into a reference state with regard to temperature and humidity.
Contamination-free: Absence of foreign matter, both on a treated surface (i.e., cleanliness), or which could migrate through the bulk to a bonded interface with time.
Craze: Defect at or under the surface of a plastic, attributable to apparent cracks bridged by polymeric material of reduced (apparent) density.
Creep: The time-dependent increase in strain resulting from a sustained load.
Crystallinity: Presence of three-dimensional order at the level of molecular dimensions.
Cure: To set or harden by means of a chemical reaction.

Cure time: Time required to affect a cure at a given temperature.
Cure temperature: Temperature at which a polymeric system is exposed in order to achieve curing.
Degradation: Change in the chemical structure of a polymeric material involving a deleterious change in properties.
Delamination: Separation of layers (i.e., planar defect) in a laminate.
Deterioration: Permanent change in the physical properties of a material evident by impairment of these properties.
Diffusivity: The transport of chemical species, such as a liquid or gas, within a solid due to concentration differences. Diffusivity is generally temperature dependent.
Dimensional stability: Consistency of dimensions of a material part or specimen under environmental conditions.
Dissolution: Process of absorption of the chemical in the polymer and depends on the affinity (interaction energy) of the polymer for the chemical, the volume available for absorption and the concentration of chemical.
Durability: The endurance of joint strength relative to the required service conditions.
Environmental test: Test to assess the performance of an assembly under service conditions.
Fibre: Particle of relatively short length, characterised by a high ratio of length to thickness or diameter.
Filler: Relatively inert material (e.g., talc) added to a plastic or resin to modify its strength, fire resistance or other qualities, or to lower costs.
Fillet: Portion of an adhesive that bridges the adherends outside the bond-line.
Glass transition: A reversible change in an amorphous polymer or in amorphous regions of a partially crystalline polymer from (or to) a viscous or rubbery condition to (or from) a hard and relatively brittle one.
Hygroscopic: Material capable of absorbing and retaining environmental moisture.
Interface: The region where two materials are in intimate contact. Interfaces can be solid-solid (cured adhesive joint), solid-liquid (uncured adhesive joint), solid-gas (exposed adherend), liquid-gas (open adhesive) or liquid-liquid (insoluble liquids).
Interphase: The region near an interface where the properties of materials are altered from their bulk properties due to the presence of the interface.
ISO: International Standards Organisation.
Laminate: Product made by bonding together two or more layers (plies) of material or materials.
Permeability: Property of a material transmitting gases and liquids by passage through one surface and out at another surface by diffusion and sorption processes.
Plasticisation: Increase in softness, flexibility, and extensibility of an adhesive.
Polymeric material: A material whose continuous phase consists of long-chain organic molecules.
Porosity: A condition of trapped pockets of air, gas, or vacuum within a solid material.
Post-cure: Further treatment by time and/or temperature of an adhesive to obtain the required properties by curing.

Primer: A coating applied to a surface, prior to the application of an adhesive, to improve the performance of the bond.

Reinforced plastic: Polymer (plastic) with high-strength fibres embedded in the composition, resulting in some strength properties greatly superior to those of the base resin.

Sealant: An interlaminar layer of polymeric material applied for the purpose of filling gaps and insulating the interior of the joint from external environments. Sealants are not used to provide load bearing capacity although adhesives can also act as sealants.

Semi-crystalline: Polymer containing crystalline and amorphous phases.

Shelf life: The period for which the components of the adhesive may be stored, under the conditions specified by the manufacturer, without being degraded.

Soundness: Freedom from weak and loosely attached surface layers.

Stability: The stability of surface layers and oxides, towards water, organic compounds, and elevated temperatures, as a function of time following treatment.

Strain: Unit change due to force in size of body relative to its original size.

Stress: Force exerted per unit area at a point within a plane.

Stress-strain diagram (or curve): A diagram in which corresponding values of stress and strain are plotted against each other.

Structural bond: A bond, which is capable of sustaining in a structure a specified strength level under a combination of stresses for a specified time.

Substrate: An adherend, a material upon which an adhesive is applied.

Surface preparation (or treatment): Physical and/or chemical treatments applied to adherends to render them suitable or more suitable for adhesive bonding.

Swelling: Increase in volume of a test specimen immersed in a liquid or exposed to a vapour.

Thermoplastic: A material that can be repeatedly softened by heating.

Thermoset: A resin that is substantially infusible and insoluble after being cured.

Traveller: A test specimen used for example to measure moisture content because of environmental conditioning.

Uniformity: Visible or measurable consistency of the other characteristics, and of the regularity of a treated surface area.

Weathering: Effects on a material of exposure to outdoor conditions.

Yield strain: The strain, below which a material acts in an elastic manner, and above which it begins to exhibit permanent deformation.

Yield stress: The stress (either normal or shear) at which a marked increase in deformation occurs without an increase in load.

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Chapter 1

Introduction and scope

Introduction

Lifetime prediction is an important consideration in the selection of materials systems and the design of structures. The design approach for lifetime prediction of engineering polymers, such as composites or structural adhesives, is developing continuously but still relies on 'knockdown factors' or 'rules of thumb' generated from mechanical tests on conditioned samples.

Chemical exposure, in particular moisture exposure, is a key mechanism for degradation in polymer systems. An understanding of permeation of chemical species is essential for developing testing methodologies and accelerated ageing protocols for polymeric materials. The process of permeation of chemicals through polymers is a combination of two interrelated processes, dissolution in the polymer and diffusion through the polymer. Dissolution is the process of absorption of the chemical in the polymer and depends on the affinity (interaction energy) of the polymer for the absorbing molecules, the volume available for absorption and the concentration of absorbing chemical. There is a limit to the amount of the chemical that can be absorbed under any set of conditions – the solubility. Diffusion is the concentration gradient driven process whereby the absorbed molecules are transported within the polymer and diffusion properties are characterised via diffusion coefficients. A review [1] of the extensive body of literature on permeation and diffusion in polymers [e.g., 2-6] emphasised the strong need for reliable test methods to measure the diffusion of gases and liquids in polymers. Permeation properties are required under relevant service conditions, which may include transient and varying levels of chemical exposure, temperature, pressure, and stress.

Often, especially in thick sections, the time taken for deleterious species to diffuse in sufficient concentrations to critical regions is the rate-determining step in the ageing process. Accurate modelling of the absorption of moisture into engineering polymers is needed to design exposure procedures and carry out reliable lifetime predictions. This needs to be supported by good quality data obtained under representative conditions. The techniques described in this Guide focus on diffusion as part of a wider investigation of accelerated ageing of polymer materials [7].

The time dependent concentration of chemical species in a component can be predicted using diffusion modelling approaches [2-6]. A common assumption used in interpreting diffusion measurements is Fickian diffusion - the steady state flux of diffusant per unit area (J) per unit time (t) is a function of the concentration gradient (concentration, ϕ, per unit length, x) and Fick's first law is expressed:

$$\frac{dJ}{dt} = -D\frac{d\phi}{dx} \qquad (1)$$

Where the diffusion coefficient *D* does not depend on concentration then Fick's second law (Equation 2) can be used to determine the time dependence of the concentration of the diffusant in the sample.

$$\frac{dJ}{dt} = -D\frac{d^2\phi}{dx^2} \quad (2)$$

The diffusion coefficient *D*(*T*) is temperature dependent, increasing the temperature (*T*) should increase the rate of diffusion and accelerate the ageing of the system.

Scope

This Good Practice Guide covers techniques for measuring the absorption and diffusion of moisture in polymeric materials, which include plastics, polymer matrix composites (PMCs) and adhesives.

The applicable standards for these measurements is ISO 62 (Plastics - Determination of Water Absorption) [8] and ASTM D570 (Standard Test Method for Water Absorption of Plastics) [9]. The ISO Standard includes an Appendix for determining the diffusion coefficient that is absent from the ASTM Standard. Chapter 2 of this guide describes these methods and explores the factors that influence the accuracy of the results obtained. Chapter 3 outlines a method for analysing the results of measurements and the calculation of Fickian diffusion properties. Environmental factors, such as stress and temperature, will affect diffusion and methods for assessing these effects are covered in Chapter 4.

Chapter 5 describes factors that affect measurements in non-homogenous and non-isotropic materials systems, such as polymeric composites and adhesive joints. Sources of uncertainties are described in Chapter 6. Chapter 7 provides a summary of key points. Chapter 8 lists standards for assessing permeation and diffusion in polymers. These standards enable the measurement of properties for comparison or specification. However, the standards do not cover all the aspects of measurement required to provide data for design.

Measurements of moisture absorption in a rubber-toughened epoxy adhesive and in a film, adhesive are described to illustrate some of the techniques employed.

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Chapter 2

Experimental procedures

- Introduction
- Specimens
- Exposure conditions and times
- Weighing and balance requirements
- Specimen preparation before testing
- Immersion and mass measurement
- Completion of tests

Introduction

ISO 62 [8] and ASTM D 570 [9] are standard measurement methods for water absorption by immersion. The absorption of liquids into polymers is followed through mass uptake (or gravimetric) measurements. Since liquid densities are comparable with polymer densities the mass changes should be measurable. Mass increases of the order of a few percent of the original mass of the polymer are typical in systems with an affinity for the liquid [2-5].

This approach can also be applied to study diffusion of vapours (e.g., water vapour) in polymers; pre-conditioned samples are exposed to a controlled atmosphere (vapour concentration and temperature) and periodically weighed [10-13]. The analysis approach described in Chapter 3 can be used to calculate solubility and diffusion coefficients. Direct contact with a liquid rather than its vapour normally leads to greater levels of absorption (higher saturation concentrations) and, therefore, condensation of vapour on the surface will affect results.

Specimens

The standards recommend a series of preferred sample geometries for flat sheets (either directly moulded or cut from larger sections), rod and tubes to enable comparison of water absorption properties. The procedures for assessing flat sheets are described in this guide but the processes and items to consider are common for all of sample types.

For example, the geometries for flat sheets are specified as:

- The ISO 62 standard specimen is a square 60 mm × 60 mm × 1 mm thick.
- The preferred test specimen for ASTM D 570 is a 50.8 mm diameter disk with a thickness of 3.2 mm.

Standards	Geometric Parameter	Dimension (mm)	Manufacture Tolerance (mm)	Measurement Tolerance (mm)
ISO 62 [8]	Length	60	± 2	± 0.1
	Width	60	± 2	± 0.1
	Thickness	1	± 0.05	± 0.1
ASTM D570 [9]	Radius	25.4	Not stated	± 0.0252
	Thickness	3.2	± 0.15	± 0.025

Table 1. Standard specimen dimensions for flat sheets

Dimensions and tolerances allowed are shown in Table 1. The tolerances on length, width and radius are wide as these dimensions have little significant effect on the results. The thickness (and accuracy of the measured thickness) is much more critical for comparing materials (and samples tested at different labs) and for the calculation of diffusion coefficients. It is good practice to measure the thickness to an accuracy of 1% or better, regardless of the tolerances specified in the standards.

Deviations from the standard dimensions are allowed for but must be recorded. Examples where samples may need to deviate from the standard dimensions include:

- Laminates, where the lay-up needs to be representative of the material.
- Highly absorbing plastics where saturation may be approached very rapidly may be better measured using thicker samples.
- Where the material properties are known or suspected to be thickness or manufacturing process dependent and the sample needs to be prepared to be representative.

Changing the thickness of the test specimen may result in the need to use different values for the other dimensions (i.e., length and width or radius). Factors than need to be considered in selecting new specimen dimensions include:

- Maintaining a similar ratio of edge to face area to the standard specimen (e.g., for the ISO square a length to thickness ratio of 60).
- Ensuring the mass of the sample is such that the change in mass on absorption can be measured with sufficient accuracy.
- Ensuring the sample fits on the balance.
- Ensuring the sample fits in the exposure system.
- Controlling and measuring the dimensions to sufficient accuracy, in particular the level of uncertainty in the thickness can increase significantly with reducing thickness.
- The time taken to reach saturation – this increases with the square of thickness.

Exposure conditions and times

The standards specify a set of standard exposure conditions (temperature and time) that allow for comparing different materials. These are:

Room temperature immersion (23 ± 2 °C) (ISO and ASTM)	Immerse for 24 ± 1 hours then weigh. Re-immerse and repeat for increasing intervals (e.g., 24h, 48h, 96h, 192h, then weekly etc.) until saturation. ASTM specifies a 2-hour (120 ± 4 minute) exposure for materials having a high rate of absorption or for thin samples. Samples can be re-immersed for measurement at 24 hours (and subsequent intervals).
Boiling water immersion (ISO and ASTM)	Immerse for 30 ± 2 minutes in boiling water remove and place in water at room temperature to cool for 15 ± 1 minute, then weigh. After weighing the procedure is repeated until saturation is reached. ASTM also specifies a 2-hour (120 ± 4 minute) boiling water exposure.

Immersion at 50 °C (ASTM)	Immersion period is specified as 48 ± 1 hours.
Exposure under standard laboratory conditions of 23 ± 2 °C and 50 ± 5% RH (ISO)	Follows the intervals from room temperature immersion.

Note 1: Appropriate safety precautions should be taken when working with boiling water.

Other exposure conditions may also be specified [14, 15]. For example, the military consider the worst worldwide environment to be represented by 70 °C and 85% RH (relative humidity). The standard exposures and intervals may not be appropriate for obtaining diffusion data for design and alternative procedures more clearly reflecting the service conditions may need to be considered.

- Time to reach saturation depends on the square of thickness and therefore exposure timescales will need to be considered in light of the sample dimensions. A maximum sample thickness of 1 mm is recommended by ISO [8] to ensure that test durations do not exceed one week for typical D values for polymers (ca. 10-12 m^2s^{-1}).
- The exposure temperature should reflect the application temperature.
- Multiple temperature exposures may be needed to build up a picture of the full behaviour of the material.
- High temperatures may cause chemical or phase changes in the polymer, which could limit the possibility of extrapolating behaviour from one temperature to another.
- Where possible, the exposure intervals should match these in the standards to enable comparability with standard data.
- If multiple specimens are to be exposed in a study then the exposure intervals for each of the specimens should be consistent. The start of the exposures may need to be staggered to allow mass measurements to be carried out efficiently.

Weighing and balance requirements

The ISO and ASTM standards require the use of a balance capable of reading to 0.1 mg. Typically, the dry masses of the specimens referred to in the standards will be in the range 2 g – 10 g. Thus, the sensitivity of the concentration measurement will be at least 0.005%, which is more than adequate if absorption levels are greater than 1%. If specimens with lower masses (< 1 g) are used, e.g., using very thin samples, or saturation concentrations are low (< 1%) then a higher resolution balance (e.g., with a resolution of 0.01 mg) may be necessary.

Procedures for weighing good practice [16] should be followed. The balance used should have a capacity such that the mass of the specimen is neither at the lower or upper end of the balance range (i.e., the sample mass is within 10%-90% of the full scale of the balance). The total mass of sample expected at saturation should also be considered. The balance should be calibrated over the expected range of masses. An enclosure around the balance pan to eliminate drafts is recommended.

To minimise reproducibility problems, it is recommended that the same balance be used throughout the test programme. The samples should be placed in the same position on the balance each time a measurement is made.

Specimen preparation before testing

If test specimens are machined then care should be taken to avoid damage to the surfaces (e.g., cracking). Rough surfaces should be smoothed, for example by polishing with fine glass paper.

In materials with anisotropic diffusion properties (e.g., fibre reinforced plastics where faces cut normal to the fibre direction in composites may have significantly higher diffusion properties) erroneous results can be obtained if absorption through exposed edges is significantly different to absorption through surfaces. For this reason, the ratio of edge area to surface area of samples should be minimised.

Where edge effects are of concern then edges can be sealed (e.g., by bonding aluminium foil to the edges or applying a barrier coating). The additional mass of the sealing material needs to be accounted for when analysing results. Any coating/foil used for sealing the edges must:

- Be applied as a thin layer to avoid becoming a significant component of the mass of the system.
- Have a significantly lower permeability than the sample; if it does not then the thin layer will not act as a barrier to diffusion.
- Be applied carefully so as to not overlap the main faces of the sample.

The second requirement usually means that sealing coatings are not commonly used for isotropic materials. However, for systems where diffusion is directionally dependent and diffusion through the edges may be high (e.g., composites) sealing may be necessary.

The samples should be dried to constant mass, M0, before testing. Standards recommend drying at 110 °C for 1 hour or at 50 °C for 24 hours then cooling in a desiccator prior to measuring mass (and testing). Drying cycles should be repeated until constant mass (i.e., change in mass between successive measurements is less than 0.1 mg). The lower temperature should be used if there are worries about thermal stability or changing the state of cure of the material.

Immersion and mass measurement

Samples should be immersed in a sufficient volume of liquid such that the samples are fully immersed and any species leaching from the samples are sufficiently diluted. ISO 62 specifies at least 300 ml per test specimen and a minimum of 8 ml of fluid per square cm of surface area. The fluid should be topped up or replaced regularly to ensure that the correct immersion conditions are maintained.

Samples of the same composition can be placed in the same container provided that the minimum volume of fluid per sample is maintained. Samples should not make any significant contact with each other or the container. A 'rack' manufactured from a material that does not degrade in the fluid (e.g., stainless steel) can be used to maintain separation. Where the samples have densities less than the fluid, a means of weighting the samples needs to be used. A stainless-steel mesh cage is recommended in IS0 62.

After immersion for the fixed period (at constant temperature), the sample is removed from the medium and surface liquid wiped off using a dry cloth or paper before immediately weighing (in a weighing bottle for very thin samples). Assessing the total removal of liquid from the surface of the sample is judged by the appearance of the surface and from the appearance of the drying cloth. Therefore, it is subjective and a potential source of uncertainty in the measurements. It is much easier to dry and to judge dryness of smooth surfaces than textured surfaces.

Samples removed from the exposure medium will lose absorbed moisture continuously during the period that they are out from the medium. The loss of absorbed moisture is a diffusion driven process depending on the difference between the surface moisture concentration and the equilibrium moisture concentration for the material in the laboratory environment (generally 23 ± 2°C and 50 ± 5% relative humidity). If this loss of absorbed material is low, then samples can then be returned to the medium for continuing exposure. This requires that the time out of the medium be minimised. Acceptable periods of time that the samples can be out of the exposure medium will be sample and material specific. The periods out of exposure should be insignificant compared to exposure periods between each weighing.

The date, time and mass readings should be recorded. Any changes to the samples (e.g., discolouration, blistering, cracking) should be noted.

It is recommended that the shape of the uptake curve be monitored by plotting the increase in mass divided by the initial mass, measured at each time intervals, against time (see Chapter 3).

Completion of tests

Saturation mass, M_∞, is defined when the weight gains from three successive measurements differ by less than 1% of the overall weight gain. The saturation moisture content C_s is simply:

$$C_s = \frac{(M_\infty - M_0)}{M_0} \quad (3)$$

Loss of water-soluble matter from test samples may also affect results. This can be checked by reconditioning (drying) the sample back to constant mass M_c and comparing against the original mass M_0.

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Chapter 3

Data analysis

- Moisture absorption curves
- Calculation of diffusion coefficients
- Correcting for edge effects

Moisture absorption curves

The absorbed moisture concentration $C(t)$ is calculated from the mass $M(t)$, initial mass M_0 and the reconditioned mass M_c. If there is no loss of water-soluble matter (or reconditioned mass data are not available) then use $M_c = M_0$.

$$C(t) = \frac{M(t) - M_c}{M_0} \tag{4}$$

$C(t)$ is often expressed as a percentage of the specimen dry mass. The plot of $C(t)$ against time has a decreasing slope that asymptotically approaches a saturation concentration at large time. There is a limit to the amount of the moisture that can be absorbed under any set of conditions (i.e., solubility).

A common approach is to plot $C(t)$ against square root of time since a linear section at the start of the curve is indicative of Fickian diffusion. The "apparent" diffusion coefficient D_a (uncorrected for edge effects) for a polymer specimen can be determined from the initial linear region of the Fickian diffusion curve. Figure 1 shows absorption curves measured for the example epoxy at different temperatures. Reducing the sample thickness and/or increasing the exposure temperature decrease the time required to reach saturation (i.e., initial gradient of the diffusion curves increases with temperature). The saturation concentration does not appear to depend on the sample thickness but seems to decrease with increasing temperature.

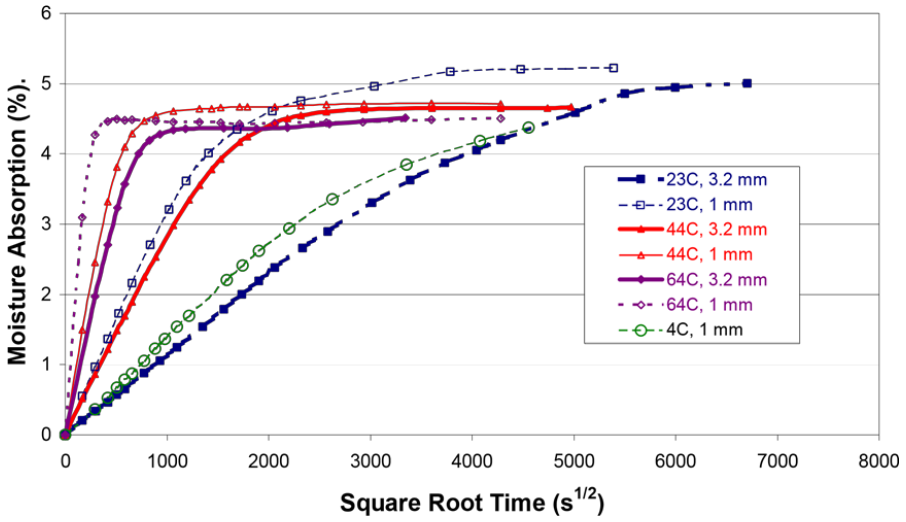

Figure 1. Moisture absorption curves measured by mass uptake

Calculation of diffusion coefficients

Through consideration of the 1-D diffusion case, analytical solutions for the temporal and spatial distribution of moisture concentration $C(t)$ at a distance x from the mid-plane can be derived [17, 18]:

$$\frac{C(t)}{C_s} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)}exp\left[\frac{-(2n+1)^2\pi^2 Dt}{4l^2}\right]cos\left[\frac{(2n+1)\pi x}{2l}\right] \quad (5)$$

Here, l is the half thickness of the film and D is the Fickian diffusion constant. However, as experimental determination of point moisture concentrations is difficult to measure experimentally, this expression is integrated with respect to x to generate an expression in terms of mass gain as a function of time:

$$\frac{C(t)}{C_s} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)}exp\left[\frac{-(2n+1)^2\pi^2 Dt}{4l^2}\right] \quad (6)$$

By assuming a one-dimensional Fickian process a method has been derived [4,5,17] for calculating the "apparent" diffusion coefficient D_a, which is not corrected for edge effects, is calculated from the moisture concentration versus time measurements, $C(t)$, and the sample thickness, h:

$$D_a = \frac{\pi}{16}\left[\frac{h(C(t_2) - C(t_1))}{C_s(\sqrt{t_2} - \sqrt{t_1})}\right]^2 \quad (7)$$

where C_s is the saturation concentration (or percentage) of moisture. If the starting point is a dry sample at time zero, then t_1 and $C(t_1)$ can be eliminated, and the fractional mass uptake $C(t_2)/C_s$ plotted as a function of $\sqrt{t_2}$ has a slope proportional to ${D_a}^{1/2}$.

$$\frac{C(t_2)}{C_s} = {D_a}^{1/2}\frac{4\sqrt{t_2}}{h\sqrt{\pi}} \quad (8)$$

For Fickian diffusion, this plot is approximately linear (e.g., Figure 2, until $C(t_2)$ approaches $0.7C_s$). D_a can be calculated from the square of the slope. Alternatively, if a full diffusion curve is not available then D_a can be evaluated from single point values of $C(t_2)$ and t_2 if a value for C_s is known or can be estimated with reasonable accuracy.

