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NPL REPORT MAT 111

HYDROGEN GAS PERMEABILITY THROUGH POLYMER COMPOSITES – TEST SET-UP DEVELOPMENT

S GIANNIS, AS MAXWELL, F OMONIYI, M G VEERABHADRAPPA

JUNE 2022

Department for
Business, Energy
& Industrial Strategy

FUNDED BY BEIS

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S Giannis, A S Maxwell, F Omoniyi, M G Veerabhadrappa
Materials and Mechanical Metrology Department

ISSN 1754-2979

DOI: https://doi.org/10.47120/npl.MAT111

National Physical Laboratory
Hampton Road, Teddington, Middlesex, TW11 0LW

This work was funded by the UK Government's Department for Business, Energy and Industrial Strategy (BEIS) through the UK's National Measurement System programmes.

Approved on behalf of NPLML by
Fernando Castro, Head of Science - Materials and Mechanical Metrology Department

CONTENTS

1 INTRODUCTION

With the United Kingdom aiming to achieve net zero by 2050, there needs to be a major shift towards renewable energy sources. Increased renewable energy production, however, presents new challenges: (a) how can we store energy produced by intermittent sources such as wind and solar? and (b) how can transport systems and industries that rely on energy-dense fuels switch to renewable energy? Hydrogen may well be the best answer to both questions. Today, hydrogen is largely produced from petrochemical sources. However, if renewable energy can be used to create hydrogen gas via water electrolysis, the energy can effectively be locked up in the gas and stored. Like conventional fuels, hydrogen has a much higher energy density (see Figure 1) than other energy storage technologies such as batteries allowing it to be used like a conventional fuel. However, unlike conventional fuels, hydrogen does not produce carbon dioxide and other harmful emissions responsible for polluting our atmosphere.

The transportation and storage of hydrogen comes with its own challenges, being an odourless, colourless gas and highly flammable, containment and leak prevention is critical. As hydrogen is the smallest molecule in existence, permeation through polymeric and polymer composite materials is extremely rapid compared to other gases. Permeability is therefore a key design challenge for polymer and composite containment and transmission systems. Moreover, permeation and absorption of hydrogen in such systems is not well understood or evaluated in a standardised manner. As a result, there is a need to develop methodologies to evaluate hydrogen gas permeation, with emphasis given to high-pressure hydrogen, in polymer-based systems.

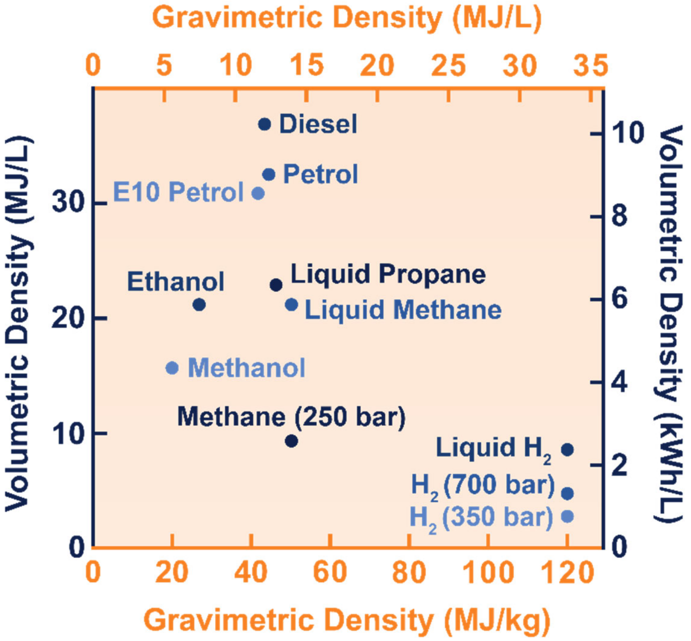

Figure 1. Comparison of specific energy (energy per mass or gravimetric density) and energy density (energy per volume or volumetric density) for several fuels.

