Report

Review of Measurement and Modelling of Permeation and Diffusion in Polymers

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ABSTRACT

Diffusion and permeation in polymeric materials is of fundamental importance in many applications and is the subject of considerable scientific interest. Measurement methods for determining permeation through polymer sheets and within polymeric materials have been reviewed. An overview of the generic mechanisms involved reveals dependence of these properties on a wide range of factors, some relating to the materials others to the exposure environments. There can often be an interrelationship between factors, for example the combination of stress and chemical exposure is often a critical degradation mechanism in the service performance of polymeric structures. Dispersed phases and interfaces play important roles in the mass transport process but the mechanisms are not well understood, limiting predictive capabilities. Modelling is used to supplement experimental measurements, improving understanding and enabling extrapolation of behaviour over timescales and in large components that are not experimentally convenient.

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1. INTRODUCTION

1.1 BACKGROUND

Polymers are widely used for coatings, components and structures in many sectors of industry, providing decorative finish, corrosion resistance, low weight and mechanical strength with reasonable lifetime cost. Chemical attack is recognised as potential route for degradation in materials systems (whether through reactions with the polymer itself or materials protected by plastic barrier films). Although polymers, in the main, have good chemical resistance there is free volume between the polymer chains through which chemicals can permeate. The ingress of chemicals into polymers can have a critical effect on the service performance of a component or structure. The permeation of chemicals within a polymer component may affect the mechanical performance of the material, degrade the material or product that the polymer should protect (e.g. corrosion of coated steel or spoiling of packaged foodstuffs), damage the interface between the polymer and another material (e.g. adhesive joints) or pollute the environment (e.g. diffusion leakage from storage vessels). Therefore, understanding the diffusion and permeation process is critical to developing reliable plastics, polymer composites, coatings and adhesive joints for use in demanding environments.

Chemical exposure is a key mechanism for degradation in plastics; an understanding of permeation is essential for developing testing methodologies and accelerated ageing protocols for plastics. 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 molecule, the volume available for absorption and the external concentration. There is a limit to the amount of the chemical that can be absorbed under any particular 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. There is an extensive body of literature on permeation and diffusion in plastics and other polymers, e.g. [1-5], reflecting a strong industrial 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 and load.

Plastics are often used as multi-layer films of different materials, to obtain the desired mixture of properties (e.g. in food packaging for mechanical strength, barrier performance, surface finish and food contact approval). Therefore, permeation through multi-layers is an important issue in the design of many products (e.g. plastic bottles). Low permeability materials are particularly difficult to characterise accurately, since the time required to make measurements can be excessive. The effects of the service environment, particularly applied stress, on permeability are not well understood but are thought to be significant for performance. The interaction of load and chemical exposure can have significant synergistic effects on material lifetimes (for example Environmental Stress Cracking (ESC) failures cost UK industry in excess of £100 million per year). Permeation along interfaces may occur in many applications (adhesive joints, coatings and laminated structures) but not currently measured owing to a lack of suitable techniques. Modelling of diffusion in polymers, particularly large or complex components, is often undertaken to develop understanding of the accumulation of chemicals in polymeric components and provide prediction of performance degradation.

1.2   PROJECT SCOPE

During the formulation exercise for the DTI National Measurements System's *Measurements for Materials Performance* programme, from surveys and workshops, it became apparent that there was considerable interest in the issue of permeation in polymers from a multitude of perspectives. Project F07 "Permeation, absorption and desorption of liquids and gases in polymer and multi-layer systems" was formulated to address measurement issues surrounding permeation.

The objectives of project F07 are to:

1) Develop methods for assessing the ingress of chemicals into polymeric materials.
2) Improve understanding of the influence of environment on permeation rates.
3) Assess the effect of interfaces on transport of chemicals in polymeric systems, such as multi-layer coatings, laminates or adhesive joints.
4) Assist in the development of reliable accelerated ageing methodologies for polymeric systems.

As mentioned earlier, there is a substantial body of literature on diffusion and permeation in polymers [e.g. 1-5]. A review of this literature has been undertaken and this report summarises the mechanisms for transport of molecules in polymers, measurement methods, modelling approaches and factors affecting permeation. It does not set out to exhaustively cover the whole body of research on permeation in polymers. High permeability, 'porous' polymers are often found in the form of membranes and perform many important roles within biological systems, gas/chemical separation plants and chemical reactors (e.g. fuel cells) where permeation is the key to their functionality. Diffusion in liquids (e.g. colloids, polymer solutions, blends) is another area of importance. However, these applications and materials are not included in the scope of this project, which concentrates on permeation in 'solid' polymers used in protective or structural roles. The review concentrates on the transport of small molecules (whether gas or liquid) but it is recognised that there are many applications where transport of ions or larger molecules (e.g. biological molecules or even nanoparticles) is of interest. Strictly speaking, all polymers are 'porous' to some degree as the random, entanglements of polymer chains leave very small pores (free volume) into which molecules can diffuse.

1.3   INDUSTRIAL CONTEXT OF PERMEABILITY

The uptake and transport of small molecules in polymer systems can be of profound importance to the service performance of the material or component. Permeability is a critical performance issue in many industries, including petrochemical, construction, water, gas, transport, electronics, medical and packaging, where the rate of permeation of chemicals from the environment to the product (or vice versa) needs to be minimised or controlled. The financial consequences of permeation can include:

- Reduced shelf life of foodstuffs, beverages and pharmaceuticals;
- Reduced reliability of electronic systems, leading to increased repair/replacement costs;
- Increased corrosion rates in poorly 'protected' systems, leading to high maintenance costs.

In addition to financial considerations, there are quality of life considerations for designers, manufacturers and end users of plastic products to consider, e.g.:

- Emission of harmful chemicals to the environment via diffusion from process, storage or transport vessels;
- Failure of safety critical systems or structures due to chemical attack.

Mass transport, often referred to as permeation, is of particular importance in many applications including:

- Permeation in packaging, particularly for foods, beverages and pharmaceuticals.
  - Contents should be retained in the packaging, including the inert atmosphere.
  - Chemicals should not diffuse or leach from the packaging materials into the contents (or vice versa).
  - External species should be excluded from the contents. This is particularly an issue where contents may be degraded through exposure to, for example, oxygen, water vapour or carbon dioxide.
- Fabrics and garments
  - Many products are marketed on the basis of their barrier performance. For example, terms such as 'waterproof' and 'windproof' are regularly used to describe fabrics and garments, with little explanation as to what these terms mean.
- Seals and sealants
  - Similar requirements as to packaging
  - Require resistance to harsh chemicals or conditions (heat/load)
- Electronic circuit boards
  - Encapsulants and conformal coatings are used to exclude water and ionic species that can damage the electrical components.
- Organic light emitting displays
  - Performance is degraded by exposure to oxygen or water vapour and thin, transparent, flexible barrier coatings are required for protection.
- Chemical/fuel storage, transport and distribution
  - Permeation of chemicals or hydrocarbon fuels is environmentally damaging and designers need to select materials and wall thickness such that emissions are minimised over service lives, which may be decades.
  - Hydrogen, being the smallest molecule, presents particular challenges for long-term storage owing to its greater diffusibility in many media.
- Separation/reaction membranes
  - Differential transport rates or molecular affinities can be exploited to effect low cost/low energy chemical separations.
    - Separation of hydrogen gas mixtures
    - Removal of VOCs from air
    - Purification of gas streams
  - Hydrogen or methane permeable membranes for fuel cells
- Structural durability – permeation is often on the critical path for service life.
  - Ingress of chemicals into a polymer can lead to a degradation of mechanical properties. For example water can plasticise many systems leading to a reduction of stiffness and strength.

- o Chemicals can diffuse to interfaces, e.g. in adhesive bond or composite material, and degrade the strength of the bond at the interface.
- o Chemicals can diffuse through protective coatings, e.g. paints, to corrode surfaces.
- Environmental Protection
  - o Permeation of waste through liners of landfill sites or chemicals/petrol from underground storage tanks may lead to contamination of ground water. Plastic liners are often used to combat this problem.
- Biotechnology
  - o The ingress of enzymes, proteins and cells in biological systems, e.g. tissue scaffolds, is important in this growing industry sector.
  - o Controlled release of pharmaceuticals.
  - o Diffusion/absorption of nano-particles in tissues.
- Stress cracking
  - o Load and chemical damage are often synergistic leading to the problem of environmental stress cracking. Uptake of chemicals under load often leads to cracks in the plastic. The increase in stress around the crack leads to increased uptake of chemical and faster crack growth rates. This can lead to significant reductions in service life than would be expected from tests loading alone or load-free chemical exposure.

Reliable techniques for testing permeability are needed to provide better specifications for materials, including protective coatings and barrier layers. These should help improve product durability and reliability. Currently little is known about the influence of internal interfaces. Any means of estimating ingress of chemicals in these critical areas will provide improved procedures for assessing the durability of adhesive joints and multi-layer systems. Enhanced understanding of permeation and the effects of stress/environment will help the development of reliable accelerated ageing protocols to evaluate new materials for long-term performance. Permeation and diffusion properties are therefore important properties in many uses of polymers. Understanding and prediction of molecular transport in these materials is important for materials specification, product design and materials development.

1.4   POLYMERIC MATERIALS

Polymers cover a wide range of materials where the principle component consists of long chain organic polymer molecules. Within this general definition the materials can exhibit a huge range of mass transport properties depending on for example:

- type of polymer,
- specific grade,
- additives and fillers,
- production process used, and
- end purpose.

Model (pure, single-phase) systems can be used to gain an understanding of diffusion mechanisms through techniques such as molecular modelling. However, most commercial polymers used are heterogeneous containing additives introduced as separate phases (e.g. toughening agents, pigments), liquids (e.g. process aids, mould release agents, plasticisers), gases (e.g. blowing agents) or inorganic solid fillers (e.g. talc, clays, pigments). The

concentration, dispersion and distribution of these additives can have a significant effect on the mass transport in plastics.

1.4.1 Plastic Films – Including Multi-layers and Coatings

Plastic films are commonly used in packaging or as coatings to protect sensitive items from the environment. The product requirements of coatings and films can be very challenging, frequently requiring optical transparency, mechanical performance, printability, barrier performance at minimum thickness and cost. The transport of molecules through thin films is normally dominated by steady state permeation – as layers are thin the time to reach equilibrium concentration is relatively short and subsequent transport rates are governed by the diffusion behaviour of the saturated film.

1.4.2 Bulk Plastics – Thick Sections

In thick sections, such as sheets, pipes and containers, since the time taken to reach equilibrium moisture content is proportional to the square of the thickness. It may take very long periods for equilibrium conditions to be reached – in many cases this can be several years. In many applications the material will see variations in the environment to which it is exposed (e.g. temperature, chemical concentrations) and the mass transport is likely to be a transient problem rather than steady state. It is difficult to test such thick sections reliably since only the early stages of the absorption and permeation curves will be achievable in realistic experimental timescales. Extrapolation of behaviour is necessary to predict long-term behaviour or permeation (e.g. to comply with environmental regulations for containers). The options available include:

- Extrapolation of short-term data to long-term behaviour. However the early stage uptake is far from saturation and any concentration dependence of properties and/or diffusion mechanisms will lead to large uncertainties.
- Testing reduced size samples and scaling results to full size through modelling, relies on being able to prepare thin samples with the same properties as thick sections.
- Accelerating mass transport mechanisms through, e.g. higher concentrations or increased temperatures. There are obvious difficulties with interpreting these results in terms of service performance.

The study of mass transport in thick sections often involves modelling, requiring good quality data and appropriate models. Concentration mapping of diffusion in thick sections can help improve confidence in the model predictions.

1.4.3 Adhesive Joints

Adhesives, although often used as thin layers, are complicated to measure and model as they normally form a 'sandwich layer' between other materials. Thus diffusion and permeation is a multi-material problem, complicated by the presence of interfaces. Moisture diffusion is of particular importance principally because of its widespread occurrence and the fact that the polar groups in the adhesive, responsible for conferring adhesive properties, also make the adhesive hydrophilic. Accelerated moisture exposure tests, using high temperatures and high concentrations, are often carried out to assess service performance. The time taken for moisture to diffuse to a critical interface is often considered a rate-determining step in the degradation of joint performance.

There are several possible mechanisms whereby water may enter and alter a joint:

Water can enter a joint by:
- Diffusion though the adhesive;
- Transport along the interface – wicking;
- Capillary action through cracks and crazes in the adhesive; or
- Diffusion through the adherend if it is permeable, e.g. polymeric composites.

Subsequent weakening can then occur by:
- Altering the properties of the adhesive in a reversible manner, e.g. plasticisation;
- Altering the properties of the adhesive in an irreversible manner, e.g. causing hydrolysis, cracking or crazing;
- Attacking the adhesive/adherend interface either by displacing the adhesive or by hydrating the metal or metal oxide surface of the adherend or inducing corrosion of the metal surface weakening the surface layer;
- Osmotic swelling causing blistering at the surface; or
- Inducing swelling stresses in the adhesive joints – volumetric expansions of 10% are possible.

1.4.4 Polymer Matrix Composites

Polymer resins highly filled with fibres or fabrics to improve their mechanical performance are known as polymer matrix composites (PMCs). The high level of filler material in composites is likely to lead to permeation and diffusion properties that differ significantly from unfilled or lightly filled materials. Composites tend to be used as thick sections, leading to complications in testing and modelling outlined in Section 1.4.3. In addition, composites are often laid up as laminates with interfaces between the layers playing an important role in diffusion behaviour. High performance structural PMCs are often made from thermosetting resins, such as epoxies that tend to be hydrophilic, filled with inorganic fibres (e.g. glass or carbon). Exposure to moisture may lead to degradation of the fibre-resin adhesion or degradation of the fibres themselves, weakening the composite. The orientation of the fibres may lead to mass transport properties, which depend on the fibre orientation. Transport in the direction of the fibres may be very different to that normal to the fibres.

1.4.5 Seals and Sealants

Seals and sealants are used to prevent or restrict mass transport through gaps in components and structures. Whilst the primary concern is preventing leaks, they must have sufficient barrier properties to function effectively. There are many standards for testing seals and sealed components, such as pipes and storage vessels, for leaks. These are not addressed within the scope of this review, which concentrates on materials.

Seals are physical components, such as O-rings or gaskets, normally made from compressible materials such as rubbers (natural or synthetic), polymers (e.g. PTFE) or silicone rubber. Under compression they will conform to the surfaces being sealed. Permeation may be an issue depending on the relative rate of diffusion through the material compared to 'leaks' at the joint. One concern regarding permeation of chemicals into the seal is that chemical reactions may damage the material or physical interactions such as swelling may physically displace the seal leading to leakage.

2. PERMEABILITY MECHANISMS

Permeation is a mass transport process in which molecules transfer through the polymer from the 'exterior' environment to the 'interior' environment, or vice versa, through diffusive processes, Figure 1. Mass uptake transport in polymers proceeds through a combination of:

- Dissolution of molecules in the polymer following absorption at the surface.
- Diffusion of molecules through the material, driven by concentration gradients.
- Desorption from the surface of the material.

The exterior and interior environments at the surface of the polymer can be a combination of vacuum, gas atmospheres, liquids or other solids. The external boundary conditions will have a significant effect on the permeation behaviour.
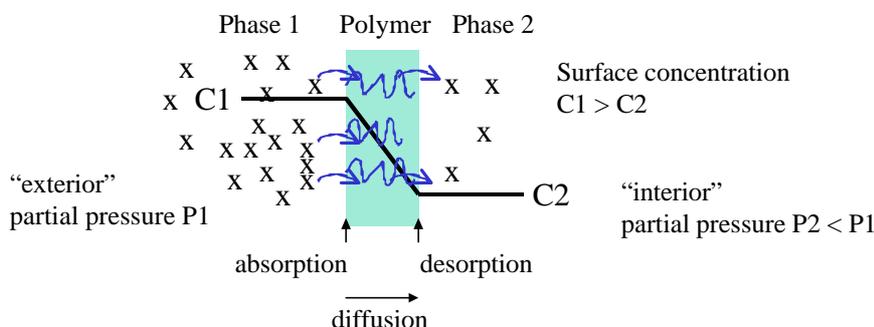
Figure 1: Schematic of permeation and diffusion process

The permeability of a molecule in a polymer is normally defined as the product of the solubility and mobility (diffusion) [1]. Each of these processes is a thermodynamic process, net changes in state occurring if energetically favourable – individual molecules may adsorb, desorb and diffuse in any direction but the ensemble average and equilibrium states are determined by thermodynamic energy considerations and mass transport is driven by differences from equilibrium in species concentrations or partial pressures. Mass transport of small molecules can occur in polymers as there is intrinsic 'porosity' of the polymer matrix caused by random nature of the polymer networks formed and the vibration of the molecular chains leaving sites into which small molecules can adsorb. Polymers are can be manufactured deliberately as porous materials (e.g. foams or membranes) but even nominally solid, homogeneous polymers are likely to be porous to some degree owing to defects, inclusions and different phases, which leave pores, voids and cracks capable of accommodating molecules. The theory and many practical applications of molecular transport in plastics have been covered extensively by Crank [1, 2]. The absorption of chemicals, in particular moisture, in composites has been described by Springer [3, 4].

Many studies (e.g. [1, 5, 6]) have indicated that the mobility and solubility of small molecules in glassy polymers depend on the free volume present in the polymer. Molecules will absorb more readily and be more mobile in polymer matrixes with high free volumes than in polymers with low free volumes. The free volume depends on the nature of the polymer and also on the physical state of the polymer, including molecular orientation and physical ageing effects.

2.1   DISSOLUTION AND ABSORPTION

In order for molecules to undergo transport within a polymer they must 'dissolve' in the solid. If the species does not 'dissolve' in the polymer then diffusion is irrelevant.   The basic mechanism for diffusion, present in all polymers, is occupation of the free volume between the polymer chains. This may be supplemented by additional mechanisms. If a mixture of species is absorbing then there will be competition between the species for absorption sites and, possibly, interactions between the chemicals.

Dissolution is a thermodynamic process where the solubility is determined by the enthalpy change on dissolution of the molecule in the polymer matrix (ΔH_s) and the volume available for occupation. A common assumption is that the surface layer reaches saturation instantly on exposure and that uptake rates are governed by the rate at which absorbed material diffuses from the surface. The amount of molecules absorbing in the component will reach equilibrium concentration in a time that depends on the dimensions of the component and the diffusion behaviour.

Ideal sorption of gases (including vapour) in a polymer follows Henry's law where the concentration adsorbed C is directly proportional to the pressure of the gas P [1]:

$$C = SP \tag{1}$$

The coefficient S is the solubility parameter, which varies with temperature T according to:

$$S = S_0 \exp\left(\frac{-\Delta H_s}{RT}\right) \tag{2}$$

Although many gas/plastic combinations have been observed to follow ideal absorption behaviour, there are many polymer/gas or polymer/liquid combinations that do not obey ideal sorption behaviour. One reason proposed to account for these observations is that there is more than one sorption mechanism operating. Two-mode models have been proposed for gas dissolution in glassy amorphous polymers consisting of ordinary absorption into the polymer matrix and additional 'anomalous' adsorption into micro voids or fillers in the material [1]. In these models, it is assumed that the total concentration is the sum of the concentrations of two thermodynamically distinct populations; molecules dissolved in the matrix and molecules adsorbed into 'holes'.

$$C = SP + C_H \tag{3}$$

It is thought that adsorption into micro voids occurs through a Langmuir isotherm.   The concentration of molecules in holes C_H depends on saturation level C'_H, hole affinity constant b and pressure P.

$$C_H = \frac{C'_H bP}{1 + bP} \tag{4}$$

Equations (3) and (4) can be combined and rewritten in the form of Henry's law with an effective solubility parameter S' which has pressure dependence:

$$S' = \frac{C'_H}{P} + S \tag{5}$$

At high pressures, the matrix solubility parameter S dominates as holes become saturated.

It has been observed [7] that the solubility of water vapour in plastics can increase, over that predicted from Henry's law predictions from low concentration uptake, above a critical relative humidity. This increase was attributed to water 'condensation' into clusters at sites that become available above this critical humidity.

2.2   DIFFUSION

Diffusion is the net transport of matter in a system by means of random molecular motion, which acts to remove chemical potential differences and will eventually produce an equilibrium state of concentration (C_∞). The motion of a molecule dissolved in a polymer can be thought of as a series of random walks between absorption sites [8]. The diffusing species is sometimes known as the diffusant or permeant. The rate of diffusion is proportional to the concentration gradient of the diffusant. General formulations for diffusion and mass transport are outlined in Appendix I.