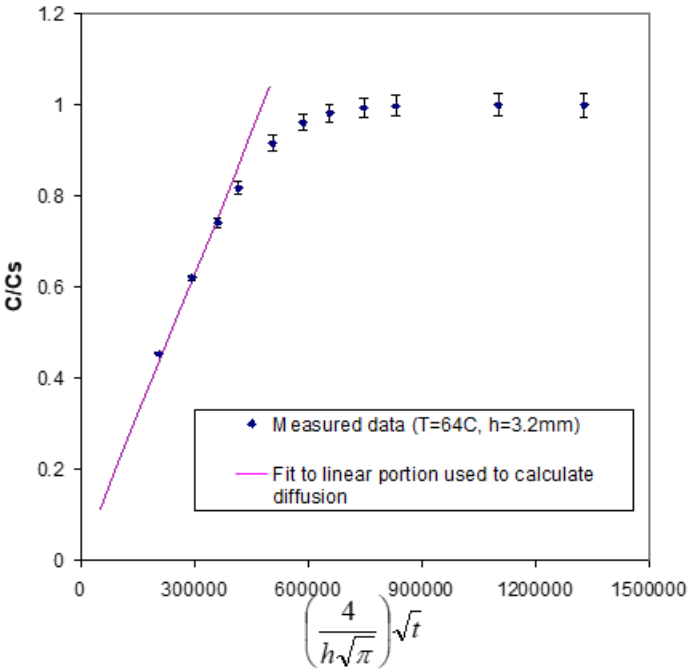

Figure 2. A linear fit to the absorption data up to C/Cs = 0.7 used to calculate D_a (See Equation 8)

Figure 2 shows mean absorption values obtained from three 3.2mm thick epoxy samples exposed simultaneously at 64 °C. The error bars represent one standard deviation and are ~2% - 4% of the mean. A straight line was fitted to the data up to an approximate value of C/C_s of 0.7 (72 hours exposure). Only three absorption measurements lie in this range.

Equation 6 can be expanded and approximated to calculate moisture concentration as a function of time. Where $Dt/h^2 > 0.05$, Equation 5 reduces to:

$$C(t_2) = C_s\left[1 - \frac{8}{\pi} exp\left[-\pi^2\left(\frac{D_a t_2}{h^2}\right)\right]\right] \quad (9)$$

The following approximation is also commonly used [17]:

$$C(t_2) = C_s\left[1 - exp\left[-7.3\left(\frac{D_a t_2}{h^2}\right)\right]\right]^{3/4} \quad (10)$$

Table 2 shows the calculate slopes and apparent diffusion coefficients for each of the three specimens. These were averaged and standard deviations calculated. The coefficients of variation for C_s and Da are 2.7% and 4.8%, respectively.

Sample	Saturation C_s (%)	Slope ($ms^{-1/2}$)	Apparent Diffusion Coefficient D_a (m^2s^{-1})
1	4.28	2.00×10^{-6}	4.20×10^{-12}
2	4.33	2.06×10^{-6}	4.24×10^{-12}
3	4.52	2.14×10^{-6}	4.57×10^{-12}
Mean	4.37	2.08×10^{-6}	4.33×10^{-12}
SD	± 0.12	$\pm 0.05 \times 10^{-6}$	$\pm 0.21 \times 10^{-12}$
CoV	2.7%	2.4%	4.8%

Table 2. Diffusion properties determined from Figure 2
(SD = standard deviation and CoV = coefficient of variation)

Correcting for edge effects

The one-dimensional approximation ignores additional diffusion of moisture through the edges of the sample. Edge effects are minimised by ensuring the samples have a large ratio of face area to edge area. Edge effects can also be minimised by sealing the edges.

A correction was derived by Shen and Springer [17] to account for edge effects. The true one-dimensional diffusion coefficient D_x can be calculated from the apparent diffusion coefficient Da and the length l, width b and thickness h of the plaques using a correction factor E.

$$D_x = ED_a = D_a\left(1 + \frac{h}{l} + \frac{h}{b}\right)^{-2} \tag{11}$$

For example, the correction factors for 1 mm and 3.2 mm thick squares with 50 mm sides are 0.925 and 0.786, respectively. As Table 3 shows, applying the correction factor narrows the differences between D_x values obtained from the two different thicknesses. However, the values obtained from the thicker specimens are still greater than those obtained from the thinner samples, suggesting that in this case there may be a greater flux through the edges than the faces.

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Chapter 4

Effect of temperature and stress

- Representing relevant service conditions
- Effect of temperature
- Effect of tensile stress
- Determining the effect of hydrostatic pressure

Representing relevant service conditions

In many applications, materials will be simultaneously exposed to moisture and stress. Many degradation processes are known to accelerate under the combination of load and exposure. For example, the residual strength of composite samples that are immersed in water under constant load decreases much more rapidly than specimens loaded in air or specimens immersed but not loaded [7]. The degradation of the material strength may have been accelerated by enhanced moisture diffusion in stressed materials.

Effect of temperature

Diffusion coefficients depend on temperature. The diffusion coefficient $D(T)$ is temperature dependent and for ideal systems follows an Arrhenius relationship, with an energy barrier to diffusion E_D.

$$D(T) = D_0 \, exp\left(-\frac{E_D}{kT}\right) \tag{12}$$

Therefore, increasing the temperature T should increase the rate of diffusion and accelerate the ageing of the system. k is Boltzmann's constant and the material parameters D_0 and E_D can be determined by plotting log $D(T)$ against $1/T$. Table 3 shows diffusion coefficients determined for an epoxy adhesive at different temperatures. Figure 3 shows a plot of logarithm of diffusion coefficient plotted against $1/T$ determined for an epoxy adhesive. This is linear suggesting that the Arrhenius coefficients holds for this range of temperatures.

Sample Thickness (mm)	Temperature (°C)	Apparent D_a (m^2s^{-1})	Saturation Concentration (%)	Corrected D_x (m^2s^{-1})
1	4	1.28×10^{-14}	5.2*	1.19×10^{-14}
1	23	6.89×10^{-14}	5.2	6.38×10^{-14}
1	44	5.69×10^{-13}	4.7	5.24×10^{-13}
1	64	3.23×10^{-12}	4.5	2.99×10^{-12}
3.2	23	9.02×10^{-14}	5.2	7.09×10^{-14}
3.2	44	7.23×10^{-13}	4.7	5.80×10^{-13}
3.2	64	4.02×10^{-12}	4.5	3.16×10^{-12}

Table 3. Diffusion properties determined from bulk sample
(Saturation not reached, value for 23 °C used to calculate the diffusion coefficient)*

Using this relationship and the data in Figure 3, the effect of changing the exposure temperature on diffusion coefficient can be calculated. Standard room temperature for materials testing is defined as 23 ± 2 °C. Calculated values for D at 21 °C and 25 °C are approximately 20% different to the value at 23 °C.

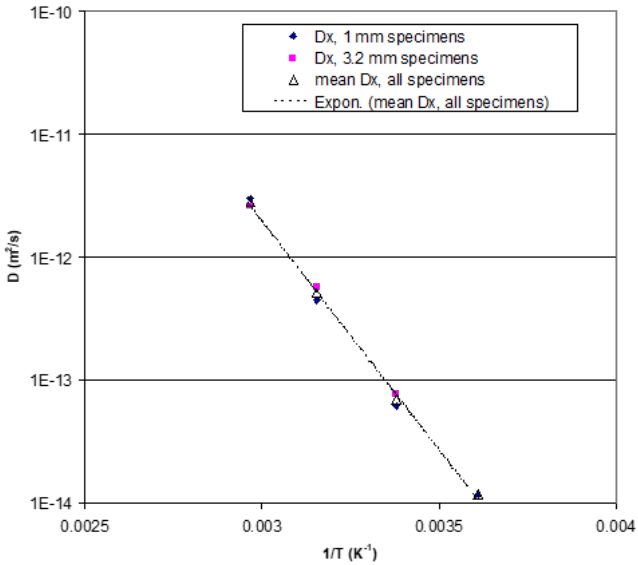

Figure 3. Temperature dependence of the diffusion coefficient

Effect of tensile stress

Specimens can be tested in liquid cells and deadweight loading frames that are used for environmental stress cracking tests for polymers or self-stressing fixtures, Figure 4. In the deadweight loading frames stress is applied using calibrated weights and in the self stressing fixtures through calibrated springs.

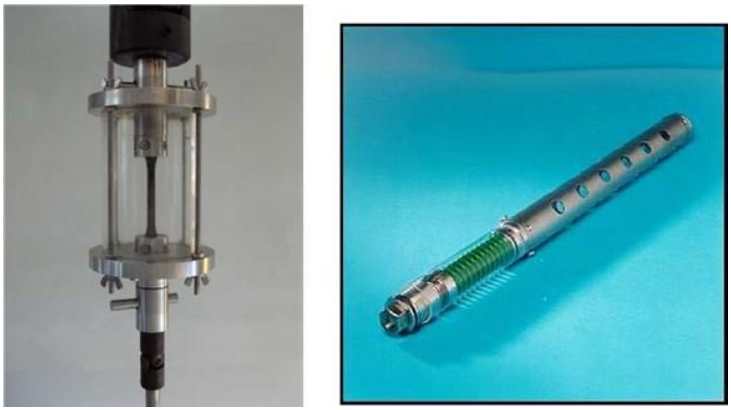

Figure 4. Liquid cell (left) and self-stressing fixture (right) for assessing properties of polymers under combined stress and chemical exposure

The square plaque used for standard moisture diffusion measurements is unsuitable for the controlled application of load in a test. Therefore, measurements of moisture uptake under tensile stress should be carried out using either dog-bone specimens [19] or parallel strips. Although the shape of the dog-bone specimen is not suitable for accurate calculation of diffusion coefficients, the uptake results can be readily compared to determine 'acceleration' factors.

Experiments should be undertaken to assess whether variability of clamping samples in the grips has a significant effect on uptake. Specimens clamped but with no applied stress should be compared with control unclamped specimens exposed at the same time. The difference between measured uptakes in unloaded specimens was found to be negligible, suggesting that the serrated grip faces did not significantly restrict absorption of moisture in the tabs in the series of tests reported.

Figure 5 shows the uptake curves measured with the example epoxy at 23 °C under different levels of tensile stress plotted against square root of time. The absorption increases with increasing stress, with very significant increases and non-linear absorption observed at high stress levels around the yield stress (i.e., between 20 MPa and 25 MPa). The epoxy adhesive is known to yield in tension through a cavitation process initiating around 20 MPa. This level of stress also corresponds with increasing creep rate in the material.

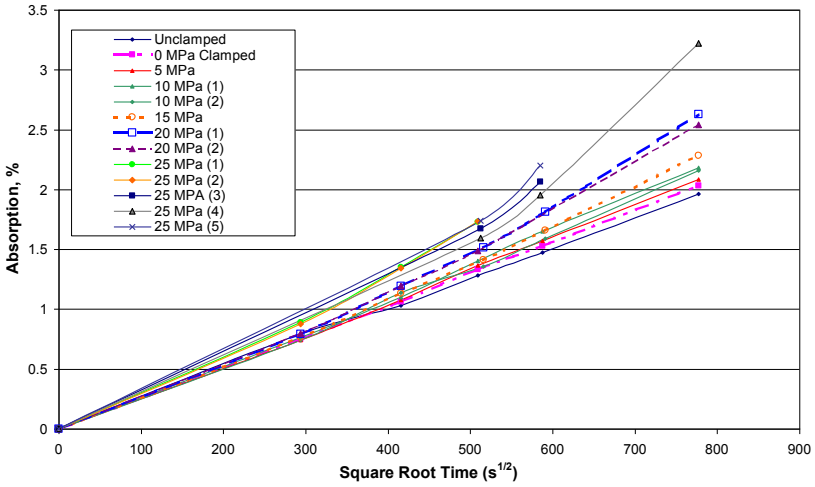

Figure 5: Effect of tensile stress on moisture absorption of epoxy at 23 °C

For the samples under load, part of the increase in absorption with stress may be due to changes in the geometry of the sample, i.e., an increase exposed area from the increase in length due to creep and shorter diffusion paths resulting from decreased width and thickness due to Poisson's contraction.

The geometrical effect can be checked by approximating the tensile specimen as a rectangular bar (60 mm × 10 mm × 1 mm) and using Equation 9 to calculate an 'apparent' diffusion coefficient from the dimensions. Mechanical tests may need to be conducted to provide an indication how dimensions change with strain and creep tests may be required.

For the epoxy evaluated in Figure 5, creep measurements made in air using standard specimens (exposed at 50% relative humidity and containing 2.5% moisture) indicated a tensile strain of 5.4% after 72 hours under 26.2 MPa stress. This strain was taken as a good approximation for the strain under 25 MPa stress and was used with an assumed Poisson's ratio of 0.4 to calculate the dimensions of the strained bar (length 1.05 × unstressed length, width, and thickness 0.98 × original values). Equation 9 was used to predict apparent diffusion coefficients for samples with the stressed ($0.804D_x$) and unstressed dimensions ($0.802D_x$) – the difference was less than 1%.

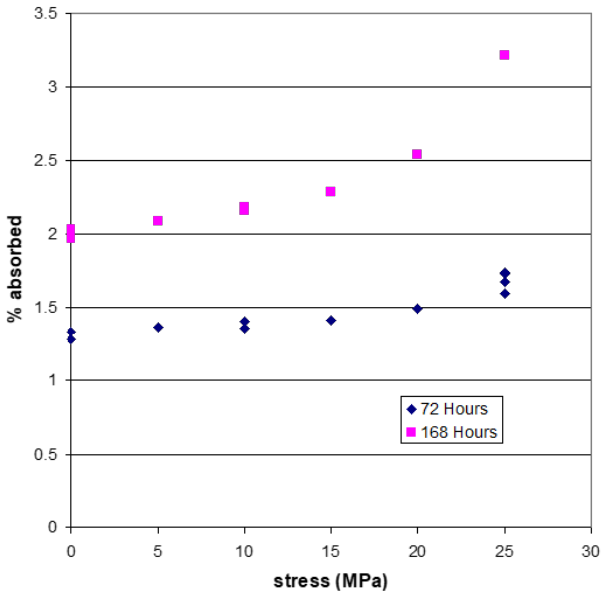

Figure 6. Effect of stress on moisture absorption

The calculated apparent diffusion coefficients and sample dimensions were used with Equation 10 to compare predicted moisture concentrations after 72 hours for 25 MPa and unstressed systems. Although there were significant discrepancies between the measured and predicted moisture uptakes, due to the assumptions made in simplifying the shape of the specimen, comparing the two sets of predictions provides further insight into changes in the diffusion behaviour under stress.

The 25 MPa system was predicted to have a moisture concentration only 1.02 times the concentration predicted for the 0 MPa system whereas the measured 72-hour moisture concentrations under stress were 1.2-1.3 times greater than those measured in the unstressed samples. The difference between the moisture concentrations measured in low stress and high stress samples increases with time, Figure 6, as diffusion in high stress samples becomes non-Fickian, as shown by the non-linearity of the high stress absorption curves in Figure 5.

Determining the effect of stress on saturation concentration would require exposing samples until saturation is reached. However, removing the sample from the apparatus for mass measurements and then reloading may lead to failure of the specimens, particularly at high stresses. Measuring the full absorption curve may require that some samples are designated for long-term exposure, and these are not removed for mass measurements, until the required exposure time has been achieved. Samples would only be used for one mass measurement; thus, fresh specimens would be needed to obtain other points on the absorption curve. This approach could potentially require a high number of specimens (particularly as repeatability between specimens may need to be established), tie up apparatus for prolonged periods and take a long time to complete.

Although very few structures would be designed to operate continuously close to the yield stress of their constituent materials there may be non-uniform stress distributions in components. Regions of high stress could be more permeable to moisture then regions of low stress, leading to preferential absorption in these areas and faster degradation.

Determining the effect of hydrostatic pressure

Diffusion properties are normally obtained at ambient pressure. However, materials may be used in applications (e.g., sub sea structures) where they are exposed to fluids under pressure. Pressure may be a further means of accelerating moisture uptake in some materials.

A system for exposing materials under pressure is shown in Figure 7. A custom-made heating jacket wrapped around the exterior of each autoclave vessel supplies any required heating. A thermostat and thermocouple probe attached to the vessel control the temperature. The accuracy of the temperature control should be confirmed by setting the thermostat to the test temperature and measuring the temperature of liquid within the unsealed vessel. A high-pressure pump is used to pressurise each vessel with air. The readings on the pump gauge and the pressure gauge of each vessel should be checked against a calibrated pressure gauge. Specimens are exposed in pressure vessels filled with water by sealing the vessels and then pressurising them to required pressure at the test temperature. In operation the pressure should be checked regularly (e.g., daily) and re-pressurised as required. It is recommended that pressure and temperature be logged automatically during tests.

Figure 7. Autoclave vessels used for conditioning specimens at elevated pressure

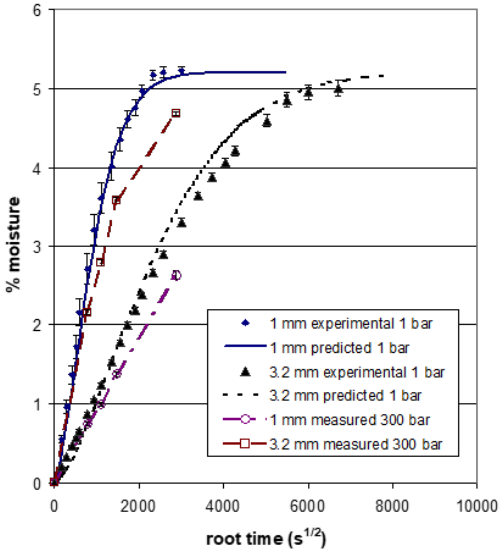

Figure 8. Measured and predicted (using Equation 10) moisture uptake at 23 °C, ambient pressure (1 bar) compared with measured moisture uptake at 23° C and 300 bar pressure

Measurements on pultruded glass-fibre reinforced polyester composite bars suggested that equilibrium moisture content could be achieved in a shorter time than at ambient pressure. Samples of the epoxy were immersed in deionised water within the autoclave. Pressure of 300 bar was applied and three 1mm and 3.2 mm thick specimens were conditioned at ambient temperature (23 °C). Owing to the time-consuming nature of the pressure and the repressurising process, samples were weighed on a weekly basis.

Figure 8 shows that moisture diffusion into the samples exposed at 300 bar is slower than for samples exposed at ambient pressure. It can be conjectured that the hydrostatic pressure may close micro voids in the sample and reduce sites and pathways for diffusion.

From these observations, it is evident that pressure may affect the diffusion of moisture into different materials in different ways. If diffusion rates under pressure are important then specific tests may need to be carried out in preference to assuming the same properties as at atmospheric pressure.

Chapter 5

Diffusion in multi-component systems

- Fibre-reinforced polymer composites
- Adhesive joints and coatings
- Multi-layer systems

Fibre-reinforced polymer composites

Diffusion in PMCs, particularly of water, has been studied extensively, with comprehensive coverage given by Springer [4, 5]. The mass transport properties will depend on the fibre material, the volume fraction of fibres and the fibre orientation. Glass and carbon fibres are normally considered to be impermeable. Transport in the direction of the fibres may be very different to that normal to the fibres. Capillary action along the fibres or the fibre resin interfaces can account for a significant proportion of initial moisture uptake. Shrinkage of the resin away from the fibres during curing could be a contributing factor to the capillary effect. Composite laminates, particularly multi-directional laminates may have a complex structure with permeation behaviour defined by a complex mixture of properties.

Diffusion in orientated fibre composite layers can be treated by a rule of mixtures approach. For a volume fraction of fibres V_f and a reasonable assumption that diffusion coefficients D_f in fibres are much less than the molecular diffusion coefficient in the polymer matrix D_m then the directional diffusion coefficients D_{11} (longitudinal) and D_{22} (transverse) can be expressed [4-5]:

$$D_{11} = (1 - V_f)D_m \tag{13}$$

$$D_{22} = \left(1 - 2\sqrt{\frac{V_f}{\pi}}\right)D_m \tag{14}$$

The diffusion coefficient for a composite is given by the following relationship [4-5]:

$$D = D_x\left(1 + \frac{h}{l}\sqrt{\frac{D_y}{D_x}} + \frac{h}{b}\sqrt{\frac{D_z}{D_x}}\right)^2 \tag{15}$$

D_x, D_y and D_z are diffusivities through the thickness, along the length and across the width of the material.

In most assessments of moisture distributions in composites, the fibres are assumed to be impermeable to moisture. Therefore, all of the water must be contained either within the matrix or bound at the fibre-matrix interface [5]. This may be applicable for glass or carbon fibres but is very unlikely to apply to natural fibres or polymer fibre reinforcements.

Adhesive joints and coatings

Diffusion in adhesive joints is often done by casting bulk sheets of adhesive and determining the diffusion properties of the bulk adhesive. These values are then used with a model [e.g., 1, 18] to predict moisture uptake into the joint. If the adherends are also permeable (e.g., composites) then their diffusion properties should be obtained and included in the model. This approach relies on:

- The bulk adhesive having the same properties as the adhesive in the joint; and
- The adhesive-adherend interface playing no role in moisture absorption and transport.

It is well established that the properties of materials near the interface, the so-called interphase, differ from those of the bulk material. Therefore, the diffusion properties in the interfacial region may not be the same as the bulk material. Few studies comparing bulk adhesive and adhesive joint diffusion have been reported. Bond et al. [20] determined diffusion coefficients for an epoxy adhesive as being 6.4 × 10-13 m^2s^{-1} when obtained from mass measurements on bulk adhesive specimens and 6.7 × 10-12 m^2s^{-1} when determined from measurements of weight gain in lap joints (1 mm thick grit blasted stainless steel adherends). These results suggest a significant contribution from the interface to diffusion. It is well recognised that diffusion of chemicals to the interface in a bond degrades bond performance [18, 20-24].

In the assessment of moisture absorption into adhesive joints the following points should be considered:

- The mass of the adherends needs to be subtracted to determine the mass of the adhesive layer - this will introduce additional uncertainties in the mass results.
- Metal adherends are likely to have significantly higher masses than the adhesive layer of interest. The total mass of the system may require that a larger capacity balance, possibly with lower resolution, be used.
- Any absorption of moisture into the adherends will contribute to measured mass gains. Traveller adherend specimens can be exposed to assess this and corrections made to calculate the moisture concentration in the adhesive layer. However, this correction will increase the uncertainty in the mass gain in the adhesive. Uncertainties can become very significant if the mass of moisture absorbed in the adherends is greater than the mass absorbed in the adhesives.
- Metallic adherends may corrode when exposed to moisture. Traveller samples can be used to determine corrections for any resulting gain in mass (or better to confirm the absence of corrosion). Uncertainties will increase due to these corrections. Traveller specimens may not detect all of the corrosion occurring in an adhesive joint. Corrosion has been observed located under adhesive bonds but not on the exposed surfaces of the same metallic adhesives [24], suggesting that chemical or stress conditions at the

interface promote corrosion. It is recommended that exposed specimens used for uptake measurements should be separated and their surfaces examined.