1.1 PROJECT SCOPE

During the formulation of the National Measurement System (NMS) programme, it became apparent that there was considerable interest in the permeability of hydrogen gas through polymer composite materials from a multitude of different perspectives concerned with the development of a hydrogen fuel-based economy. The project has therefore been developed with the following objective:

To design, construct and demonstrate the measurement capability of a cell capable of measuring the permeability of hydrogen gas through polymeric materials and to report on the permeation cell specifications, operational procedure, and test results from two materials.

2 PERMEABILITY MECHANISMS

Permeation is a mass transport process in which molecules transfer through a material from the exterior environment to the interior environment, or vice versa, through diffusive processes.

In polymers, permeation occurs through a combination of the following:

- Absorption at the surface and dissolution of the permeant molecules in the polymer,
- Diffusion of the molecules through the polymer, driven by concentration gradients, and,
- Desorption from the surface of the polymer.

Figure 2 schematically presents the above-described processes. The environments surrounding the surface of the polymer can be a combination of vacuum, gas atmospheres, liquids, or other solids and the external boundary conditions will have a significant effect on the permeation process. The permeability of a molecule in a polymer is normally defined as the product of the solubility and mobility (diffusion)[1]. The permeability of small molecules in polymers depends on the free volume present in the polymer, meaning that molecules will absorb more easily and be more mobile in polymeric materials with high free volumes. In turn, the free volume depends on the nature of the polymer and on the physical state of the polymer, including molecular orientation and physical ageing effects. The theory and many practical applications of molecular transport in polymers have been covered extensively by Crank [1, 2]; while the absorption of moisture in polymer composites has been described widely by Springer [3, 4].

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[1] Diffusion in Polymers, edited by J Crank and G S Park, Academic Press, London, 1968

[2] Crank J., The Mathematics of Diffusion, Clarendon Press, Second Edition 1975.

[3] Springer G.S., Environmental effects on composite materials, Technomic Publishing Company, Westport CT, 1981

[4] Springer G.S., Environmental effects on composite materials, Volume 2, Technomic Publishing Company, Lancaster Pa, 1984.

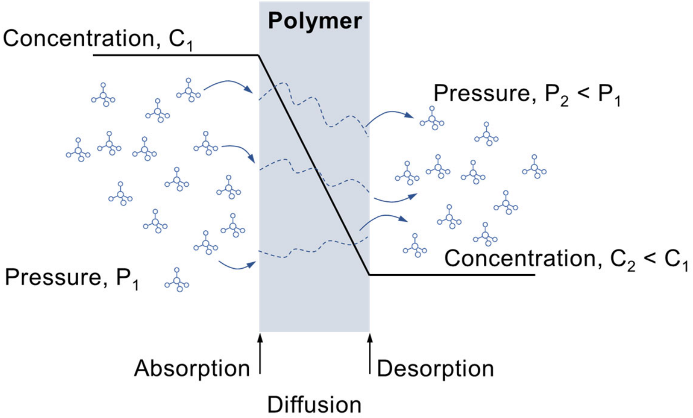

Figure 2. Permeation and diffusion process

2.1 DISSOLUTION & ADSORPTION

Dissolution is a thermodynamic process where the solubility is determined by the enthalpy change on dissolution of the molecule in the polymer and the volume available for occupation. It is commonly assumed that the surface layer of the polymer reaches saturation instantly on exposure to the molecules and that uptake rates are governed by the rate at which these diffuse from the surface. Equilibrium will be reached in a time depending on the size of the polymeric component and its diffusion characteristics.

$$c = S \cdot P \qquad \textbf{1}$$

Ideal sorption of gases (including vapour) in a polymer follows Henry's law (Eqn. 1) where the concentration, c, adsorbed is directly proportional to the pressure, P, of the gas, where S is the solubility coefficient.

2.2 DIFFUSION

Diffusion is the process by which matter is transported from one part of a system to another because of random molecular motions. The process acts to remove chemical potential differences and will eventually produce an equilibrium state of concentration.