Fick's first law of diffusion, expresses the steady state flux of diffusant per unit area (J) through a membrane as a function of the concentration gradient, where ϕ is the concentration of diffusing molecules.

$$\frac{dJ}{dt} = -D\frac{d\phi}{dx} \tag{6}$$

The proportionality constant D is known as the diffusion coefficient. The diffusion coefficient may depend on the concentration of diffusant. However, for some systems, e.g. gases above their critical temperature (fixed gases), the diffusion coefficient often does not depend on concentration, in which case Fick's second law can be used to determine the time dependence of the concentration, ϕ, of the diffusant in the sample.

$$\frac{d\phi}{dt} = D\frac{d^2\phi}{dx^2} \tag{7}$$

Diffusion following the Fick's first and second laws is termed Fickian diffusion. The diffusion coefficient is temperature dependent and for ideal systems follows an Arrhenius relationship, with an energy barrier to diffusion E_D.

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right) \tag{8}$$

For polymers, Arrhenius plots of D against 1/T are often linear but there may be discontinuities in the diffusion coefficient-temperature curves near phase transitions. For example, diffusion rates can increase significantly when the temperature is increased above the glass-to-rubber

transition temperature T_g. Diffusion can also depend on other factors, such as concentration or stress. Some of these factors are described in Section 2.5.

Fick's laws express diffusion only in terms of concentration gradients but there are indications that diffusion may also be driven by, for example, gradients in stress or temperature in the materials. These may be described using more generalised models building in Fickian diffusion. For instance, the finite element modelling package ABAQUS [9] offers a generalised diffusion model containing terms for both stress (pressure) and thermal gradient diffusion. Diffusion is assumed to be driven by the gradient of a general chemical potential, which gives the behaviour:

$$ J = -sD\left[\frac{\partial \boldsymbol{f}}{\partial x} + \boldsymbol{k}_S \frac{\partial}{\partial x}\left(\ln\left(T - T^Z\right) \right) + \boldsymbol{k}_P \frac{\partial P}{\partial x} \right] \tag{9} $$

where $\boldsymbol{J}$ is the flux, $\boldsymbol{D}(c, T, f)$ is the diffusivity; $s(T, f)$ is the solubility; $\kappa_S(c, T, f)$ is the "Soret effect" factor, providing diffusion because of temperature gradient; ϕ is the concentration, T is the temperature; T^Z is the absolute zero on the temperature scale used; $\kappa_P(c, T, f)$ is the pressure stress factor, providing diffusion driven by the gradient of the equivalent pressure stress, $P = -\sigma/3$; σ is stress; and f are other predefined field variables. The Soret effect appears to be most relevant to diffusion in liquid systems (e.g. oils, polymer solutions, melts) and little information is available on the application of the effect for diffusion in solids.

2.3   PERMEABILITY

Steady state permeability, the flux per unit pressure gradient across a polymer membrane, occurs when boundary conditions are fixed and the diffusant concentration within the membrane is in equilibrium. Henry's law states that the concentration of the diffusant in the polymer is directly proportional to the pressure on the polymer. For a polymer film of fixed thickness L, at constant temperature and gas concentrations ϕ_1 and ϕ_2 at the two surfaces ($\phi_1 > \phi_2$) then Equation (6) can be integrated across the thickness to give permeation, Q:

$$ \frac{dQ}{dt} = D\frac{\left(\boldsymbol{f}_1 - \boldsymbol{f}_2\right)}{L} \tag{10} $$

Expressing concentrations in terms of pressure then from Henry's law, Equation (6) can be written in terms of the pressure at each surface (P_1 and P_2) to express steady state permeability in terms of pressure difference:

$$ \frac{dQ}{dt} = DS\frac{\left(P_1 - P_2\right)}{L} \tag{11} $$

The product DS is known as the permeability coefficient.

In laminated systems, the total permeability of a multi-layer system (Q_L) with n layers can be simply expressed as a sum of the permeabilities (Q_i) and thickness (x_i) of all of the layers.

$$ \frac{1}{Q_L} = \frac{1}{L}\sum_{i=1}^{i=n}\frac{x_i}{Q_i} \tag{12} $$

This simple summation approach while generally effective ignores any barrier properties that may result from the interfaces between different layers. If the permeability coefficients are independent of pressure then the ordering of the layers is unimportant. However, if the permeability coefficients are pressure sensitive then their order will have a significant effect on the overall permeability coefficient (and conversely on the reliability of individual layer permeabilities calculated from experiments on multi-layers [10]). A finite difference modelling method which, when combined with inverse modelling approaches can be used to analyse the mass transport properties of multi-layers, is outlined in Appendix I.

2.4   DESORPTION

Desorption is the opposite of absorption and net desorption occurs if it is thermodynamically favoured. Normally, molecules will desorb where the concentration of the desorbing species in the atmosphere or material in contact is less than the concentration required for maintaining saturation in the polymer. Desorption may also occur across interfacial layers if the two materials in contact have very different affinities for the absorbed species. The greater the difference between the polymer surface concentration and the atmospheric concentration, the higher the desorption rate. Molecular escape rates will depend on the transport of material to the surface and thus out gassing, drying or desorption times will depend on the component dimensions and molecular diffusion behaviour.

It should be noted that desorption will not simply be the reverse of absorption, there may be considerable hysteresis if absorbed molecules are strongly bound in the polymer. Higher energies (in the form of heat) or longer times may be required for the material to return to the unexposed state.

2.5   FACTORS INFLUENCING MASS TRANSPORT

2.5.1   Polymer Chemistry

The chemical composition of the polymer matrix will have a strong influence on the solubility and diffusion properties of small molecules in the polymer matrix. Polymers with polar chemical groups, such as epoxies or nylons, will have a strong affinity for polar molecules, including water. Such materials are known to be hygroscopic. In contrast, the uptake of polar species is much lower in non-polar polymer molecules, e.g. polypropylene [1].

In polar polymer matrices, the diffusion coefficients of polar organic molecules can increase with the absorbed concentration of molecules, due to strong interactions between the molecules and polymer chains that induce structural transformations such as swelling, crazing or partial dissolution of the polymer matrix [1].

2.5.2   Free Volume

Free volume is an intrinsic property of the polymer matrix and arises from the gaps left between entangled polymer chains. Since the gaps are at the molecular scale, it is not possible to directly observe free volume. Free volume can be thought of as extremely small-scale porosity but free volume pores are dynamic and transient in nature since the size (and existence) of any individual free volume 'pore' depends on the vibrations and translations of the surrounding polymer chains. The translation of the polymer chains can open and close 'pores' and open/close channels between pores, providing 'pathways' for diffusion jumps. The

absorption and diffusion of molecules in plastics will depend to a considerable extent on the available free volume within the polymer. The greater the free volume is, the higher the capacity for absorption and the higher the mobility of the molecules within matrix. Free volume depends on the density and physical state of the polymer.

Crystallinity: Crystalline regions in polymers are more ordered than amorphous regions and free volume will be lower in these regions. It is often assumed that the crystalline region is impermeable and that the sorption depends only on the volume fraction of amorphous phase [11]. For many polymer/gas combinations it has been observed that solubility constants are directly proportional to the volume fraction of amorphous phase [5]. However, there are systems where the solubilities have been found to be higher than those expected from the volume fraction of amorphous phase, this has been attributed to the higher probability of denser regions of amorphous material crystallising preferentially leaving the residual amorphous phase with a lower density and higher concentration of 'holes' available for absorption.

Physical ageing: Physical ageing in glassy polymers occurs when a polymer is cooled to temperatures below T_g. At the elevated temperature, the polymer is in the rubbery state and the molecular configurations are in equilibrium. When the temperature is cooled through T_g conformal changes needed to maintain an equilibrium structure are restricted by the reduced mobility (increased relaxation times) at the lower temperatures. These non-equilibrium structures have relatively high mobility. However, over time the molecular structure will reconfigure to an equilibrium structure through the physical ageing process. The effect of physical ageing is to reduce chain mobility and free volume of the polymer, which reduces the mobility and solubility of diffusing molecules.

Molecular orientation: When a polymer is processed by a method that produces a preferred molecular orientation (e.g. by hot drawing, extrusion, injection moulding) then the free volume will differ from a random orientated polymer. If the polymer is semi-crystalline, orientation can cause enhanced crystallisation and, hence, reduced free volume. In amorphous polymers, orientation can elongate the free volume voids and lead to directional dependence of mobility, i.e. increased mobility in the direction of drawing and reduced transverse mobility.

2.5.3 Porosity and Voids

Pores and voids are on a larger size scale than free volume and are 'permanent' features, independent of polymer chain motion. Pores/voids tend to result from the generation of 'defects', e.g. included air, arising during processing but can also be generated in service (e.g. stress generated crazing or chemical swelling). The volume fraction of voids in a sample will depend on the imposed stress state. Hydrostatic tensile stress will tend to open voids whilst hydrostatic compressive stresses will close voids.

Pores, like free volume, offer sites into which molecules can absorb and are far less of a barrier to transport than solid polymer. Pores may also provide sites into which liquids and vapours can condense and thereby dramatically increase their uptake. A high level of porosity will increase permeability through increasing both the solubility and the effective diffusion coefficient. If pores are linked (open pores), then diffusion rates through these channels will be lead to very much greater permeation than if the pores are isolated (closed pores).

2.5.4   Filler Particles

Practically every polymeric material used in practical applications will contain filler particles and fibres introduced to modify their physical and processing properties. Fibres are added to polymer matrix composites to provide mechanical reinforcement, inorganic particles are used to control shrinkage, rubber particles are used to increase toughness and nanoparticles, such as exfoliated clays, are postulated to improve a range of properties including barrier performance.

Filler particles can influence the molecular absorption behaviour in two principal ways. Where the solubility of the filler differs from the polymer matrix then the absorption can be either increased or decreased depending on the relative solubility of the molecule in the matrix and filler. Most common inorganic filler particles (e.g. glass or carbon fibres, talc, clays, silica) can usually be considered as impermeable in comparison to polymer matrix. However, organic filler particles (e.g. rubber toughening agents, process agents, natural fibres) may have higher solubilities than the matrix. The overall effect on the component behaviour will depend on the concentration of filler and can be characterised through a 'rule of mixtures' approach provided that the solubility of the diffusant in each phase is known. However, this approach ignores any role that may be played by the interface between the filler and the matrix.

If the diffusing molecules have an affinity for the surfaces of the filler particles then the interface between the filler and the matrix may provide absorption sites for the molecules, increasing the overall solubility. Surface energies of the filler particles and diffusing molecules may be greater than greater than the polymer matrix, encouraging preferential absorption at the surfaces. There can be a large increase in solubility of molecular species that strongly interact with the surfaces of inorganic fillers. For example, inorganic fillers with hydrophilic or polar surface sites would have a strong affinity for water (and other polar molecules) and substantially increase the overall solubility of the polymer system. Nano-composite materials show substantially higher moisture absorption than the base polymer, and, studies on montmorrillonite clay nano-composites show that the extent of absorption depends strongly on the surface properties of the treated nano-particles [11]. In this situation, the overall effect on absorption is likely to depend strongly on the surface area of the filler phase.

The presence of filler particles can also affect the diffusion behaviour. Diffusing molecules would need to work their way around impermeable particles, increasing path lengths and reducing mass transport rates. Improved barrier properties from nano-sized fillers would be expected from the increased lengths of diffusion paths.

Diffusion in polymer matrix composites (PMCs), particularly of water, has been studied extensively, with comprehensive coverage given by Springer [3, 4]. The mass transport properties will depend on the volume fraction of fibres and the fibre orientation. Transport in the direction of the fibres may be very different to that normal to the fibres. 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 been treated by a rule of mixtures approach. For a volume fraction of fibres V_f and a reasonable assumption that molecular 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 [3, 4]:

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

$$D_{22} = \left(1 - 2\sqrt{\frac{V_f}{p}}\right)D_m \qquad\qquad (13)$$

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 [4]. This may be applicable for glass or carbon fibres but is very unlikely to apply to natural fibres or polymer fibre reinforcements (e.g. aramides).

Some materials, in particular composites, can exhibit anisotropic diffusion behaviour. This is normally modelled with a single solubility parameter determined from the saturation concentration and directionally dependent diffusion coefficients. Several researchers [e.g. 3, 4, 12-14] have presented three-dimensional FE methodologies for simulating Fickian diffusion, often with temperature-dependent diffusion coefficients, for predicting moisture diffusion in composite materials.

Particles lead to the presence of internal interfaces within the material that may play a role in the diffusion process. Strong affinities between surfaces and diffusing molecules may provide a driving potential for diffusion in addition to concentration gradients (or supply regions where the local concentration of diffusing molecules far exceeds the solubility limit of the matrix). Strong interactions between surfaces and diffusing molecules may allow for increased rates of diffusion along the interfaces. Conversely, strong interactions between diffusing molecules and particle surfaces may reduce permeation rates. Strongly absorbed molecules will need to overcome an energy barrier to desorb, and thus are likely to be far less mobile than molecules dissolved in the polymer matrix. This mechanism, combined with the increased diffusion path lengths due to the particles, is supported by observation that the addition of nano-fillers (such as clays) can significantly increase the solubility of moisture in plastics but reduce permeability of these materials to water [11].

2.5.5 Temperature

Temperature has an effect on the permeability and diffusion properties of small molecules in polymers, e.g. Figure 2 [15]. As the temperature increases, the mobility of the molecular chains increases and thermal expansion leads to a reduced density. Therefore, the free volume in the system will increase, leading to an increased solubility. Absorption and diffusion normally follow Arrhenius behaviour.

The coefficient S is the solubility parameter, which varies with temperature T according to Equation (2). The diffusion coefficient D is temperature dependent and for ideal systems follows an Arrhenius relationship, Equation (8), with an energy barrier to diffusion E_D.

These functions suggest predictable relationships between solubility, diffusion, permeation and temperature. However, phase changes in polymers can significantly change mass transport properties. For example, a discontinuity is normally observed in the absorption-temperature curve at the glass transition temperature with higher absorption into the rubber phase above T_g. Raising the temperature increases diffusion coefficients as free volume becomes greater and the higher vibrational energies of the polymer chains and permeant molecules increase the energetic potential for translating between absorption sites. Diffusion coefficients normally

follow Arrhenius behaviour but there may be discontinuous behaviour near phase transitions. Figure 3 shows diffusion coefficients and saturation levels for water in an epoxy adhesive [16]. The highest test temperature (90 °C) is slightly greater than T_g (85 °C), both diffusion coefficient and moisture uptake are substantially greater than they are for temperatures below T_g. There are some circumstances where increasing temperature may reduce solubility, e.g. high temperatures may reduce condensation of liquid molecules within pores reducing the quantity that can be absorbed by this mechanism.
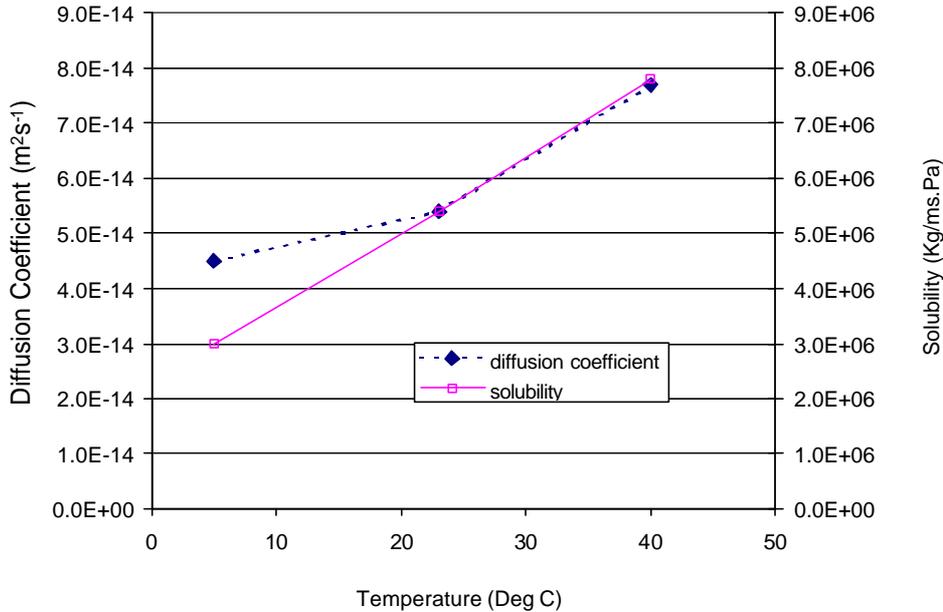

Figure 2: Effect of temperature on oxygen permeation in PET [15]
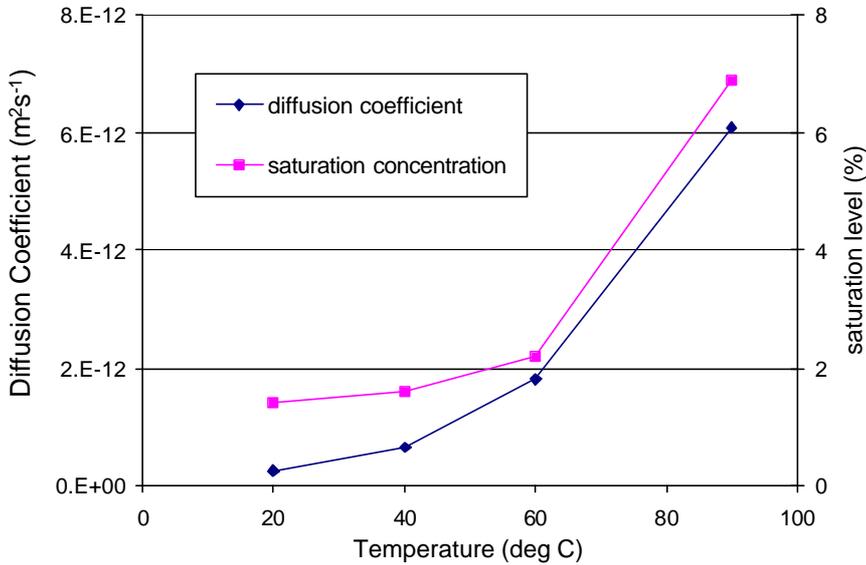

Figure 3: Effect of temperature on moisture diffusion in an epoxy [16]

2.5.6   Mechanical Stress and Strain

In service, many polymers will experience both stress and chemical exposure. Most permeation or mass uptake experiments are carried out free of external stress, although there may be unquantified internal, residual stresses, arising from processing, present in the materials. The effect on molecular solubility and mobility will depend on the type of stress applied. Hydrostatic tensile stress is expected to increase free volume and open internal voids or crazes, providing additional sites into which molecules can absorb. Conversely, hydrostatic compressive stress will reduce solubility by closing internal sites.