- Adsorption in joints is mainly through the edges and the resulting long diffusion path lengths to the centre of the joint mean that the time to reach saturation may be extremely high.
- If all edges are available for absorption then there is a two-dimensional diffusion situation. The analysis approach outlined in Chapter 3 is not appropriate and a much more complex analysis procedure is needed to calculate diffusion coefficients. A simpler approach might be to seal off two (opposite) edges leaving a one-dimensional diffusion situation.

Multi-layer systems

Overall absorption into multi-layer systems can be measured using the same methods that are used for homogeneous, isotropic systems. The measurements will produce an average saturation value and diffusion coefficient. Obtaining data on individual layers in a multi-layer system is difficult. Each layer will have a different saturation concentration and diffusion coefficient. Layer thickness may be extremely difficult to measure, particularly in very thin films.

In steady state moisture permeation measurements [1,10-13], where there is a high concentration on one side of the film and low concentration on the other (e.g., liquid and air), a constant flux per unit concentration gradient across the film occurs when boundary conditions are fixed and the moisture concentration within the membrane is in equilibrium.

Figure 9 shows, schematically, one-dimensional diffusion in a multi-layer system.

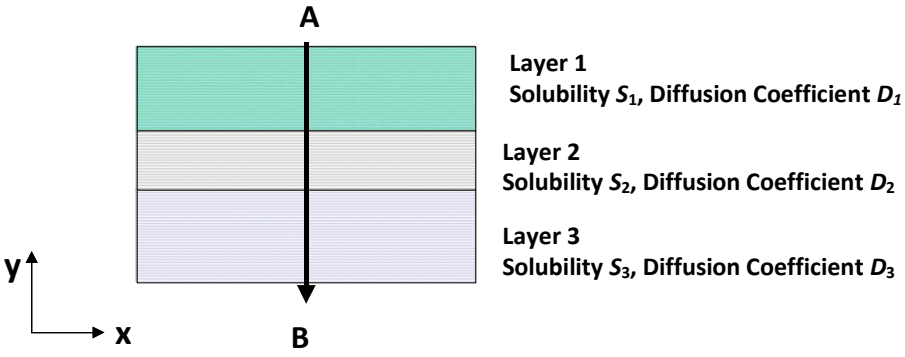

Figure 9. One-dimensional diffusion through a multi-layer system

For a layer of total thickness *L*, at constant temperature and gas concentrations ϕ_1 and ϕ_2 at *A* and *B*, respectively (assuming $\phi_1 > \phi_2$) then Equation 1 can be integrated across the thickness using an average diffusion coefficient D to give permeation rate or permeability:

$$\frac{dQ}{dt} = D\frac{\phi_1 - \phi_2}{L} \tag{16}$$

When one side is in contact with liquid then ϕ_1 is the saturation concentration of the material in contact with the liquid.

In laminated systems, the total permeability of a multi-layer system Q_L with *n* layers can be calculated from the series permeation 'resistance' of each layer and expressed as a sum of the diffusion coefficients D_i and thickness x_i of all of the layers.

$$\frac{1}{Q_L} = \frac{1}{L}\sum_{j=1}^{n}\frac{x_i}{D_i} \tag{17}$$

In cases where the diffusion coefficients of only one of the layers is unknown, then Equation 17 can be used to calculate the diffusion coefficient of the unknown layer.

Determining saturation concentrations of internal layers presents a problem. In the onedimensional diffusion situation illustrated in Figure 9 the moisture concentration in any layer can never exceed the saturation concentration of the preceding layer(s), since diffusion requires a concentration gradient. If both surfaces are exposed then the concentration in internal layers can never exceed those of the layers outside of them.

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Chapter 6

Estimating uncertainties in diffusion coefficients

- Estimating uncertainties
- Uncertainty in specimen dimensions
- Uncertainty in elapsed time
- Uncertainty in moisture concentration
- Exposure temperature
- Material variability
- Changes occurring post material manufacture
- Example uncertainty calculations

Estimating uncertainties

Uncertainties in measurements should be combined according to the methods described in UKAS M3003 [25]. The significance of uncertainties ΔV in the different measured values V used to calculate the diffusion coefficient can be examined by using the expanded uncertainties from Equation 7 and the simplifying assumption that t_1 is zero:

$$\left(\frac{\Delta D}{D}\right)^2 = 2x\left[\left(\frac{\Delta h}{h}\right)^2 + \left(\frac{\Delta C_s}{C_s}\right)^2 + \left(\frac{\Delta(C(t_2) - C(t_1))}{(C(t_2) - C(t_1))}\right)^2 + 0.5x\left(\frac{\Delta t_2}{t_2}\right)^2\right] \qquad (18)$$

Uncertainties will arise from:

- Calibration and resolution uncertainties of the measurement instruments;
- Variations in test procedure (repeatability and reproducibility); and
- Sample variability

Normal distributions are assumed in these calculations, implying a coverage factor of 2 should be used.

Uncertainty in specimen dimensions

The accuracy of the thickness measurement is the most important of the dimensions in determining diffusion coefficients. Uncertainty in sample thickness h arises from two sources.

Resolution and calibration of thickness measuring device:- measurements should be made using instruments such as callipers and micrometers with sufficient accuracy so that this uncertainty is low relative to the measurement. Devices with a resolution of 0.01 mm contribute a relative uncertainty of ± 0.5% for a 1 mm thick specimen, likely to be acceptable for most measurements. Higher resolution instruments are recommended for thinner specimens.

Variations of sample thickness:- samples should have uniform thickness for accurate determination of diffusion coefficients. Thickness should be measured and recorded at several locations on the sample (both at the edges and centre). A minimum of five locations is recommended but if the maximum and minimum readings differ significantly (e.g., by more than 3-5%) then additional measurements should be made. The mean and standard deviation of the thickness should be determined. If the standard deviation in the measurements is high then this will have a significant effect on the overall uncertainty and further preparation (including polishing) should be considered to reduce the thickness variations.

Uncertainties in the other dimensions contribute to the overall uncertainty budget through the correction for edges (Equation 11). The uncertainty in the edge correction factor E can be calculated as:

$$\Delta E^2 = 2x\left(\left[\left(\frac{\Delta h}{h}\right)^2 + \left(\frac{\Delta l}{l}\right)^2\right]\left(\frac{h}{l}\right)^2 + \left[\left(\frac{\Delta h}{h}\right)^2 + \left(\frac{\Delta b}{b}\right)^2\right]\left(\frac{h}{b}\right)^2\right) \quad (19)$$

For example, for square plaques (with sides l = b = 50 ± 1 mm) with thicknesses of 1 ± 0.05 mm and 3.2 ± 0.1 mm the correction factors are 0.925 ± 0.003 and 0.786 ± 0.007, respectively.

Uncertainty in elapsed time

Since the samples are typically exposed over periods of days or weeks the accuracy and resolution required of time measurement is not critical. Recording the date and time of the start of the exposure and each measurement should be sufficient. There will be some uncertainty due to the periods when the sample is removed from exposure for the purposes of mass measurements. Since this period is unlikely to be more than 15 minutes and measurements are unlikely to be made more often than daily then the relative uncertainty in elapsed time is unlikely to exceed 1%. Records should be made of the time at which the sample is measured and returned to the exposure and elapsed time can be calculated to omit these periods.

Where measurements are made with less than 24 hours of exposure the uncertainty in time measurement may become more significant. In such measurements, it is advisable to use a stopwatch for time measurements and to ensure that the time that the sample is taken out of exposure for measurement is minimised (e.g., a minute or less). A 15 minute uncertainty in an 8 hour exposure leads to a relative uncertainty of 3%.

For most exposures, the uncertainty in the time measurement is negligible and can be ignored in the uncertainty estimation.

Uncertainty in moisture concentration

Uncertainties in the mass measurement lead to uncertainties in the concentration gain, $C(t_2)C(t_1)$, and the saturation concentration, C_s, terms. In most cases $C(t_1)$ is zero and $M(t_1)$ is the dry mass of the sample. Concentration $C(t)$ is defined in Equation 4 from the measured mass gain divided by the dry mass. The uncertainties in concentrations (both $C(t)$ and C_s) are defined from the uncertainties in the mass measurements. The uncertainty in the mass gain is expressed:

$$\Delta(M(t_2) - M(t_1))^2 = \Delta\big(M(t_1)\big)^2 + \Delta\big(M(t_2)\big)^2 \quad (20)$$

Resolution of the weighing balance: Provided a sufficiently sensitive balance is used then the uncertainty in concentration due to the resolution of the balance is only likely to be significant for very small changes in concentration.

For example if the balance has a resolution of 0.1mg then the resolution uncertainty in mass ΔM is taken as 0.05 mg. Equation 20 then produces an uncertainty of 0.071 mg in the mass gain. If a sample with an initial dry mass of 2.5 g gains 0.1% moisture then the relative uncertainty in the 2.5 mg mass change is 2.8%. At 1% moisture absorption this reduces to 0.28% uncertainty in the 25 mg mass gain. The uncertainty in the dry mass measurement is negligible in this case (0.05 mg in 2500 mg) and can be ignored in determining the uncertainty in concentration.

The significance of the resolution uncertainties is minimised if:

- The resolution of the balance is much smaller than the mass changes.
- A specimen with a large area is used to increase the mass of polymer and, thence, the size of the mass gain for a given concentration.
- Specimens are sufficiently thick - reducing the thickness will reduce the mass of material and hence the mass of moisture absorbed.
- Moisture absorption is high.

Measurement repeatability: Since the moisture content in the samples are continually changing whether in or out of the exposure medium, assessing repeatability of mass measurement of the samples is not recommended. Replicate specimens should be exposed under the same conditions and measured after the same exposure durations to assess repeatability in measured concentrations. The standard deviation in the measurements should be included in the uncertainty budget.

If the repeatability (or reproducibility between operators) of the weighing process is considered to be a concern then this should be assessed through repeat measurements using an unchanging specimen with similar mass and dimensions to the exposed specimens. A sample that has been left to achieve equilibrium in the weighing laboratory is ideal for this purpose.

Procedural variations: Factors such as the drying of specimen surfaces and time between removing the sample from exposure and weighing will lead to reproducibility uncertainties in the results. All surface moisture must be removed prior to weighing since it would lead to an overestimate of absorbed moisture concentration. Moisture will desorb from dried surfaces into the atmosphere, leading to diffusion of moisture from the sample. The rate of moisture loss will depend on the concentration of moisture in the sample and the diffusion properties of the material. Therefore, the procedure used for each weighing should be as consistent as possible. The importance of the procedure and procedural variations may differ appreciably between materials.

For example, the epoxy adhesive studied had a smooth, flat and poorly wetted surface that became dry to the touch (with no noticeable residual moisture transfer to the cloth) after brief wiping. Consequently, the weighings could be carried out within a controllable, short period of time and the resulting scatter in absorption between different samples were small (typically less than ±3% of the measurement).

However, in another example, it proved very difficult to obtain reliable uptake measurements for bulk plaque samples prepared with different numbers of plies of a film adhesive, Figure 10. These samples had rough textured surfaces and appeared to be well wetted by water. It took considerably longer to dry the surfaces of the samples (i.e. until no transfer to the drying cloth was observed). Figure 11 illustrates possible variations in 'moisture concentration' that could occur from the drying and weighing process. Two samples were weighed at variable time intervals after removal from the water. A point is indicated on each of the two curves when it was considered that all surface moisture had been removed – this is the value used as the concentration in the moisture absorption measurement. However, it is clear that the mass of the sample is changing rapidly during this period and there must be a large uncertainty in this value.

As a result of this, the moisture uptake curves were noisy and there was considerable scatter between specimens, as shown in Figure 10. The standard deviations in the concentration measurements were typically between 10-20%. The diffusion coefficients calculated differed considerably, with a factor of 10 between the values for 1 ply and 4 ply samples, Table 4. Some of that difference may reflect real differences between the samples.

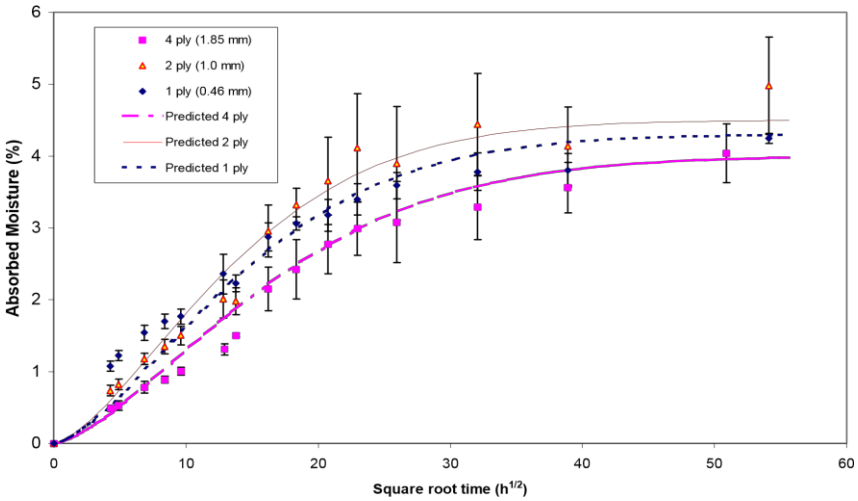

Figure 10. Moisture absorption curves obtained for film adhesive samples
(predicted curves were generated using Equation 10 and the data in Table 4)

Number of Plies	Thickness (mm)	C_s (%)	D_a (m^2s^{-1})
1	0.46	4.3	1.5×10^{-14}
2	1.00	4.5	8.1×10^{-14}
4	1.85	4.0	1.9×10^{-13}
Average	-	4.3 ± 0.3	$1.0 \pm 0.9 \times 10^{-13}$

Table 4. Diffusion parameters determined from Figure 10

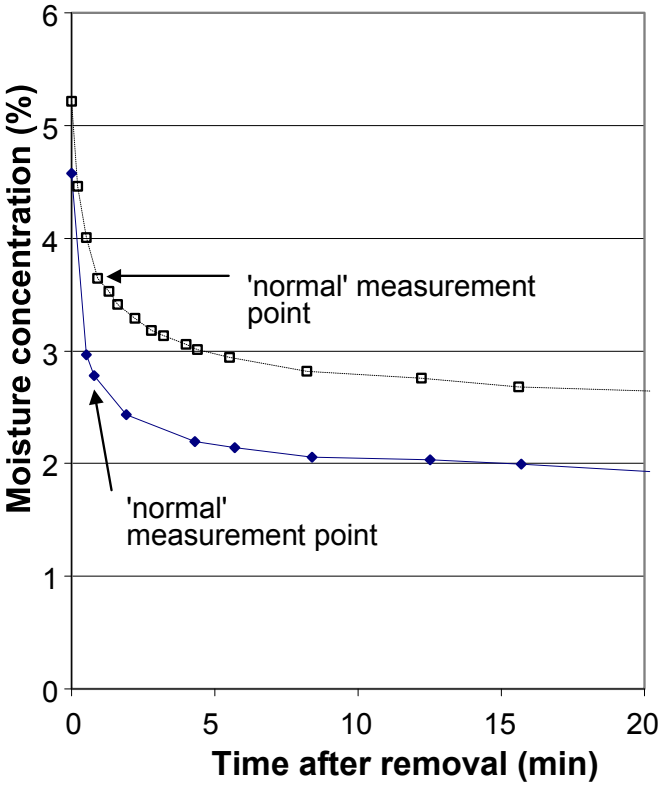

Figure 11. Effect of time out of exposure and drying on measured moisture concentrations

Exposure temperature

The saturation concentrations and diffusion coefficients of polymeric materials are sensitive to temperature. Table 3 shows that the diffusion coefficient of the example epoxy studied increases by a factor of ca. 40 on increasing the temperature from 23 °C to 64 °C. Therefore, as Table 5 shows, even relatively small differences between exposure temperatures can have a significant effect on the diffusion coefficient.

Therefore, it is good practice to maintain and monitor the exposure temperature, using accurate and calibrated instruments, throughout the measurements.

Temperature (°C)	Predicted D_x (m^2s^{-1})	Variation of D_x (% of 23° C Value)
21	6.33×10^{-12}	81.9
22	7.22×10^{-14}	90.5
22.5	7.59×10^{-14}	95.1
23	7.98×10^{-14}	100
23.5	8.38×10^{-14}	105
24	8.81×10^{-14}	110
25	9.72×10^{-14}	122

Table 5. Variation of predicted diffusion coefficient with small temperature changes (D_x predicted from Figure 3)

Material variability

In order to produce relevant information the samples used to assess diffusion behaviour should have the same properties as the materials in the components and structures for which the data will be used. The properties of polymeric materials are affected by the way they have been processed. When the samples are taken from directly from the component of interest and tested, then there should be little concern about the reliability of the results. However, many samples will be manufactured specifically for testing, often using a different process than the components of ultimate interest.

Factors that should be taken into consideration when deciding whether a sample is representative of a component or structure include:

- Composition – same material (including grade of polymer, type and proportion of filler/fibre, toughening agents, processing agents, etc.);
- Lay-up (e.g., for composite laminates or multi-layer films);
- State of cure;
- Degree of crystallinity;
- Processing conditions; and
- Extent of defects including delaminations and voids.

One example where processing conditions could have a significant effect on properties is in the state of cure of thermosetting polymers (including composites). The state of cure can vary within materials (particularly in thick sections where the centre may not reach as high a temperature as the exterior, or may exceed the exterior temperature if large amounts of heat are generated by exothermic reactions) or between samples, particularly if thicknesses differ.

Thin specimens are often preferred for diffusion studies as saturation will be reached much sooner than in thick sections, but there is a danger that the cure state in the thin sections may not match those of the thick sections leading to results of dubious relevance.

For example, Figure 12 shows moisture absorption in two samples of 2-ply film adhesive that were cured under different conditions. One sample (Sample 1) was cured for 20 minutes in an oven preheated at 165 °C. This sample reached 165 °C, as measured by a thermocouple embedded in the mould, towards the end of the sure period. The other sample (Sample 2) was left to continue curing for a further 20 minutes, giving a total of 40 minutes in the oven at 165 °C. The manufacturer's data sheet specified curing for 15 minutes at 165 °C, which is unclear whether the time refers to total time (including heating) or the time that the specimen is actually at the cure temperature (excluding heating). Glass transition temperature T_g for samples cured under both conditions were determined using DSC (differential scanning calorimetry [26]). T_g was 84 °C for sample 1 cured for the shorter time period and 90 °C for sample 2 cured for the longer period. Second and third DSC runs on the samples were carried out and Tg for each sample reached 96 °C, suggesting that neither sample was fully cured.

At equivalent exposure times, there is approximately twice as much moisture absorbed into the sample 1 than into sample 2. It is also apparent that the two samples will have significantly different saturation levels. These major differences exist despite what could be seen as fairly minor differences in cure state.

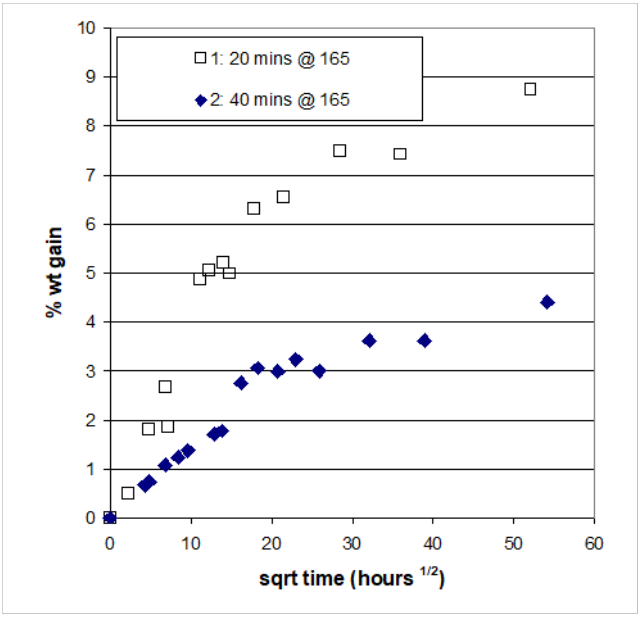

Figure 12. Effect of cure conditions on moisture absorption

Changes occurring post material manufacture

Post-curing: The curing process that occurs when manufacturing components from polymers that cross-link through cure reactions (e.g., thermosets, may not fully cure the materials). Therefore, polymers may continue to cure post manufacture, changing their moisture absorption properties, potentially very significantly (e.g., as indicated in Figure 12). This is more likely to occur where the material is kept or exposed at temperatures at or above its glass transition temperature (where higher molecular mobility makes interaction of unreacted groups more likely). For example:

- Room temperature cured systems, e.g., adhesives, will continue to cure slowly after the material is nominally 'cured' (in practice having reached a sufficient state of mechanical performance).
- Elevated temperature cured systems exposed to elevated temperatures.

Curing can be completed through a deliberate post cure, e.g., heating the material significantly above T_g for sufficient time to ensure completion of reactions. Completeness of cure can be checked by thermal analysis methods [26].

Physical ageing: The structure of polymers continues to evolve through molecular relaxation and realignments after completion of the component 'manufacture' in a process known as physical ageing. Thus, the mobility of polymer chains decreases with time after high temperature processing until an equilibrium structure is obtained. These structural changes are influenced by many factors, including stress and temperature. The moisture absorption kinetics of polymer systems will change with physical ageing and, therefore, it is advisable to compare results from samples having the same physical age. Materials can be 'de-aged' by heating them above their glass transition temperature for a short period of time, typically an hour.

Glass transition temperature (T_g): The properties of the polymeric material will also change with chemical ageing. For example, the T_g for a typical polyester resin will decrease by ~15-20 °C for a 2% moisture weight gain and reduced for the example epoxy by ~5 °C for a similar moisture gain. Figure 13 shows the effect of moisture content on T_g for a glass reinforced epoxy that was immersed in distilled/deionised water for prolonged periods of time at three different temperatures [27]. This reduction in T_g is induced by plasticisation (softening) of the polymer matrix and in some cases by loss of organic additives through leaching to the surrounding media.

Long periods of exposure to moisture at elevated temperatures could lead to phase changes in the polymer (e.g., a glass to rubber transition) and moisture absorption and/or transport processes not relevant to lower temperature exposure may occur. Physical ageing and stress may increase the potential for phase changes occurring during exposure. Therefore, it is advisable, when using elevated temperatures to accelerate moisture uptake, to ensure that the maximum operating temperature is below the T_g of the material (e.g., at least 30-40 °C, taking into account moisture effects).

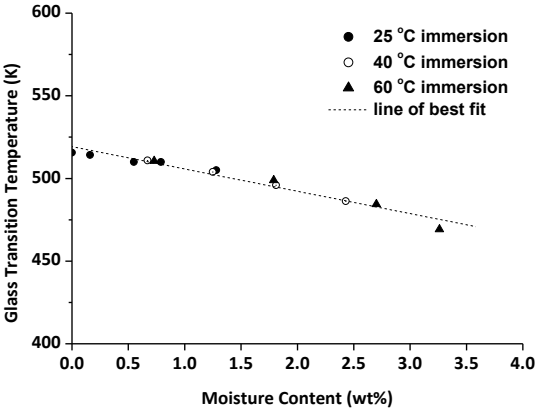

Figure 13. Glass transition temperature of F922 epoxy as a function of moisture content

Combined effects: Exposure of polymeric materials to moisture, elevated temperature, physical ageing and stress may lead to behaviour that cannot be predicted from less complex situations. In Chapter 5, samples exposed at room temperature and elevated pressure absorbed moisture more slowly than materials exposed at atmospheric pressure. However, when the temperature was increased to 64 °C (Figure 14), moisture concentrations under high pressures were found to be considerably higher than the saturation concentrations obtained at atmospheric pressure. The predicted curves in Figure 14 were calculated from Equation 10 and data in Table 3.