The flux (rate of transfer), J, of a gas in a polymeric material can be defined as the quantity of permeant, q, which crosses the membrane area, A, during time t.

$$J = \frac{q}{t}\frac{1}{A} \qquad \textbf{2}$$

Fick's first law of diffusion in isotropic materials expresses the steady-state flux of a permeant per unit area of a membrane, J, as a function of the concentration gradient dc/dx of permeating molecules across dx.

$$J = -D \cdot \frac{dc}{dx} \qquad \textbf{3}$$

The proportionality factor, D, is the diffusion coefficient. By expressing the fact that the amount of gas by unit of membrane volume is equal to the increase of the gas concentration with time, it is possible to write, in the case of unidirectional diffusion:

$$-\frac{dJ}{dx} = \frac{dc}{dt} \qquad \mathbf{4}$$

Assuming the diffusion coefficient does not depend on concentration and by combining Eqn. 3 and Eqn. 4 Fick's second law is as follows:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad \mathbf{5}$$

The diffusion coefficient is temperature dependent and for ideal systems follows an Arrhenius relationship with temperature:

$$D = D_0 \exp\cdot\left(-\frac{E_D}{RT}\right) \qquad \mathbf{6}$$

where, R is the gas constant (8.314 J mol^{-1} K^{-1}), E_D (J mol^{-1}) the activation energy and T the temperature.

2.3 PERMEATION

For steady-state permeability through a polymer sheet of finite thickness, h, it is postulated that concentrations remain constant at all points on each side of the material ($x = 0, c = c_1$ and $x = h, c = c_2$) and provided that the diffusion coefficient is constant and independent of concentration, Fick's second law reduces to:

$$\frac{\partial^2 c}{\partial x^2} = 0, \qquad \frac{dc}{dx} = constant \ \ \& \ \ c = c_1 + \frac{x}{h}(c_2 - c_1) \qquad \mathbf{7}$$

So, from Fick's first law

$$J = -D\cdot\frac{dc}{dx} = \frac{D\cdot(c_1 - c_2)}{h} \qquad \mathbf{8}$$

Expressing concentrations as pressures using Henry's Law and re-arranging, the previous equation becomes

$$\frac{q}{t}\cdot\frac{1}{A} = \frac{D\cdot s\cdot(P_1 - P_2)}{h} = \frac{Pe}{h}\cdot(P_1 - P_2) \qquad \mathbf{9}$$

where, dq/dt, is the rate of flow of permeant, A, is the permeated area, P_1, is the high pressure applied to the sheet at constant temperature, T, P_2 is the low pressure having permeated through the sheet also at constant T, s is the solubility coefficient and $Pe = D\cdot s$ is the permeation coefficient.

2.4 DESOPRTION

Desorption is the opposite of adsorption and net desorption occurs if it is thermodynamically favoured. Normally, molecules will desorb where the concentration of the desorbing species in the atmosphere is less than the concentration required for maintaining saturation in the polymer. The greater the difference between the two concentration levels, the higher the desorption rate. Desorption will not simply be the reverse of adsorption, there may be considerable hysteresis if adsorbed 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 initial, unsaturated state.

3 EVALUATION OF TRANSPORT COEFFICIENTS

3.1 STEADY STATE

The simplest technique to determine the diffusion coefficient is based on Fick's first law. Consider the gas diffusion through a polymer sheet of finite thickness h, both surfaces of which are respectively maintained to gas concentrations c_1 and c_2. At the beginning of the experiment, the flux and the gas concentration in every point of the membrane vary with time. When the steady state is reached, Fick's first law states that the concentration varies linearly across the membrane and that the gas flux is the same in every section of the membrane. Generally, c_2 is maintained to 0 and the membrane thickness as well as the applied pressure are known. Therefore, if the value of c_1 is known, the diffusion coefficient can be directly obtained by measurement of the permeant flux (Eqn. 8). Though, in many systems, the surface concentrations are unknown, whereas the pressures P_1 and P_2 on each membrane face are known, with, P_1 highly greater than P_2. By considering, the gas amount, q, that crossed the polymer membrane of area A and of thickness h during the time t, the permeability coefficient can be calculated from Eqn. 9 as:

$$Pe = \frac{q \cdot h}{t \cdot A \cdot (P_1 - P_2)} \qquad 10$$

3.2 TIME LAG METHOD (NON-STEADY STATE)

When a gas is applied under pressure to one of the polymer sides, before reaching the steady state, the flux and the concentration vary with time in every point inside the polymer sheet. The concentration is given by[5]:

$$c = c_1 + \frac{x}{h}(c_2 - c_1) + \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{c_2 \cos n\pi - c_1}{n}\sin n\pi\frac{x}{h} \cdot exp\left[-\frac{Dn^2\pi^2 t}{h^2}\right] \qquad 11$$