The results from standard permeation tests may not truly represent the properties of materials in service. Results from tests performed with applied tensile stresses have been reported in the literature. Boersma et al [6] studied the effects of tensile stress applied to plastic films on their oxygen permeation properties and reported an increase in permeation rate with stress, (see Figure 4). Michaeli et al [17] tested polymer films with and without plasma deposited barrier coatings at different levels of strain. In both cases, gas permeability increased with strain with much greater effect for the coated material. Unstrained, the coated sample had permeability around 20% of that of the uncoated sample. At 5-8% strain the differences between the two samples was insignificant. The large increases in gas permeability in the coated sample could be correlated with the strains where microscopic cracks begin to form in the brittle barrier film.
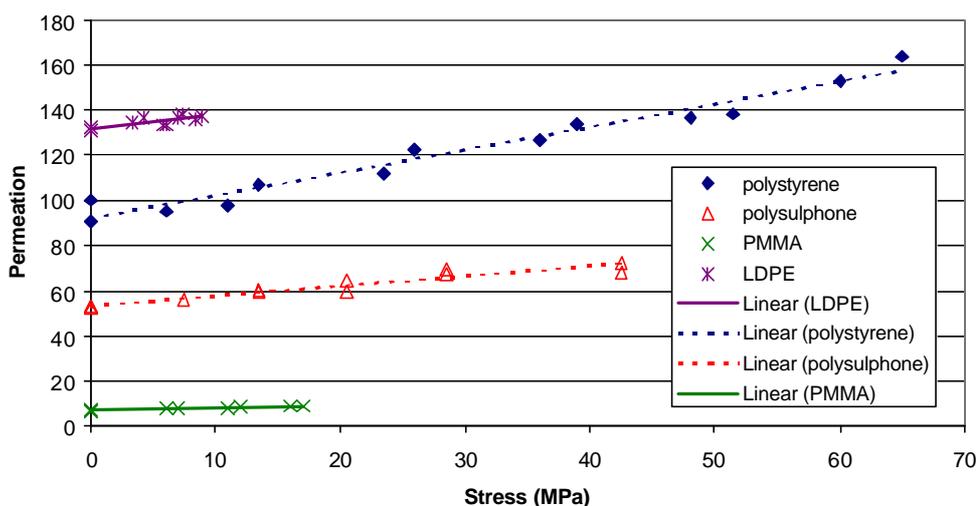
Figure 4:   Effect of applied stress on oxygen permeability ($cm^3.mm.atm^{-1}.day^{-1}$ per m^2 of surface) for various plastic films [6]

Combined stress and chemical exposure is known to lead to enhanced degradation of polymers and polymer structures. Plastics that are stressed in contact with chemicals can experience environmental stress cracking failures in conditions, which individually, would not be a problem [18]. The combination of stress and chemical exposure is known to degrade the mechanical performance of adhesive joints [16, 18-26] far more rapidly than either factor independently. The effect of absorbed chemicals (usually moisture) on stress levels within polymer structures has been modelled using stress-free Fickian diffusion coefficients and concentration dependent mechanical properties [3, 4, 13, 22-26] but studies on the effect of stress on diffusion behaviour are comparatively rare. Crocombe *et al* [26] measured the uptake of moisture in stressed bulk samples of epoxy adhesive using mass uptake experiments. They found a positive correlation between stress and solubility but, unexpectedly, a negative correlation between stress and diffusion coefficients, Figure 5, although there was a comment

that the large uncertainties in the diffusion coefficient values made it difficult to draw reliable conclusions.
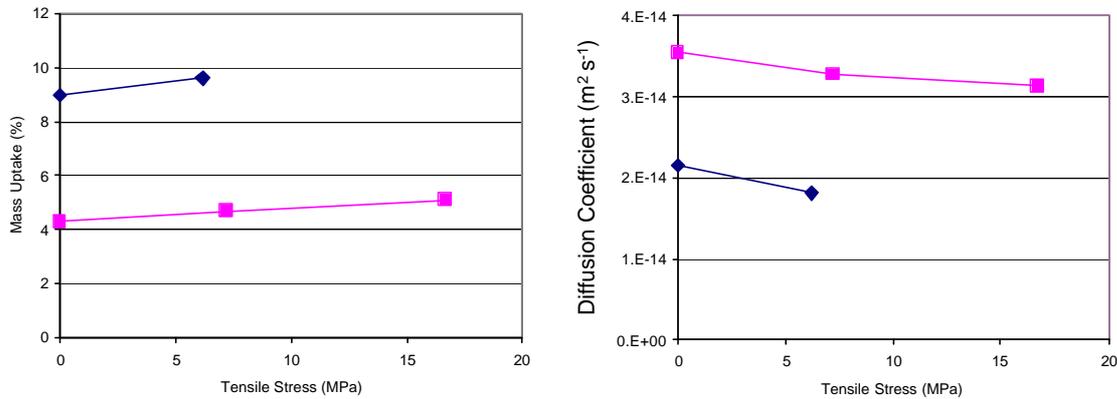
Figure 5: Effect of stress on solubility and diffusion coefficients [26]

2.5.7   Concentration

Henry's law for ideal gas absorption states that solubility is directly proportional to the external gas pressure. It was noted earlier that some systems seem to exhibit two stage absorption processes; a Henry's law type process at low concentrations and a second process occurring once a critical concentration is reached [1]. Although Henry's law does not always apply, the equilibrium concentration of absorbed molecules will increase with external concentration. This is true for exposure to gases and vapours. Liquid ingress may result from contact with fluids or exposure to their vapours. It is generally not possible to relate solubility of vapours to solubility of the liquid – contact with the latter always results in higher saturation concentrations, although diffusion coefficients may be similar. In experiments where samples are exposed to vapour it is important that vapour does not condense on the sample surface since higher absorption will occur via this route.
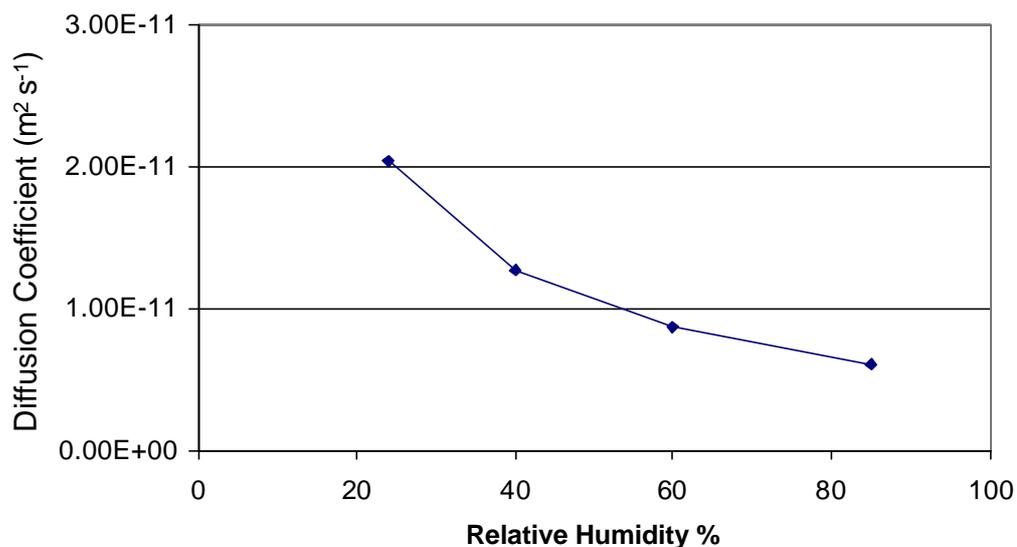
Figure 6: Effect of relative humidity on moisture diffusion coefficient [27]

The solubility of water or organic vapours is often not directly proportional to the vapour pressure, i.e. Henry's law is not obeyed. Saturation vapour concentration C_∞ can be fitted as a power law of vapour concentration ϕ in many cases [3]:

$$C_\infty = a\phi^b \qquad\qquad (14)$$

where a and b are found from isothermal absorption experiments in atmospheres with different vapour concentrations. Springer [3] reported that many studies found that the exponent b for moisture absorption fell within the range 1 – 2 and for many of the systems investigated the absorption was approximately directly proportional to vapour concentration (analogous to Henry's law). The amount of liquid absorbed during immersion cannot be predicted from the vapour absorption characteristics. The most common liquid encountered by polymer systems is water, ubiquitous in the natural environment, and the subject of numerous studies and standard measurement methods.

Diffusion coefficients can be highly dependent on concentration if there is a significant interaction between the diffusing species and the polymer. The concentration of diffusing molecules within the polymer may influence their diffusion properties. Diffusion is driven by concentration gradients and so, initially, high external concentrations imply high concentration at the surface causing large concentration gradients and, hence, rapid diffusion. As time progresses, the system will reach an equilibrium concentration determined by the solubility and external concentration. Increasing equilibrium concentrations may then have positive or negative effect on permeation rates through the material. For example, if the polymer swells in response to absorption of the diffusing molecules then increasing concentrations may increase the diffusion mobility by causing additional free volume as the polymer swells further. In the absence of such interactions, increasing concentrations in the material may lead to 'crowding' of absorption sites, reducing diffusion. Gravimetric uptake measurements of water into an epoxy [27] shown in Figure 6 illustrate the phenomenon of increasing concentration leading to a reduction in diffusion coefficient.

Studies indicate that some materials/exposure conditions can be modelled as Fickian processes characterised by a saturation concentration and single diffusion constant. However, many have revealed non-Fickian behaviour. Loh et al [22] proposed a dual Fickian process to explain moisture uptake in a rubber toughened epoxy adhesive. Each process was characterised by a diffusion constant and saturation level (the sum of saturation levels equalled the equilibrium moisture content of the samples). The values for the diffusion coefficients and saturation coefficients were obtained by iterative regression fits to the moisture uptake curves under different exposures. A non-Fickian model for glassy polymers derived from visco-elastic behaviour of polymers that expressed diffusion coefficients as a Prony series sum of relaxations has been proposed [28, 29]. Other approaches to define moisture concentration dependent diffusion coefficients [e.g. 27] have also been developed. Non-linear solubility curves have been observed in polymer systems with high levels of inorganic fillers. These curves were non-linear at all relative humidity levels, suggesting that the excess sites (assumed to be at the surfaces of the filler particles) were available at all humidity levels [19].

2.5.8   Exposure to Mixed Diffusants

Permeation and diffusion tests are generally performed with exposure to a single chemical species under defined, normally constant, conditions. However, real service life is unable to be as simple, for instance in food and beverage packaging the plastics will be exposed to mixtures

of chemicals contained in their contents. Alternatively, pre-exposure to one chemical may lead to a change in mass transport properties of a second chemical. The presence of a pre-absorbed species may block sites where the second molecule may adsorb thereby reducing solubility or alternatively increase solubility through swelling the polymer or disrupting bonds that could block absorption by the second species. For example, exposure of plastics to aqueous solutions with low pH and other ionic concentrations affects permeability of other species [30].

2.5.9   Molecule Sizes

Small gas molecules have higher diffusion coefficients than larger molecules as larger molecules require larger holes and hence have higher activation energies for diffusion. Where the penetrant has a molecule size smaller than the monomer unit of the polymer and the interaction between the components is weak then diffusive progression requires only a weak effect, such as limited rotational oscillation of a very few monomer units, in order to create sufficient space for the penetrant to jump from one space to another. Penetrant molecules that are comparable in size to the monomer units require cooperative movements by several monomer units to facilitate translation.

Although not considered in depth in this review, the transport of small particles within polymeric materials is a diffusion problem. There is obvious interest in understanding the movement of species such as cells, enzymes and proteins in biomaterials such as tissue scaffolds or gels. The growing use of nano-particles in plastics may require better measurement and understanding of their diffusive migration, leaching behaviour and absorption through tissue, e.g. skin or lungs, in order to address health issues (real or perceived) that could limit their acceptability.

2.5.10   Role of Interfaces

As discussed earlier, permeation through a polymeric material can be described using functions that represent the solubility and diffusion constants. Many polymers may not exhibit ideal behaviour but non-linear functions can be used to represent non-Fickian behaviour. Similarly, most polymers used in practical applications are filled and can be considered to be multi-phase systems with many internal interfaces at the micro/nano-scale. The permeation properties of such systems would be very difficult to represent from first principles. Accounting for the properties of all the different materials and surfaces would be a very complex task. Fortunately, the properties of the materials system can be measured as an ensemble and these properties, sometimes directionally dependent, can be used for most purposes. Rule of mixtures approaches can be used to estimate the effects of varying volume fractions of dispersed phases.

Materials systems containing macro-scale interfaces cannot usually be treated as a single ensemble material as the size scale and geometry of the different materials will have an effect whether or not the interfaces have diffusion properties. Systems that have macro-scale interfaces include:

- Adhesive joints
- Laminates
- Coatings
- Multi-layer films
- Long-fibre composites

- Woven fabric composites

Where macroscopic interfaces occur, the analysis is less straightforward but amenable to analysis if the interfaces play no role in the process. Figure 7 shows schematically the likely differences between diffusion in a multi-layer with interfaces through the thickness, case (i), and parallel to the layers, case (ii).

Case (i) is analogous to a multi-layer film or coating. Diffusion occurs in series and concentration is uniform in the x-direction. Ignoring any 'properties' that the interface may have, the overall diffusion could be modelled simply as a series of 1-dimensional analyses, using the concentration at each interface as the boundary condition for the next layer. Case (ii) is perhaps more representative of an adhesive joint, long-fibre composite or laminate. Diffusion occurs into all three layers in parallel. This situation would need to be considered as a 2-dimensional problem, the permeation rates within each layer would be different and therefore there would be concentration gradients across each interface, leading to diffusion between the layers. This would accelerate uptake in the less permeable materials.

However, these analyses become unreliable should the interfaces affect mass transport processes. There is evidence that impermeable inorganic filler particles in polymers increase the uptake of polar solvents and moisture through strong affinities between the surface and the molecules increasing available sites for absorption. It is not unreasonable to assume that similar mechanisms will occur at macroscopic interfaces between dissimilar materials (e.g. metal-adhesive or metal-coating bonds). In which case, high saturation concentrations at the interfaces would alter diffusion boundary conditions, encouraging increased permeation rates. The effects may not be particularly significant in case (i), particularly if the material layers are thick but in case (ii) a strong absorption at the interface may provide a fast diffusion channel along the interface. Diffusion from this interface would increase concentrations in the interior of the sample at a higher rate than would be expected from bulk material properties.
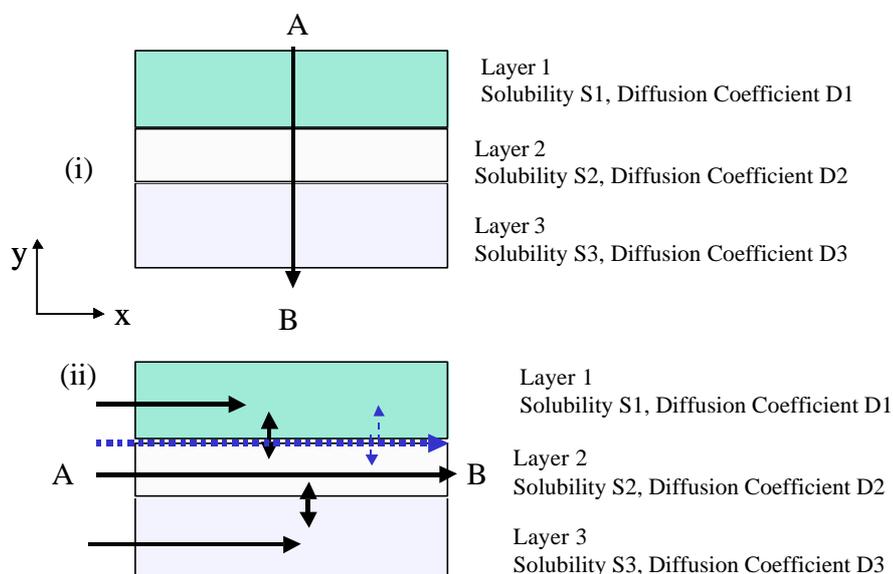

Figure 7: Diffusion in multi-layer systems with interfaces (i) through thickness diffusion in series: interfaces only have an effect if they provide an additional barrier; (ii) diffusion along layers, in parallel: diffusion possible between layers and along interfaces.

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 are unlikely to be the same as the bulk material. Bond et al [31] determined diffusion coefficients for an epoxy adhesive as being 6.4×10^{-13} $m^2 s^{-1}$ when obtained from mass measurements on bulk adhesive specimens and 6.7×10^{-12} $m^2 s^{-1}$ 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 diffusion along the interface, supported by dielectric constant measurements indicating a significant difference in water concentration across the thickness of the glue line. However, there is little else in the way of quantitative data in the literature on the role that is played by interfaces in the diffusion process, although it is well recognised that diffusion of chemicals to the interface in a bond degrades bond performance [16, 19-26, 32]. High diffusion of chemicals, e.g. moisture, into the interfacial layer is generally undesirable as interfacial bond strength can degrade through many mechanisms [32] including:

(i)   Rupture of interfacial secondary bonds;
(ii)   Rupture of interfacial primary bonds;
(iii)   Hydration and weakening of the oxide layer on metallic substrates;
(iv)   the hydrolytic attack on a boundary layer of adhesive, adjacent to the interface – this boundary layer may have a different chemical/physical structure to that of the bulk adhesive due to the presence of the adjacent substrate surface;
(v)   Hydrolysis of the primary bonds of any primer present - leading to a cohesive failure through the primer layer;
(vi)   Moisture induced swelling of material close to the interface imposing stress at the interface.

2.5.11 Leaching of Additives

The permeation of additives in a polymeric material may become an issue in some applications, particularly for food contact, pharmaceutical or medical use. Additives that remain as liquids or gases within the polymer are likely to be capable of moving within the polymer matrix or even of being leached from the polymer (this process is known as migration). Chemicals leaching from additives may also diffuse within the matrix as a result of reactions between the additives and the diffusant. Leaching from additives may be 'activated' as a result of environmental conditions (e.g. temperature or chemical concentrations). Additives that are 'solids' are less likely to migrate within the polymer matrix unless they undergo dissolution in the matrix (either in the polymer or through ingress of other chemicals) or if their size is comparable to the sizes of pores or voids in the polymer (this may become an issue with nano-particles).

3.   PERMEATION MEASUREMENT METHODS

3.1   OVERVIEW

There are many measurement methods and several standard techniques for determining mass transport in polymers [1, 10]. The most suitable method will depend on the type of sample, the permeating chemical species and the likely rate of permeation. The most appropriate methods will differ according to the type and thickness of the sample, for example different methods are suitable for foams, thin film membranes and solid sheets.

The main measurement methods can be divided into two general classes. Those that determine the mass transport within a material by sensing the time dependent distribution of molecules in the sample material and those that determine the mass transport properties from the rate at which molecules permeate through the material.

Sensing Within Materials Methods: The permeating species accumulates within the sample material over a period of time and diffusion behaviour is determined from the spatial and temporal distribution of the permeant concentration.   The permeant concentration can be measured directly (e.g. using a quantitative spectroscopic technique) or indirectly (e.g. using gravimetric determinations). Techniques have also been developed that monitor changes in the physical properties of the polymer (e.g. mechanical or optical properties).

Permeation methods: Permeation measurements can be split into two basic types. Quasi-isostatic methods determine permeation through the sample under varying concentration differences. A permeant current flows through one side of the cell. The permeant accumulates in the other side of the cell and the amount accumulating is quantified by a physical sensor or analytic chemistry technique, Figure 8. The concentrations in the cell will reach equilibrium given sufficient time and the concentration gradient will fall during the test. Isostatic methods test permeation through the sample material under constant concentration gradients.   A permeant gas current flows through one side of the cell (the permeant may be a mixture of gases), and through the other side a carrier gas takes the permeant passing through the polymer to the sensor, Figure 9. In some methods the detector side may be under reduced pressure or even a vacuum. The concentration gradient across the sample is constant throughout the test (provided that the flowing sample concentrations are maintained).

All permeation methods use the same basic principle: one side of the sample is exposed to the gas or vapour to be studied (feeding side); this can be done statically or with a continuous stream of permeant gas to maintain a constant pressure/concentration. On the detector side the permeating gas or vapour is swept away with a carrier gas (usually nitrogen) and fed into a sensor. The detector is often specific to the permeating species. In many applications, rather than measuring the absolute quantity of the mixture permeant in the carrier gas, a relative difference between the mixture of the permeant and carrier gas and the pure carrier gas is used. The permeability of the membrane is determined from the amount or rate of permeation and experimental parameters such as time, sample area, sample thickness, pressure difference, concentrations, etc. the permeability of the membrane can be calculated. There are several commercial suppliers of permeability measurement instruments suitable for studying plastics. Appendix II lists some commercial permeability measurement instruments. Inclusion in (or exclusion from) this list does not imply any particular recommendation (or rejection) of instruments but merely reflects information available when this report was being compiled.

permeant sample

material sample

sampling

sealed cell
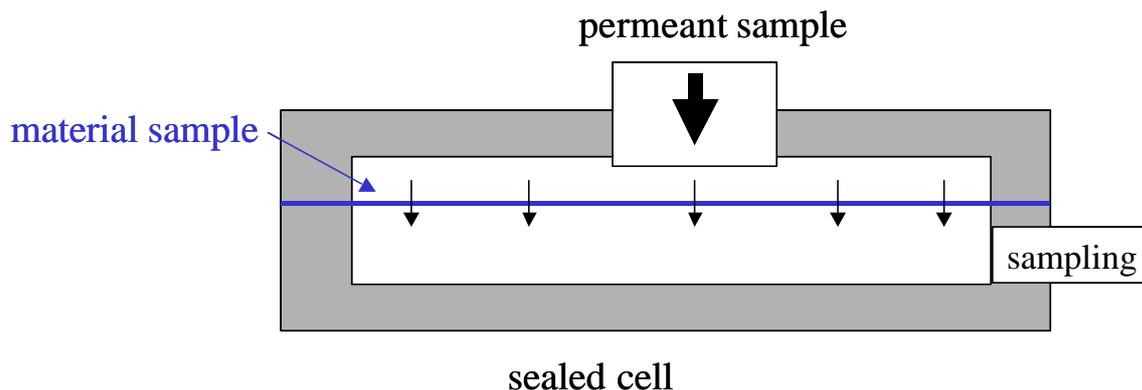
Figure 8: Quasi-isostatic method

permeant sample

material sample

detector

sealed cell

carrier gas
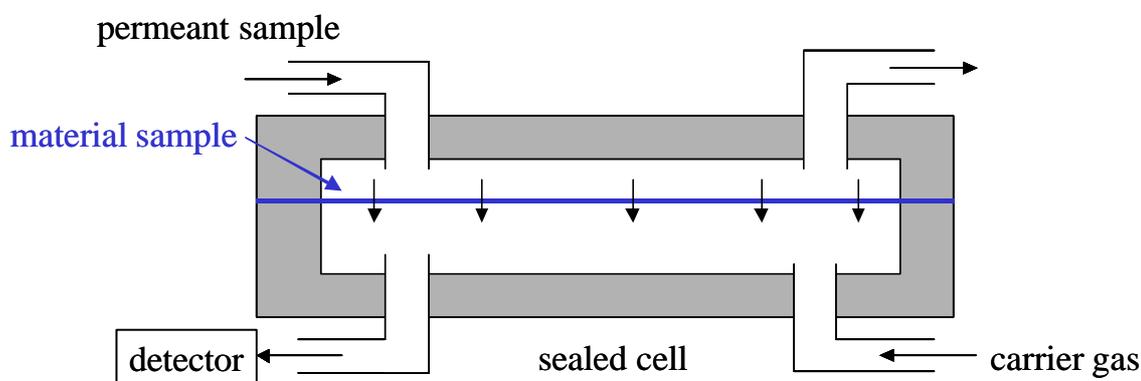
Figure 9: Isostatic method

Many methods for measuring the permeability of a membrane or film work by a sensor continuously generating a signal, which is related to the amount or to the rate of transmission rate of the gas or vapour through the membrane. The choice of sensor will depend on the species to be sensed, the level of accuracy required and cost considerations. Various detection methods are outlined in Appendix III.