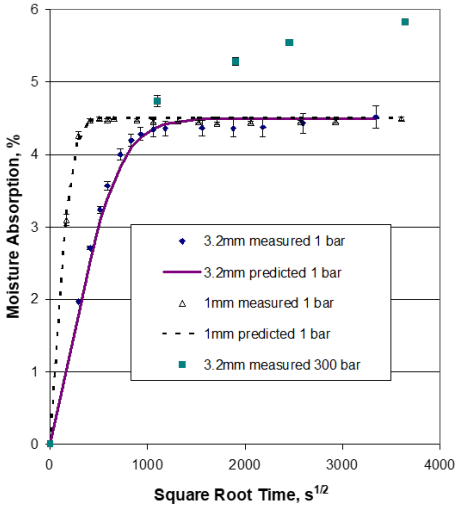

Figure 14. Measured and predicted moisture uptake at 64 °C, ambient pressure (1 bar) compared with measured moisture uptake at 64° C and 300 bar pressure

In addition to the high pressure the test specimens were several months older than the atmospheric test specimens, having been prepared at the same time but not tested until significantly later. It is possible that the moisture and elevated temperature combined with the physical ageing and high pressure to cause phase changes not occurring in younger and unstressed materials.

Example uncertainty calculations

As an example, the calculation of the diffusion coefficient for a 1 mm thick sample of the rubber toughened epoxy exposed at 23 ± 2 °C is used in conjunction with Equation 18 (see below).

$$\left(\frac{\Delta D}{D}\right)^2 = 2x\left[\left(\frac{\Delta h}{h}\right)^2 + \left(\frac{\Delta C_s}{C_s}\right)^2 + \left(\frac{\Delta(C(t_2) - C(t_1))}{(C(t_2) - C(t_1))}\right)^2 + 0.5x\left(\frac{\Delta t_2}{t_2}\right)^2\right]$$

Calculated D_a = 6.89 × 10^{-14} m^2s^{-1} (Table 3)

Sample plaque (dimensions): l = b = 50 ± 1 mm; h = 1.0 ± 0.05 mm

Dimensions measured using digital callipers with resolution 0.01 mm, which is insignificant compared with the variability in dimensions, i.e.:

$$\Delta l = \Delta b = \pm\sqrt{1^2 + 0.005^2} \approx \pm\ 1.0$$

$$\Delta h = \pm\sqrt{0.05^2 + 0.005^2} \approx \pm\ 0.05$$

$$\frac{\Delta h}{h} = 0.05$$

C_s was 5.20% with a standard deviation of ± 0.07%; t_2 was 393 ± 3 hours; $C(t_2)$ was 3.61% with a standard deviation of ± 0.19%

M_0 was 3.055 g; mass gain at t_2 was 0.110 ± 0.005 g, and mass gain at saturation was 0.1595 ± 0.0008 g.

Balance resolution = 0.1 mg which, when used in Equation 20 to calculate uncertainties in the mass gain, is insignificant compared with the variability in mass gain measurements and ignored.

Although $C(t_1)$ was taken to be zero, a standard deviation in $C(t_1)$ of ± 0.07% was assumed, the same as the standard deviation in the saturation value. This was included to account for possible variability in the 'dry' state (which may arise from the drying time being insignificant to ensure complete drying and the possible the pick up of moisture from the atmosphere before the first weighing).

Thus:

$$\Delta\big(C(t_2) - C(t_1)\big) = \sqrt{0.19^2 + 0.07^2} = 0.20, \quad \frac{\Delta\big(C(t_2) - C(t_1)\big)}{\big(C(t_2) - C(t_1)\big)} = 0.055$$

$$\frac{\Delta D_a}{D_a} = \sqrt{2x[(0.05)^2 + (0.019)^2 + (0.055)^2 + 0.5x(0.0076)^2]} = 0.109$$

$$\frac{\Delta t_2}{t_2} = 0.0076$$

Therefore, excluding temperature uncertainty, the uncertainty in Da can be calculated from Equation 17:

$$\frac{\Delta D_a}{D_a} = \sqrt{2x[(0.05)^2 + (0.019)^2 + (0.055)^2 + 0.5x(0.0076)^2]} = 0.109$$

Assuming a coverage factor of 2 then the uncertainty in the value of D_a is 21.8%, thus the value of D_a (taking the uncertainty into account) is **6.9 ± 1 .5x10^{-14} m^{2}s^{-1}**.

The uncertainty in D_x is of a similar order, as the uncertainty in the correction factor is negligible.

The uncertainty due to temperature can be included using the data presented in Table 5. A ± 2 °C difference in temperature causes a maximum of 22% in the value for *D* at a temperature of 23 °C. This can be combined with the calculated uncertainty in D_a (10.9%) using the squaring and adding process (and applying a coverage factor of 2) to yield an estimated uncertainty in the value of D at 23 °C of:

$$\frac{\Delta D(T = 23)}{D(T = 23)} = 2x\sqrt{0.109^2 + 0.22^2} = 0.49$$

Therefore, the value of D_a at 23 °C is **6.9 ± 3.4 ×1 0^{-14} m^{2}s^{-1}**.

In this case the uncertainty could be considerably reduced by tighter control of the exposure temperature. A temperature tolerance of ± 1 °C reduces the relative uncertainty to 0.3, i.e., D_a = 6.9 ± 2.1 × 10^{-14} m^{2}s^{-1} and a temperature tolerance of ± 0.5 °C reduces the relative uncertainty to 0.24 (Da = 6.9 ± 1.7 × 10^{-14} m^{2}s^{-1}), which is little more than the uncertainty due to the non-temperature factors.

Chapter 7

Conclusions

- Key points
- Concluding remarks

Key points

The measurement of moisture absorption and diffusion is, in principle, straightforward to carry out. It requires only the capability to manufacture representative specimens to the required tolerances, measure their dimensions to the required accuracy and make mass measurements at the required time intervals. However, there are several key points to recognise when making measurements.

- **Variations in sample processing** can cause large differences in moisture absorption and diffusion behaviour.
- **Replicate samples** should be tested to improve the reliability of the results and provide some indication of the effects of procedural and material variations.
- The **sample thickness** is the specimen dimension that should be controlled most carefully to minimise uncertainties.
- The **weighing procedure**, and in particular the period the sample is dried for after being taken from exposure, can lead to significant variability in results.
- It is much more difficult to remove all the surface moisture from samples with textured surfaces than from smooth samples. Thus **surface texture** of samples should be controlled.
- Diffusion in polymers depends on **temperature** and any variation in temperature is likely to have significant influence on the accuracy of the results. Temperatures should be controlled and monitored within appropriate tolerances to ensure accuracy: within ± 0.5 °C is recommended.
- The molecular structure of polymers reorganises following processing and the properties will be **time-dependent** to some extent. Ageing of polymers, especially when combined with elevated temperature and/or stress, may lead to unexpected changes in behaviour.

Concluding remarks

The use of simple gravimetric techniques and a one-dimensional Fickian analysis for determining moisture and diffusion have been described. Reasonable accuracy can be obtained provided that good quality samples are available and the procedures outlined in this guide are followed.

Standards

ISO Standards

Plastics

Permeation

ISO 2528	Sheet Materials — Determination of Water Vapour Transmission Rate (WVTR) - Gravimetric (Dish) Method.
ISO 7783-1	Paints and Varnishes - Determination of Water-Vapour Transmission Rate - Part 1: Dish Method for Free Films.

Effects of liquids

ISO 62	Plastics – Determination of Water Absorption.
ISO 175	Plastics - Determining the Effect of Liquid Chemical Including Water.
ISO 483	Plastics - Small Enclosures for Conditioning and Testing Using aqueous Solutions to Maintain Relative Humidity at Constant Value.
ISO 4611	Plastics - Determination of the Effect of Exposure to Damp Heat, Water Spray and Salt.

Thermal degradation

ISO 176	Plastics - Determination of Loss of Plasticizers — Activated Carbon Method.
ISO 177	Plastics - Determination of Migration of Plasticizers.
ISO 291	Plastics - Standard Atmospheres for Conditioning and Testing.
ISO 305	Determination of Thermal Stability of Polyvinyl Chloride Related Chlorine Containing Polymers, and their Compounds - Discoloration Method.
ISO 554	Standard Atmospheres for Conditioning and/or Testing - Specification.
ISO 1137	Plastics: Determination of Behaviour in a Ventilated Tubular Oven.
ISO 2578	Plastics: Determination of Time/Temperature Limits after Exposure to Prolonged Action of Heat.

Environmental stress cracking (ESC)

ISO 4599	Plastics: Determination of Time/Temperature Limits after Exposure to Prolonged Action of Heat Plastics - Determination of Resistance to Environmental Stress Cracking (ESC) - Bent Strip Method.
ISO 4600	Plastics - Determination of Environmental Stress Cracking (ESC) - Ball and Pin.

ISO 6252 Plastics - Determination of Resistance to Environmental Stress Cracking (ESC) - Constant Tensile Stress Method.

ISO 16770 Plastics - Determination of Environmental Stress Cracking (ESC) of Polyethylene - Full-Notch Creep Test (FNCT).

ISO 22088-5 Plastics - Determination of Resistance to Environmental Stress Cracking (ESC) - Part 5: Constant Tensile Deformation Method.

ISO 22088-6 Plastics - Determination of Resistance to Environmental Stress Cracking (ESC) - Part 6: Slow Strain Rate Method.

Weathering

ISO 877 Plastics - Determination of Resistance to Change upon Exposure under Glass to Daylight.

ISO 2579 Plastics - Instrumental Evaluation of Colour Differences.

ISO 3577 Plastics - Recommended Practice for Spectrophotometry and Calculation of Colour in CIE Systems.

ISO 3558 Plastics - Assessment of the Colour of Near-White or Near-Colourless Materials.

ISO 4582 Plastics - Determination of Changes in Colour and Variations in Properties and Exposure to Daylight under Glass, Natural Weathering or Laboratory Light Sources.

ISO 4607 Plastics - Methods of Exposure to Natural Weathering.

ISO 4892 Plastics - Methods of Exposure to Laboratory Light Sources.

ISO 9370 Guide for the Iinstrumental Determination of Radiant Exposure in Weathering Tests.

ISO TR 9673 Solar Radiation and Its Measurements for Determining Outdoor Weather Exposure Levels.

ISO 11403-3 Plastics - Acquisition and Presentation of Comparable Multipoint Data - Part 3: Environmental Influences on Properties.

Biological attack

ISO 846 Plastics — Evaluation of the Action of Microorganisms.

Mechanical (Creep)

ISO 899-1 Plastics - Determination of Creep Behaviour - Part 1: Tensile Creep.

ISO 899-2 Plastics - Determination of Creep Behaviour - Part 2: Flexural Creep by Three-Point Loading.

Rubbers

Thermal degradation

ISO 188 Rubber, Vulcanized or Thermoplastic - Accelerated Ageing and Heat Resistance Tests.

ISO 6914 Rubber, Vulcanized or Thermoplastic - Determination of Ageing Characteristics by Measurement of Stress Relaxation in Tension.

Effect of liquids

ISO 1817 Rubber, Vulcanized or Thermoplastic - Determination of the Effect of Liquids.

Weathering

ISO 4665-1 Assessment of Change in Properties after Exposure to Natural Weathering or Artificial Light.

ISO 4665-2 Methods of Exposure to Natural Weathering.

ISO 4665-3 Methods of Exposure to Artificial Weathering.

Effect of ozone

ISO 1431-1 Resistance of Ozone Cracking - Static Strain Test

ISO 1431-2 Resistance to Ozone Cracking - Dynamic Strain Test.

ISO 1431 -3 Determination of Ozone Concentration.

Biological degradation

ISO 846 Determination of Behaviour under the Action of Fungi and Bacteria - Evaluation by Visual Examination or Measurement of Change in Mass or Physical Properties.

Mechanical (stress relaxation in compression)

ISO 3384 Determination of Stress Relaxation in Compression at Normal and High Temperatures.

ISO 6056 Determination of Compression Stress Relaxation (Rings).

Composites

ISO 75-3 Plastics - Determination of Temperature of Deflection Under Load. Part 3: High-Strength Thermosetting Laminates and Long-Fibre-Reinforced plastics.

ISO 13003 Fibre-Reinforced Plastics - Determination of Fatigue Properties under Cyclic Loading Conditions.

ISO 21746 Composites and Metal Assemblies - Galvanic Corrosion Tests of Carbon Fibre Reinforced Plastics (CFRPs) Related Bonded or Fastened Structures in Artificial Atmospheres - Salt Spray Tests.

ISO 22836 Fibre-Reinforced Composites - Method for Accelerated Moisture Absorption and Supersaturated Conditioning by Moisture Using Sealed Pressure Vessel.

Note: *The standards listed in this section refer specifically to fibre-reinforced composites. More general standards covering both plastics and composites are given in the section on ISO plastic related standards.*

Adhesives

ISO 9142 Adhesives - Guide to the Selection of Standard Laboratory Ageing Conditions for Testing Bonded Joints.

ISO 9664 Test Methods for Fatigue Properties of Structural Adhesives in Tensile Shear.

ISO 10354 Adhesives - Characterisation of Durability of Structural Adhesive Assemblies - Wedge Rupture Test.

ISO 10363 Hot Melt adhesives - Determination of Thermal Stability.

ISO 14615 Adhesives - Durability of Structural Adhesive Joints - Exposure to Humidity and Temperature under Load.

BSI and EN Standards

Composites

BS EN 2378 Fibre Reinforced Plastics - Determination of Water Absorption by Immersion in Demineralised Water.

BS EN 2489 Fibre reinforced Plastics - Determination of the Action of Liquid Chemicals.

BS EN 2823 Fibre Reinforced Plastics - Determination of the Effect of Exposure to Humid Atmosphere on Physical and Mechanical Characteristics.

ASTM Standards

Plastics

Permeation

ASTM E96 Water Vapor Transmission Standard Test Methods.

ASTM D1653 Standard Test Methods for Water Vapor Transmission of Organic Coating Films.

Thermal degradation

ASTM D1203 Standard Test Methods for Volatile Loss From Plastics Using Activated Carbon Methods.

ASTM D2115 Standard Practice for Oven Heat Stability of Poly (Vinyl Chloride) Compositions.

ASTM D3045 Standard Practice for Heat Aging of Plastics Without Load.

Effects of liquids

ASTM D543 Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents.

ASTM D570 Standard Test Method for Water Absorption of Plastics.

ASTM D1712 Standard Practice for Resistance of Plastics to Sulfide Staining.

Environmental stress cracking (ESC)

ASTM D1693 Standard Test Method for Environmental Stress-Cracking of Ethylene Plastics.

ASTM F1248 Standard Test Method for Determination of Environmental Stress Crack Resistance (ESCR) of Polyethylene Pipe.

Weathering

ASTM D1435 Standard Practice for Outdoor Weathering of Plastics.

ASTM D1499 Standard Practice Filtered Open-Flame Carbon-Arc Type Exposures of Plastics.

ASTM D2565 Standard Practice for Xenon Arc Exposure of Plastics Intended for Outdoor Applications.

ASTM D4329 Standard Practice for Fluorescent UV Exposure of Plastics.

ASTM D4364 Standard Practice for Performing Outdoor Accelerated Weathering Tests of Plastics Using Concentrated Sunlight.

ASTM G24 Standard Practice for Conducting Exposures to Daylight Filtered Through Glass.

ASTM G156 Standard Practice for Selecting and Characterizing Weathering Reference Materials Used to Monitor Consistency of Conditions in an Exposure Test.

ASTM G178 Standard Practice for Determining the Activation Spectrum of a Material (Wavelength Sensitivity to an Exposure Source) Using the Sharp Cut-On Filter or Spectrographic Technique.

Biological attack

ASTM G21 Standard Practice for Determining Resistance of Synthetic Polymeric Materials to Fungi.

Creep

ASTM D2990 Standard Test Methods for Tensile, Compressive, and Flexural Creep and Creep-Rupture of Plastics.

Rubber

Thermal degradation

ASTM D454 Standard Test Method for Rubber Deterioration by Heat and Air Pressure.

ASTM D572 Standard Test Method for Rubber—Deterioration by Heat and Oxygen.

ASTM D573 Standard Test Method for Rubber—Deterioration in an Air Oven.

ASTM D865 Standard Test Method for Rubber-Deterioration by Heating in Air (Test Tube Enclosure).

Effects of liquids

ASTM D471 Standard Test Method for Rubber Property-Effect of Liquids.

ASTM D1460 Standard Test Method for Rubber Property-Change in Length During Liquid Immersion.

ASTM D3137 Standard Test Method for Rubber Property-Hydrolytic Stability.

Weathering

ASTM D518 Standard Test Method for Rubber Deterioration Surface Cracking.

Effect of ozone

ASTM D1149 Standard Test Method for Rubber DeteriorationSurface Ozone Cracking in a Chamber.

ASTM D1171 Standard Test Method for Rubber DeteriorationSurface Ozone Cracking Outdoors or Chamber (Triangular Specimens).

Mechanical stress relaxation in compression

ASTM F38 Standard Test Methods for Creep Relaxation of a Gasket Material.

Composites

ASTM C480 Standard Test Method for Flexure Creep of Sandwich Constructions.

ASTM D1151 Standard Practice for Effect of Moisture and Temperature on Adhesive Bonds.

ASTM D1828 Standard Practice for Atmospheric Exposure of Adhesive Joints Stressed in Peel.

ASTM D2295 Standard Test Method for Strength Properties of Adhesives in Shear by Tension Loading at Elevated Temperatures (Metal-to-Metal).

ASTM D2918 Standard Test Method for Durability Assessment of Adhesive Joints Stressed in Peel.

ASTM D2919 Standard Test Method for Determining Durability of Adhesive Joints Stressed in Shear by Tension Loading.

ASTM D5229 Standard Test Method for Moisture Absorption Properties and Equilibrium Conditioning of Polymer Matrix Composite Materials.

ASTM D7792 Standard Practice for Freeze/Thaw Conditioning of Pultruded Fiber Reinforced Polymer (FRP) Composites Used in Structural Designs.

Adhesives

BS EN 1465 Adhesives – Determination of Tensile Lap-Shear Strength of Rigid-to-Rigid Bonded Assemblies.

BS 5350-A1 Methods of Test for Adhesives - Part A1: Adherend Preparation.

BS 7079 General Introduction to Standards for Preparation of Steel Substrates Before Application of Paints and Related Products.

BS EN 2243-5 Non-Metallic Materials Structural Adhesives Test Method Part 5: Ageing Tests.

BS EN 13887 Structural Adhesives. Guidelines for Surface Preparation of Metal and Plastics Prior to Adhesive Bonding.

BS EN 26922 Adhesives - Determination of Tensile Strength of Butt Joints.

ASTM Standards

Plastics

Mechanical

ASTM D695 Standard Test Method for Compressive Properties of Rigid Plastics.

ASTM D2990 Standard Test Methods for Tensile, Compressive, and Flexural Creep and Creep-Rupture of Plastics.

Environmental conditioning and testing

ASTM D543 Standard Practices for Evaluating the resistance of Plastics for Chemical Reagents.

ASTM D570 Standard Test Method for Water Absorption of Plastics.

ASTM D618 Standard Practice for Conditioning Plastics for Testing.

Environmental stress cracking (ESC)

ASTM D1693 Standard Test Method for Environmental Stress-Cracking of Ethylene Plastics.

ASTM F1248 Standard Test Method for Determination of Environmental Stress Crack Resistance (ESCR) of Polyethylene Pipe.

Adhesives

Thermal degradation

ASTM D1151 Standard Practice for Effect of Moisture and Temperature on Adhesive Bonds.

ASTM D2295 Standard Test Method for Strength Properties of Adhesives in Shear by Tension Loading at Elevated Temperatures (Metal-to-Metal).

ASTM D4498 Standard Test Method for Heat-Fail Temperature in Shear of Hot Melt Adhesives.

ASTM 4502 Standard Test Method for Heat and Moisture Resistance of Wood-Adhesive Joints.

Chemical resistance

ASTM D896 Standard Practice for Resistance of Adhesive Bonds to Chemical Reagents.

Environmental conditioning and testing

ASTM D1151 Standard Practice for Effect of Moisture and Temperature on Adhesive Bonds.

ASTM D1183 Standard Practices for Resistance of Adhesives to Cyclic Laboratory Aging Conditions.

ASTM D1828 Standard Practice for Atmospheric Exposure of Adhesive Joints Stressed in Peel.

ASTM D2295 Standard Test Method for Strength Properties of Adhesives in Shear by Tension Loading at Elevated Temperatures (Metal-to-Metal).

ASTM D2918 Standard Test Method for Durability Assessment of Adhesive Joints Stressed in Peel.

ASTM D2919 Standard Test Method for Determining Durability of Adhesive Joints Stressed in Shear by Tension Loading.

ASTM D3434 Standard Test Method for Multiple-Cycle Accelerated Aging Test (Automatic Boil Test) for Exterior Wet Use Wood Adhesives.

ASTM D3632 Standard Test Method for Accelerated Aging of Adhesive Joints by the Oxygen-Pressure Method.

ASTM D3762 Standard Test Method for Adhesive-Bonded Surface Durability of Aluminium (Wedge Test).

ASTM D4498 Standard Test Method for Heat-Fail Temperature in Shear of Hot Melt Adhesives.

Creep

ASTM D1780 Standard Practice for Conducting Creep Tests of Metal-to-Metal Adhesives.

ASTM D2293 Standard Test Method for Creep Properties of Adhesives in Shear by Compression Loading (Metal-to-Metal).

ASTM D2294 Standard Test Method for Creep Properties of Adhesives in Shear by Tension Loading (Metal-to-Metal).

Surface treatment

ASTM D2093 Standard Practice for Preparation of Surfaces of Plastics Prior to Adhesive Bonding.

ASTM D2651 Standard Guide for Preparation of Metal Surfaces for Adhesive Bonding.

Useful contacts

Useful contacts

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Abstract

Accurate modelling of the absorption of moisture into engineering polymers is needed to design exposure procedures for durability assessment and carry out reliable lifetime predictions. This needs to be supported by good quality data obtained under representative conditions. This Guide describes methods for measuring the absorption and diffusion of moisture in polymeric materials, including plastics, adhesives, and composites. Factors that will affect moisture absorption, including service conditions (temperature, pressure, and stress) and the manufacture process (e.g., state of cure), are also covered.

NPL has made every effort to ensure all information contained in this Good Practice Guide was correct at the time of publication. NPL is not responsible for any errors, omissions, or obsolescence, and does not accept any liability arising from the use of this Good Practice Guide.