While the total amount of permeant substance q which has passed through the sheet is obtained by:

$$q = D\frac{t}{h}(c_1 - c_2) + \frac{2h}{\pi^2}\sum_{n=1}^{\infty}\frac{c_1 \cos n\pi - c_2}{n^2}\left\{1 - exp\left[-\frac{Dn^2\pi^2 t}{h^2}\right]\right\} \qquad 12$$

In the most common experimental arrangements c_2 = 0 and when t tends towards very long times, the steady state is reached, and the exponential term becomes negligible leading to:

$$q = \frac{c_1 \cdot D}{h}\left(t - \frac{h^2}{6D}\right) \qquad 13$$

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[5] Stancel A.F., Diffusion through Polymers, in Polymers Science and Materials, Wiley Interscience, 1971. p.247-274.

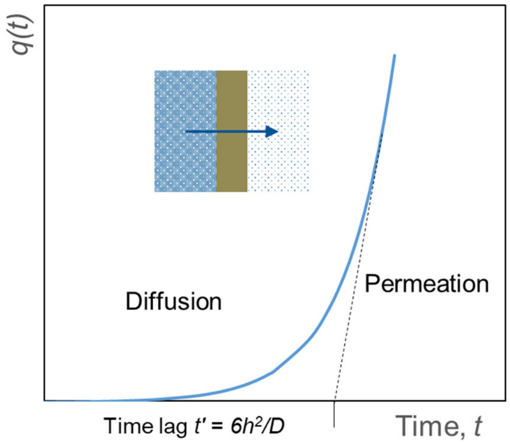

Figure 3. Theoretical curve of a permeation experiment.

This has an intercept t' on the time axis given by Eqn. 14 and is called the “time lag” (see Figure 3).

$$t' = \frac{h^2}{6D} \tag{14}$$

According to Eqn. 14 it is possible to deduce the diffusion coefficient. In steady state, Eqn. 10 provides the permeability coefficient, and the solubility coefficient is calculated as Pe over D.

3.3 ANALYSIS OF SORPTION-DESORPTION TESTS

When a polymeric film of thickness h, is immersed in a penetrant, the concentration, C, in the material is given, at time t, by the solution of Fick’s second law (Eqn. 5), which for unidirectional diffusion is:

$$\frac{c}{c_1} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\cdot exp\left[-\frac{D(2n+1)^2\pi^2 t}{h^2}\right]\cdot \cos\frac{(2n+1)\pi x}{h} \tag{15}$$

This equation does not consider the diffusion towards the edges of the membrane, as far as the thickness of the film is very small compared to the other dimensions. Eqn. 15 can be integrated to obtain the mass of penetrant, $M(t)$, absorbed by the sample at time t, assuming that the temperature and the pressure are constant. If D is assumed to be constant, the following relation is obtained:

$$\frac{M(t)}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\cdot exp\left[-\frac{D(2n+1)^2\pi^2 t}{h^2}\right] \tag{16}$$

where, M_∞ is the mass of the diffusing species adsorbed by the material at equilibrium. For $M(t) / M_\infty < 0.6$ the above equation simplifies to:

$$\frac{M(t)}{M_\infty} = \frac{4}{h}\left(\frac{D}{\pi}\right)^{1/2}\sqrt{t} \tag{17}$$

The slope of the $M(t)$ vs. $\sqrt{t}$ for $M(t) / M_\infty < 0.6$ (linear diffusion) is given by Eqn. 18 and provides a practical measure of the diffusion coefficient (Figure 4).