The amount of permeant detected by the sensor is proportional to the amount of molecules that permeate through the polymer, and it is quantified as transmission rate, permeance, or permeability coefficient. Permeability coefficients can be expressed in a variety of units, for example with normalisation for sample dimensions permeation properties can be expressed in units of:

- Mass of material permeating times sample thickness per time per unit area of surface;
- Volume of gas (at standard temperature and pressure) permeating times sample thickness per time per unit area of surface; or
- Number of moles permeating times sample thickness per time per unit area of surface

These terms are of course interchangeable as conversions between mass, volume and number of moles can be readily derived but this variety of units for permeation makes ready comparison between results reported in the literature somewhat complex (particularly as results are sometimes reported without normalisation for sample dimensions).

3.2 SENSING WITHIN MATERIALS

Many methods have been proposed for determining mass transport properties through measuring changes in the properties of the material with exposure time and position. The spatial and temporal distribution of the permeant concentration can be used to determine diffusion properties. The permeant concentration can be measured directly (e.g. using a quantitative spectroscopic technique) or indirectly (e.g. using gravimetric determinations). Techniques have also been developed that use changes in the physical properties of the polymer (e.g. mechanical or optical properties).

Many chemicals will affect the thermo-mechanical properties of the polymer matrix in which they are absorbed [1-5]. Examples of this include swelling, plasticisation (leading to loss of stiffness and strength) and reduction in glass transition temperature in many polymers with the ingress of water. Whilst these changes in properties are usually seen as an undesired consequence of chemical exposure, monitoring these property changes will provide information on chemical concentrations that could be used to investigate diffusion. Mechanical property measurements usually require a reasonable quantity of materials and are, in general, destructive tests, at the very least altering the concentration of the absorbing species. Therefore, many test samples are likely to be needed. In many cases, with a possible exception of adhesive joints or very low solubilities, it is difficult to see any advantage of mechanical measurements over gravimetric measurements for determination of diffusion properties. The methods described in this section are included more to illustrate the effects of chemical uptake than to describe measurement methods. Thermo-mechanical approaches average the response over a volume rather than providing information on concentration distributions.

3.2.1 Mass Uptake Measurements

Absorption of liquids into polymers can be followed through mass uptake (or gravimetric) measurements, since liquid densities are large compared with gas densities. 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 [1, 23, 25]. However, if the material samples (or components of the material) are soluble in the liquid then mass loss due to leaching of material can lead to errors in the absorption measurements [10].

ASTM D 570 [33] and ISO 62 [34] are standards that outline measurement methods for water absorption by immersion. Standard sized samples should be dried to constant mass, m_0 (at 110°C or 50°C depending on the thermal stability of the material) and stored in a desiccator before testing. 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 before immediately weighing (in a weighing bottle for very thin samples). Samples can then be returned to the medium for continuing exposure provided that the time out of the medium is minimised. The balance used should be have a resolution of 0.1 mg or better [34], which can be relaxed to 1 mg if water absorption is greater than 1 %. The increase in mass divided by the initial mass, measured at regular time intervals, is plotted against time in order to define the absorption curve. Saturation mass uptake m_s is defined when the weight gain from 3 successive measurements differ by less than 1% of the overall weight gain and saturation moisture content C_s is simply m_s/m_0.

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.

The relative mass uptake at time 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 then $m_c = m_0$.

$$m_r(t) = \frac{m(t) - m_c}{m_0} \tag{15}$$

Diffusion plots are obtained by plotting $m_r(t)/m_s$ against a function of $\sqrt{t}$ divided by thickness, d. The initial portion of the curve (normally the portion up to $m_r(t)/m_s = 0.5$) is linear and the diffusion coefficient D is determined from the slope. The time required to reach saturation depends on d^2. A maximum sample thickness of 1 mm is recommended [34] to ensure that test durations do not exceed one week for typical D values for polymers (ca. 10^{-12} m^2s^{-1}).

ISO 62 [34] provides guidance on verifying Fickian diffusion; a log-log plot of $m_r(t)/m_s$ against the dimensionless diffusion value, $D\pi^2t/d^2$ and compared with the theoretical curve.

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 [22]:

$$\frac{c(t)}{c_s} = 1 - \frac{4}{p}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)}\exp\left[\frac{-D(2n+1)^2p^2t}{4l^2}\right]\cos\left[\frac{(2n+1)px}{2l}\right] \tag{16}$$

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:

$$\frac{m_r(t)}{c_s} = 1 - \frac{8}{p^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[\frac{-D(2n+1)^2p^2t}{4l^2}\right] \tag{17}$$

which can be approximated for the initial part of the diffusion curve as:

$$\frac{m_r(t)}{c_s} = \frac{2}{l}\sqrt{\frac{Dt}{p}} \tag{18}$$

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. The same analysis approach 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.

In materials with anisotropic diffusion properties (e.g. fibre reinforced plastics) erroneous results may 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, but the additional mass of the sealing material needs to be accounted for when analysing results. Any sealing materials used should have insignificant moisture absorbance.

3.2.2 Glass Transition Temperature

The absorption of many chemicals will reduce the glass transition temperature T_g of polymers. T_g of thermoset polymers such as epoxies are known to vary with moisture content. T_g can be measured using either Dynamic mechanical thermal analysis (DMTA) or differential scanning calorimetry (DSC) measurements. Figure 9 shows DMTA measurements that were carried out on a hot/wet conditioned glass-fibre reinforced composite [14]. Each specimen had been immersed in deionised water at elevated temperatures (i.e. 25, 40 or 60 °C) for a selected period (either 1, 2, 3 or 6 weeks).

The results, presented in Figure 10, show that moisture reduces T_g with the shift in temperature being related to moisture content and independent of exposure temperature. The moisture uptake- T_g shift can be represented by the following linear relationship [14]:

$$T_{gw} = T_{gd} - gM \qquad (19)$$

where T_{gd} is the glass transition temperature of the dry material, T_{gw} is the glass transition temperature of the conditioned (or wet) material, g is the temperature shift (in K) per unit moisture absorbed and M is the amount of moisture absorbed (wt %). The value of g in this case is 13.5 K.
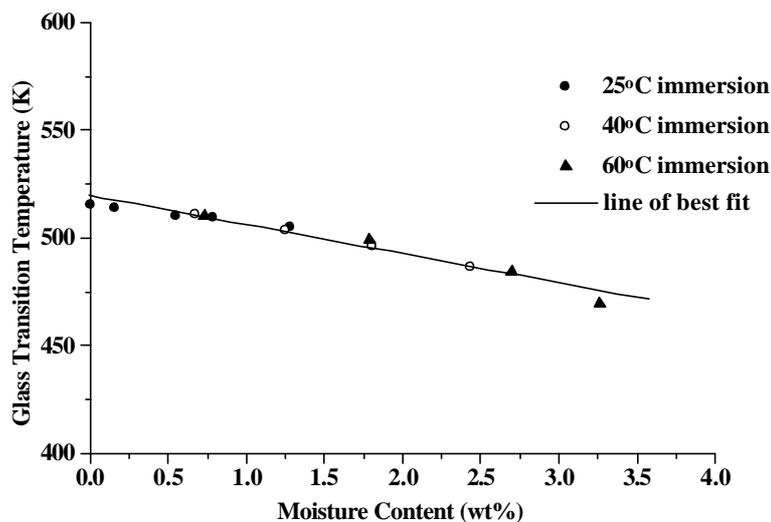

Figure 10: Glass transition temperature of a composite as a function of moisture content [14]

T_g measurement requires that samples be removed for testing, which makes this measurement a destructive test. DSC measurements require less of material (milligrams) and are therefore less

invasive than DMTA samples (rectangular bars) but such small samples may not be truly representative of the whole component (e.g. for PMCs). Developments in nano-indentation measurement capabilities offer the possibility of carrying out T_g measurements in-situ but these techniques will be limited to near surface regions, in common with sampling for DSC or DMTA.

3.2.3   Material Strength

It is possible to relate the rate of degradation of tensile strength with the rate of moisture uptake (i.e. diffusivity D), as shown in Figure 10 [14]. The diffusivity D is a function of absolute temperature T and is given by the Arrhenius relation:

$$D = D_O \exp^{-E/RT} \qquad (20)$$

D_0 is a constant, E is the activation energy of diffusion and R is the ideal gas constant. If the natural logarithm of the half-life $t_{1/2}$, the time taken for tensile strength to degrade to 50% of the dry strength under environmental exposure, is plotted against the diffusion coefficient at the temperature of exposure then a linear relationship is found [14].

The relationship between tensile strength half-life, $t_{1/2}$, and diffusivity, D, can be approximated by the following empirical relationship (see Figure 11):

$$\ln t_{1/2} = A - BD \qquad (21)$$

Here, constants A and B have values of 9 and 168,662, respectively. Such an approach could be used to assess moisture content but would rely on a great deal of destructive testing.
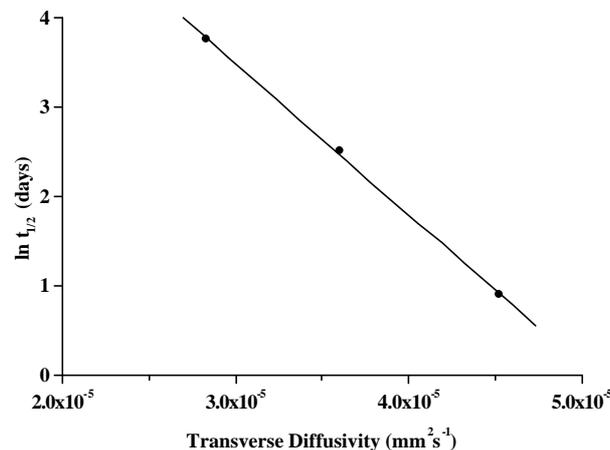
Figure 11: Tensile strength half-life as a function of diffusivity for E-glass/polyester [14]

3.2.4   Stiffness and Modulus

Uptake of many chemicals, particularly water, reduces the modulus of polymers. This is linked to the reduction in T_g with uptake. Modulus can be measured in a variety of ways, most obviously using standard tensile test methods, such as ISO 527 [35]. Changes in mechanical modulus have been used to assess fluid uptake in adhesive joints. The changes in joint

stiffness were correlated with the concentration dependant change in modulus of bulk samples [36]. The results for adhesive joints produced diffusion coefficients of similar magnitudes to the bulk material.

Stiffness changes can also be followed through ultrasonic modulus measurements. The speed of sound in a material is dependent on its density and modulus. Time of flight measurements, of pulses generated and detected by ultrasound transducers, can reveal changes in the speed of sound. This is exploited in the use of ultrasound velocity measurements in cure monitoring applications [37] but may also be sufficiently sensitive to monitor changes due to chemical uptake. Measurements of ultrasound transmission at different locations could be used to map spatial distributions of chemical concentration. The resolution would depend on the diameter of the ultrasonic transducer.

3.2.5   Sample Swelling

Many chemicals can cause swelling of polymers. This is often a problem for long term performance as a swollen polymer has the effect of:
- Being less dense
  - Increased permeability to molecular transport;
  - Reduced mechanical and thermal performance
- Increasing stress, potentially weakening the component
  - Internal stress in the polymer
  - Applied stress on parts in contact, e.g. adherends
- Shape distortion
  - Loss of sealing ability
  - Change of fit

Swelling may also be used to track uptake, through measurement of dimensional changes of samples, if a relationship between swelling and liquid content is known. Swelling strains of the order of 1-3% have been reported for epoxy adhesives [22].

3.2.6   Optical Properties

The change in optical properties of a polymer with concentration of absorbing molecules may be used to quantify the concentration provided that suitable calibration curves are available. Beers law stating that optical absorption is proportional to concentration of absorbing species (for a fixed path length) may apply if the primary absorption bands of the diffusing species and the polymer are sufficiently separate. Optical transmission properties depend on the plastic being transparent to the optical wavelength selected. This will tend to rule out opaque plastics, which will tend to include most filled materials, limiting applications.

Reflection spectroscopy methods can be used to study the chemical composition of the surface of opaque materials and may be used in combination with sample sectioning to determine through-thickness distributions. However, the value of such measurements is open to question since freshly exposed surfaces are likely to swiftly reach an equilibrium concentration based on the makeup of the atmosphere. This is a limitation with any surface analysis technique.

Refractive Index: Absorption of chemicals will alter the refractive index of transparent polymers with the magnitude of the change in refractive index being related to the concentration. Refractive index measurements made on transparent plastics will deliver

quantitative information on concentrations provided that changes in refractive index can be attributed to changes in concentration. These measurements can be used to map concentrations in two dimensions but not through the thickness in the direction of transmission, which may limit applicability in many types of exposure test. The spatial resolution will depend on the diameter of light beam used.

Interference Fringe Patterns: Variations in refractive index will produce changes in interference fringe patterns generated from internal reflections in the film. Swelling in polymers induced by absorbed species will cause density/optical path length changes that will alter fringe patterns. Therefore, changes in interference film patterns could be used to 'map' diffusion in thin films.

Infra-red Spectroscopy: Infra-red (IR) spectroscopy provides qualitative and quantitative chemical analysis data, particularly useful polymer chemistry. IR provides a fingerprint of the adhesive or coating composition in any physical state that can be compared with databases of spectra to enable characterisation of molecular state. IR is a commonly available laboratory technique. Water content of polymers and adhesives can be quantified using infra-red spectroscopy [38]. However, the characteristic OH vibrational bands of water are difficult to resolve from OH groups on many polymer chains. The IR bands of deuterated water (D_2O) can be more easily resolved. Thus D_2O can be used in place of water to probe diffusion. Gravimetric measurements suggest that the mass uptake of D_2O is similar to water and there is an assumption from this that the diffusion coefficient of D_2O is about 10% lower than that of H_2O. Many polymers will not be transparent to IR. Therefore, only surfaces (by reflection) or thin layers (by transmission) can be probed without embedding fibre optic sensors, which limits the applicability. The combination of spectroscopy with embedded optical fibres, as a means of probing within materials, is of great interest. Wapner and Grundmeir [39] used FTIR transmission microscopy measurements to determine the diffusion of D_2O into a thin layer of adhesive sandwiched between two transparent silicon wafers. They were able to map water concentrations in the adhesive layer, measuring the evolution of concentration with distance from the exposed edge to calculate diffusion coefficients. The resolution of measurement was determined by the spatial resolution of the beam diameter (100μm).

Fibre Optics: Fibre optic sensors can be embedded within materials to allow structural health, conditioning or cure monitoring. Developments in evanescent wave techniques allow spectroscopic study of the chemical nature of material in contact with the fibre [38, 40]. This can be used to study chemical reactions during cure [40] but could also be used detect and quantify migrating molecules provided that peaks can be resolved from the polymer matrix. Uptake of chemicals can also be monitored through physical interactions between the fibre cladding and the chemical – for example water will swell the cladding leading to a change in refractive index [38]. With suitable calibration, this refractive index change can be related to water content. Care should be taken with fibre optic sensors so that additional paths for diffusion ingression do not arise from the placement of the sensor.
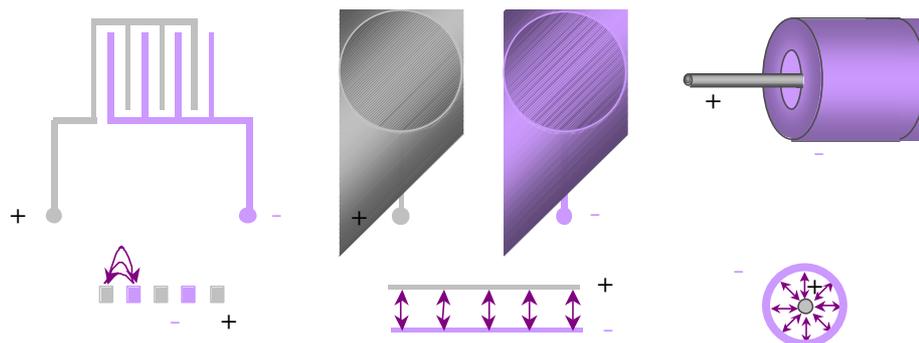
Figure 12: Dielectric sensor types – interdigitated, parallel plate and coaxial

3.2.7 Electrical Measurements

Dielectric spectroscopy probes the complex impedance of insulating materials. Molecular relaxation in polymers can be studied through dielectric relaxation spectroscopy, which enables changes in polymer networks to be followed, for example during cure [41]. Dielectric spectroscopy may be able to determine concentration changes through changes in the dielectric relaxation of the polymer chains but far more usefully through the changes in electrical signal due to the diffusing molecules. Water, like other polar molecules, has high dielectric constant in comparison to polymers and so the ingress of water will lead to an increase in electrical permittivity. The dielectric properties of both the polymer and water are frequency dependent, which complicates interpretation, but in many systems it should be possible to select a single frequency where the change in permittivity can be easily correlated with water content. Dielectric water sensing was demonstrated on an earlier DTI project [38]. Dielectric sensors can take various forms, Figure 12:

- parallel plates applied externally to the sample, measuring the full volume;
- interdigitated sensors either embedded in the sample or applied to an exterior surface, measuring local properties; or
- coaxial sensors, embedded in the sample, measuring local properties.

Electrochemical sensors are often used in permeation instruments as sensors for quantifying permeation through plastic films but sensors embedded within samples could be used to monitor changes in chemical concentration. Electrochemical sensors have been used to monitor corrosion in reinforced concrete (due to chloride ion diffusion), demonstrating the principle. However, it is unlikely that the commercial sensors used in the concrete would be suitable for plastics without further development.

3.2.8 Other Methods for Detecting Chemical Ingress in Polymers

Many other methods have been proposed in the scientific literature for characterising absorption of chemicals into polymer for example:

X-ray Diffraction (XRD): Predecki and Barrett [42] described an X-ray diffraction measurement for assessing moisture distribution in composites. The technique relies on detecting residual strain changes in the filler particles (from lattice spacing). The presence of moisture near the filler particles plasticises the matrix, allowing the relaxation of residual strains in the fibre, which are detected through diffraction peak shifts. This method requires

extensive knowledge of the properties of the fibre and a model relating relaxation to water content.

Nuclear Reaction Analysis (NRA): This moisture profiling technique relies on the detection of high energy protons emitted due to the nuclear reaction between ^{3}He ions and absorbed deuterium atoms (originating from the conditioning D_2O-H_2O mixture). Samples were exposed for a fixed duration and then sectioned under liquid nitrogen to expose the inner surface [43]. These surfaces were scanned using a ^{3}He ion beam to determine the concentration of moisture with depth. Measurements were in agreement with Fickian diffusion predictions.