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Contents

Glossary of Terms (Based on BSI and ASTM Definitions)

Accelerated ageing test: Short-term test designed to simulate the effects of longer-term service conditions.
Adherend: Body that is or intended to be held to another body by an adhesive.
Adherend failure: Failure of a joint in the body of the adherend.
Adhesion (or adherence): State in which two surfaces are held together by interfacial bonds.
Adhesive: Non-metallic substance capable of joining materials by surface bonding (adhesion), the bonding possessing adequate internal strength (cohesion).
Adhesive failure: Failure of an adhesive bond, such that separation appears to be at the adhesive/adherend interface.
Ageing: Irreversible chemical and physical processes occurring in a material in the course of time.
Amorphous: Non-crystalline or devoid of crystalline structure.
Amorphous regions: Regions within a polymeric material that, on the basis of X-ray diffraction or other suitable techniques, do not show any evidence of crystalline structure.
ASTM: American Society for Testing and Materials.
Bond: The union of materials by adhesives.
Bond-line: The layer of adhesive, which attaches two adherends.
Bond strength: The unit of load applied to tension, compression, flexure, peel, impact, cleavage, or shear, required to break an adhesive assembly with failure occurring in or near the plane of the bond.
Breaking stress: Stress at the moment of rupture of a specimen.
Brittle failure: Failure in which the fracture surface exhibits no permanent material deformation to the naked eye (e.g., stretching, elongation and necking down).
BSI: British Standards Institute
Bulk adhesive: The adhesive unaltered by the adherend.
Cleavage: Mode of application of a force to a joint between rigid adherends, which is not uniform over the whole area, but results in a stress concentrated at one edge.
Cohesion: The ability of the adhesive to resist splitting or rupture.
Cohesive failure: Failure within the body of the adhesive (i.e., not at the interface).
Composite: Solid product consisting of two or more distinct phases, including a binding material (matrix) and a particulate or fibrous material.
Conditioning: A series of operations intended to bring a sample or specimen into a reference state with regard to temperature and humidity.
Contamination-free: Absence of foreign matter, both on a treated surface (i.e., cleanliness), or which could migrate through the bulk to a bonded interface with time.
Craze: Defect at or under the surface of a plastic, attributable to apparent cracks bridged by polymeric material of reduced (apparent) density.
Creep: The time-dependent increase in strain resulting from a sustained load.
Crystallinity: Presence of three-dimensional order at the level of molecular dimensions.
Cure: To set or harden by means of a chemical reaction.

Cure time: Time required to affect a cure at a given temperature.
Cure temperature: Temperature at which a polymeric system is exposed in order to achieve curing.
Degradation: Change in the chemical structure of a polymeric material involving a deleterious change in properties.
Delamination: Separation of layers (i.e., planar defect) in a laminate.
Deterioration: Permanent change in the physical properties of a material evident by impairment of these properties.
Diffusivity: The transport of chemical species, such as a liquid or gas, within a solid due to concentration differences. Diffusivity is generally temperature dependent.
Dimensional stability: Consistency of dimensions of a material part or specimen under environmental conditions.
Dissolution: Process of absorption of the chemical in the polymer and depends on the affinity (interaction energy) of the polymer for the chemical, the volume available for absorption and the concentration of chemical.
Durability: The endurance of joint strength relative to the required service conditions.
Environmental test: Test to assess the performance of an assembly under service conditions.
Fibre: Particle of relatively short length, characterised by a high ratio of length to thickness or diameter.
Filler: Relatively inert material (e.g., talc) added to a plastic or resin to modify its strength, fire resistance or other qualities, or to lower costs.
Fillet: Portion of an adhesive that bridges the adherends outside the bond-line.
Glass transition: A reversible change in an amorphous polymer or in amorphous regions of a partially crystalline polymer from (or to) a viscous or rubbery condition to (or from) a hard and relatively brittle one.
Hygroscopic: Material capable of absorbing and retaining environmental moisture.
Interface: The region where two materials are in intimate contact. Interfaces can be solid-solid (cured adhesive joint), solid-liquid (uncured adhesive joint), solid-gas (exposed adherend), liquid-gas (open adhesive) or liquid-liquid (insoluble liquids).
Interphase: The region near an interface where the properties of materials are altered from their bulk properties due to the presence of the interface.
ISO: International Standards Organisation.
Laminate: Product made by bonding together two or more layers (plies) of material or materials.
Permeability: Property of a material transmitting gases and liquids by passage through one surface and out at another surface by diffusion and sorption processes.
Plasticisation: Increase in softness, flexibility, and extensibility of an adhesive.
Polymeric material: A material whose continuous phase consists of long-chain organic molecules.
Porosity: A condition of trapped pockets of air, gas, or vacuum within a solid material.
Post-cure: Further treatment by time and/or temperature of an adhesive to obtain the required properties by curing.

Primer: A coating applied to a surface, prior to the application of an adhesive, to improve the performance of the bond.

Reinforced plastic: Polymer (plastic) with high-strength fibres embedded in the composition, resulting in some strength properties greatly superior to those of the base resin.

Sealant: An interlaminar layer of polymeric material applied for the purpose of filling gaps and insulating the interior of the joint from external environments. Sealants are not used to provide load bearing capacity although adhesives can also act as sealants.

Semi-crystalline: Polymer containing crystalline and amorphous phases.

Shelf life: The period for which the components of the adhesive may be stored, under the conditions specified by the manufacturer, without being degraded.

Soundness: Freedom from weak and loosely attached surface layers.

Stability: The stability of surface layers and oxides, towards water, organic compounds, and elevated temperatures, as a function of time following treatment.

Strain: Unit change due to force in size of body relative to its original size.

Stress: Force exerted per unit area at a point within a plane.

Stress-strain diagram (or curve): A diagram in which corresponding values of stress and strain are plotted against each other.

Structural bond: A bond, which is capable of sustaining in a structure a specified strength level under a combination of stresses for a specified time.

Substrate: An adherend, a material upon which an adhesive is applied.

Surface preparation (or treatment): Physical and/or chemical treatments applied to adherends to render them suitable or more suitable for adhesive bonding.

Swelling: Increase in volume of a test specimen immersed in a liquid or exposed to a vapour.

Thermoplastic: A material that can be repeatedly softened by heating.

Thermoset: A resin that is substantially infusible and insoluble after being cured.

Traveller: A test specimen used for example to measure moisture content because of environmental conditioning.

Uniformity: Visible or measurable consistency of the other characteristics, and of the regularity of a treated surface area.

Weathering: Effects on a material of exposure to outdoor conditions.

Yield strain: The strain, below which a material acts in an elastic manner, and above which it begins to exhibit permanent deformation.

Yield stress: The stress (either normal or shear) at which a marked increase in deformation occurs without an increase in load.

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Chapter 1

Introduction and scope

Introduction

Lifetime prediction is an important consideration in the selection of materials systems and the design of structures. The design approach for lifetime prediction of engineering polymers, such as composites or structural adhesives, is developing continuously but still relies on 'knockdown factors' or 'rules of thumb' generated from mechanical tests on conditioned samples.

Chemical exposure, in particular moisture exposure, is a key mechanism for degradation in polymer systems. An understanding of permeation of chemical species is essential for developing testing methodologies and accelerated ageing protocols for polymeric materials. The process of permeation of chemicals through polymers is a combination of two interrelated processes, dissolution in the polymer and diffusion through the polymer. Dissolution is the process of absorption of the chemical in the polymer and depends on the affinity (interaction energy) of the polymer for the absorbing molecules, the volume available for absorption and the concentration of absorbing chemical. There is a limit to the amount of the chemical that can be absorbed under any set of conditions – the solubility. Diffusion is the concentration gradient driven process whereby the absorbed molecules are transported within the polymer and diffusion properties are characterised via diffusion coefficients. A review [1] of the extensive body of literature on permeation and diffusion in polymers [e.g., 2-6] emphasised the strong need for reliable test methods to measure the diffusion of gases and liquids in polymers. Permeation properties are required under relevant service conditions, which may include transient and varying levels of chemical exposure, temperature, pressure, and stress.

Often, especially in thick sections, the time taken for deleterious species to diffuse in sufficient concentrations to critical regions is the rate-determining step in the ageing process. Accurate modelling of the absorption of moisture into engineering polymers is needed to design exposure procedures and carry out reliable lifetime predictions. This needs to be supported by good quality data obtained under representative conditions. The techniques described in this Guide focus on diffusion as part of a wider investigation of accelerated ageing of polymer materials [7].

The time dependent concentration of chemical species in a component can be predicted using diffusion modelling approaches [2-6]. A common assumption used in interpreting diffusion measurements is Fickian diffusion - the steady state flux of diffusant per unit area (J) per unit time (t) is a function of the concentration gradient (concentration, ϕ, per unit length, x) and Fick's first law is expressed:

$$\frac{dJ}{dt} = -D\frac{d\phi}{dx} \qquad (1)$$

Where the diffusion coefficient *D* does not depend on concentration then Fick's second law (Equation 2) can be used to determine the time dependence of the concentration of the diffusant in the sample.

$$\frac{dJ}{dt} = -D\frac{d^2\phi}{dx^2} \quad (2)$$

The diffusion coefficient *D*(*T*) is temperature dependent, increasing the temperature (*T*) should increase the rate of diffusion and accelerate the ageing of the system.

Scope

This Good Practice Guide covers techniques for measuring the absorption and diffusion of moisture in polymeric materials, which include plastics, polymer matrix composites (PMCs) and adhesives.

The applicable standards for these measurements is ISO 62 (Plastics - Determination of Water Absorption) [8] and ASTM D570 (Standard Test Method for Water Absorption of Plastics) [9]. The ISO Standard includes an Appendix for determining the diffusion coefficient that is absent from the ASTM Standard. Chapter 2 of this guide describes these methods and explores the factors that influence the accuracy of the results obtained. Chapter 3 outlines a method for analysing the results of measurements and the calculation of Fickian diffusion properties. Environmental factors, such as stress and temperature, will affect diffusion and methods for assessing these effects are covered in Chapter 4.

Chapter 5 describes factors that affect measurements in non-homogenous and non-isotropic materials systems, such as polymeric composites and adhesive joints. Sources of uncertainties are described in Chapter 6. Chapter 7 provides a summary of key points. Chapter 8 lists standards for assessing permeation and diffusion in polymers. These standards enable the measurement of properties for comparison or specification. However, the standards do not cover all the aspects of measurement required to provide data for design.

Measurements of moisture absorption in a rubber-toughened epoxy adhesive and in a film, adhesive are described to illustrate some of the techniques employed.

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Chapter 2

Experimental procedures

- Introduction
- Specimens
- Exposure conditions and times
- Weighing and balance requirements
- Specimen preparation before testing
- Immersion and mass measurement
- Completion of tests

Introduction

ISO 62 [8] and ASTM D 570 [9] are standard measurement methods for water absorption by immersion. The absorption of liquids into polymers is followed through mass uptake (or gravimetric) measurements. Since liquid densities are comparable with polymer densities the mass changes should be measurable. Mass increases of the order of a few percent of the original mass of the polymer are typical in systems with an affinity for the liquid [2-5].

This approach can also be applied to study diffusion of vapours (e.g., water vapour) in polymers; pre-conditioned samples are exposed to a controlled atmosphere (vapour concentration and temperature) and periodically weighed [10-13]. The analysis approach described in Chapter 3 can be used to calculate solubility and diffusion coefficients. Direct contact with a liquid rather than its vapour normally leads to greater levels of absorption (higher saturation concentrations) and, therefore, condensation of vapour on the surface will affect results.

Specimens

The standards recommend a series of preferred sample geometries for flat sheets (either directly moulded or cut from larger sections), rod and tubes to enable comparison of water absorption properties. The procedures for assessing flat sheets are described in this guide but the processes and items to consider are common for all of sample types.

For example, the geometries for flat sheets are specified as:

- The ISO 62 standard specimen is a square 60 mm × 60 mm × 1 mm thick.
- The preferred test specimen for ASTM D 570 is a 50.8 mm diameter disk with a thickness of 3.2 mm.

Standards	Geometric Parameter	Dimension (mm)	Manufacture Tolerance (mm)	Measurement Tolerance (mm)
ISO 62 [8]	Length	60	± 2	± 0.1
	Width	60	± 2	± 0.1
	Thickness	1	± 0.05	± 0.1
ASTM D570 [9]	Radius	25.4	Not stated	± 0.0252
	Thickness	3.2	± 0.15	± 0.025

Table 1. Standard specimen dimensions for flat sheets

Dimensions and tolerances allowed are shown in Table 1. The tolerances on length, width and radius are wide as these dimensions have little significant effect on the results. The thickness (and accuracy of the measured thickness) is much more critical for comparing materials (and samples tested at different labs) and for the calculation of diffusion coefficients. It is good practice to measure the thickness to an accuracy of 1% or better, regardless of the tolerances specified in the standards.

Deviations from the standard dimensions are allowed for but must be recorded. Examples where samples may need to deviate from the standard dimensions include:

- Laminates, where the lay-up needs to be representative of the material.
- Highly absorbing plastics where saturation may be approached very rapidly may be better measured using thicker samples.
- Where the material properties are known or suspected to be thickness or manufacturing process dependent and the sample needs to be prepared to be representative.

Changing the thickness of the test specimen may result in the need to use different values for the other dimensions (i.e., length and width or radius). Factors than need to be considered in selecting new specimen dimensions include:

- Maintaining a similar ratio of edge to face area to the standard specimen (e.g., for the ISO square a length to thickness ratio of 60).
- Ensuring the mass of the sample is such that the change in mass on absorption can be measured with sufficient accuracy.
- Ensuring the sample fits on the balance.
- Ensuring the sample fits in the exposure system.
- Controlling and measuring the dimensions to sufficient accuracy, in particular the level of uncertainty in the thickness can increase significantly with reducing thickness.
- The time taken to reach saturation – this increases with the square of thickness.

Exposure conditions and times

The standards specify a set of standard exposure conditions (temperature and time) that allow for comparing different materials. These are:

Room temperature immersion (23 ± 2 °C) (ISO and ASTM)	Immerse for 24 ± 1 hours then weigh. Re-immerse and repeat for increasing intervals (e.g., 24h, 48h, 96h, 192h, then weekly etc.) until saturation. ASTM specifies a 2-hour (120 ± 4 minute) exposure for materials having a high rate of absorption or for thin samples. Samples can be re-immersed for measurement at 24 hours (and subsequent intervals).
Boiling water immersion (ISO and ASTM)	Immerse for 30 ± 2 minutes in boiling water remove and place in water at room temperature to cool for 15 ± 1 minute, then weigh. After weighing the procedure is repeated until saturation is reached. ASTM also specifies a 2-hour (120 ± 4 minute) boiling water exposure.

Immersion at 50 °C (ASTM)	Immersion period is specified as 48 ± 1 hours.
Exposure under standard laboratory conditions of 23 ± 2 °C and 50 ± 5% RH (ISO)	Follows the intervals from room temperature immersion.

Note 1: Appropriate safety precautions should be taken when working with boiling water.

Other exposure conditions may also be specified [14, 15]. For example, the military consider the worst worldwide environment to be represented by 70 °C and 85% RH (relative humidity). The standard exposures and intervals may not be appropriate for obtaining diffusion data for design and alternative procedures more clearly reflecting the service conditions may need to be considered.

- Time to reach saturation depends on the square of thickness and therefore exposure timescales will need to be considered in light of the sample dimensions. A maximum sample thickness of 1 mm is recommended by ISO [8] to ensure that test durations do not exceed one week for typical D values for polymers (ca. 10-12 m^2s^{-1}).
- The exposure temperature should reflect the application temperature.
- Multiple temperature exposures may be needed to build up a picture of the full behaviour of the material.
- High temperatures may cause chemical or phase changes in the polymer, which could limit the possibility of extrapolating behaviour from one temperature to another.
- Where possible, the exposure intervals should match these in the standards to enable comparability with standard data.
- If multiple specimens are to be exposed in a study then the exposure intervals for each of the specimens should be consistent. The start of the exposures may need to be staggered to allow mass measurements to be carried out efficiently.

Weighing and balance requirements

The ISO and ASTM standards require the use of a balance capable of reading to 0.1 mg. Typically, the dry masses of the specimens referred to in the standards will be in the range 2 g – 10 g. Thus, the sensitivity of the concentration measurement will be at least 0.005%, which is more than adequate if absorption levels are greater than 1%. If specimens with lower masses (< 1 g) are used, e.g., using very thin samples, or saturation concentrations are low (< 1%) then a higher resolution balance (e.g., with a resolution of 0.01 mg) may be necessary.

Procedures for weighing good practice [16] should be followed. The balance used should have a capacity such that the mass of the specimen is neither at the lower or upper end of the balance range (i.e., the sample mass is within 10%-90% of the full scale of the balance). The total mass of sample expected at saturation should also be considered. The balance should be calibrated over the expected range of masses. An enclosure around the balance pan to eliminate drafts is recommended.

To minimise reproducibility problems, it is recommended that the same balance be used throughout the test programme. The samples should be placed in the same position on the balance each time a measurement is made.

Specimen preparation before testing

If test specimens are machined then care should be taken to avoid damage to the surfaces (e.g., cracking). Rough surfaces should be smoothed, for example by polishing with fine glass paper.

In materials with anisotropic diffusion properties (e.g., fibre reinforced plastics where faces cut normal to the fibre direction in composites may have significantly higher diffusion properties) erroneous results can be obtained if absorption through exposed edges is significantly different to absorption through surfaces. For this reason, the ratio of edge area to surface area of samples should be minimised.

Where edge effects are of concern then edges can be sealed (e.g., by bonding aluminium foil to the edges or applying a barrier coating). The additional mass of the sealing material needs to be accounted for when analysing results. Any coating/foil used for sealing the edges must:

- Be applied as a thin layer to avoid becoming a significant component of the mass of the system.
- Have a significantly lower permeability than the sample; if it does not then the thin layer will not act as a barrier to diffusion.
- Be applied carefully so as to not overlap the main faces of the sample.

The second requirement usually means that sealing coatings are not commonly used for isotropic materials. However, for systems where diffusion is directionally dependent and diffusion through the edges may be high (e.g., composites) sealing may be necessary.

The samples should be dried to constant mass, M0, before testing. Standards recommend drying at 110 °C for 1 hour or at 50 °C for 24 hours then cooling in a desiccator prior to measuring mass (and testing). Drying cycles should be repeated until constant mass (i.e., change in mass between successive measurements is less than 0.1 mg). The lower temperature should be used if there are worries about thermal stability or changing the state of cure of the material.

Immersion and mass measurement

Samples should be immersed in a sufficient volume of liquid such that the samples are fully immersed and any species leaching from the samples are sufficiently diluted. ISO 62 specifies at least 300 ml per test specimen and a minimum of 8 ml of fluid per square cm of surface area. The fluid should be topped up or replaced regularly to ensure that the correct immersion conditions are maintained.

Samples of the same composition can be placed in the same container provided that the minimum volume of fluid per sample is maintained. Samples should not make any significant contact with each other or the container. A 'rack' manufactured from a material that does not degrade in the fluid (e.g., stainless steel) can be used to maintain separation. Where the samples have densities less than the fluid, a means of weighting the samples needs to be used. A stainless-steel mesh cage is recommended in IS0 62.

After immersion for the fixed period (at constant temperature), the sample is removed from the medium and surface liquid wiped off using a dry cloth or paper before immediately weighing (in a weighing bottle for very thin samples). Assessing the total removal of liquid from the surface of the sample is judged by the appearance of the surface and from the appearance of the drying cloth. Therefore, it is subjective and a potential source of uncertainty in the measurements. It is much easier to dry and to judge dryness of smooth surfaces than textured surfaces.

Samples removed from the exposure medium will lose absorbed moisture continuously during the period that they are out from the medium. The loss of absorbed moisture is a diffusion driven process depending on the difference between the surface moisture concentration and the equilibrium moisture concentration for the material in the laboratory environment (generally 23 ± 2°C and 50 ± 5% relative humidity). If this loss of absorbed material is low, then samples can then be returned to the medium for continuing exposure. This requires that the time out of the medium be minimised. Acceptable periods of time that the samples can be out of the exposure medium will be sample and material specific. The periods out of exposure should be insignificant compared to exposure periods between each weighing.

The date, time and mass readings should be recorded. Any changes to the samples (e.g., discolouration, blistering, cracking) should be noted.

It is recommended that the shape of the uptake curve be monitored by plotting the increase in mass divided by the initial mass, measured at each time intervals, against time (see Chapter 3).

Completion of tests

Saturation mass, M_∞, is defined when the weight gains from three successive measurements differ by less than 1% of the overall weight gain. The saturation moisture content C_s is simply:

$$C_s = \frac{(M_\infty - M_0)}{M_0} \quad (3)$$

Loss of water-soluble matter from test samples may also affect results. This can be checked by reconditioning (drying) the sample back to constant mass M_c and comparing against the original mass M_0.

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Chapter 3

Data analysis

- Moisture absorption curves
- Calculation of diffusion coefficients
- Correcting for edge effects

Moisture absorption curves

The absorbed moisture concentration $C(t)$ is calculated from the mass $M(t)$, initial mass M_0 and the reconditioned mass M_c. If there is no loss of water-soluble matter (or reconditioned mass data are not available) then use $M_c = M_0$.

$$C(t) = \frac{M(t) - M_c}{M_0} \tag{4}$$

$C(t)$ is often expressed as a percentage of the specimen dry mass. The plot of $C(t)$ against time has a decreasing slope that asymptotically approaches a saturation concentration at large time. There is a limit to the amount of the moisture that can be absorbed under any set of conditions (i.e., solubility).

A common approach is to plot $C(t)$ against square root of time since a linear section at the start of the curve is indicative of Fickian diffusion. The "apparent" diffusion coefficient D_a (uncorrected for edge effects) for a polymer specimen can be determined from the initial linear region of the Fickian diffusion curve. Figure 1 shows absorption curves measured for the example epoxy at different temperatures. Reducing the sample thickness and/or increasing the exposure temperature decrease the time required to reach saturation (i.e., initial gradient of the diffusion curves increases with temperature). The saturation concentration does not appear to depend on the sample thickness but seems to decrease with increasing temperature.

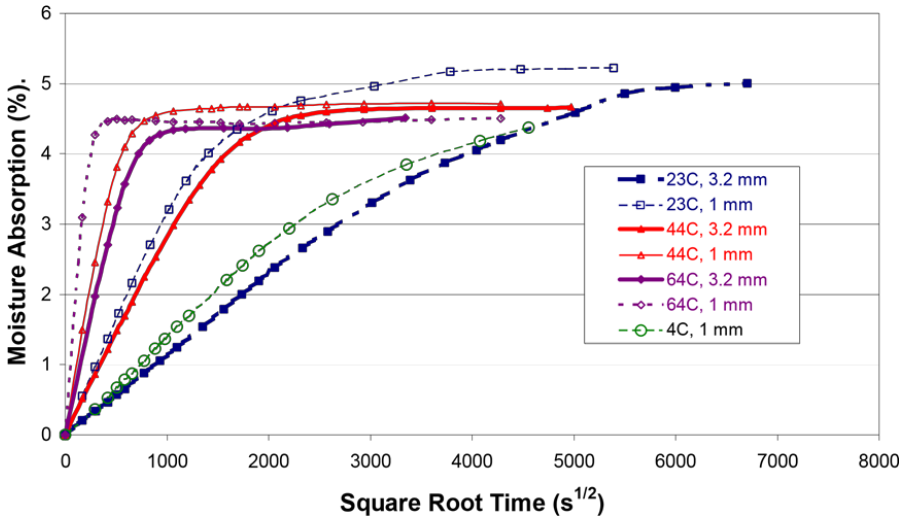

Figure 1. Moisture absorption curves measured by mass uptake

Calculation of diffusion coefficients

Through consideration of the 1-D diffusion case, analytical solutions for the temporal and spatial distribution of moisture concentration $C(t)$ at a distance x from the mid-plane can be derived [17, 18]:

$$\frac{C(t)}{C_s} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)}exp\left[\frac{-(2n+1)^2\pi^2 Dt}{4l^2}\right]cos\left[\frac{(2n+1)\pi x}{2l}\right] \quad (5)$$

Here, l is the half thickness of the film and D is the Fickian diffusion constant. However, as experimental determination of point moisture concentrations is difficult to measure experimentally, this expression is integrated with respect to x to generate an expression in terms of mass gain as a function of time:

$$\frac{C(t)}{C_s} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)}exp\left[\frac{-(2n+1)^2\pi^2 Dt}{4l^2}\right] \quad (6)$$

By assuming a one-dimensional Fickian process a method has been derived [4,5,17] for calculating the "apparent" diffusion coefficient D_a, which is not corrected for edge effects, is calculated from the moisture concentration versus time measurements, $C(t)$, and the sample thickness, h:

$$D_a = \frac{\pi}{16}\left[\frac{h(C(t_2) - C(t_1))}{C_s(\sqrt{t_2} - \sqrt{t_1})}\right]^2 \quad (7)$$

where C_s is the saturation concentration (or percentage) of moisture. If the starting point is a dry sample at time zero, then t_1 and $C(t_1)$ can be eliminated, and the fractional mass uptake $C(t_2)/C_s$ plotted as a function of $\sqrt{t_2}$ has a slope proportional to ${D_a}^{1/2}$.

$$\frac{C(t_2)}{C_s} = {D_a}^{1/2}\frac{4\sqrt{t_2}}{h\sqrt{\pi}} \quad (8)$$

For Fickian diffusion, this plot is approximately linear (e.g., Figure 2, until $C(t_2)$ approaches $0.7C_s$). D_a can be calculated from the square of the slope. Alternatively, if a full diffusion curve is not available then D_a can be evaluated from single point values of $C(t_2)$ and t_2 if a value for C_s is known or can be estimated with reasonable accuracy.