$$slope = \frac{4M_\infty}{h}\left(\frac{D}{\pi}\right)^{1/2} \quad 18$$

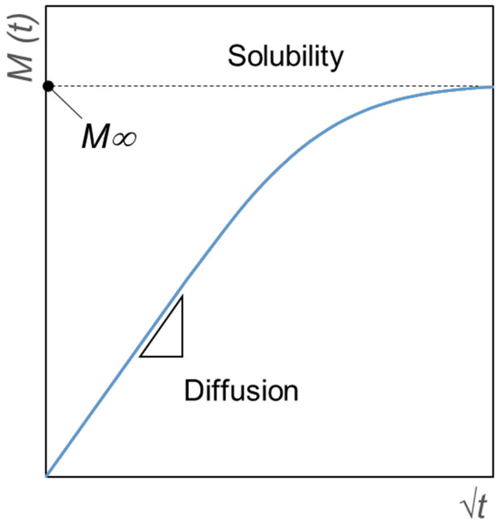

Figure 4. Theoretical curve of a sorption experiment.

The volume of penetrant (e.g., gas) at equilibrium, V_∞ in cm^3 (Standard, Temperature and Pressure -STP), can be obtained from the value of M_∞ by the following relation:

$$V_\infty = \frac{M_\infty - M_i}{M_{gas}} \cdot 22400 \quad 19$$

The constant 22 400 corresponds to the volume in cm^3 occupied by a mole of gas in the standard conditions of pressure and temperature. M_i is the initial mass of the sample and M_{gas} is the molar mass of the penetrant gas. The solubility coefficient (in cm^3 (STP)/ cm^3 MPa) is then obtained by:

$$S = \frac{V_\infty}{PV_{pol}} = \frac{M_\infty - M_i}{PV_{pol}M_{gas}} \cdot 22400 \quad 20$$

where P is the applied gas pressure and V_{pol} the volume of the polymeric film.

4 PERMEATION MEASUREMENT METHODS

There are many measurement methods and several standard techniques for determining mass transport in polymers that can also be applicable to polymer composites.

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

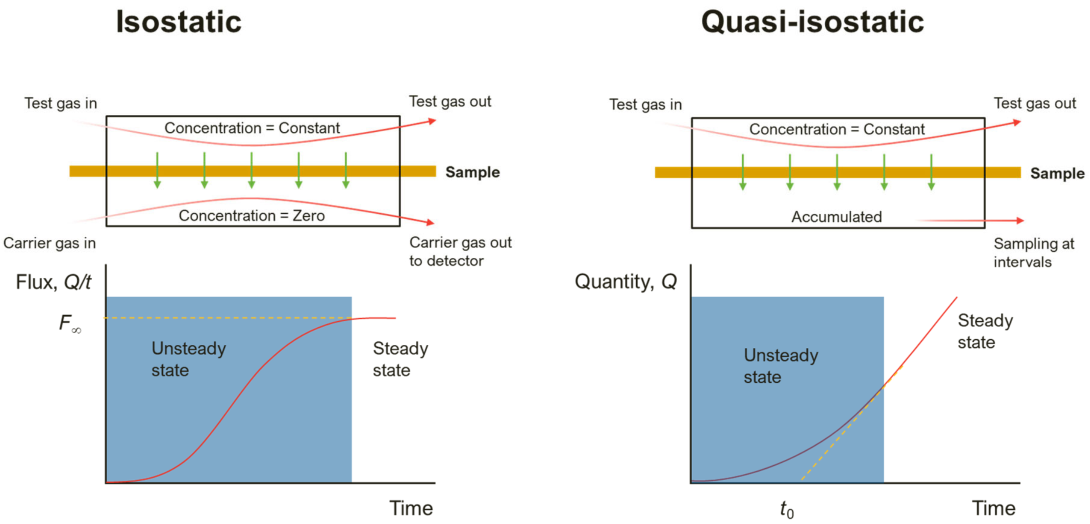

Figure 5. Isostatic and quasi-isostatic permeation methods.