Nuclear Magnetic Resonance (NMR): The concentration of deuterium hydrogen nuclei can be determined using magnetic resonance scanners, suggesting that through using deuterated probe chemicals NMR may be a potential method for characterising concentration profiles.

Surface Analysis: Various surface analytical methods, such as secondary ion mass spectroscopy (SIMS), Auger spectroscopy or X-ray photo spectroscopy (XPS), can be used to provide quantitative data on molecules absorbed in surface layers. Such techniques may be used to map the distribution of molecules permeating through membranes or films. Samples may be sectioned and examined using surface analysis methods but it should be recognised that sectioning and exposing interior surfaces may affect the behaviour of the system.

Reactive Films: Films that react with diffusion chemicals can be applied to the surfaces of samples (either permeation films or 1-dimensional diffusion systems) to determine concentrations at the surfaces. For example, thin reactive layers of potassium, deposited on one side of a polymer film sample, react with molecules of gas (e.g. oxygen, water vapour) diffusing through the film and corrode the reactive layer to various extent at various places, proportionally to the amount of the gas passed. The "permeation map" thus created can be visualized with optical microscopy.

Radioactivity: Radioactive isotopes such as tritium can be detected after permeation by using counters to detect the products of radioactive decay [44].

3.2.9 Embedded Sensors

Most of the methods available for determining concentrations within materials provide information averaged over the whole sample (e.g. gravimetric or mechanical), averaged through the thickness (e.g. optical transmission) or at the surface only (e.g. surface spectroscopy). Some novel sensing methods, such as fibre optic, electrochemical and dielectric, can be used as embedded sensors within materials to measure local concentrations in the interior of the material. If several sensors are used in different locations in the specimen then measurements of diffusion flux can be made. In order to successfully use embedded sensors, the sensor should be small in comparison to the component. To provide valid results, embedded sensors should not interfere with the diffusion in the component. The sensors should not act as sinks or reservoirs for the diffusant (e.g. by consuming or releasing sensed molecules). When designing tests using embedded sensing it should be remembered that the cabling might act as a diffusion channel.

3.3. PERMEATION MEASUREMENT METHODS

There are several general types of permeation measurement that are commonly used, many of these specified as standards by bodies such as ISO, BSI or ASTM. The methods are arbitrarily classified here as Water Vapour Transmission Rate (WVTR) and Gas Permeability but it is recognised that WVTR measurements can be regarded as a subset of gas permeability techniques. Permeation tests rely on differences in concentration of the permeating species on either side of the membrane to provide the 'potential difference' that drives the permeating flux. The increase in concentration of permeating species is determined either through a general method such as pressure changes, mass changes or by using a detector specific to the species being studied. Detector types are summarised in Appendix III, inclusion in (or exclusion from) this list does not imply particular recommendation (or rejection) of any technique but merely reflects information available when this report was being compiled.
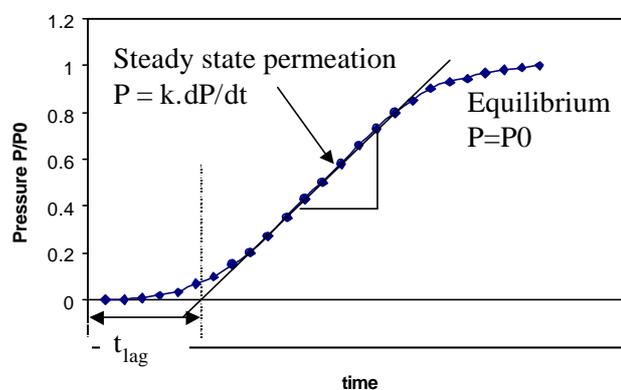
Figure 13: Illustrative permeation curve

The feed side is exposed (at $t = t_0$) to the permeant and the amount permeating through the sample is measured through an increase in concentration at the detector side. Figure 13 illustrates a typical permeation detection curve, characterising permeation through pressure change. There is a short delay in detecting an increase in concentration, characterised by the "time-lag" t_{lag}, while the first molecules diffuse through the membrane. The concentration and rate of change in concentration continues to increase as further molecules permeate through the sample. The rate of increase in pressure levels off when the concentration in the sample reaches equilibrium and the concentration time plot becomes linear. The linear portion of the curve is called steady state permeation. Permeation will remain at this rate in an isostatic test. As shown, the rate of permeation may level off as concentration reaches equilibrium, decreasing the concentration gradient across the sample, in quasi-isostatic tests.

The time-lag t_{lag} is a measure for the diffusion coefficient and can be determined by extrapolating the linear portion of the pressure curve to P = 0. The slope of the linear part of the P(t) curve can be used to calculate the permeation coefficient. The solubility and diffusion coefficients can be calculated from these results.

3.4   WATER VAPOUR TRANSMISSION RATE (WVTR)

There are several standard methods available for the determination of water vapour transmission through thin samples [45-54] or for exposing samples to standard conditioning atmospheres [55-58]. All WVTR methods follow the basic principle of exposing one side of the sample to an elevated level of water vapour and measuring the quantity permeating through the sample – different methods are employed for measuring the amount of moisture transmitted. In experiments where absolute concentrations are maintained (isostatic methods) there will be a transient, increasing rate of transmission as the moisture saturates the sample before a steady state transmission rate is obtained. In accumulation (quasi-static) experiments where the concentration of vapour is allowed to build up on the detector side the transmission rate will decrease as the water vapour concentration approaches equilibrium with the input or feed side. Between the start and end transients, there will be an approximately linear region in the transmission curve where the transmission rate is close to steady state permeation.

In all methods the sample cell should be tightly sealed from the external environment in order to prevent extraneous transfer of material to or from the detector side. The materials used in the construction of the cell should not react with either water vapour or any carrier gas. The materials should not absorb water or carrier gases. Stainless steel is a suitable material for the cell and plumbing. An inert material such as Viton rubber is recommended for seals. Wax is sometimes used for sealing samples, particularly where it is not possible to use pressure to seal, but can take a skilled technician to manufacture a good quality seal. The efficiency of seals or the inertness of measurement cells can be established by running tests with an impermeable material (e.g. glass or metal sheet) replacing the test sample.

ASTM standards adopt the following definitions:

- Water vapour transfer rate (WVTR): is the mass transfer rate of water vapour per unit area and is normally expressed in gm^{-2} per day.
- Permeance: the ratio of WVTR to the difference in vapour pressure between the two sides of the sample, normally expressed in gm^{-2} per day per mm Hg.
- Permeability: is the product of permeance and test samples thickness. This assumes that permeance is inversely proportional to thickness. Permeability is normally expressed in $g\ cm\ m^2$ per day per mm Hg (or in SI units $\mu g\ m\ N^{-1}\ h^{-1}$).

3.4.1   ASTM Standard E 398 Accumulation Method

Although ASTM E 398 has been withdrawn as an ASTM standard there are many commercial instruments in use (and still being manufactured) that use this method. The accumulation method of WVTR measurement is a proven approach for medium/high barriers. The test method, shown in Figure 13, involves a chamber containing a source of water that is separated from an accumulation chamber by the sample under test. The introduction of a dry purge gas, such as nitrogen, is used to control the relative humidity (RH) within the accumulation chamber, which fluctuates between a low set point and a high set point in response to purge.

When the test begins, the valves open to allow a stream of dry purge gas to flow through the upper chamber, reducing the RH in the chamber until the low RH is reached. The valves are closed and the humidity level within the chamber increases gradually in response to permeation through the film, Figure 14. When the high RH set point is reached, the valves are opened once again and the cycle repeats. The WVTR is based on the number of seconds or minutes

required for the RH within the chamber to reach the high set point. When the WVTR is stable over repeated cycles, the ?lm is at equilibrium.
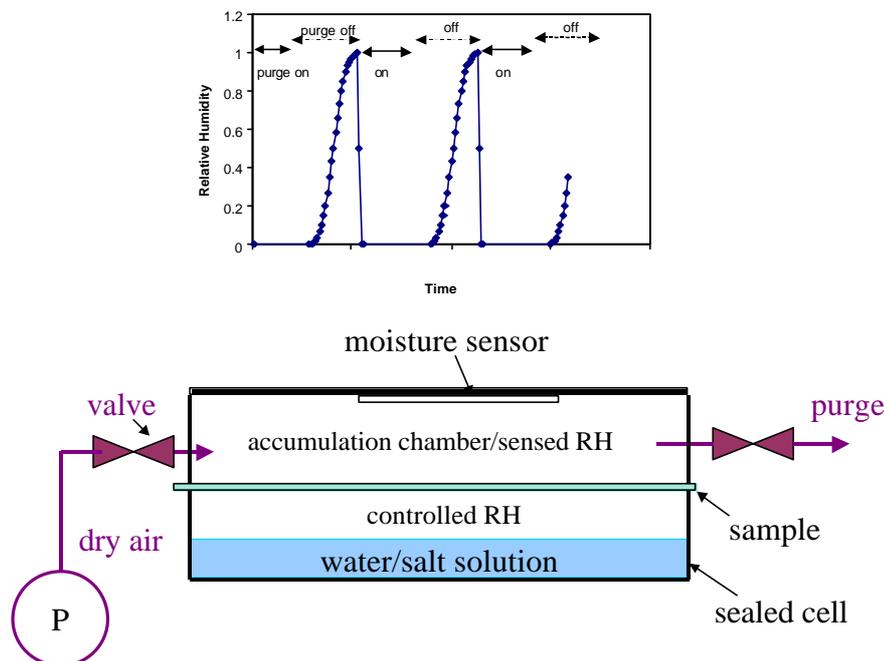
Figure 14: ASTM 398 Method

3.4.2 Water Vapour Transmission Rate Through Plastic Film and Sheeting Using a Modulated Infrared Sensor

In ASTM F 1249-01 [47] and ISO 15106-2 [51], water or aqueous solution, is placed in 'wet' side of the cell, producing a humid atmosphere, and dry carrier gas is blown at a constant, controlled flow rate through the 'dry' side of the cell to sweep the diffusing water molecules to the detector (Figure 15). These are isostatic permeation methods provided that the sample in the 'wet' cell does not become exhausted during the test. The methods require an IR detector (where IR absorption at the fixed wavelength is proportional to vapour concentration) to determine the water vapour concentration in the gas. This detector signal, E_s, will be constant when steady state permeation is occurring. The initial instrument reading E_0 is determined with no water in the 'wet' cell. The instrument is calibrated for known flow rates against the signal E_R determined for a reference film of known WVTR (whose permeation has been determined using a gravimetric dish method) to produce a calibration factor, C. The calculation of WVTR then becomes simply:

$$WVTR = \frac{S(E_S - E_0)}{(E_R - E_0)}\frac{A_R}{A_S} \qquad (22)$$

where A_R and A_S are, respectively, the transmission areas of the reference and sample films. If these areas, and the dry cell and reference sample signals are constants then the analysis reduces can be carried out using a single calibration constant C:

$$WVTR = C(E_s - E_0) \qquad (23)$$

The relative humidity can be controlled on the 'wet' side of the cell through the use of appropriate salt solutions (distilled water gives 100% RH). The cell is maintained at a constant temperature during tests. Permeance is determined from the WVTR divided by the water vapour partial pressure gradient across the film and the permeability coefficient, for homogeneous samples, is calculated from the permeance multiplied by the film thickness.
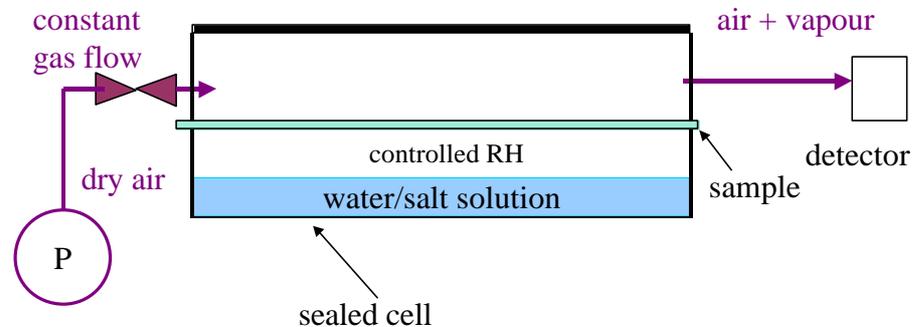

Figure 15: WVTR technique using an IR detector

3.4.3 Water Vapour Transmission Rate of Flexible Barrier Materials Using an Infrared Detection Technique

ASTM F 372 [48] specifies a test method for rapid determination of the WVTR of films (this ASTM method appears to have been written specifically for a commercial (Mocon) instrument, giving operating procedures in an appendix). A schematic of the test arrangement is shown in Figure 16. Two humid chambers are separated from the test chamber by the sample material being tested. The concentration of moisture in the test chamber is monitored by IR absorbance. Before running a test, the sample chamber is purged with dry gas. At time t = 0 the purge is switched off and the test chamber sealed. The increase in moisture concentration in the chamber is monitored. The time for a given increase in the water vapour concentration is determined. Following this the chamber is purged again and the cycle repeated until a constant time (to within ± 5%) is obtained for the given concentration gain, following a similar procedure to ASTM E 398. The instrument is calibrated using standard films (whose permeation properties are determined from gravimetric measurements) and analysis methods similar to those outlined in section 3.4.2 are used to calculate WVTR.

3.4.4 Evaluation of Solubility, Diffusivity and Permeability of Flexible Barrier Materials to Water Vapour

ASTM F 1770 [49] outlines procedures for determining the mass transfer properties of vapour in films. The method assumes Fickian behaviour in the determination of solubility, diffusivity and permeation constants. One side of the sample is exposed to a specific water vapour pressure in a constant temperature cell using a constant flow of humid gas. Molecules diffuse through the sample and are swept by a (dry) carrier gas to the detector (unspecified in the standard). The detector is calibrated using reference samples and atmospheres with known moisture content. The WVTR rate is determined from the linear region of the flux-time plot, which has similar features to Figure 13. Fickian models are used to calculate diffusion coefficients and from these solubility coefficients. The standard outlines how the test can be performed at different temperatures in order to calculate activation energies from Arrhenius fits.
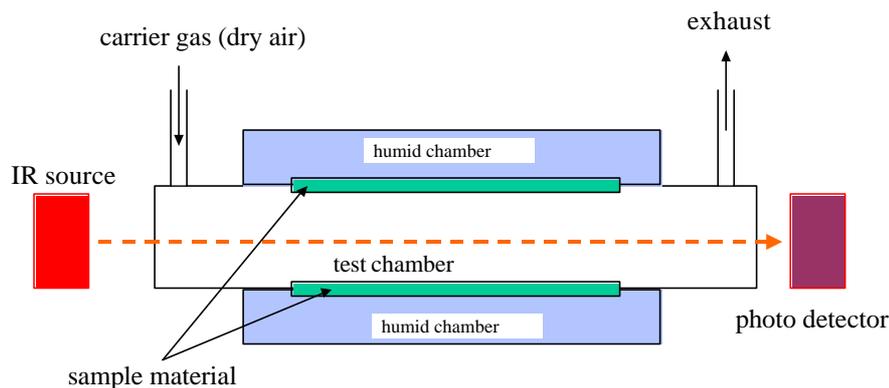
Figure 16: ASTM F372 method

3.4.5   Water Vapour Transmission of Materials (Gravimetric Techniques)

ASTM D 1653 [45], ASTM E 96 [46], EN ISO 7783-1 [53] and ISO 2528 [54], specify gravimetric methods for the determination of WVTR. In each case the sample is used to 'seal' an impermeable cell (Figure 17). Changes of mass are related to water vapour transport through the sample. The mass can be measured either continuously by placing the cell on a dedicated balance or periodically by removing from the controlled atmosphere for a brief period of time to weigh. Removing the sample from the environment introduces an element of uncertainty into the measurement as the steady state permeation conditions are interrupted. Mass transfer rates will change or even reverse during the weighing period. The accuracy of results will become worse the longer (or more variable) the 'out period' for weighing. In-situ weighing is intrinsically more accurate, although more expensive, providing the balance is stable. Gravimetric methods are used to determine the WVTR properties of reference films required for many if the other standard methods.

The desiccant or dry cup method maintains a 'dry' atmosphere in the cell by placing desiccant (e.g. anhydrous calcium chloride) in the cell. Moisture diffusing through the sample from the more humid external environment absorbs in the desiccant, thus increasing the mass of the cell. Provided the desiccant does not become saturated then under steady stare permeation the rate of mass increase will be linear with time.

The water or wet cup method uses a controlled 'wet' atmosphere in the cell by filling the base with distilled water or a standard salt solution. Water diffusing from the cell into the dryer external environment leads to a net loss in mass. Under steady stare permeation the rate of mass loss will be linear with time. The wet cell method can allow finer control of water vapour gradients across the sample than the dry cell.

3.4.6   Volatile Liquids

Gravimetric methods can be used to measure permeation of volatile liquid vapours (e.g. organic solvents) through plastic films. Sensor techniques for permeation measurement can also be used but no standards exist for these measurements. Methods for measurement and control of solvent concentrations on either side of the film are not as well established as the techniques for water.
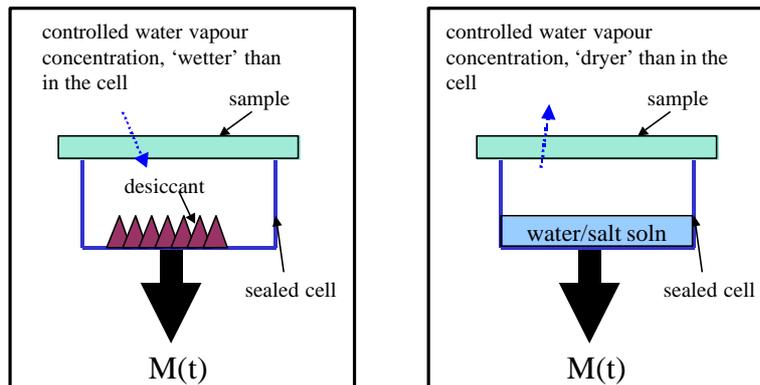
Figure 17: Dry and wet cup methods for gravimetric WVTR measurement

3.5   GAS PERMEATION TESTS

3.5.1   Atmospheric Pressure – Manometric Methods

EN ISO 2556 [59] and ASTM D 1434 [60] specify methods for determining gas permeation rates using pressure changes that are monitored using a manometer. In this method the test gas is contained within the feed chamber at atmospheric pressure. The chamber on the opposite side of the sample is evaluated and hermetically sealed. As gas diffuses through the film, the pressure, as determined by the height of the manometer mercury column, at the low-pressure side increases. After an initial delay, the pressure-time curve will become linear and the permeability can be calculated from the rate of pressure increase. This method measures the total flow of gas through the sample and does now determine permeation of individual components of mixtures.

3.5.2   Constant Volume Methods

ISO method ISO 15105-1 [61] is similar to the manometric method except that a differential pressure transducer is used in place of the manometer. The permeant side of the cell is effectively at constant volume throughout the test (except for negligible changes due to the deflection of the transducer diaphragm).

3.5.3   Constant Pressure Methods

ASTM D 1434 [60] provides for a constant pressure measurement of permeation. The basic system design is the same as the manometric method. The permeant side is maintained at atmospheric pressure whilst an increased gas pressure is applied to the feed side, typically 2

bar or greater. The diffusion of gas through the sample leads to increase in volume (at constant pressure) on the low-pressure side, which is measured by displacement of the manometer fluid. The volume-time plot is used to calculate gas transmission rates and permeability coefficients.

3.5.4 Carrier Gas Methods

Carrier gas methods (e.g. ISO 15105-1 [61]) often referred to as 'dynamic' methods, permit gas to flow across either side of the sample at equal pressures. The test gas flows in the feeder side of the permeation cell whilst a carrier gas flows through the diffusant side at a constant flow rate. The carrier gas sweeps the permeating test gas to a detector, which is normally specific to the test gas (see Appendix III). Thermal conductivity or thermistor sensors can be used as general sensors for most gases.

3.5.5 Mass Spectrometry Methods

Mass spectrometers can be used as the sensor system in permeation experiments, combining high sensitivity with simultaneous measurements of different species [62]. In one mass spectrometer method the sample gas is introduced into a closed gas cell, which is then sealed. The opposite side of the sample is evacuated, drawing gas molecules through the sample. The partial pressures of the gases permeating from the gas cell are measured as a function of time using a mass spectrometer. Since the cell is sealed, the gas pressure within the cell will decay with time and, hence, the flux of gas permeating will decay with time. The decay of the partial pressure of each component can be used determine the permeability coefficient of that component. Since the determination of different species is simultaneous, this method can be used to study the diffusion of mixtures. This method has high sensitivity to all materials provided that mass/charge ratios of species or fragments are not the same (e.g. N_2 and CO have an atomic mass of 28 and cannot be distinguished). Mass spectrometry offers very high sensitivity with accurate quantified detection possible to gas pressures below 10^{-10} Pa.