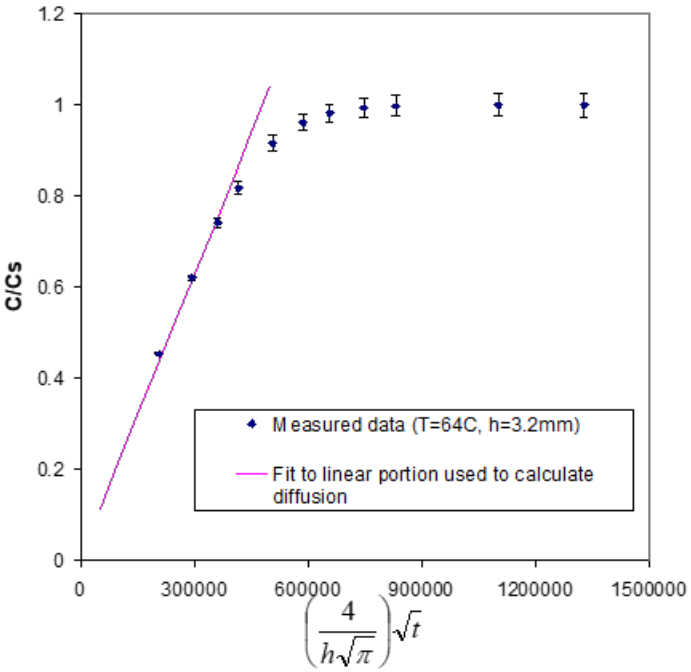

Figure 2. A linear fit to the absorption data up to C/Cs = 0.7 used to calculate D_a (See Equation 8)

Figure 2 shows mean absorption values obtained from three 3.2mm thick epoxy samples exposed simultaneously at 64 °C. The error bars represent one standard deviation and are ~2% - 4% of the mean. A straight line was fitted to the data up to an approximate value of C/C_s of 0.7 (72 hours exposure). Only three absorption measurements lie in this range.

Equation 6 can be expanded and approximated to calculate moisture concentration as a function of time. Where $Dt/h^2 > 0.05$, Equation 5 reduces to:

$$C(t_2) = C_s\left[1 - \frac{8}{\pi} exp\left[-\pi^2\left(\frac{D_a t_2}{h^2}\right)\right]\right] \quad (9)$$

The following approximation is also commonly used [17]:

$$C(t_2) = C_s\left[1 - exp\left[-7.3\left(\frac{D_a t_2}{h^2}\right)\right]\right]^{3/4} \quad (10)$$

Table 2 shows the calculate slopes and apparent diffusion coefficients for each of the three specimens. These were averaged and standard deviations calculated. The coefficients of variation for C_s and Da are 2.7% and 4.8%, respectively.

Sample	Saturation C_s (%)	Slope ($ms^{-1/2}$)	Apparent Diffusion Coefficient D_a (m^2s^{-1})
1	4.28	2.00×10^{-6}	4.20×10^{-12}
2	4.33	2.06×10^{-6}	4.24×10^{-12}
3	4.52	2.14×10^{-6}	4.57×10^{-12}
Mean	4.37	2.08×10^{-6}	4.33×10^{-12}
SD	± 0.12	$\pm 0.05 \times 10^{-6}$	$\pm 0.21 \times 10^{-12}$
CoV	2.7%	2.4%	4.8%

Table 2. Diffusion properties determined from Figure 2
(SD = standard deviation and CoV = coefficient of variation)

Correcting for edge effects

The one-dimensional approximation ignores additional diffusion of moisture through the edges of the sample. Edge effects are minimised by ensuring the samples have a large ratio of face area to edge area. Edge effects can also be minimised by sealing the edges.

A correction was derived by Shen and Springer [17] to account for edge effects. The true one-dimensional diffusion coefficient D_x can be calculated from the apparent diffusion coefficient Da and the length l, width b and thickness h of the plaques using a correction factor E.

$$D_x = ED_a = D_a\left(1 + \frac{h}{l} + \frac{h}{b}\right)^{-2} \tag{11}$$

For example, the correction factors for 1 mm and 3.2 mm thick squares with 50 mm sides are 0.925 and 0.786, respectively. As Table 3 shows, applying the correction factor narrows the differences between D_x values obtained from the two different thicknesses. However, the values obtained from the thicker specimens are still greater than those obtained from the thinner samples, suggesting that in this case there may be a greater flux through the edges than the faces.

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Chapter 4

Effect of temperature and stress

- Representing relevant service conditions
- Effect of temperature
- Effect of tensile stress
- Determining the effect of hydrostatic pressure

Representing relevant service conditions

In many applications, materials will be simultaneously exposed to moisture and stress. Many degradation processes are known to accelerate under the combination of load and exposure. For example, the residual strength of composite samples that are immersed in water under constant load decreases much more rapidly than specimens loaded in air or specimens immersed but not loaded [7]. The degradation of the material strength may have been accelerated by enhanced moisture diffusion in stressed materials.

Effect of temperature

Diffusion coefficients depend on temperature. The diffusion coefficient $D(T)$ is temperature dependent and for ideal systems follows an Arrhenius relationship, with an energy barrier to diffusion E_D.

$$D(T) = D_0 \, exp\left(-\frac{E_D}{kT}\right) \tag{12}$$

Therefore, increasing the temperature T should increase the rate of diffusion and accelerate the ageing of the system. k is Boltzmann's constant and the material parameters D_0 and E_D can be determined by plotting log $D(T)$ against $1/T$. Table 3 shows diffusion coefficients determined for an epoxy adhesive at different temperatures. Figure 3 shows a plot of logarithm of diffusion coefficient plotted against $1/T$ determined for an epoxy adhesive. This is linear suggesting that the Arrhenius coefficients holds for this range of temperatures.

Sample Thickness (mm)	Temperature (°C)	Apparent D_a (m^2s^{-1})	Saturation Concentration (%)	Corrected D_x (m^2s^{-1})
1	4	1.28×10^{-14}	5.2*	1.19×10^{-14}
1	23	6.89×10^{-14}	5.2	6.38×10^{-14}
1	44	5.69×10^{-13}	4.7	5.24×10^{-13}
1	64	3.23×10^{-12}	4.5	2.99×10^{-12}
3.2	23	9.02×10^{-14}	5.2	7.09×10^{-14}
3.2	44	7.23×10^{-13}	4.7	5.80×10^{-13}
3.2	64	4.02×10^{-12}	4.5	3.16×10^{-12}

Table 3. Diffusion properties determined from bulk sample
(Saturation not reached, value for 23 °C used to calculate the diffusion coefficient)*

Using this relationship and the data in Figure 3, the effect of changing the exposure temperature on diffusion coefficient can be calculated. Standard room temperature for materials testing is defined as 23 ± 2 °C. Calculated values for D at 21 °C and 25 °C are approximately 20% different to the value at 23 °C.

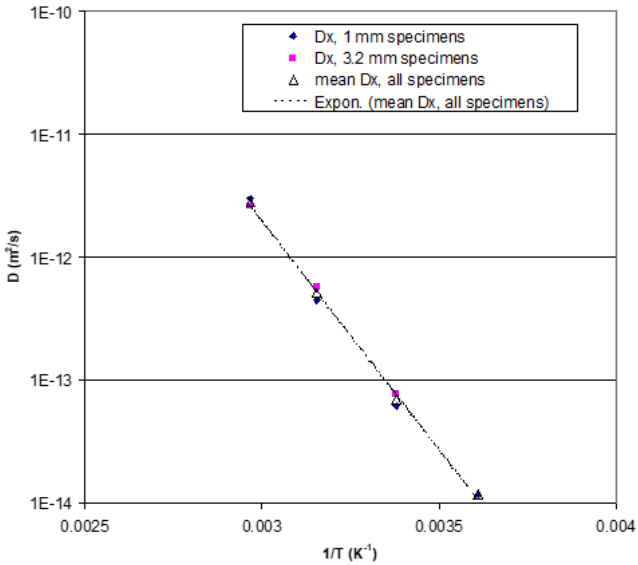

Figure 3. Temperature dependence of the diffusion coefficient

Effect of tensile stress

Specimens can be tested in liquid cells and deadweight loading frames that are used for environmental stress cracking tests for polymers or self-stressing fixtures, Figure 4. In the deadweight loading frames stress is applied using calibrated weights and in the self stressing fixtures through calibrated springs.

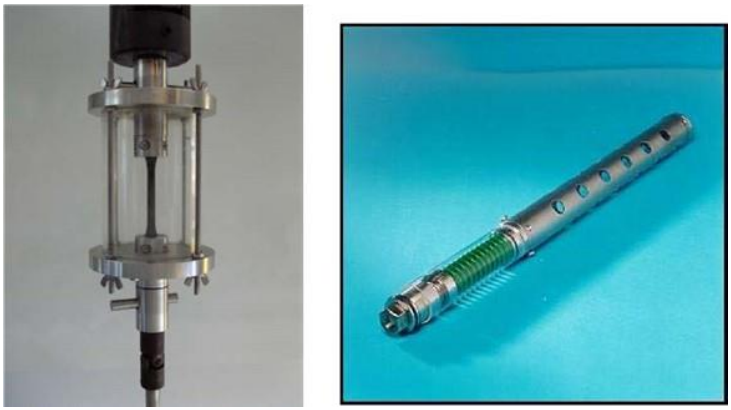

Figure 4. Liquid cell (left) and self-stressing fixture (right) for assessing properties of polymers under combined stress and chemical exposure

The square plaque used for standard moisture diffusion measurements is unsuitable for the controlled application of load in a test. Therefore, measurements of moisture uptake under tensile stress should be carried out using either dog-bone specimens [19] or parallel strips. Although the shape of the dog-bone specimen is not suitable for accurate calculation of diffusion coefficients, the uptake results can be readily compared to determine 'acceleration' factors.

Experiments should be undertaken to assess whether variability of clamping samples in the grips has a significant effect on uptake. Specimens clamped but with no applied stress should be compared with control unclamped specimens exposed at the same time. The difference between measured uptakes in unloaded specimens was found to be negligible, suggesting that the serrated grip faces did not significantly restrict absorption of moisture in the tabs in the series of tests reported.

Figure 5 shows the uptake curves measured with the example epoxy at 23 °C under different levels of tensile stress plotted against square root of time. The absorption increases with increasing stress, with very significant increases and non-linear absorption observed at high stress levels around the yield stress (i.e., between 20 MPa and 25 MPa). The epoxy adhesive is known to yield in tension through a cavitation process initiating around 20 MPa. This level of stress also corresponds with increasing creep rate in the material.

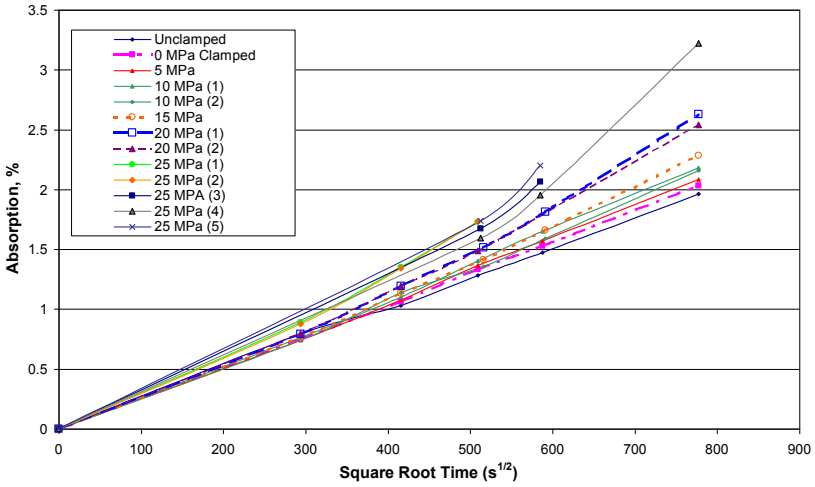

Figure 5: Effect of tensile stress on moisture absorption of epoxy at 23 °C

For the samples under load, part of the increase in absorption with stress may be due to changes in the geometry of the sample, i.e., an increase exposed area from the increase in length due to creep and shorter diffusion paths resulting from decreased width and thickness due to Poisson's contraction.

The geometrical effect can be checked by approximating the tensile specimen as a rectangular bar (60 mm × 10 mm × 1 mm) and using Equation 9 to calculate an 'apparent' diffusion coefficient from the dimensions. Mechanical tests may need to be conducted to provide an indication how dimensions change with strain and creep tests may be required.

For the epoxy evaluated in Figure 5, creep measurements made in air using standard specimens (exposed at 50% relative humidity and containing 2.5% moisture) indicated a tensile strain of 5.4% after 72 hours under 26.2 MPa stress. This strain was taken as a good approximation for the strain under 25 MPa stress and was used with an assumed Poisson's ratio of 0.4 to calculate the dimensions of the strained bar (length 1.05 × unstressed length, width, and thickness 0.98 × original values). Equation 9 was used to predict apparent diffusion coefficients for samples with the stressed ($0.804D_x$) and unstressed dimensions ($0.802D_x$) – the difference was less than 1%.

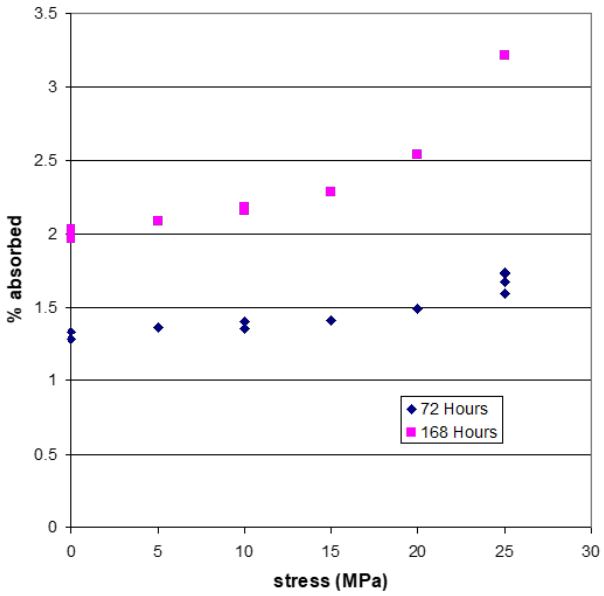

Figure 6. Effect of stress on moisture absorption

The calculated apparent diffusion coefficients and sample dimensions were used with Equation 10 to compare predicted moisture concentrations after 72 hours for 25 MPa and unstressed systems. Although there were significant discrepancies between the measured and predicted moisture uptakes, due to the assumptions made in simplifying the shape of the specimen, comparing the two sets of predictions provides further insight into changes in the diffusion behaviour under stress.

The 25 MPa system was predicted to have a moisture concentration only 1.02 times the concentration predicted for the 0 MPa system whereas the measured 72-hour moisture concentrations under stress were 1.2-1.3 times greater than those measured in the unstressed samples. The difference between the moisture concentrations measured in low stress and high stress samples increases with time, Figure 6, as diffusion in high stress samples becomes non-Fickian, as shown by the non-linearity of the high stress absorption curves in Figure 5.

Determining the effect of stress on saturation concentration would require exposing samples until saturation is reached. However, removing the sample from the apparatus for mass measurements and then reloading may lead to failure of the specimens, particularly at high stresses. Measuring the full absorption curve may require that some samples are designated for long-term exposure, and these are not removed for mass measurements, until the required exposure time has been achieved. Samples would only be used for one mass measurement; thus, fresh specimens would be needed to obtain other points on the absorption curve. This approach could potentially require a high number of specimens (particularly as repeatability between specimens may need to be established), tie up apparatus for prolonged periods and take a long time to complete.

Although very few structures would be designed to operate continuously close to the yield stress of their constituent materials there may be non-uniform stress distributions in components. Regions of high stress could be more permeable to moisture then regions of low stress, leading to preferential absorption in these areas and faster degradation.

Determining the effect of hydrostatic pressure

Diffusion properties are normally obtained at ambient pressure. However, materials may be used in applications (e.g., sub sea structures) where they are exposed to fluids under pressure. Pressure may be a further means of accelerating moisture uptake in some materials.

A system for exposing materials under pressure is shown in Figure 7. A custom-made heating jacket wrapped around the exterior of each autoclave vessel supplies any required heating. A thermostat and thermocouple probe attached to the vessel control the temperature. The accuracy of the temperature control should be confirmed by setting the thermostat to the test temperature and measuring the temperature of liquid within the unsealed vessel. A high-pressure pump is used to pressurise each vessel with air. The readings on the pump gauge and the pressure gauge of each vessel should be checked against a calibrated pressure gauge. Specimens are exposed in pressure vessels filled with water by sealing the vessels and then pressurising them to required pressure at the test temperature. In operation the pressure should be checked regularly (e.g., daily) and re-pressurised as required. It is recommended that pressure and temperature be logged automatically during tests.

Figure 7. Autoclave vessels used for conditioning specimens at elevated pressure

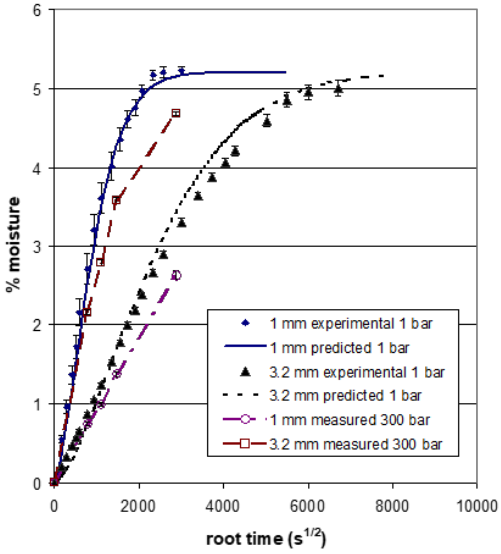

Figure 8. Measured and predicted (using Equation 10) moisture uptake at 23 °C, ambient pressure (1 bar) compared with measured moisture uptake at 23° C and 300 bar pressure

Measurements on pultruded glass-fibre reinforced polyester composite bars suggested that equilibrium moisture content could be achieved in a shorter time than at ambient pressure. Samples of the epoxy were immersed in deionised water within the autoclave. Pressure of 300 bar was applied and three 1mm and 3.2 mm thick specimens were conditioned at ambient temperature (23 °C). Owing to the time-consuming nature of the pressure and the repressurising process, samples were weighed on a weekly basis.

Figure 8 shows that moisture diffusion into the samples exposed at 300 bar is slower than for samples exposed at ambient pressure. It can be conjectured that the hydrostatic pressure may close micro voids in the sample and reduce sites and pathways for diffusion.

From these observations, it is evident that pressure may affect the diffusion of moisture into different materials in different ways. If diffusion rates under pressure are important then specific tests may need to be carried out in preference to assuming the same properties as at atmospheric pressure.

Chapter 5

Diffusion in multi-component systems

- Fibre-reinforced polymer composites
- Adhesive joints and coatings
- Multi-layer systems

Fibre-reinforced polymer composites

Diffusion in PMCs, particularly of water, has been studied extensively, with comprehensive coverage given by Springer [4, 5]. The mass transport properties will depend on the fibre material, the volume fraction of fibres and the fibre orientation. Glass and carbon fibres are normally considered to be impermeable. Transport in the direction of the fibres may be very different to that normal to the fibres. Capillary action along the fibres or the fibre resin interfaces can account for a significant proportion of initial moisture uptake. Shrinkage of the resin away from the fibres during curing could be a contributing factor to the capillary effect. Composite laminates, particularly multi-directional laminates may have a complex structure with permeation behaviour defined by a complex mixture of properties.

Diffusion in orientated fibre composite layers can be treated by a rule of mixtures approach. For a volume fraction of fibres V_f and a reasonable assumption that diffusion coefficients D_f in fibres are much less than the molecular diffusion coefficient in the polymer matrix D_m then the directional diffusion coefficients D_{11} (longitudinal) and D_{22} (transverse) can be expressed [4-5]:

$$D_{11} = (1 - V_f)D_m \tag{13}$$

$$D_{22} = \left(1 - 2\sqrt{\frac{V_f}{\pi}}\right)D_m \tag{14}$$

The diffusion coefficient for a composite is given by the following relationship [4-5]:

$$D = D_x\left(1 + \frac{h}{l}\sqrt{\frac{D_y}{D_x}} + \frac{h}{b}\sqrt{\frac{D_z}{D_x}}\right)^2 \tag{15}$$

D_x, D_y and D_z are diffusivities through the thickness, along the length and across the width of the material.

In most assessments of moisture distributions in composites, the fibres are assumed to be impermeable to moisture. Therefore, all of the water must be contained either within the matrix or bound at the fibre-matrix interface [5]. This may be applicable for glass or carbon fibres but is very unlikely to apply to natural fibres or polymer fibre reinforcements.

Adhesive joints and coatings

Diffusion in adhesive joints is often done by casting bulk sheets of adhesive and determining the diffusion properties of the bulk adhesive. These values are then used with a model [e.g., 1, 18] to predict moisture uptake into the joint. If the adherends are also permeable (e.g., composites) then their diffusion properties should be obtained and included in the model. This approach relies on:

- The bulk adhesive having the same properties as the adhesive in the joint; and
- The adhesive-adherend interface playing no role in moisture absorption and transport.

It is well established that the properties of materials near the interface, the so-called interphase, differ from those of the bulk material. Therefore, the diffusion properties in the interfacial region may not be the same as the bulk material. Few studies comparing bulk adhesive and adhesive joint diffusion have been reported. Bond et al. [20] determined diffusion coefficients for an epoxy adhesive as being 6.4 × 10-13 m^2s^{-1} when obtained from mass measurements on bulk adhesive specimens and 6.7 × 10-12 m^2s^{-1} when determined from measurements of weight gain in lap joints (1 mm thick grit blasted stainless steel adherends). These results suggest a significant contribution from the interface to diffusion. It is well recognised that diffusion of chemicals to the interface in a bond degrades bond performance [18, 20-24].