In this work the focus is on the second category, the permeation measurement methods. These can be divided into two basic types: (a) isostatic test methods where the material tested is under constant concentration gradients. A test gas, or mixture, flows through one side of the sample in the cell and through the other side a carrier gas takes the permeant passing through the polymer to a detector (Figure 5). In some cases, the detector side may be under reduced pressure or even a vacuum, though the concentration gradient across the sample is constant throughout the test provided that the flow concentrations are maintained, and (b) quasi-isostatic methods which determine permeation through the sample under varying concentration differences. A test gas, or mixture, flows through one side of the sample in the cell. The permeant accumulates in the other side of the cell and the amount accumulating is quantified by a physical sensor or analytical chemistry technique (Figure 5). The concentrations in the cell will reach equilibrium provided sufficient time is allowed and the concentration gradient will continuously decrease during the test.

There are several general types of permeation measurement that are commonly used and have been specified as standards by bodies such as ASTM, ISO, BSI or DIN. A number of these standards are summarised in Appendix 1. Generally, permeation tests rely on differences in concentration of the permeating species on either side of a sample 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.

4.1 GAS PERMEATION TESTS

Manometric Method

ASTM D1434 specifies method 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 side of the cell at atmospheric pressure. The cell on the opposite side of the sample is hermetically sealed and evacuated. 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.

Constant Volume Method

This is like the manometric method except that a differential pressure transducer is used in place of the manometer (e.g., ISO 15105-1). 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.

Constant Pressure Methods

ASTM D1434 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 of the cell, typically 2 bar or greater. The diffusion of gas through the sample leads to an increase in volume (at constant pressure) on the low-pressure side, which is measured by displacement of the manometer fluid.

Carrier Gas Methods

Carrier gas methods (e.g., ISO 15105-2) 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.

Standards for Gas Specific Test Methods

In addition to the main generic gas permeability test standards listed above, there are also numerous standards for specific gases in particular, oxygen, carbon dioxide, and water vapour. Standards specific to oxygen, including ASTM D3985, ASTM F1307, ASTM F1927 and ASTM F 2622 involve the use of oxygen sensors, such as a coulometric or zirconium dioxide sensor to measure the oxygen present in the carrier gas. This provides an extremely sensitive measurement of oxygen but is unsuitable for use with hydrogen.

The two test standards specific to carbon dioxide ASTM F2476 and DIN 53380-4, use infrared sensors to detect the carbon dioxide in a nitrogen carrier gas. Unfortunately, this technique also cannot be used for hydrogen gas as infrared sensors are unable to detect diatomic molecules like hydrogen as they do not absorb infrared radiation.

Measurement of water vapour through polymer films and sheets has been standardised using a range of different techniques. A relatively simple test described in ASTM E96 and DIN 53122 is to use an open dish which is sealed with the sample and placed in a controlled environment. The dish can either be filled with water and diffusion determined by weighing the dish to calculate moisture loss, or a desiccant placed in the dish and the dish weighed to assess the amount of water that diffuses into the dish. A more sensitive technique that works on the same principle is the calcium corrosion test method (ISO 1506-7), which measures the rate of reaction of calcium with water. In this technique a calcium film is deposited on to the test specimen and the calcium sealed allowing moisture diffusion only through the specimen. Water vapour transmission is then determined from changes in the properties of the calcium after it has been exposed in an environmental chamber. Numerous measurement techniques have also been standardised that use carrier gases. These include ASTM F1249 and ISO 15106-2 which use pressure-modulated infrared sensors, ISO 15106-3 which uses an electrolytic sensor, ISO 15106-4 which uses gas-chromatographic sensors and ISO 15106-6 which uses atmospheric pressure ionization mass spectrometers. Techniques that use an accumulation method include ASTM F1249 and ISO 15106-1 which use humidity sensors to measure dynamic relative humidity and ISO 15106-5 that uses pressure sensors to measure the pressure exerted by water vapour diffusing into the accumulation chamber. Many of these tests are unsuitable for hydrogen gas, however gas-chromatography and the use of pressure sensors will be described later.

5 FACTORS INFLUENCING TEST ACCURACY

Sealing of the Permeation Cell

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 nearly impermeable sample materials e.g., metals, glass.

Calibration of Detectors/Instruments

All sensors in the permeation set-up, 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.

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 is 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. 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.

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.

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.