3.5.6 Oxygen Transmission Using a Coulometric Sensor

ASTM D 3895 [63] and ISO 15105-2 [64] are isostatic test methods. Pure oxygen flow in the feed side of the permeation cell, diffuses through the sample and is swept by the pure nitrogen carrier gas to the solid state sensor, where the oxygen concentration is determined through current generated by electrochemical reactions.

3.6 FACTORS INFLUENCING ACCURACY

3.6.1 Sealing of the Permeation Cell

It goes without saying that any ingress of species from the external environment or egress of species to the external environment can lead to significant errors in the measurement of permeation. The permeation cell and all associated pipe work, valves, joints, detectors, etc. should be impermeable to the species under test within the time frame of the permeation experiment. One method of checking the sealing is to perform tests using 'impermeable' sample materials such as metals or glass.

3.6.2 Calibration of Detectors/Instruments

All sensors in the permeation equipment, e.g. temperature, pressure, flow and chemical sensors, should be calibrated to obtain accurate and traceable measurements. Gas detectors can be calibrated against reference gas samples, supplied by national measurement institutes such as NIST, NPL or PTB.

Commercial WVTR or permeation apparatus procedures often specify calibration of the instrument using a reference film of known permeability to calibrate the detector, carrier gas flow and permeability cell as a single system. Reference films for WVTR can be calibrated using gravimetric methods. Reference films should have permeation properties similar to the samples being tested. The reference film materials should be stable over time. Storage and handling procedures should avoid any conditions that may lead to changes in the reference film.

3.6.3 Condition of the Test Sample

Permeation depends on the thickness of the sample, variability in the thickness of the sample, either from undulations in thickness of a single sample or sample-to-sample variations, can lead to uncertainty in the results. Therefore, it is important to measure the thickness of the sample to high accuracy. For 'thick' films of approximately 1 mm or greater then micrometers capable of measuring to within 1 µm are suitable for thickness determination. However for very 'thin' films (< 100 µm), micrometers do not have the required level of accuracy.

Preparation of the test sample can affect the permeability. Chemically similar polymer samples may have very different permeation properties as production processes can affect free volume, mobility and molecular orientation. Test samples should be prepared identically to production material.

The physical condition of the film is also important. Any damage to the surface or pinholes through the sample will lead to increased permeation. Samples need to be handled carefully before testing and when being mounted in the permeation cell. Thin samples may need to be supported to prevent bowing or stretching if pressure differentials or high gas flow rates are used. Any support used should not interfere with the permeation mechanism, e.g. by providing an additional barrier. Filter paper is sometimes recommended as a support material.

Samples, particularly composites and multi-layer or coated films, may have directionally dependent solubility and permeability. These should always be tested in the orientation of intended use (i.e. the correct surface in contact with the test gas).

Preconditioning of test samples should be carefully controlled. Samples exposed to uncontrolled, ambient conditions will absorb moisture from the atmosphere. It is known that the presence of absorbed moisture can significantly increase gas permeation rates in hydrophilic polymers such as nylon or PET [1, 15]. Therefore, samples need to be conditioned in order to achieve stable and known moisture content before tests begin. This may be accomplished by drying to constant mass or conditioning in a fixed temperature/humidity atmosphere until equilibrium is reached. Strain and thermal history may also be a source of measurement uncertainty. Molecular mobility, and thus permeability is influenced by the physical age of the polymer. The application of strain, in particular irrecoverable plastic strains, may change the properties of the plastic.

3.6.4 Carrier Gases

Carrier gases should not influence the results or interact with the sample. Care should be taken to ensure that the concentration of test species in the carrier gas is extremely low, preferably zero. There should be no constituents of the carrier gas that will be 'detected' by the detector used and therefore inflate the measurement. Similarly, the carrier gas should not contain any species that would poison the detector, thereby reducing detection efficiency.

Water vapour, even if not the test species, is often undesirable as it may interact with the detector or the sample (e.g. through swelling) and it is good practice to dry the carrier gas before it is passed into the permeation cell. This can be done by passing the gas through a desiccant filled filter.

Background level checks can be performed using an impermeable material as a sample. The detector signals obtained using the impermeable sample can be subtracted from test results to 'zero' the instrument. This practice assumes that the background level is low in comparison to the concentration of permeating sample. However, if the correction for background levels is significant in comparison to the measured values then there will be considerable uncertainty in the determined permeation rate.

3.6.5 Low Permeation Levels

Materials with extremely good barrier performance present significant measurement challenges. The sample may take an extremely long period of time to reach equilibrium saturation and, hence, steady state permeation. Such tests require that expensive instruments be dedicated for considerable periods of time and can be extremely costly. Tests that run for long periods of time also increase the risk of permeation of the external environment.

Even when steady state permeation is achieved, the flux may be extremely low and detectors may have insufficient sensitivity or stability to provide accurate quantitative concentration measurements. Calibration of the sensor may not be possible for low concentrations. The flux level is proportional to area and so can be increased by increasing the sample size, although the extent to which this can be done is limited by the size of the permeation cell. Permeation rates depend inversely on thickness, using reduced thickness samples can increase the flux but it may not be economic or possible to make the same material at different thickness. Increased pressure differentials, for example by evacuating the detector side or pressurising the feed side, will also increase the flux but there is a risk that the film may deform/stretch, affecting the permeation performance.

3.6.6   Materials Used in the Apparatus

The materials used in constructing the permeation apparatus must not influence the measurement. There should be no chemical reactions or absorption involving the test molecule and the materials used in the apparatus that could deplete the flux of material permeating or being detected. Also, under the test conditions, there should be no release or evolution of molecular species that could be 'detected' as permeating. In practice, when measuring permeation of water vapour, oxygen or carbon dioxide, metals used to construct the cell should be corrosion resistant (e.g. stainless steel) and any plastics/seals should not have significant uptake of the permeating species.

3.6.7   Edge Effects

There should be no flow of permeant (or other molecules) around or through the edges of the sample from the feed side of the cell to the detection side of the cell or the external environment (or vice versa). In practice, this means that either the edges of the sample should be sealed or that the cell is designed so that only a small window of sample is available for permeation, leaving a diffusion length through the edge that is many times that through the thickness so that permeation from the edges is negligible.

3.6.8   Temperature

Equilibrium (saturation) concentrations and diffusion coefficients depend on temperature, as free volume and molecular mobility are temperature dependent. For a typical diffusion activation energy of 35 kJ/mol an increase of 15°C can lead to a doubling of permeation [62]. There also may be discontinuities in the absorption-temperature or diffusion-temperature curves at the glass transition temperature with higher sorption occurring above T_g. Temperature gradients within a material can also provide a driving force for permeation. Permeation experiments should therefore be performed under stable, thermostatically controlled conditions (covering the sample, sample chamber, carrier/feed gases) in order to optimise accuracy. The temperature dependence of permeation properties can be determined from experiments performed at different controlled temperatures.

3.6.9   Stress

The effect on solubility and molecular mobility will depend on the type of stress applied. Hydrostatic tensile stress is expected to increase free volume and open internal voids or crazes, providing additional sites into which molecules can absorb. Conversely, hydrostatic compressive stress will reduce solubility by closing internal sites. Tensile stresses tend to open internal voids or crazes, providing additional sites into which molecules can absorb. Moisture and gas permeation rates for plastic films have been observed to increase with the application of strain [11, 17]. Very significant increases in permeability can occur with brittle polymer films if the strains are sufficient to cause micro cracking in addition to free volume increase [17]. Significant strain effects may also occur if applied gas pressures (or gas pressure differentials) lead to significant deformation of plastic film samples [11]. Samples can be supported with porous supports to prevent excessive deformation.

A modified permeation cell for testing plastic films under different imposed tensile stress levels is shown in Figure 18 [6, 17]. Tests on gas permeation performed using such apparatus showed that permeation rates increase with applied stress.
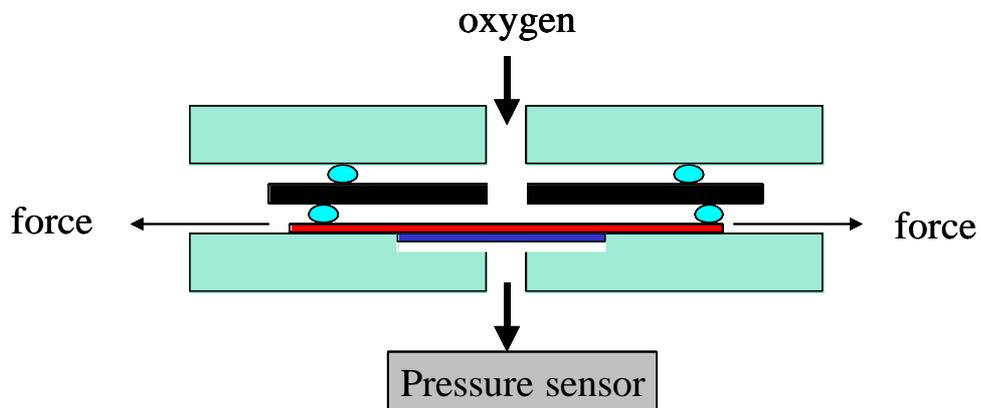
Figure 18: Schematic of a permeation cell for testing films at different stress levels

Crocombe et al [26] performed mass uptake experiments on bulk epoxy adhesive specimens immersed in distilled water under different levels of tensile stress imposed by a self-stressing fixture. The results, for 2 different adhesives (Figure 5), showed an increase in maximum water content with stress and what appeared to be a reduction in diffusion coefficient with increasing stress (although it was stated that there were high levels of uncertainty in the determination of diffusivity D and that it would be reasonable to assume a constant diffusion constant). Figure 19 shows a self-stressing fixture suitable for use in assessing durability of materials and components under combined load and environmental exposure.

Figure 19: Self stressed tube for combined environment/stress testing

4. MODELLING DIFFUSION

Modelling of permeation and diffusion is of interest in many applications. Diffusion is included in Finite Element (FE) models of components and structures to predict service life performance. Modelling helps interpret experimental results, particularly for complex test samples (such as multi-layer systems). Mass diffusion in materials can be considered mathematically analogous to thermal diffusion in solids. An NPL developed software model for heat transfer TherMOL has been used for modelling heat transfer in multi-layer systems. Through comparison with experimental data and inverse modelling techniques this package can be used to extract information on heat transfer coefficients between different layers that are not easily amenable to direct measurement. This model is being adapted for use to solve mass diffusion problems and the mathematical theory and implementation of boundary conditions are described in Appendix I. Molecular modelling is being used in academic research to better understand diffusion mechanisms and there has been some success in predicting solubilities and diffusion coefficients in model systems [8, 65].

4.1 MODELLING MOISTURE UPTAKE

Modelling the uptake of moisture by composites and adhesive joints, being of particular interest to the aerospace industry, has been, in conjunction with moisture dependant properties, the focus of studies to predict long-term effects on strength and stiffness [e.g. 3, 4, 13, 22, 25, 28, 29]. Degradation of mechanical properties dues to moisture concentration and moisture induced swelling can be incorporated in these analyses to provide more realistic stress states under load. Studies have considered exposure under constant environments (constant concentration and temperatures) and varying environments. These allow detailed analyses that are not generally possible to duplicate through experimental means. In large components, the required time to reach concentrations of interest may be many years and certainly beyond the likely time available for testing. Detailed analysis of moisture distribution in complex shapes is very difficult to do experimentally and modelling may be the only practical route.

Springer [66] analysed moisture distributions in composite components simulating a 20-year service life of an aircraft exposed to changing humidity and temperature. Models of moisture ingress into composite skinned panels showed that:
- under transient conditions the centre will eventually reach a quasi-steady state concentration about which the moisture content fluctuates, in was predicted to take 10 years to reach this state;
- the moisture distribution never attains a steady state and after long period of times most of the fluctuations occur in the surfaces;
- constant temperature / constant humidity exposure could not produce the moisture distribution achieved in steady state tests;
- the steady state moisture distribution and moisture content in the centre of the samples produced by transient conditions can be approximated by constant ambient conditions but the required relative humidity cannot be determined *a priori* beforehand.

Materials are normally modelled as continuous phases with averaged diffusion properties, generally ignoring fillers or other phases. Interfaces between materials are not assigned diffusion properties. Some materials, in particular composites, can exhibit anisotropic diffusion behaviour. This is normally modelled with a single solubility parameter determined from the saturation concentration and directionally dependent diffusion coefficients. Several researchers [12, 13, 66] have presented three-dimensional FE methodologies for simulating

Fickian diffusion, often with temperature-dependent diffusion coefficients, for predicting moisture diffusion in composite materials.

Several methodologies have been proposed to account for non-Fickian diffusion [22-24, 27-29]. The different approaches to diffusion calculations may be divided into two general groups, those building upon Fick's Law and those developed with non-Fickian principals.

Loh *et al* [22] presented a model incorporating Fickian diffusion in two stages to simulate moisture uptake in a rubber toughened epoxy adhesive whose mass uptake profile did not fit the standard Fickian model. The proposed mechanism for the first stage was absorption in the polymer matrix and the second stage involved volumetric swelling that occurs at higher moisture levels. Each process was modelled using a separate diffusion constant and saturation level. These constants could be determined using least squares fitting routines. Gravimetric test results showed that deviations from Fickian behaviour appeared to diminish with sample thickness and final saturation levels were higher in the thicker samples. These behaviours were attributed to possible differences in chemical and physical structure of thin film and bulk specimens, voids are more likely in thick samples and cure states may be differ. The dual stage uptake process was modelled using two separate standard Fickian diffusion FE analyses [22]. Moisture dependent mechanical properties were incorporated and used to predict the swelling and bending of a bi-material (metal-adhesive) beam exposed to moisture with good success.

Hambly *et al* [23] described experimentally observed diffusion with a modified Fickian model that operated with a variable diffusion coefficient that is a function of concentration of diffusant with in the adhesive. Thin plaques of two epoxy adhesives were immersed in distilled water at 22 °C and 55 °C and weighed periodically. Mass uptake was found to lag behind the Fickian prediction using a single diffusion coefficient. Regression fits to the data were used to determine concentration dependent diffusion coefficients. A single 'dry' diffusion coefficient was used to model uptake until water content reached 2/3 of saturation and a variable (decreasing) diffusion coefficient used above this. In one case, for one of the adhesives at the higher immersion temperature, mass losses were observed in long-term uptake experiments and attributed to leaching of soluble components from the adhesive. An estimate of mass loss due to this leaching was made through extrapolating the mass loss curve at the end of the test to zero time but this condition was excluded from subsequent analysis. Diffusion coefficients (single fit and 'dry' values) increased significantly in each adhesive system when the temperature increased from 22 °C to 55 °C.

Roy *et al* [28, 29] proposed a methodology for characterisation of non-Fickian diffusion coefficients from moisture weight gain data for a polymer below its T_g. This was based on irreversible thermodynamics and visco-elasticity theory to derive governing equations for history-dependent diffusion in visco-elastic polymers. Subsequently, these diffusion coefficients were used for predicting moisture concentration profiles through the thickness of a polymer. The model used this to predict two stage uptake observed in graphite/epoxy composites.

The absorption of moisture or organic solvents into polymeric materials is known to lead to swelling, causing internal stress in the material that could contribute to failure. Internal stress due to swelling is likely to be a problem in adhesive joints where expansion is constrained by rigid adherends. This phenomenon can be included in FE models by empirical relationships derived from experimental measurements of swelling strain as a function of uptake [22, 24].

Stress will influence diffusion rates in materials. In adhesive joints, studies have shown that the combination of stress and chemical exposure can have synergistic effects in accelerating the degradation of interfaces [20, 32]. Gledhill *et al* [20] proposed that a critical concentration of water in interfacial regions must be attained for bonds to fail. The implication of this is that diffusion is the rate-determining step in the degradation process and that diffusion modelling can be used to predict lifetimes. Lam *et al* [24] proposed a model for stress-assisted hydration of adhesive bonds. Failure depended on the saturation water content, concentration gradients, stress gradients and on the peak stress. After comparing with crack growth results it was concluded that the bond degradation is governed by time-dependent stress-assisted hydration rather than water concentration alone. The effect of moisture concentration on fracture toughness [67] and the threshold energy for crack growth can be modified to include a diffusion term.

Materials and structures may fail cohesively owing to exposure to the environment. Chemical or moisture absorption can degrade the mechanical performance of materials, plasticisation due to swelling or disruption of networks leads to (reduced) modulus, yield stress and failure stress values, which depend on the concentration of the absorbed species [14, 25]. Thus, mechanical properties can vary within a material or component with time and position. The time and spatial distribution of the absorbent can be calculated from the diffusion properties using FE and, together with concentration dependent mechanical behaviour, used to predict the effects of exposure on the stress state of a loaded structure [25]. The effort required to obtain data over a sufficient range of concentrations can be significant, a shortcut can be to determine the mechanical performance of fully saturated material to model the 'worst case' scenario [68].

4.2 FINITE ELEMENT METHODS

Finite element modelling packages often include the capability for modelling mass transport in components through diffusion models. Finite element modeling has been used in many studies to predict the rate of ingress of chemicals (generally moisture) into components and structures, such as adhesive joints. Predictions of concentration distributions at different time steps are obtained and, together with measured relationships between absorbed concentration and mechanical properties, used to predict the degradation of mechanical performance. During early stages of exposure the plasticisation of near surface material can allow load shedding from stress concentrations leading to improved mechanical strength, this phenomenon has been observed in experimental studies and the mechanisms confirmed by FE modeling [25].

There are many FE software packages that can be used for modelling diffusion behaviour. For brevity, this section describes only the use of the general FE package ABAQUS [9]. This system has been used in many studies reported in the literature [e.g. 22, 23]. In a mass diffusion analysis:

- transient or steady-state diffusion of one material through another is modelled; and
- temperature and/or pressure-driven mass diffusion can be included.

The governing equations for mass diffusion are based on extensions of Fick's equations and allow for nonuniform solubility of the diffusing substance in the base material and for mass diffusion driven by gradients of temperature and pressure. The basic solution variable (used as the degree of freedom at the nodes of the mesh) is the "normalized concentration" (often also referred to as the "activity" of the diffusing material):

$$f = \frac{c}{s} \tag{24}$$

where c is the mass concentration of the diffusing material and s is its solubility in the matrix material. When the mesh includes dissimilar materials that share nodes, the normalized concentration is continuous across the interface between the different materials.

The diffusion problem is defined from the requirement of mass conservation for the diffusing phase:

$$\int_V \frac{dc}{dt} dV + \int_S n.J ds = 0 \tag{25}$$

where V is any volume whose surface, S is the outward normal to n, J is the flux of concentration of the diffusing phase, and n.J is the concentration flux leaving S.

Diffusion is assumed to be driven by the gradient of a general chemical potential, which gives the behaviour

$$J = -sD\left[\frac{\partial f}{\partial x} + k_S \frac{\partial}{\partial x}\left(\ln\left(T - T^Z\right)\right) + k_P \frac{\partial P}{\partial x}\right] \tag{26}$$

where $D(c, T, f)$ is the diffusivity; $s(T, f)$ is the solubility; $\kappa_S(c, T, f)$ is the "Soret effect" factor, providing diffusion because of temperature gradient; T is the temperature; T^Z is the absolute zero on the temperature scale used; $\kappa_P(c, T, f)$ is the pressure stress factor, providing diffusion driven by the gradient of the equivalent pressure stress, $P = -\sigma/3$; σ is stress; and f are any other predefined field variables that the modeller may require.

Whenever **D**, κ_S, or κ_P depends on concentration, the problem becomes non-linear and the system of equations becomes non-symmetric. A non-symmetric matrix storage and solution scheme is invoked automatically when a mass diffusion analysis is performed.

An extended form of Fick's law can be used as an alternative to the general chemical potential:

$$J = -D\left(\frac{\partial c}{\partial x} + s k_P \frac{\partial P}{\partial x}\right) \tag{27}$$

Further details of implementing mass diffusion within an ABAQUS analysis are given in Appendix IV.

4.2 MOLECULAR DYNAMICS

Molecular dynamics is a technique that may be capable of predicting dissolution and diffusion properties of small molecules in polymer systems. This is a new field with growing possibilities for accurate predictive capabilities provided that computing power, reliable models and fundamental properties become available. In most work reported to date, simulations model interactions with very few polymer units and so applicability to real materials may be limited.