In the assessment of moisture absorption into adhesive joints the following points should be considered:

- The mass of the adherends needs to be subtracted to determine the mass of the adhesive layer - this will introduce additional uncertainties in the mass results.
- Metal adherends are likely to have significantly higher masses than the adhesive layer of interest. The total mass of the system may require that a larger capacity balance, possibly with lower resolution, be used.
- Any absorption of moisture into the adherends will contribute to measured mass gains. Traveller adherend specimens can be exposed to assess this and corrections made to calculate the moisture concentration in the adhesive layer. However, this correction will increase the uncertainty in the mass gain in the adhesive. Uncertainties can become very significant if the mass of moisture absorbed in the adherends is greater than the mass absorbed in the adhesives.
- Metallic adherends may corrode when exposed to moisture. Traveller samples can be used to determine corrections for any resulting gain in mass (or better to confirm the absence of corrosion). Uncertainties will increase due to these corrections. Traveller specimens may not detect all of the corrosion occurring in an adhesive joint. Corrosion has been observed located under adhesive bonds but not on the exposed surfaces of the same metallic adhesives [24], suggesting that chemical or stress conditions at the

interface promote corrosion. It is recommended that exposed specimens used for uptake measurements should be separated and their surfaces examined.

- Adsorption in joints is mainly through the edges and the resulting long diffusion path lengths to the centre of the joint mean that the time to reach saturation may be extremely high.
- If all edges are available for absorption then there is a two-dimensional diffusion situation. The analysis approach outlined in Chapter 3 is not appropriate and a much more complex analysis procedure is needed to calculate diffusion coefficients. A simpler approach might be to seal off two (opposite) edges leaving a one-dimensional diffusion situation.

Multi-layer systems

Overall absorption into multi-layer systems can be measured using the same methods that are used for homogeneous, isotropic systems. The measurements will produce an average saturation value and diffusion coefficient. Obtaining data on individual layers in a multi-layer system is difficult. Each layer will have a different saturation concentration and diffusion coefficient. Layer thickness may be extremely difficult to measure, particularly in very thin films.

In steady state moisture permeation measurements [1,10-13], where there is a high concentration on one side of the film and low concentration on the other (e.g., liquid and air), a constant flux per unit concentration gradient across the film occurs when boundary conditions are fixed and the moisture concentration within the membrane is in equilibrium.

Figure 9 shows, schematically, one-dimensional diffusion in a multi-layer system.

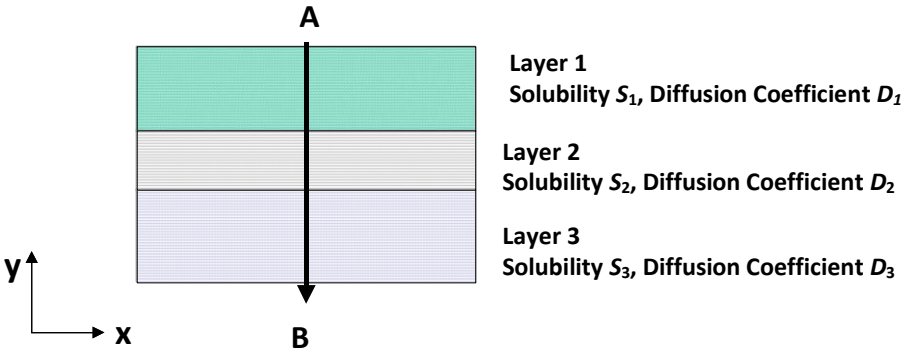

Figure 9. One-dimensional diffusion through a multi-layer system

For a layer of total thickness *L*, at constant temperature and gas concentrations ϕ_1 and ϕ_2 at *A* and *B*, respectively (assuming $\phi_1 > \phi_2$) then Equation 1 can be integrated across the thickness using an average diffusion coefficient D to give permeation rate or permeability:

$$\frac{dQ}{dt} = D\frac{\phi_1 - \phi_2}{L} \tag{16}$$

When one side is in contact with liquid then ϕ_1 is the saturation concentration of the material in contact with the liquid.

In laminated systems, the total permeability of a multi-layer system Q_L with *n* layers can be calculated from the series permeation 'resistance' of each layer and expressed as a sum of the diffusion coefficients D_i and thickness x_i of all of the layers.

$$\frac{1}{Q_L} = \frac{1}{L}\sum_{j=1}^{n}\frac{x_i}{D_i} \tag{17}$$

In cases where the diffusion coefficients of only one of the layers is unknown, then Equation 17 can be used to calculate the diffusion coefficient of the unknown layer.

Determining saturation concentrations of internal layers presents a problem. In the onedimensional diffusion situation illustrated in Figure 9 the moisture concentration in any layer can never exceed the saturation concentration of the preceding layer(s), since diffusion requires a concentration gradient. If both surfaces are exposed then the concentration in internal layers can never exceed those of the layers outside of them.

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Chapter 6

Estimating uncertainties in diffusion coefficients

- Estimating uncertainties
- Uncertainty in specimen dimensions
- Uncertainty in elapsed time
- Uncertainty in moisture concentration
- Exposure temperature
- Material variability
- Changes occurring post material manufacture
- Example uncertainty calculations

Estimating uncertainties

Uncertainties in measurements should be combined according to the methods described in UKAS M3003 [25]. The significance of uncertainties ΔV in the different measured values V used to calculate the diffusion coefficient can be examined by using the expanded uncertainties from Equation 7 and the simplifying assumption that t_1 is zero:

$$\left(\frac{\Delta D}{D}\right)^2 = 2x\left[\left(\frac{\Delta h}{h}\right)^2 + \left(\frac{\Delta C_s}{C_s}\right)^2 + \left(\frac{\Delta(C(t_2) - C(t_1))}{(C(t_2) - C(t_1))}\right)^2 + 0.5x\left(\frac{\Delta t_2}{t_2}\right)^2\right] \qquad (18)$$

Uncertainties will arise from:

- Calibration and resolution uncertainties of the measurement instruments;
- Variations in test procedure (repeatability and reproducibility); and
- Sample variability

Normal distributions are assumed in these calculations, implying a coverage factor of 2 should be used.

Uncertainty in specimen dimensions

The accuracy of the thickness measurement is the most important of the dimensions in determining diffusion coefficients. Uncertainty in sample thickness h arises from two sources.

Resolution and calibration of thickness measuring device:- measurements should be made using instruments such as callipers and micrometers with sufficient accuracy so that this uncertainty is low relative to the measurement. Devices with a resolution of 0.01 mm contribute a relative uncertainty of ± 0.5% for a 1 mm thick specimen, likely to be acceptable for most measurements. Higher resolution instruments are recommended for thinner specimens.

Variations of sample thickness:- samples should have uniform thickness for accurate determination of diffusion coefficients. Thickness should be measured and recorded at several locations on the sample (both at the edges and centre). A minimum of five locations is recommended but if the maximum and minimum readings differ significantly (e.g., by more than 3-5%) then additional measurements should be made. The mean and standard deviation of the thickness should be determined. If the standard deviation in the measurements is high then this will have a significant effect on the overall uncertainty and further preparation (including polishing) should be considered to reduce the thickness variations.

Uncertainties in the other dimensions contribute to the overall uncertainty budget through the correction for edges (Equation 11). The uncertainty in the edge correction factor E can be calculated as:

$$\Delta E^2 = 2x\left(\left[\left(\frac{\Delta h}{h}\right)^2 + \left(\frac{\Delta l}{l}\right)^2\right]\left(\frac{h}{l}\right)^2 + \left[\left(\frac{\Delta h}{h}\right)^2 + \left(\frac{\Delta b}{b}\right)^2\right]\left(\frac{h}{b}\right)^2\right) \quad (19)$$

For example, for square plaques (with sides l = b = 50 ± 1 mm) with thicknesses of 1 ± 0.05 mm and 3.2 ± 0.1 mm the correction factors are 0.925 ± 0.003 and 0.786 ± 0.007, respectively.

Uncertainty in elapsed time

Since the samples are typically exposed over periods of days or weeks the accuracy and resolution required of time measurement is not critical. Recording the date and time of the start of the exposure and each measurement should be sufficient. There will be some uncertainty due to the periods when the sample is removed from exposure for the purposes of mass measurements. Since this period is unlikely to be more than 15 minutes and measurements are unlikely to be made more often than daily then the relative uncertainty in elapsed time is unlikely to exceed 1%. Records should be made of the time at which the sample is measured and returned to the exposure and elapsed time can be calculated to omit these periods.

Where measurements are made with less than 24 hours of exposure the uncertainty in time measurement may become more significant. In such measurements, it is advisable to use a stopwatch for time measurements and to ensure that the time that the sample is taken out of exposure for measurement is minimised (e.g., a minute or less). A 15 minute uncertainty in an 8 hour exposure leads to a relative uncertainty of 3%.

For most exposures, the uncertainty in the time measurement is negligible and can be ignored in the uncertainty estimation.

Uncertainty in moisture concentration

Uncertainties in the mass measurement lead to uncertainties in the concentration gain, $C(t_2)C(t_1)$, and the saturation concentration, C_s, terms. In most cases $C(t_1)$ is zero and $M(t_1)$ is the dry mass of the sample. Concentration $C(t)$ is defined in Equation 4 from the measured mass gain divided by the dry mass. The uncertainties in concentrations (both $C(t)$ and C_s) are defined from the uncertainties in the mass measurements. The uncertainty in the mass gain is expressed:

$$\Delta(M(t_2) - M(t_1))^2 = \Delta\big(M(t_1)\big)^2 + \Delta\big(M(t_2)\big)^2 \quad (20)$$

Resolution of the weighing balance: Provided a sufficiently sensitive balance is used then the uncertainty in concentration due to the resolution of the balance is only likely to be significant for very small changes in concentration.

For example if the balance has a resolution of 0.1mg then the resolution uncertainty in mass ΔM is taken as 0.05 mg. Equation 20 then produces an uncertainty of 0.071 mg in the mass gain. If a sample with an initial dry mass of 2.5 g gains 0.1% moisture then the relative uncertainty in the 2.5 mg mass change is 2.8%. At 1% moisture absorption this reduces to 0.28% uncertainty in the 25 mg mass gain. The uncertainty in the dry mass measurement is negligible in this case (0.05 mg in 2500 mg) and can be ignored in determining the uncertainty in concentration.

The significance of the resolution uncertainties is minimised if:

- The resolution of the balance is much smaller than the mass changes.
- A specimen with a large area is used to increase the mass of polymer and, thence, the size of the mass gain for a given concentration.
- Specimens are sufficiently thick - reducing the thickness will reduce the mass of material and hence the mass of moisture absorbed.
- Moisture absorption is high.

Measurement repeatability: Since the moisture content in the samples are continually changing whether in or out of the exposure medium, assessing repeatability of mass measurement of the samples is not recommended. Replicate specimens should be exposed under the same conditions and measured after the same exposure durations to assess repeatability in measured concentrations. The standard deviation in the measurements should be included in the uncertainty budget.

If the repeatability (or reproducibility between operators) of the weighing process is considered to be a concern then this should be assessed through repeat measurements using an unchanging specimen with similar mass and dimensions to the exposed specimens. A sample that has been left to achieve equilibrium in the weighing laboratory is ideal for this purpose.

Procedural variations: Factors such as the drying of specimen surfaces and time between removing the sample from exposure and weighing will lead to reproducibility uncertainties in the results. All surface moisture must be removed prior to weighing since it would lead to an overestimate of absorbed moisture concentration. Moisture will desorb from dried surfaces into the atmosphere, leading to diffusion of moisture from the sample. The rate of moisture loss will depend on the concentration of moisture in the sample and the diffusion properties of the material. Therefore, the procedure used for each weighing should be as consistent as possible. The importance of the procedure and procedural variations may differ appreciably between materials.

For example, the epoxy adhesive studied had a smooth, flat and poorly wetted surface that became dry to the touch (with no noticeable residual moisture transfer to the cloth) after brief wiping. Consequently, the weighings could be carried out within a controllable, short period of time and the resulting scatter in absorption between different samples were small (typically less than ±3% of the measurement).

However, in another example, it proved very difficult to obtain reliable uptake measurements for bulk plaque samples prepared with different numbers of plies of a film adhesive, Figure 10. These samples had rough textured surfaces and appeared to be well wetted by water. It took considerably longer to dry the surfaces of the samples (i.e. until no transfer to the drying cloth was observed). Figure 11 illustrates possible variations in 'moisture concentration' that could occur from the drying and weighing process. Two samples were weighed at variable time intervals after removal from the water. A point is indicated on each of the two curves when it was considered that all surface moisture had been removed – this is the value used as the concentration in the moisture absorption measurement. However, it is clear that the mass of the sample is changing rapidly during this period and there must be a large uncertainty in this value.

As a result of this, the moisture uptake curves were noisy and there was considerable scatter between specimens, as shown in Figure 10. The standard deviations in the concentration measurements were typically between 10-20%. The diffusion coefficients calculated differed considerably, with a factor of 10 between the values for 1 ply and 4 ply samples, Table 4. Some of that difference may reflect real differences between the samples.

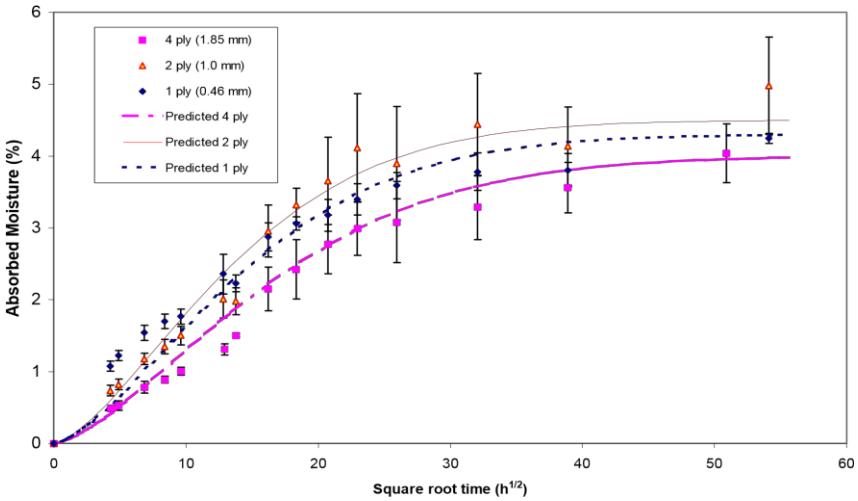

Figure 10. Moisture absorption curves obtained for film adhesive samples
(predicted curves were generated using Equation 10 and the data in Table 4)

Number of Plies	Thickness (mm)	C_s (%)	D_a (m^2s^{-1})
1	0.46	4.3	1.5×10^{-14}
2	1.00	4.5	8.1×10^{-14}
4	1.85	4.0	1.9×10^{-13}
Average	-	4.3 ± 0.3	$1.0 \pm 0.9 \times 10^{-13}$

Table 4. Diffusion parameters determined from Figure 10

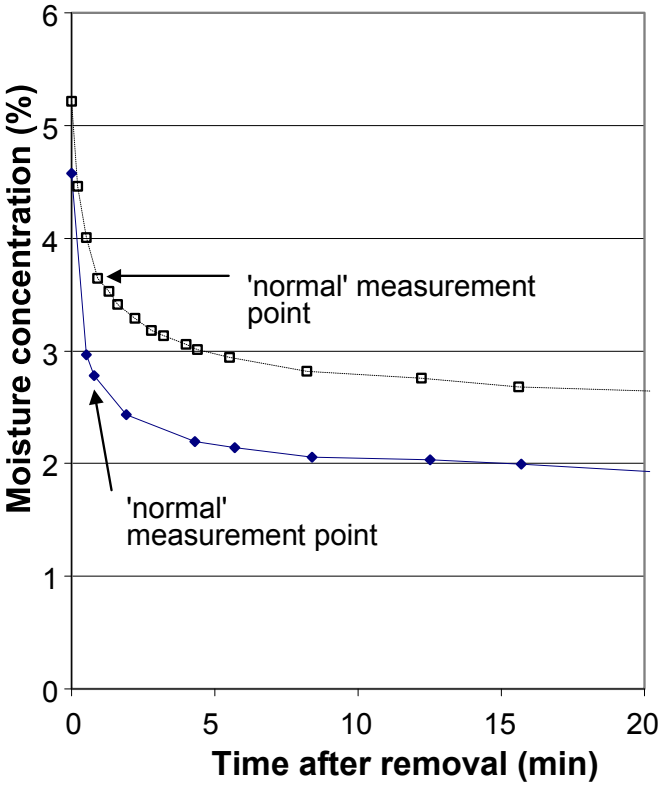

Figure 11. Effect of time out of exposure and drying on measured moisture concentrations

Exposure temperature

The saturation concentrations and diffusion coefficients of polymeric materials are sensitive to temperature. Table 3 shows that the diffusion coefficient of the example epoxy studied increases by a factor of ca. 40 on increasing the temperature from 23 °C to 64 °C. Therefore, as Table 5 shows, even relatively small differences between exposure temperatures can have a significant effect on the diffusion coefficient.

Therefore, it is good practice to maintain and monitor the exposure temperature, using accurate and calibrated instruments, throughout the measurements.

Temperature (°C)	Predicted D_x (m^2s^{-1})	Variation of D_x (% of 23° C Value)
21	6.33×10^{-12}	81.9
22	7.22×10^{-14}	90.5
22.5	7.59×10^{-14}	95.1
23	7.98×10^{-14}	100
23.5	8.38×10^{-14}	105
24	8.81×10^{-14}	110
25	9.72×10^{-14}	122

Table 5. Variation of predicted diffusion coefficient with small temperature changes (D_x predicted from Figure 3)

Material variability

In order to produce relevant information the samples used to assess diffusion behaviour should have the same properties as the materials in the components and structures for which the data will be used. The properties of polymeric materials are affected by the way they have been processed. When the samples are taken from directly from the component of interest and tested, then there should be little concern about the reliability of the results. However, many samples will be manufactured specifically for testing, often using a different process than the components of ultimate interest.

Factors that should be taken into consideration when deciding whether a sample is representative of a component or structure include:

- Composition – same material (including grade of polymer, type and proportion of filler/fibre, toughening agents, processing agents, etc.);
- Lay-up (e.g., for composite laminates or multi-layer films);
- State of cure;
- Degree of crystallinity;
- Processing conditions; and
- Extent of defects including delaminations and voids.

One example where processing conditions could have a significant effect on properties is in the state of cure of thermosetting polymers (including composites). The state of cure can vary within materials (particularly in thick sections where the centre may not reach as high a temperature as the exterior, or may exceed the exterior temperature if large amounts of heat are generated by exothermic reactions) or between samples, particularly if thicknesses differ.

Thin specimens are often preferred for diffusion studies as saturation will be reached much sooner than in thick sections, but there is a danger that the cure state in the thin sections may not match those of the thick sections leading to results of dubious relevance.

For example, Figure 12 shows moisture absorption in two samples of 2-ply film adhesive that were cured under different conditions. One sample (Sample 1) was cured for 20 minutes in an oven preheated at 165 °C. This sample reached 165 °C, as measured by a thermocouple embedded in the mould, towards the end of the sure period. The other sample (Sample 2) was left to continue curing for a further 20 minutes, giving a total of 40 minutes in the oven at 165 °C. The manufacturer's data sheet specified curing for 15 minutes at 165 °C, which is unclear whether the time refers to total time (including heating) or the time that the specimen is actually at the cure temperature (excluding heating). Glass transition temperature T_g for samples cured under both conditions were determined using DSC (differential scanning calorimetry [26]). T_g was 84 °C for sample 1 cured for the shorter time period and 90 °C for sample 2 cured for the longer period. Second and third DSC runs on the samples were carried out and Tg for each sample reached 96 °C, suggesting that neither sample was fully cured.

At equivalent exposure times, there is approximately twice as much moisture absorbed into the sample 1 than into sample 2. It is also apparent that the two samples will have significantly different saturation levels. These major differences exist despite what could be seen as fairly minor differences in cure state.

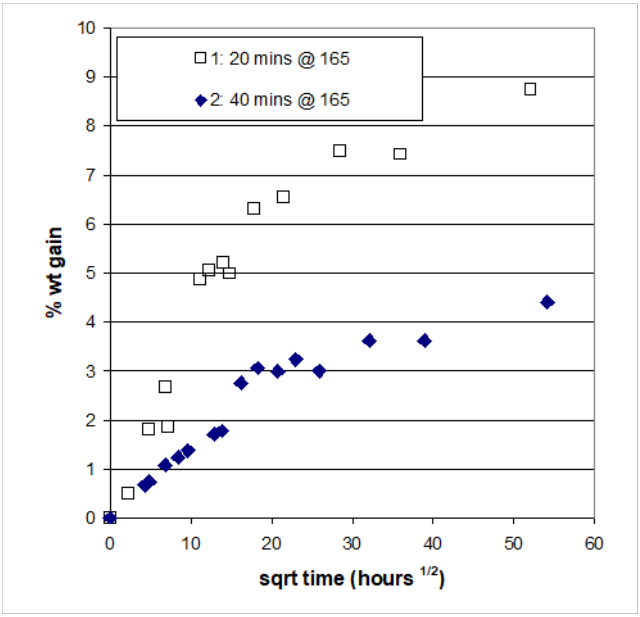

Figure 12. Effect of cure conditions on moisture absorption

Changes occurring post material manufacture

Post-curing: The curing process that occurs when manufacturing components from polymers that cross-link through cure reactions (e.g., thermosets, may not fully cure the materials). Therefore, polymers may continue to cure post manufacture, changing their moisture absorption properties, potentially very significantly (e.g., as indicated in Figure 12). This is more likely to occur where the material is kept or exposed at temperatures at or above its glass transition temperature (where higher molecular mobility makes interaction of unreacted groups more likely). For example:

- Room temperature cured systems, e.g., adhesives, will continue to cure slowly after the material is nominally 'cured' (in practice having reached a sufficient state of mechanical performance).
- Elevated temperature cured systems exposed to elevated temperatures.

Curing can be completed through a deliberate post cure, e.g., heating the material significantly above T_g for sufficient time to ensure completion of reactions. Completeness of cure can be checked by thermal analysis methods [26].

Physical ageing: The structure of polymers continues to evolve through molecular relaxation and realignments after completion of the component 'manufacture' in a process known as physical ageing. Thus, the mobility of polymer chains decreases with time after high temperature processing until an equilibrium structure is obtained. These structural changes are influenced by many factors, including stress and temperature. The moisture absorption kinetics of polymer systems will change with physical ageing and, therefore, it is advisable to compare results from samples having the same physical age. Materials can be 'de-aged' by heating them above their glass transition temperature for a short period of time, typically an hour.

Glass transition temperature (T_g): The properties of the polymeric material will also change with chemical ageing. For example, the T_g for a typical polyester resin will decrease by ~15-20 °C for a 2% moisture weight gain and reduced for the example epoxy by ~5 °C for a similar moisture gain. Figure 13 shows the effect of moisture content on T_g for a glass reinforced epoxy that was immersed in distilled/deionised water for prolonged periods of time at three different temperatures [27]. This reduction in T_g is induced by plasticisation (softening) of the polymer matrix and in some cases by loss of organic additives through leaching to the surrounding media.