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 and using reduced thickness samples can increase the flux, but it may not be economic or possible to make the same material at different thicknesses. 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.

Temperature

Equilibrium (saturation) concentrations and diffusion coefficients depend on temperature, as free volume and molecular mobility are temperature dependent (Figure 6). For a typical diffusion activation energy of 35 kJ/mol the Arrhenius relationship predicts that an increase of about 15 °C from ambient temperature can lead to a doubling of permeation rate. There also may be discontinuities in the diffusion coefficient vs. temperature curves at the glass transition temperature with higher sorption occurring above T_g. Permeation experiments should therefore be performed under stable, thermostatically controlled conditions (covering the sample, sample chamber, carrier/feed gases) to optimise accuracy. The temperature dependence of permeation properties can be determined from experiments performed at different controlled temperatures.

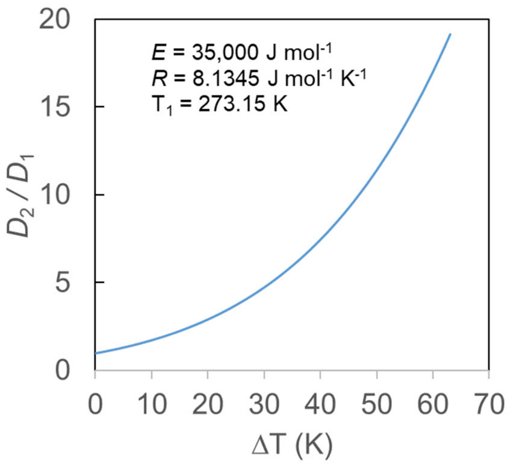

Figure 6. Change in diffusion coefficient with temperature for a typical diffusion activation energy of 35 kJ/mol.

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 a high degree of accuracy. For ‘thick’ films of 1 mm or greater, micrometre gauges capable of measuring to within 1 μm are suitable for thickness determination. However, for very ‘thin’ films (< 100 μm), micrometre gauges 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. Therefore, samples need to be conditioned 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. The effect on molecular solubility and mobility of stresses will depend on the type of stress applied. Hydrostatic tensile stress will increase free volume and open internal voids, providing additional sites into which molecules can adsorb. Conversely, hydrostatic compressive stress will reduce solubility by closing internal sites.

6 HYDROGEN PERMEATION EXPERIMENTAL SET-UP

6.1 PERMEATION CELL

The permeation cell (Figure 7, Figure 8) comprises a top and bottom plug that are clamped together in a sleeve via two locking caps. A removable sealing ring is assembled in the inside face of the top plug and is used to clamp up on a sample of polymer or composite sheet when the two locking plugs are assembled. The sealing ring seals against the plug and the sample using two sets of O-ring and back-up ring assemblies. The top plug has two ports for pressurising and venting the test gas in the test gas chamber and a thermowell for attaching a thermocouple on the top face. Two ports in the bottom plug allow for sweeping gas (nitrogen or helium) to pass through a porous support and be collected for analysis.

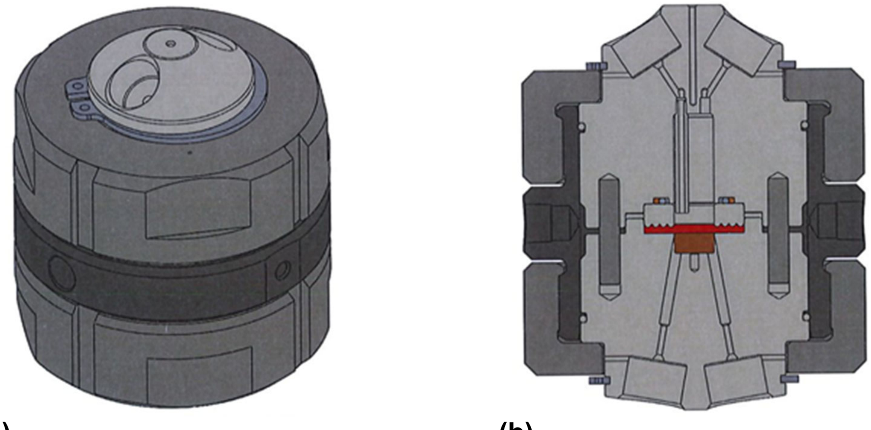
(a) (b)