Molecular dynamic simulations have been used to study the mechanisms involved in permeation. In molecular dynamics [8], diffusion can be represented by random walk phenomena characterised by self diffusion coefficients, which in fluids are commonly calculated from the Einstein relation by plotting mean squared displacement $\langle r^2 \rangle$ against time t:

$$D = \lim_{t \to \infty} \frac{\langle \Delta r^2 \rangle}{6t} \tag{28}$$

Molecular dynamic simulations suggest that diffusion occurs through a 'rattle and jump' mechanism. Plots of position of a single permeant molecule as a function of time show that the behaviour is characterised by periods of oscillation about a fixed position ('rattle') interspersed with longer 'jumps' to a new position. As the temperature is increased, the amplitude of oscillation increases and jumps become more frequent. Simulations suggest that jump events are associated with the opening of channels between sites, suggesting that polymer chain mobility is involved in the process of diffusion. Solubility of a gas in a polymer is determined from the chemical potential or free energy, which depends on the interaction energy of a virtual permeant molecule inserted at random in the sample:

Alentiev *et al* [65] reported molecular dynamics simulations for solubility and diffusion coefficients of various small chain alkanes in pure polydimethylsilmethylene (PDMSM) and found very good agreement with experimental measurements.

5. CONCLUDING REMARKS

Diffusion and permeation in polymeric materials is of fundamental importance in many applications and is the subject of much study in the scientific literature. Measurement methods for determining permeation through polymer sheets and within polymeric materials have been reviewed. An overview of the generic mechanisms involved reveals dependence of these properties on a wide range of factors, some relating to the materials others to the exposure environments. There can often be an interrelationship between factors, for example the combination of stress and chemical exposure is often a critical degradation mechanism in the service performance of structures containing polymers. Dispersed phases and interfaces play important roles in the mass transport process but the mechanisms are not well understood, limiting predictive capabilities. The effect of multiple, interacting diffusion species is limited but required for many practical applications. Modelling is used to supplement experimental measurements, improving understanding and enabling extrapolation of behaviour over timescales and in large components that are not experimentally convenient. However, the accuracy of these models requires that the dissolution and diffusion mechanisms are well understood for real materials and that accurate date are available.

There are many scientifically interesting areas of permeability and diffusion that could be studied further. However, with limited resources available it is proposed to concentrate on:

- Developing methods for determining the effects of stress on uptake and diffusion in engineering polymers used in load or pressure bearing applications.
- Understanding of the role of interfaces in the diffusion process and develop methods for characterising interfacial processes.

- Investigating methods for 'accelerating' uptake and diffusion in order to provide methods for characterising low permeability materials or thick sections.

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APPENDIX I

TRANSIENT DIFFUSION MODELLING IN THREE-DIMENSIONAL MULTI-STRUCTURED POLYMER SYSTEMS

ABSTRACT

This Appendix outlines the basic theory necessary for mass diffusion, highlighting analogies with heat diffusion, in multi-structured systems with the intention to model permeation in multi-layered polymeric systems. A finite difference modelling approach is described, which uses conservation of species to balance the species flux into a volume element together with a species generation term. The derived finite difference model may be applied to three-dimensional structures and includes constant species and constant species flux boundary conditions.

A1.1 INTRODUCTION AND BASIC THEORY

Diffusion and transport of matter in layered systems is important in such processes as moisture permeability of paint films or the degradation of the matrix in polymer composite laminates and packaging material. Many products are increasingly being made as layered systems to tailor the properties.

Multi-layer modelling has become important to determine the properties and the changes in properties of each layer when subjected to diffusion. Hedenqvist et al [1] developed a mass transfer model based on an implicit multi-step integration algorithm to include concentration-dependent diffusivities that has been applied to water diffusing in multi-layer polyesters. The model was used to predict curves for diffusivity as a function of water concentration as well as predict water desorption curves. A comprehensive review of the theoretical background of the modelling of diffusion and permeation in heterogeneous systems with polymer matrices, highlighting the analogies with heat flow and thermal conductivity, was presented by Barrer [2].

In heat transfer, numerical and analytical models combined with inverse modelling approaches have been used successfully to predict the thermal properties of layered materials such as the thermal conductivity of an oxide scale using laser flash temperature data [3]. This Appendix outlines the basic theory necessary to derive multi-layered models for mass diffusion, exploiting the analogy with heat diffusion, and outlines the basic concepts, definitions and theory are introduced for solving diffusion problems mathematically.

Incropera and DeWitt [4] provided an introduction to the basic mathematical theory and analogies with heat transfer. Crank [5] extensively reviewed analytical solutions to diffusion problems, giving solutions for different boundary conditions and geometries. Both publications have substantial sections on solving diffusion problems using finite difference numerical methods, which is particularly useful for solving more complex geometries or problems with more complicated boundary conditions and will be discussed in Section A1.2.

A1.1.1. Fick's law of diffusion

The term *mass transfer* describes the relative motion of species in a mixture due to the presence of concentration gradients. If there is a difference in the concentration of some chemical species in a mixture then *mass transfer* will occur. A species concentration gradient in a mixture provides a driving potential for transport of that species.

Mass transfer by convection is analogous to convection heat transfer and mass transfer by diffusion is analogous to conductive heat transfer. Mass diffusion can occur in liquids, solids and gases, with diffusion occurring more readily in gases than liquids and more readily in liquids than solids.

The same physical mechanism is associated with heat transfer and mass transfer by diffusion and the corresponding rate equations are of the same form. The rate equation for mass diffusion is known as Fick's (first) Law of Diffusion [6] and this is analogous to Fourier's law [7]. The mathematical theory of diffusion in isotropic substances is based on the hypothesis that the rate of transfer of diffusing substance through a unit area of a section is proportional to the concentration gradient measured normal to the section. For a binary mixture of species A and B we may write Fick's law, as:

$$\mathbf{j}_A = -\rho D_{AB} \nabla m_A \ , \tag{A1.1}$$

where $\mathbf{j}_A$ is the rate of transfer per unit area of species A perpendicular to the direction of transfer and is commonly known as the mass flux. D_{AB} is the diffusion coefficient between species A and B and is sometimes referred to as mass diffusivity, and m_A is the concentration of the diffusing substance such that

$$m_A = \frac{\rho_A}{\rho} \ . \tag{A1.2}$$

The mixture mass density ρ in Equations (A1.1) and (A1.2) is defined simply as

$$\rho = \rho_A + \rho_B \ . \tag{A1.3}$$

where ρ_A and ρ_B are the densities of the species A and B respectively. If it is assumed that ρ is a constant then

$$\rho \frac{dm_A}{dx} = \rho \frac{d}{dx}\left(\frac{\rho_A}{\rho}\right) = \frac{d\rho_A}{dx} \ . \tag{A1.4}$$

hence Fick's law in Equation (A1.1) may be written

$$\mathbf{j}_A = -D_{AB} \nabla \rho_A \ , \tag{A1.5}$$

It is sufficient in most cases of gases diffusing into solids to use the simplified version of Fick's law in Equation (A1.5).

A1.1.2. Conservation of species

Consider an element of volume, bounded by a control surface through which matter may pass, in the form of a rectangular parallelepiped whose sides are parallel to the axes of coordinates and are of lengths dx, dy and dz such that the volume of the element is simply:

$$dV = dx\ dy\ dz \qquad (A1.6)$$

Conservation of species is analogous to conservation of energy. Any species may enter and leave the control volume due to diffusion across the control surface; these processes are surface phenomena represented by $\dot{M}_{A,in}$ and $\dot{M}_{A,out}$ respectively. The same species A may also be generated (for example from chemical reactions), $\dot{M}_{A,g}$, and accumulated and stored, $\dot{M}_{A,st}$, within the control volume. The conservation equation may then be expressed as a rate of transfer of mass as:

$$\dot{M}_{A,st} = \dot{M}_{A,in} - \dot{M}_{A,out} + \dot{M}_{A,g} \qquad (A1.7)$$

where $\dot{M}_{A,st}$ is defined as:

$$\dot{M}_{A,st} \equiv \frac{dM_{A,st}}{dt}\ . \qquad (A1.8)$$

Consider now a general case of mass transfer in a solid with the mass $M = M(x, y, z, t)$ varying with position (x,y,z) and time. The rate at which the amount of diffusing substance in the element increases is:

$$\dot{M}_{A,st} = \frac{d\rho_A}{dt} dxdydz\ , \qquad (A1.9)$$

$$\dot{M}_{A,in} = \dot{M}_{A,x} + \dot{M}_{A,y} + \dot{M}_{A,z}\ , \qquad (A1.10)$$

$$\dot{M}_{A,out} = \dot{M}_{A,x+dx} + \dot{M}_{A,y+dy} + \dot{M}_{A,z+dz}\ , \qquad (A1.11)$$

where $\dot{M}_{A,x}$, $\dot{M}_{A,y}$ and $\dot{M}_{A,z}$ are the mass diffusion transfer rates into the solid at positions x, y, z respectively and $\dot{M}_{A,x+dx}$, $\dot{M}_{A,y+dy}$ and $\dot{M}_{A,z+dz}$ are the mass diffusion transfer rates out of the solid at positions x+dx, y+dy and z+dz respectively. Applying conservation of species at any instant t in the solid and inserting the Equations (A1.8) and (A1.9) into Equation (A1.7) results in:

$$\left(\dot{M}_{A,x} - \dot{M}_{A,x+dx}\right) + \left(\dot{M}_{A,y} - \dot{M}_{A,y+dy}\right) + \left(\dot{M}_{A,z} - \dot{M}_{A,z+dz}\right) + \dot{M}_{A,g} = \frac{\partial \rho_A}{\partial t} dxdydy\ . (A1.12)$$

The mass fluxes j_x, j_y and j_z in the x, y and z directions respectively are defined as the rate of mass transfer per unit area perpendicular to the direction of transfer and may be written in terms of the mass transfer rates:

$$\dot{M}_{A,x} \; = \; j_{A,x} dydz, \quad \dot{M}_{A,x+dx} \; = \; j_{A,x+dx} dydz,$$

$$\dot{M}_{A,y} \; = \; j_{A,y} dxdz, \quad \dot{M}_{A,y+dy} \; = \; j_{A,y+dy} dxdz, \qquad (A1.13)$$

$$\dot{M}_{A,z} \; = \; j_{A,z} dydz, \quad \dot{M}_{A,z+dz} \; = \; j_{A,z+dz} dydz.$$

The rate at which species A is generated, independent of diffusion across the control volume is:

$$\dot{M}_{A,g} = \dot{N}_A dxdydy \quad , \qquad (A1.14)$$

where $\dot{N}_A$ is the rate of increase of the mass of species A per unit volume of the mixture. Inserting the mass fluxes in Equation (A1.13) into the energy balance in Equation (A1.12) gives:

$$\left(j_{A,x} - j_{A,x+dx}\right)dydz + \left(j_{A,y} - j_{A,y+dy}\right)dxdz$$
$$+ \left(j_{A,z} - j_{A,z+dz}\right)dxdy + \dot{N}_A dxdydy = \frac{\partial \rho_A}{\partial t} dxdydz \qquad (A1.15)$$

The mass fluxes at opposite surfaces can be expressed as Taylor series expansions, neglecting higher order terms, such that:

$$j_{A,x+dx} = j_{A,x} + \frac{\partial j_{A,x}}{\partial x} dx \quad , \qquad (A1.16)$$

$$j_{A,x+dy} = j_{A,y} + \frac{\partial j_{A,y}}{\partial y} dy \quad , \qquad (A1.17)$$

$$j_{A,z+dz} = j_{A,z} + \frac{\partial j_{A,z}}{\partial z} dz \quad . \qquad (A1.18)$$

Inserting Equations (A1.16) – (A1.18) into Equation (A1.15) yields:

$$-\left[\frac{\partial\left(\mu_{A,x} dydz\right)}{\partial x} dx + \frac{\partial\left(\mu_{A,y} dxdz\right)}{\partial y} dy + \frac{\partial\left(\mu_{A,z} dxdy\right)}{\partial z} dz \right] + \dot{N}_A = \frac{\partial \rho_A}{\partial t} dxdydz \quad .(A1.19)$$

For a constant volume we can write Equation (A1.19) as:

$$-\left[\frac{\partial j_{A,x}}{\partial x} + \frac{\partial j_{A,y}}{\partial y} + \frac{\partial j_{A,z}}{\partial z} \right] + \dot{N}_A = \frac{\partial \rho_A}{\partial t} \quad , \qquad (A1.20)$$

where from Equation (A1.1) we have:

$$\frac{\partial}{\partial x}\left(\rho D_{AB}\frac{\partial m_A}{\partial x}\right)+\frac{\partial}{\partial y}\left(\rho D_{AB}\frac{\partial m_A}{\partial y}\right)+\frac{\partial}{\partial z}\left(\rho D_{AB}\frac{\partial m_A}{\partial z}\right)+\dot{N}_A=\frac{\partial \rho_A}{\partial t}\ .\ \text{(A1.21)}$$

If D_{AB} and ρ are constant then we may write Equation (A1.21) using Equation (A1.2) as:

$$\frac{\partial^2 \rho_A}{\partial x^2}+\frac{\partial^2 \rho_A}{\partial y^2}+\frac{\partial^2 \rho_A}{\partial z^2}+\frac{\dot{N}_A}{D_{AB}}=\frac{1}{D_{AB}}\frac{\partial \rho_A}{\partial t}\ .\qquad\text{(A1.22)}$$

Equation (A1.22) is known as the mass diffusion equation and is analogous to the heat diffusion equation.

A1.1.3. Molar form of the mass diffusion equation

In many applications it is more useful to use the molar form of the mass diffusion equation and for this case Fick's law of diffusion [8] is defined as:

$$\mathbf{f}_A=-CD_{AB}\nabla\xi_A\ ,\qquad\text{(A1.23)}$$

where $\mathbf{f}_A$ is the molar flux of species A and ξ_A is the species mole fraction defined simply as:

$$\xi_A=\frac{C_A}{C}\ .\qquad\text{(A1.24)}$$

The total molar concentration C in Equation (A1.24) is defined simply as:

$$C=C_A+C_B\ .\qquad\text{(A1.25)}$$

where C_A and C_B are the molar concentrations of the species A and B respectively. When C is a constant then:

$$C\nabla\xi_A=\nabla\left(\frac{C_A}{C}\right)=\nabla C_A\ .\qquad\text{(A1.26)}$$

hence Fick's law may be written:

$$\mathbf{f}_A=-D_{AB}\nabla C_A\ ,\qquad\text{(A1.27)}$$

Using a similar derivation as in Section A1.2.2 based on conservation of species, the molar form of the mass diffusion equation for a constant molar concentration is:

$$\left[\frac{\partial^2 C_A}{\partial x^2}+\frac{\partial^2 C_A}{\partial y^2}+\frac{\partial^2 C_A}{\partial z^2}\right]+\frac{\dot{S}_A}{D_{AB}}=\frac{1}{D_{AB}}\frac{\partial C_A}{\partial t}\ .\qquad\text{(A1.29)}$$

where $\dot{S}_A$ is the rate of increase of the molar concentration of the species A due to chemical reactions and is analogous to the mass density rate parameter $\dot{N}_A$. It is sufficient in most cases of gases diffusing into solids to use the simplified version of molar form of Fick's law in Equation (A1.27) and the associated mass diffusion equation in Equation (A1.29). The mass diffusion equation in Equation (A1.29) may be rewritten in terms of cylindrical coordinates (r, θ, z) as:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 C_A}{\partial \theta^2} + \frac{\partial^2 C_A}{\partial z^2} + \frac{\dot{S}_A}{D_{AB}} = \frac{1}{D_{AB}}\frac{\partial C_A}{\partial t} \ . \qquad (A1.30)$$

From here on the molar form of the mass diffusion equation will be used, where it is assumed that the system has a constant total molar concentration C and diffusivity D_{AB}.

A1.1.4. Initial and boundary conditions

The initial molar concentration of species A at time t=0 for a system represented by cylindrical coordinates is given by:

$$C_A(x, y, z, 0) = C_A^{ini} \ , \qquad (A1.31)$$

and in cylindrical coordinates is simply

$$C_A(r, \theta, z, 0) = C_A^{ini} \ , \qquad (A1.32)$$

There are two main types of boundary conditions that may be applied to Equations (A1.29) and (A1.30) and both have analogies with similar boundary conditions in heat transfer.

The first boundary condition is where the concentration of the species at the surface is kept constant and this is analogous to the constant temperature boundary condition in heat transfer. For a constant concentration the boundary condition on the x axis for the molar form of the mass-diffusion equation is:

$$C_A(x_{surf}, y, z, t) = C_A^{surf} \ . \qquad (A1.33)$$

where x_{surf} is the x value of the surface/boundary C_A^{surf} is constant over time. The second boundary condition is a constant species flux, which is analogous to constant heat flux boundary conditions in heat transfer, at the surface. Using Fick's law we may write

$$-D_{AB}\frac{\partial C_A(x, y, z, t)}{\partial x}\bigg|_{x=surf} = \Phi_A^{surf} \ . \qquad (A1.34)$$

where Φ_A^{surf} is constant over time. Both types of boundary conditions in Equations (A1.31) and (A1.32) may be extended without loss of generality to y and z directions. It is worth noting that for cylindrical systems (r, θ, z) boundary conditions have the same form of the

constant molar concentration and species flux as in Equations (A1.31) and (A1.32) respectively, however for the r and z directions only.

A1.2 NUMERICAL METHODS AND APPLICATIONS TO MULTI-STRUCTURED SYSTEMS

Although there exist many analytical solutions to the mass diffusion equation with various boundary conditions, see Crank [5], more complicated multi-layered or multi-material structures are solved more easily using numerical methods. For determining mass diffusion in systems where the geometry is generally static the most suitable approach is to use finite difference methods.

A1.2.1 Overview

Finite difference methods are a numerical solution technique that effectively split the material system up into a grid where each cell or element has constant properties for any discrete time interval. The properties of each cell may be different and may also change between each time interval. However for any cell and particular time interval the solution of each cell is reduced to that of a homogeneous system with constant boundary conditions. The mass diffusion equation of the reduced system may then be solved by applying linear mass transfer techniques. It should be noted that by discretisation of the system in both space and time is an approximation and so it is preferable to have as small as possible time steps and grid spacing to reduce errors in the solution.

The model described in this section uses a non-standard approach to finite differences. The multi-structured system contains interfaces and boundaries that only occur at the edge of a prescribed grid in which each grid contains a set pattern of cells. Each cell represents an actual volume of the multi-structured system and the value of the molar concentration or mass density for each cell is represented by a node, which is assumed to lie in the centre of the cell. Using this method it ensures that a node never lies on a boundary or interface and that every calculation for each cell requires that of a homogeneous material only. This approach means that only one type of cell is necessary and simplifies programming for multi-structured systems. However, the limitation of this technique is in integrating non-linear boundary conditions within a time step and this can only be solved using the standard approach by introducing boundary cells where the cell node is on the boundary.

The finite difference model described in this section uses an explicit solution method, which means that the concentration of A at each node is written as a function of the concentration of A of the nodes at the end of the previous time step. The equation at a node is derived by considering the species flux into and out of a small element surrounding the node and stating that any net species flux into or out of the element raises or lowers the concentration of A of that element accordingly.

A1.2.2 Geometry

In order to calculate the distribution of the concentration of species A numerically it is necessary to describe the material by a discretised grid or mesh. If we consider a node which represents a cell volume of dimensions $\left(\Delta x_{ijk}, \Delta y_{ijk}, \Delta z_{ijk}\right)$ in a three-dimensional cuboid x-y-z grid consisting of $i = 1...nx$, $j = 1...ny$ and $k = 1...nz$ nodes in the x-, y- and z-directions respectively. It is assumed that the adjoining nodes have dimensions of $\left(\Delta x_{i\pm1jk}, \Delta y_{ijk}, \Delta z_{ijk}\right)$, $\left(\Delta x_{ijk}, \Delta y_{ij\pm1k}, \Delta z_{ijk}\right)$ and $\left(\Delta x_{ijk}, \Delta y_{ijk}, \Delta z_{ijk\pm1}\right)$.