Long periods of exposure to moisture at elevated temperatures could lead to phase changes in the polymer (e.g., a glass to rubber transition) and moisture absorption and/or transport processes not relevant to lower temperature exposure may occur. Physical ageing and stress may increase the potential for phase changes occurring during exposure. Therefore, it is advisable, when using elevated temperatures to accelerate moisture uptake, to ensure that the maximum operating temperature is below the T_g of the material (e.g., at least 30-40 °C, taking into account moisture effects).

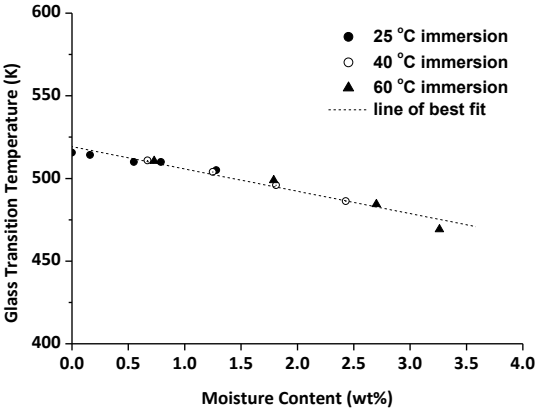

Figure 13. Glass transition temperature of F922 epoxy as a function of moisture content

Combined effects: Exposure of polymeric materials to moisture, elevated temperature, physical ageing and stress may lead to behaviour that cannot be predicted from less complex situations. In Chapter 5, samples exposed at room temperature and elevated pressure absorbed moisture more slowly than materials exposed at atmospheric pressure. However, when the temperature was increased to 64 °C (Figure 14), moisture concentrations under high pressures were found to be considerably higher than the saturation concentrations obtained at atmospheric pressure. The predicted curves in Figure 14 were calculated from Equation 10 and data in Table 3.

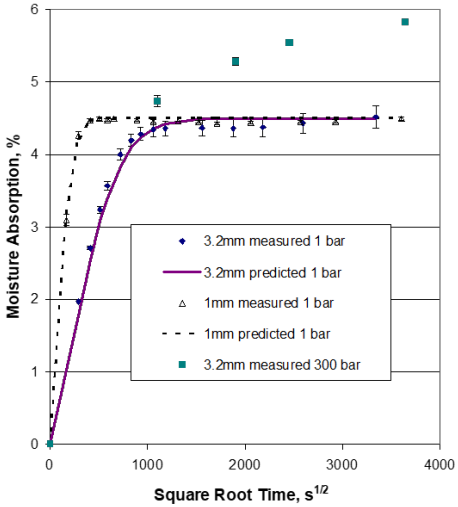

Figure 14. Measured and predicted moisture uptake at 64 °C, ambient pressure (1 bar) compared with measured moisture uptake at 64° C and 300 bar pressure

In addition to the high pressure the test specimens were several months older than the atmospheric test specimens, having been prepared at the same time but not tested until significantly later. It is possible that the moisture and elevated temperature combined with the physical ageing and high pressure to cause phase changes not occurring in younger and unstressed materials.

Example uncertainty calculations

As an example, the calculation of the diffusion coefficient for a 1 mm thick sample of the rubber toughened epoxy exposed at 23 ± 2 °C is used in conjunction with Equation 18 (see below).

$$\left(\frac{\Delta D}{D}\right)^2 = 2x\left[\left(\frac{\Delta h}{h}\right)^2 + \left(\frac{\Delta C_s}{C_s}\right)^2 + \left(\frac{\Delta(C(t_2) - C(t_1))}{(C(t_2) - C(t_1))}\right)^2 + 0.5x\left(\frac{\Delta t_2}{t_2}\right)^2\right]$$

Calculated D_a = 6.89 × 10^{-14} m^2s^{-1} (Table 3)

Sample plaque (dimensions): l = b = 50 ± 1 mm; h = 1.0 ± 0.05 mm

Dimensions measured using digital callipers with resolution 0.01 mm, which is insignificant compared with the variability in dimensions, i.e.:

$$\Delta l = \Delta b = \pm\sqrt{1^2 + 0.005^2} \approx \pm\ 1.0$$

$$\Delta h = \pm\sqrt{0.05^2 + 0.005^2} \approx \pm\ 0.05$$

$$\frac{\Delta h}{h} = 0.05$$

C_s was 5.20% with a standard deviation of ± 0.07%; t_2 was 393 ± 3 hours; $C(t_2)$ was 3.61% with a standard deviation of ± 0.19%

M_0 was 3.055 g; mass gain at t_2 was 0.110 ± 0.005 g, and mass gain at saturation was 0.1595 ± 0.0008 g.

Balance resolution = 0.1 mg which, when used in Equation 20 to calculate uncertainties in the mass gain, is insignificant compared with the variability in mass gain measurements and ignored.

Although $C(t_1)$ was taken to be zero, a standard deviation in $C(t_1)$ of ± 0.07% was assumed, the same as the standard deviation in the saturation value. This was included to account for possible variability in the 'dry' state (which may arise from the drying time being insignificant to ensure complete drying and the possible the pick up of moisture from the atmosphere before the first weighing).

Thus:

$$\Delta\big(C(t_2) - C(t_1)\big) = \sqrt{0.19^2 + 0.07^2} = 0.20, \quad \frac{\Delta\big(C(t_2) - C(t_1)\big)}{\big(C(t_2) - C(t_1)\big)} = 0.055$$

$$\frac{\Delta D_a}{D_a} = \sqrt{2x[(0.05)^2 + (0.019)^2 + (0.055)^2 + 0.5x(0.0076)^2]} = 0.109$$

$$\frac{\Delta t_2}{t_2} = 0.0076$$

Therefore, excluding temperature uncertainty, the uncertainty in Da can be calculated from Equation 17:

$$\frac{\Delta D_a}{D_a} = \sqrt{2x[(0.05)^2 + (0.019)^2 + (0.055)^2 + 0.5x(0.0076)^2]} = 0.109$$

Assuming a coverage factor of 2 then the uncertainty in the value of D_a is 21.8%, thus the value of D_a (taking the uncertainty into account) is **6.9 ± 1 .5x10^{-14} m^{2}s^{-1}**.

The uncertainty in D_x is of a similar order, as the uncertainty in the correction factor is negligible.

The uncertainty due to temperature can be included using the data presented in Table 5. A ± 2 °C difference in temperature causes a maximum of 22% in the value for *D* at a temperature of 23 °C. This can be combined with the calculated uncertainty in D_a (10.9%) using the squaring and adding process (and applying a coverage factor of 2) to yield an estimated uncertainty in the value of D at 23 °C of:

$$\frac{\Delta D(T = 23)}{D(T = 23)} = 2x\sqrt{0.109^2 + 0.22^2} = 0.49$$

Therefore, the value of D_a at 23 °C is **6.9 ± 3.4 ×1 0^{-14} m^{2}s^{-1}**.

In this case the uncertainty could be considerably reduced by tighter control of the exposure temperature. A temperature tolerance of ± 1 °C reduces the relative uncertainty to 0.3, i.e., D_a = 6.9 ± 2.1 × 10^{-14} m^{2}s^{-1} and a temperature tolerance of ± 0.5 °C reduces the relative uncertainty to 0.24 (Da = 6.9 ± 1.7 × 10^{-14} m^{2}s^{-1}), which is little more than the uncertainty due to the non-temperature factors.

Chapter 7

Conclusions

- Key points
- Concluding remarks

Key points

The measurement of moisture absorption and diffusion is, in principle, straightforward to carry out. It requires only the capability to manufacture representative specimens to the required tolerances, measure their dimensions to the required accuracy and make mass measurements at the required time intervals. However, there are several key points to recognise when making measurements.

- **Variations in sample processing** can cause large differences in moisture absorption and diffusion behaviour.
- **Replicate samples** should be tested to improve the reliability of the results and provide some indication of the effects of procedural and material variations.
- The **sample thickness** is the specimen dimension that should be controlled most carefully to minimise uncertainties.
- The **weighing procedure**, and in particular the period the sample is dried for after being taken from exposure, can lead to significant variability in results.
- It is much more difficult to remove all the surface moisture from samples with textured surfaces than from smooth samples. Thus **surface texture** of samples should be controlled.
- Diffusion in polymers depends on **temperature** and any variation in temperature is likely to have significant influence on the accuracy of the results. Temperatures should be controlled and monitored within appropriate tolerances to ensure accuracy: within ± 0.5 °C is recommended.
- The molecular structure of polymers reorganises following processing and the properties will be **time-dependent** to some extent. Ageing of polymers, especially when combined with elevated temperature and/or stress, may lead to unexpected changes in behaviour.

Concluding remarks

The use of simple gravimetric techniques and a one-dimensional Fickian analysis for determining moisture and diffusion have been described. Reasonable accuracy can be obtained provided that good quality samples are available and the procedures outlined in this guide are followed.

Standards

ISO Standards

Plastics

Permeation

ISO 2528	Sheet Materials — Determination of Water Vapour Transmission Rate (WVTR) - Gravimetric (Dish) Method.
ISO 7783-1	Paints and Varnishes - Determination of Water-Vapour Transmission Rate - Part 1: Dish Method for Free Films.

Effects of liquids

ISO 62	Plastics – Determination of Water Absorption.
ISO 175	Plastics - Determining the Effect of Liquid Chemical Including Water.
ISO 483	Plastics - Small Enclosures for Conditioning and Testing Using aqueous Solutions to Maintain Relative Humidity at Constant Value.
ISO 4611	Plastics - Determination of the Effect of Exposure to Damp Heat, Water Spray and Salt.

Thermal degradation

ISO 176	Plastics - Determination of Loss of Plasticizers — Activated Carbon Method.
ISO 177	Plastics - Determination of Migration of Plasticizers.
ISO 291	Plastics - Standard Atmospheres for Conditioning and Testing.
ISO 305	Determination of Thermal Stability of Polyvinyl Chloride Related Chlorine Containing Polymers, and their Compounds - Discoloration Method.
ISO 554	Standard Atmospheres for Conditioning and/or Testing - Specification.
ISO 1137	Plastics: Determination of Behaviour in a Ventilated Tubular Oven.
ISO 2578	Plastics: Determination of Time/Temperature Limits after Exposure to Prolonged Action of Heat.

Environmental stress cracking (ESC)

ISO 4599	Plastics: Determination of Time/Temperature Limits after Exposure to Prolonged Action of Heat Plastics - Determination of Resistance to Environmental Stress Cracking (ESC) - Bent Strip Method.
ISO 4600	Plastics - Determination of Environmental Stress Cracking (ESC) - Ball and Pin.

ISO 6252 Plastics - Determination of Resistance to Environmental Stress Cracking (ESC) - Constant Tensile Stress Method.

ISO 16770 Plastics - Determination of Environmental Stress Cracking (ESC) of Polyethylene - Full-Notch Creep Test (FNCT).

ISO 22088-5 Plastics - Determination of Resistance to Environmental Stress Cracking (ESC) - Part 5: Constant Tensile Deformation Method.

ISO 22088-6 Plastics - Determination of Resistance to Environmental Stress Cracking (ESC) - Part 6: Slow Strain Rate Method.

Weathering

ISO 877 Plastics - Determination of Resistance to Change upon Exposure under Glass to Daylight.

ISO 2579 Plastics - Instrumental Evaluation of Colour Differences.

ISO 3577 Plastics - Recommended Practice for Spectrophotometry and Calculation of Colour in CIE Systems.

ISO 3558 Plastics - Assessment of the Colour of Near-White or Near-Colourless Materials.

ISO 4582 Plastics - Determination of Changes in Colour and Variations in Properties and Exposure to Daylight under Glass, Natural Weathering or Laboratory Light Sources.

ISO 4607 Plastics - Methods of Exposure to Natural Weathering.

ISO 4892 Plastics - Methods of Exposure to Laboratory Light Sources.

ISO 9370 Guide for the Iinstrumental Determination of Radiant Exposure in Weathering Tests.

ISO TR 9673 Solar Radiation and Its Measurements for Determining Outdoor Weather Exposure Levels.

ISO 11403-3 Plastics - Acquisition and Presentation of Comparable Multipoint Data - Part 3: Environmental Influences on Properties.

Biological attack

ISO 846 Plastics — Evaluation of the Action of Microorganisms.

Mechanical (Creep)

ISO 899-1 Plastics - Determination of Creep Behaviour - Part 1: Tensile Creep.

ISO 899-2 Plastics - Determination of Creep Behaviour - Part 2: Flexural Creep by Three-Point Loading.

Rubbers

Thermal degradation

ISO 188 Rubber, Vulcanized or Thermoplastic - Accelerated Ageing and Heat Resistance Tests.

ISO 6914 Rubber, Vulcanized or Thermoplastic - Determination of Ageing Characteristics by Measurement of Stress Relaxation in Tension.

Effect of liquids

ISO 1817 Rubber, Vulcanized or Thermoplastic - Determination of the Effect of Liquids.

Weathering

ISO 4665-1 Assessment of Change in Properties after Exposure to Natural Weathering or Artificial Light.

ISO 4665-2 Methods of Exposure to Natural Weathering.

ISO 4665-3 Methods of Exposure to Artificial Weathering.

Effect of ozone

ISO 1431-1 Resistance of Ozone Cracking - Static Strain Test

ISO 1431-2 Resistance to Ozone Cracking - Dynamic Strain Test.

ISO 1431 -3 Determination of Ozone Concentration.

Biological degradation

ISO 846 Determination of Behaviour under the Action of Fungi and Bacteria - Evaluation by Visual Examination or Measurement of Change in Mass or Physical Properties.

Mechanical (stress relaxation in compression)

ISO 3384 Determination of Stress Relaxation in Compression at Normal and High Temperatures.

ISO 6056 Determination of Compression Stress Relaxation (Rings).

Composites

ISO 75-3 Plastics - Determination of Temperature of Deflection Under Load. Part 3: High-Strength Thermosetting Laminates and Long-Fibre-Reinforced plastics.

ISO 13003 Fibre-Reinforced Plastics - Determination of Fatigue Properties under Cyclic Loading Conditions.

ISO 21746 Composites and Metal Assemblies - Galvanic Corrosion Tests of Carbon Fibre Reinforced Plastics (CFRPs) Related Bonded or Fastened Structures in Artificial Atmospheres - Salt Spray Tests.

ISO 22836 Fibre-Reinforced Composites - Method for Accelerated Moisture Absorption and Supersaturated Conditioning by Moisture Using Sealed Pressure Vessel.

Note: *The standards listed in this section refer specifically to fibre-reinforced composites. More general standards covering both plastics and composites are given in the section on ISO plastic related standards.*

Adhesives

ISO 9142 Adhesives - Guide to the Selection of Standard Laboratory Ageing Conditions for Testing Bonded Joints.

ISO 9664 Test Methods for Fatigue Properties of Structural Adhesives in Tensile Shear.

ISO 10354 Adhesives - Characterisation of Durability of Structural Adhesive Assemblies - Wedge Rupture Test.

ISO 10363 Hot Melt adhesives - Determination of Thermal Stability.

ISO 14615 Adhesives - Durability of Structural Adhesive Joints - Exposure to Humidity and Temperature under Load.

BSI and EN Standards

Composites

BS EN 2378 Fibre Reinforced Plastics - Determination of Water Absorption by Immersion in Demineralised Water.

BS EN 2489 Fibre reinforced Plastics - Determination of the Action of Liquid Chemicals.

BS EN 2823 Fibre Reinforced Plastics - Determination of the Effect of Exposure to Humid Atmosphere on Physical and Mechanical Characteristics.

ASTM Standards

Plastics

Permeation

ASTM E96 Water Vapor Transmission Standard Test Methods.

ASTM D1653 Standard Test Methods for Water Vapor Transmission of Organic Coating Films.

Thermal degradation

ASTM D1203 Standard Test Methods for Volatile Loss From Plastics Using Activated Carbon Methods.

ASTM D2115 Standard Practice for Oven Heat Stability of Poly (Vinyl Chloride) Compositions.

ASTM D3045 Standard Practice for Heat Aging of Plastics Without Load.

Effects of liquids

ASTM D543 Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents.

ASTM D570 Standard Test Method for Water Absorption of Plastics.

ASTM D1712 Standard Practice for Resistance of Plastics to Sulfide Staining.

Environmental stress cracking (ESC)

ASTM D1693 Standard Test Method for Environmental Stress-Cracking of Ethylene Plastics.

ASTM F1248 Standard Test Method for Determination of Environmental Stress Crack Resistance (ESCR) of Polyethylene Pipe.

Weathering

ASTM D1435 Standard Practice for Outdoor Weathering of Plastics.

ASTM D1499 Standard Practice Filtered Open-Flame Carbon-Arc Type Exposures of Plastics.

ASTM D2565 Standard Practice for Xenon Arc Exposure of Plastics Intended for Outdoor Applications.

ASTM D4329 Standard Practice for Fluorescent UV Exposure of Plastics.

ASTM D4364 Standard Practice for Performing Outdoor Accelerated Weathering Tests of Plastics Using Concentrated Sunlight.

ASTM G24 Standard Practice for Conducting Exposures to Daylight Filtered Through Glass.

ASTM G156 Standard Practice for Selecting and Characterizing Weathering Reference Materials Used to Monitor Consistency of Conditions in an Exposure Test.

ASTM G178 Standard Practice for Determining the Activation Spectrum of a Material (Wavelength Sensitivity to an Exposure Source) Using the Sharp Cut-On Filter or Spectrographic Technique.

Biological attack

ASTM G21 Standard Practice for Determining Resistance of Synthetic Polymeric Materials to Fungi.

Creep

ASTM D2990 Standard Test Methods for Tensile, Compressive, and Flexural Creep and Creep-Rupture of Plastics.

Rubber

Thermal degradation

ASTM D454 Standard Test Method for Rubber Deterioration by Heat and Air Pressure.

ASTM D572 Standard Test Method for Rubber—Deterioration by Heat and Oxygen.

ASTM D573 Standard Test Method for Rubber—Deterioration in an Air Oven.

ASTM D865 Standard Test Method for Rubber-Deterioration by Heating in Air (Test Tube Enclosure).

Effects of liquids

ASTM D471 Standard Test Method for Rubber Property-Effect of Liquids.

ASTM D1460 Standard Test Method for Rubber Property-Change in Length During Liquid Immersion.

ASTM D3137 Standard Test Method for Rubber Property-Hydrolytic Stability.

Weathering

ASTM D518 Standard Test Method for Rubber Deterioration Surface Cracking.

Effect of ozone

ASTM D1149 Standard Test Method for Rubber DeteriorationSurface Ozone Cracking in a Chamber.

ASTM D1171 Standard Test Method for Rubber DeteriorationSurface Ozone Cracking Outdoors or Chamber (Triangular Specimens).

Mechanical stress relaxation in compression

ASTM F38 Standard Test Methods for Creep Relaxation of a Gasket Material.

Composites

ASTM C480 Standard Test Method for Flexure Creep of Sandwich Constructions.

ASTM D1151 Standard Practice for Effect of Moisture and Temperature on Adhesive Bonds.

ASTM D1828 Standard Practice for Atmospheric Exposure of Adhesive Joints Stressed in Peel.

ASTM D2295 Standard Test Method for Strength Properties of Adhesives in Shear by Tension Loading at Elevated Temperatures (Metal-to-Metal).

ASTM D2918 Standard Test Method for Durability Assessment of Adhesive Joints Stressed in Peel.

ASTM D2919 Standard Test Method for Determining Durability of Adhesive Joints Stressed in Shear by Tension Loading.

ASTM D5229 Standard Test Method for Moisture Absorption Properties and Equilibrium Conditioning of Polymer Matrix Composite Materials.

ASTM D7792 Standard Practice for Freeze/Thaw Conditioning of Pultruded Fiber Reinforced Polymer (FRP) Composites Used in Structural Designs.

Adhesives

BS EN 1465 Adhesives – Determination of Tensile Lap-Shear Strength of Rigid-to-Rigid Bonded Assemblies.

BS 5350-A1 Methods of Test for Adhesives - Part A1: Adherend Preparation.

BS 7079 General Introduction to Standards for Preparation of Steel Substrates Before Application of Paints and Related Products.

BS EN 2243-5 Non-Metallic Materials Structural Adhesives Test Method Part 5: Ageing Tests.

BS EN 13887 Structural Adhesives. Guidelines for Surface Preparation of Metal and Plastics Prior to Adhesive Bonding.

BS EN 26922 Adhesives - Determination of Tensile Strength of Butt Joints.

ASTM Standards

Plastics

Mechanical

ASTM D695 Standard Test Method for Compressive Properties of Rigid Plastics.

ASTM D2990 Standard Test Methods for Tensile, Compressive, and Flexural Creep and Creep-Rupture of Plastics.

Environmental conditioning and testing

ASTM D543 Standard Practices for Evaluating the resistance of Plastics for Chemical Reagents.

ASTM D570 Standard Test Method for Water Absorption of Plastics.

ASTM D618 Standard Practice for Conditioning Plastics for Testing.

Environmental stress cracking (ESC)

ASTM D1693 Standard Test Method for Environmental Stress-Cracking of Ethylene Plastics.

ASTM F1248 Standard Test Method for Determination of Environmental Stress Crack Resistance (ESCR) of Polyethylene Pipe.

Adhesives

Thermal degradation

ASTM D1151 Standard Practice for Effect of Moisture and Temperature on Adhesive Bonds.

ASTM D2295 Standard Test Method for Strength Properties of Adhesives in Shear by Tension Loading at Elevated Temperatures (Metal-to-Metal).

ASTM D4498 Standard Test Method for Heat-Fail Temperature in Shear of Hot Melt Adhesives.

ASTM 4502 Standard Test Method for Heat and Moisture Resistance of Wood-Adhesive Joints.

Chemical resistance

ASTM D896 Standard Practice for Resistance of Adhesive Bonds to Chemical Reagents.

Environmental conditioning and testing

ASTM D1151 Standard Practice for Effect of Moisture and Temperature on Adhesive Bonds.

ASTM D1183 Standard Practices for Resistance of Adhesives to Cyclic Laboratory Aging Conditions.

ASTM D1828 Standard Practice for Atmospheric Exposure of Adhesive Joints Stressed in Peel.

ASTM D2295 Standard Test Method for Strength Properties of Adhesives in Shear by Tension Loading at Elevated Temperatures (Metal-to-Metal).

ASTM D2918 Standard Test Method for Durability Assessment of Adhesive Joints Stressed in Peel.

ASTM D2919 Standard Test Method for Determining Durability of Adhesive Joints Stressed in Shear by Tension Loading.

ASTM D3434 Standard Test Method for Multiple-Cycle Accelerated Aging Test (Automatic Boil Test) for Exterior Wet Use Wood Adhesives.

ASTM D3632 Standard Test Method for Accelerated Aging of Adhesive Joints by the Oxygen-Pressure Method.

ASTM D3762 Standard Test Method for Adhesive-Bonded Surface Durability of Aluminium (Wedge Test).

ASTM D4498 Standard Test Method for Heat-Fail Temperature in Shear of Hot Melt Adhesives.

Creep

ASTM D1780 Standard Practice for Conducting Creep Tests of Metal-to-Metal Adhesives.

ASTM D2293 Standard Test Method for Creep Properties of Adhesives in Shear by Compression Loading (Metal-to-Metal).

ASTM D2294 Standard Test Method for Creep Properties of Adhesives in Shear by Tension Loading (Metal-to-Metal).

Surface treatment

ASTM D2093 Standard Practice for Preparation of Surfaces of Plastics Prior to Adhesive Bonding.

ASTM D2651 Standard Guide for Preparation of Metal Surfaces for Adhesive Bonding.

Useful contacts

Useful contacts

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