A1.2.3. Explicit finite difference equation for the concentration of species

For simplicity the species flux contribution from each node is assumed to be *into* the node in all directions and can be calculated using Fick's law, which for a constant diffusion coefficient D in the x-direction is:

$$\phi = -D\frac{\partial C}{\partial x} \; . \tag{A1.35}$$

where ϕ is the molar flux and C is the molar concentration. We take this opportunity to simplify the notation used, from here on a variable with no subscripts will be assumed to be associated with the $(i,j,k)^{th}$ node, for example $\Delta x_{ijk} \equiv \Delta x$. Any variable associated with an adjacent node to the $(i,j,k)^{th}$ node will be indicated only by the subscript of the direction for which it is adjacent, for example $\Delta x_{j-1jk} \equiv \Delta x_{j-1}$. This can be seen more clearly in Figure A1.1.
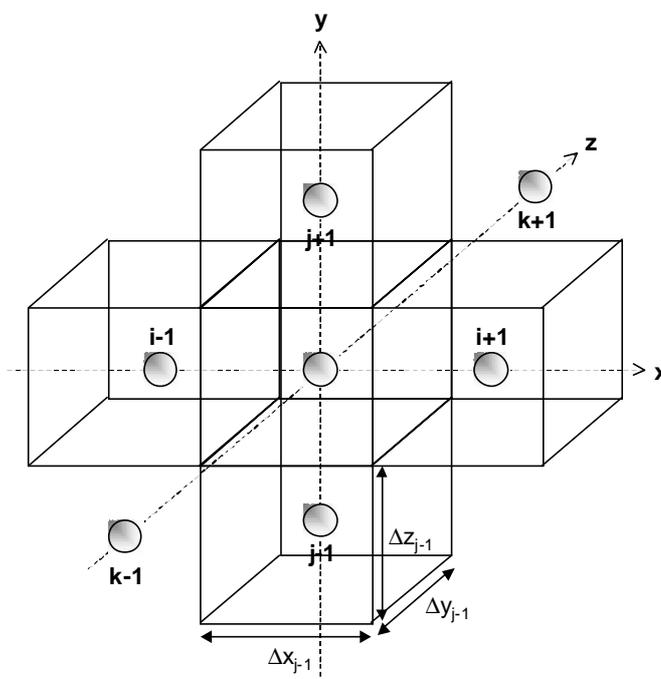

Figure A1.1: Three-dimensional node structure

The simplified notation is extended to the species fluxes where for example the flux from the $(i+1,j,k)^{th}$ node to the $(i,j,k)^{th}$ node will be simplified to ϕ_{i+1}. Assuming that in all directions the fluxes travel towards the $(i,j,k)^{th}$ node then the species transfer rates into the $(i,j,k)^{th}$ node, denoted by $\dot{S}_{in}$, is:

$$\dot{S}_{in} = (\phi_{i+1} + \phi_{i-1})\Delta y \Delta z + (\phi_{j+1} + \phi_{j-1})\Delta x \Delta z + (\phi_{z+1} + \phi_{z-1})\Delta x \Delta y \ , \qquad \text{(A1.37)}$$

where the rate of change of species stored in the control volume $\dot{S}_{st}$ is simply:

$$\dot{S}_{st} = \frac{dC}{dt}\Delta x \Delta y \Delta z = \frac{(C^{p+1} - C^p)}{\Delta t}\Delta x \Delta y \Delta z \ . \qquad \text{(A1.38)}$$

In Equation (A1.38) the time differential may be calculated explicitly where the superscripts p and p+1 represent the species concentration at the time p and p+1. Defining a conservation of the rate of species similar to Equation (A1.7), we may write:

$$\dot{S}_{st} = \dot{S}_{in} + \dot{S}_{g} \ , \qquad \text{(A1.39)}$$

where $\dot{S}_{g}$ is the contribution to the rate of change of species from internal chemical reactions. Inserting Equation (A1.38) in Equation (A1.39) and rearranging gives a finite difference representation of the concentration of species at a time period p+1:

$$C^{p+1} = C^p + \left(\frac{\Delta t}{\Delta x \Delta y \Delta z}\right)\left(\dot{S}_{in} + \dot{S}_{g}\right) \ , \qquad \text{(A1.40)}$$

where $\dot{S}_{in}$ is calculated by Equation (A1.37) from the species fluxes $\phi_{i\pm1}, \phi_{j\pm1}, \phi_{k\pm1}$, each which must be derived depending on the type of the surrounding node.

3.4. Solid nodes

In this model solid nodes are defined simply as nodes, which represent solid cell volumes. For these nodes Fick's law may be used to calculate the species flux into an adjacent solid node. For a solid node (i,j,k) that is completely surrounded by internal nodes of different material diffusivities, the fluxes from each adjacent node are:

$$\phi_{i\pm1} = \frac{2\left(D_{i\pm1}\Delta x_{i\pm1} + D\Delta x\right)\left(C_{i\pm1}^p - C^p\right)}{\left(\Delta x_{i\pm1} + \Delta x\right)^2}$$

$$\phi_{j\pm1} = \frac{2\left(D_{j\pm1}\Delta y_{j\pm1} + D\Delta y\right)\left(C_{j\pm1}^p - C^p\right)}{\left(\Delta y_{j\pm1} + \Delta y\right)^2} \quad , \quad\quad\quad (A1.41)$$

$$\phi_{z\pm1} = \frac{2\left(D_{k\pm1}\Delta z_{k\pm1} + D\Delta z\right)\left(C_{k\pm1}^p - C^p\right)}{\left(\Delta z_{k\pm1} + \Delta z\right)^2}$$

The fluxes in Equation (A1.41) are inserted into Equation (A1.37) to and the species concentration over time may then be calculated in an incremental fashion using Equation (A1.40).

A1.2.5. Boundary nodes

Non-solid nodes are used to describe boundary conditions that may be applied to solid nodes. They effectively have zero cell volume and are only there to represent a boundary condition type, they are sometimes referred to as ghost nodes. The species flux ϕ_{surf} in the x-direction from a constant species boundary condition, where the species concentration on the boundary is held at C_{surf}, would be

$$\phi_{surf} = \frac{2D\left(C_{surf} - C^p\right)}{\Delta x} \quad . \quad\quad\quad (A1.42)$$

The value for ϕ_{surf} would be inserted into Equation (A1.37) depending on which side of the $(i,j,k)^{th}$ node the boundary node is. For example if there is no solid $(i+1,j,k)^{th}$ node then the edge of the cell on that side is a boundary and if held at a constant species concentration then the flux from the $(i+1,j,k)^{th}$ ghost node would be $\phi_{i+1} = \phi_{surf}$, where ϕ_{surf} is calculated by Equation (A1.42). For applying a constant species flux at the boundary then simply put $\phi_{i+1} = \phi_{surf}$ in Equation (A1.37) where ϕ_{surf} is the value of the species flux at the boundary.

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APPENDIX II COMMERCIAL EQUIPMENT SUPPLIERS

This section describes permeation measurement instruments available commercially. The presence of a supplier or instrument does not indicate any endorsement by NPL. Similarly, the list is not exhaustive and the absence of any supplier/instrument is only due to a lack of information found from various searches rather than a judgement on the system. Further information is available from the manufacturers at the website addresses given.

MOCON http://www.mocon.com/

MOCON is a global provider of permeation systems and services designed to assess materials and processes. The company develops, manufactures and markets instrumentation, and also provides consulting and development services.

The PERMTRAN-W range of instruments determines water vapour transmission rates. The feed side of the instrument is cycled between low and high humidity set points and the resulting transmission of moisture measured using an IR detector. Instruments are available which conform to ASTM Standard E-398 (Accumulation Method) and ASTM F-1249 /Tappi T-557. Calibration is traceable to NIST. The PERMATRAN-C range assesses carbon dioxide (CO_2) transmission rates. The OX-TRAN range uses proprietary, high accuracy COULOX® coulometric-type sensors for oxygen transmission measurements. Instruments comply with ASTM standards D-3985, F-1927 and F-1307 and calibration is traceable to NIST standards.

VTI CORPORATION http://www.vticorp.com/products/WPA-100.htm

The WPA-100, water permeability analyser from VTI measures water vapour transmission rate (WVTR) through films, blisters, foil, and various packaging material. Temperature ranges from 23° C to 50° C and humidity ranges from 2% to 98% RH are used. Experiments yield information for initial moisture content, drying, kinetics, diffusion and steady state permeability

LYSSY http://www.lyssy.com/

Lyssy supply instruments for water vapour, oxygen and carbon dioxide transmission measurement. General manometric gas permeability testers comply with standards ASTM D 1434, DIN 53380 and ISO 2556. Gravimetric water vapour permeability test systems are also supplied.

ILLINOIS INSTRUMENTS
http://www.illinoisinstruments.com/moisture-permeation-analyzers.html

Illinois Instruments Series 400 Moisture Permeation Analysers provide moisture transmission measurements, over a wide range of temperature from –110°C to +20°C, using an aluminium oxide sensor.

SYSTECH INSTRUMENTS http://www.systechinstruments.com

Systech instruments manufacture a range of modular systems for the precise analysis of the oxygen permeation performance of packaging film. Pure oxygen is fed above the sample and nitrogen below. Molecules of oxygen, diffusing through the film, are carried by the nitrogen to

a precision sensor that directly measures oxygen content. Calibration can be by both standard gas and NIST traceable films

TECHNOLOX http://www.technolox.com

Technolox manufacture MicropermM4 gas permeation instruments. Gas samples are fed to the feed side of the cell whilst the diffusant side of the cell is evacuated. Gas molecules permeating through the cell are detected using a mass spectrometer.

Versaperm www.versaperm.com

Manufacture WVTR Meters

APPENDIX III: DETECTORS

Detector Type	Species Detected	Principal	Comments
IR Spectroscopy	Various in particular carbon containing molecules	Molecular groups absorb light at characteristic frequencies in the IR region. From Beers law, the intensity of light absorbed is proportional to concentration of absorbing molecules.	Versatile, continuous method for determining organic molecules, CO_2, etc. However, accuracy for trace amounts may be limited and corrections for drift may be needed. Calibration would be via reference gas mixtures.
Mass Spectroscopy	Various	Mass spectroscopy sorts molecules according to their mass/charge ratios. The number of molecules for each ratio is counted on arrival at the detector.	Mass spectroscopy is a very sensitive but costly technique.
Pressure sensing	Various	Absolute gas pressure difference across the membrane used to drive diffusion – increase in pressure on the low-pressure side measured. Sensors can be manometric, piezoelectric or electro-mechanical	Can be extremely sensitive to total gas flow but has no selectivity for distinguishing individual species.
Gas Chromatography	Various	The diffusing gas is collected and analysed using a gas chromatograph.	Can quantify relative proportions of gases. Requires sufficient sample volume for accurate measurements.
Mass Sensing	Various	The increase in mass of absorbents on the diffusant side of the permeation cell can be determined either off line or continuously. Resonant mass sensors and surface acoustic wave surface sensors can have extremely good mass resolution.	Most obviously useful for water vapour. Usefulness for molecules will depend on absorbents used. MEMS sensors are under development but few commercial systems yet.
Thermal Conductivity	Various	Thermal conductivity is measured with a sensor that employs four matched filaments arranged as a Wheatstone bridge that change resistance according to the thermal conductivity of the gas passing over it. Since each gas has a known thermal conductivity, the thermal conductivity can be deconvoluted .to determine the mixture.	Gas content needs to be known to make measurements and measurement compares conductivity to a known sample. Highest resolution is between gases having large thermal conductivity differences (normally H or He from other gases).
Capacitive	Various (high dielectric permittivity)	Gas absorbs into porous layer between two electrodes. Capacitance is proportional to quantity and dielectric constant of gas.	Most obviously useful for moisture (high dielectric constant).
Semiconductor	Various	The resistance of some semiconductive metal oxides change with the absorption of gas molecules.	Used in monitoring for gas or LPG leaks.
Photo Ionisation	Various	High-energy UV photons (<300 um) will ionise some gases (e. g. toluene, trichloroethyene) but not others (e.g. air, methane). The ions collected by e-field produce a current proportional to gas concentration.	Sensitive (< 1 ppm) but not selective. Special UV lamps costly and have limited life (also high power)

Detector Type	Species Detected	Principal	Comments
Fluorescence	Various	UV light impinges on some organics produces a fluorescent light proportional to ambient gas concentration (e.g. oxygen)	High sensitivity (because photo-detectors are sensitive). Applicable only to a few gases (but used with many biological materials where it can be sensitive and selective). Few commercial sensors using this technology are available.
Electrochemical sensor	Oxygen	Covers a range of sensors, some specific types are described below. Principally used for oxygen but also applications for H, CO, CO_2, etc. Solid-state coulometric sensors are used in many commercial permeation instruments. Electrochemical sensors are self powered micro fuel cells. The cell consists of a casing containing a gel or electrolyte and two active electrodes: the working electrode (anode) and the counter-electrode (cathode). The top of the casing has a membrane, which can be permeated by the gas sample. Oxidization takes place at the anode and reduction at the cathode. A current is created as the positive ions flow to the cathode and the negative ions flow to the anode. Gases such as oxygen, nitrogen oxides and chlorine which are electrochemically reducible are sensed at the cathode while those which are electrochemically oxidizable such as carbon monoxide, nitrogen dioxide and hydrogen sulphide are sensed at the anode. Diffusion of gas into the solid electrolyte in the sensor cell leads to electrochemical reactions that produce a current proportional to the quantity of reactive gas.	Very sensitive method (sensitivity depends on cell type), suitable for a wide level of concentrations. Calibration is by the manufacturer. Consumption of electrolyte requires that cells be replaced regularly.
Hersh Cell	Oxygen	Electrochemical technique, relying on oxygen interacting with a silver cathode to produce a flow of OH^- ions, which generate current at a cadmium anode, proportional to oxygen flow. To prevent cadmium depletion, a platinum electrode is used to provide anodic protection. The anode potential applied is proportional to the current flow.	Sensitive method for trace quantities of oxygen (ppm < C < 1%). Reactive impurities can affect measurements (e.g. CO_2)

Detector Type	Species Detected	Principal	Comments
Zirconia Cell	Oxygen	This is a high temperature ceramic sensor, an electrochemical galvanic cell comprising of two electronically conducting, chemically inert, electrodes attached to either side of a solid electrolyte tube. The tube is completely gas tight and made of a ceramic (stabilized zirconium oxide) which, at the temperature of operation, conducts electricity by means of oxygen ions. The potential difference across the cell is proportional to the ratio of partial pressure of oxygen (P_1/P_2) and is given by the Nernst equation. $$E = \frac{RT}{4F} \ln\left(\frac{P_1}{P_2}\right),$$ where F is the Faraday constant. This equates to E = 0.0496T log (P_1/P_2)	The zirconia cell needs to be mounted in a temperature-controlled furnace. Typically oxygen concentration is measured over the range 0.01ppm to 100%. Various molecules (combustible, halogen containing molecules) can poison the cell.
Paramagnetic Sensor	Oxygen	Uses the paramagnetic susceptibility of oxygen, a physical property that distinguishes oxygen from most other common gases. Two nitrogen-filled glass spheres mounted on a suspension, which is suspended in a symmetrical non-uniform magnetic field. When the gas contains paramagnetic oxygen, the glass spheres are pushed farther away form the strongest part of the magnetic field, the torque acting on the suspension is proportional to the oxygen content of the gas.	Factory calibrated. Results can be affected by other paramagnetic molecules.
Phosphorus Pentoxide (P_2O_5)	Water vapour	Following Faraday's Law, water molecules require energy to dissociate into hydrogen and oxygen. As gas passes over the sensor, moisture is attracted to the P2O5 coating, changing the resistance of the platinum coil, due to the electrolysis of the moisture to form hydrogen gas and oxygen gas. The current flowing in the electrode is therefore proportional to the moisture dissociating.	Recombination can give false high readings if the carrier gas contains hydrogen or oxygen, which can react to form water. This is usually only a problem if the measured sample contains less that 5 ppm of moisture. P_2O_5 moisture analysers are not suitable for gases that will react with the phosphorus.
Pulsed Electrolytic Hygrometer	Water vapour	Depends on adsorption of water vapour from a known flow of gas and the simultaneous electrolysis of the adsorbed water. The normal adsorbent is a film of phosphoric acid/phosphorus pentoxide with embedded platinum wire electrodes.	

Detector Type	Species Detected	Principal	Comments
Aluminium Oxide	Water vapour	AlO_2 sensors are extremely sensitive moisture sensors. Interdigitated capacitance sensors are mounted on an AlO_2 substrate that changes both, its capacity and resistance, depending on the humidity.	The sensor has a large linear dynamic range, minimal hysteresis and the extremely short reaction time. This type of sensor is used in many commercial water permeation instruments
Carbon nano-tubes	Water vapour	The conductivity of doped carbon nanotubes varies (non-linearly) with water content. Response is very quick.ref549	Very new method, not commercially available but may give a quick method of sensing trace quantities.
Polymer micro-layers	Various	Various methods based on the interaction of permeant molecules with polymer sensor layers. The shift in spectroscopic fingerprint of the polymer molecule or increase in intermolecular spacing (detected by XRD) have been proposed.	Claims of very high sensitivities but few commercial applications yet.
Colourmetric	Various	The carrier gas is fed through an aqueous solution containing ionic species that react with the diffusant and change the colour of the solution. The colour change is measured through light absorption or spectroscopy or directly compared with a colour chart.	Low accuracy method, mostly suitable for quality control.
Radioactive isotopes	Various	The permeant gas is doped with radioactive isotopes. The flux of doped molecules through the sample is determined by the increase in radiation detected using a Geiger counter.	Obvious health, safety and regulatory concerns surrounding the use of radioactive materials.

APPENDIX IV   IMPLEMENTATION OF DIFFUSION IN ABAQUS

ABAQUS requires the definition of diffusivity behaviour (through the command *DIFFUSIVITY) and solubility properties (using the *SOLUBILITY command) in order to perform a mass diffusion analysis. Optionally, diffusion due to stress and temperature gradients can be included through the *KAPPA command (TYPE=PRESS to define pressure dependence, TYPE=TEMP to define temperature dependence. Both KAPPA options may be used with the general diffusion law.

The default, LAW=GENERAL, is chosen for "general mass diffusion behaviour"; this was used by Hinopoulos and Broughton [25]. The equations ABAQUS employ to perform the general and Fickian analyses are shown in the ABAQUS Analysis User's Manual [9]. When the general diffusivity law is selected then *KAPPA may be included to "specify the material parameters for mass diffusion driven by gradients of temperature and equivalent pressure stress".

Command	Required Data	Optional Data
*DIFFUSIVITY Isotropic, orthotropic, or fully anisotropic diffusivity can be defined. For orthotropic diffusivity three values (D_{11}, D_{22}, D_{33}) and for anisotropic diffusivity six values (D_{11}, D_{12}, D_{22}, D_{13}, D_{23}, D_{33}) of diffusivity are needed at each concentration, temperature, and field variable value. The *DIFFUSIVITY parameter LAW may be set to either GENERAL or FICK to describe the diffusion behaviour. When the FICK law is chosen then κ_S is defined automatically and on *KAPPA, TYPE=PRESS may be defined by the user.	Diffusivity, D, (ABAQUS units of L^2T^{-1}, where L = length, T = time) (Diffusivity data may be supplied an isotropic value or a set of orthotropic or ansiotropic values)	Concentration, c Temperature, T Field variables
*KAPPA (optional command) The Soret effect factor, κ_s, governs temperature-driven mass diffusion. It can be defined as a function of concentration, temperature, and/or field variables in the context of the constitutive equation presented above. The Soret effect factor cannot be specified in conjunction with Fick's law since it is calculated automatically in this case The pressure stress factor, κ_p, governs mass diffusion driven by the gradient of the equivalent pressure stress. It can be defined as a function of concentration, temperature, and/or field variables in the context of the constitutive equation presented above.	TYPE=TEMP κ_S Soret effect factor (units $F^{1/2}L^{-1}$, where F = force) **and/or** TYPE=PRESS κ_P Pressure stress factor (units $LF^{-1/2}$)	Concentration, c Temperature, T Field variables
*SOLUBILITY Solubility, s, is used to define the "normalized concentration," ϕ, of the diffusing phase in a mass diffusion process: The normalized concentration is often also referred to as the "activity" of the diffusing material, and the gradients of the normalized concentration, along with gradients of temperature and pressure stress, drive the diffusion process	Solubility s ($PLF^{-1/2}$, where P = mass concentration)	Temperature, T Field variables
*INITIAL CONDITIONS, TYPE=CONCENTRATION	NSET or node number, initial normalized concentration value at the node(s)	

Table A1.1: A summary of the model data ABAQUS requires for diffusion analysis (greater detail can be found in [9]).