Figure 7 (a) Permeation cell and (b) Section view of the permeation cell

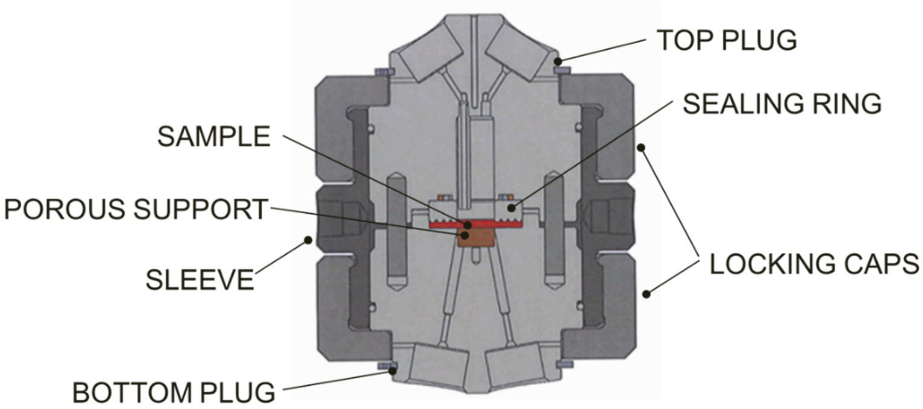

Figure 8 Permeation cell main parts

The materials used for manufacturing the various parts of the permeation cell are listed in Table 1. The cell was designed by KW Design Solutions and hydrostatically tested at a pressure of 2,838 bar at ambient temperature.

Table 1. Permeation cell materials.

Materials	
Plugs	Hastelloy C276
Sealing Ring	Hastelloy C276
Sleeve	17-5PH Stainless steel
Caps	17-5PH Stainless steel
Main seals	G92E FFKM with PEEK back-up ring
Secondary seals	VMQ 70S

6.2 EXPERIMENTAL SET-UP – GAS CHROMATOGRAPHY

The experimental set-up to measure the concentration of hydrogen gas that permeates through the polymer composite is schematically shown in Figure 9. The concentration of hydrogen that permeates through the polymer is analysed by gas chromatography (GC); two detectors were utilised- an Agilent GC with Pulse Discharge Helium Ionisation detector (PDHID, VICI, CH) using helium as a carrier gas (pre-filtered helium was utilised as carrier gas, Purity > 99.9999%, (He BIP®, Air Products)) and an Agilent GC with a thermal conductivity detector (TCD).

The GC PDHID is a non-destructive high selectivity detector that shows a linear response to both organic and inorganic compounds. It utilises a stable, low powered, pulse DC discharge in helium as an ionisation source. The GC TCD consists of an electrically heated filament in a temperature-controlled cell. The method used one Hayesep Q 80/100 mesh 2 m × 1/8” outer diameter × 2 mm inner diameter column and one Molesieve 5A 80/100 mesh 9 ft × 1/8” outer diameter × 2 mm inner diameter column with argon carrier. The loop size used for sample injection was 2 ml.

To ascertain the concentration of hydrogen permeating through the cell, NPL gravimetric gas standards in helium matrix gas were utilised in calibration of the instrument. The gas standards utilised were in-house standards prepared in accordance with ISO 6142-1.

The experimental procedure involves connecting the system as shown in Figure 9, purging the system and connecting line as well as carrying out an experiment using helium (Purity > 99.9999%, (He BIP®, Air Products)) and pure hydrogen (Purity > 99.9999%, (H2 BIP+®, Air Products)).

Leak checking and purging the system

The system is purged after the material is placed in the permeation cell as shown in Figure 8; a leak check is carried out using hydrogen and helium leak detectors to ensure that there are no leaks to the cell and the connection line. In the case of leaks the gas supply is switched off and experiments stopped till the source of the leak is identified.

The hydrogen side is purged first before a purge is carried out using hydrogen through the steps described below.

1. Ensure P1 is closed and open the hydrogen gas supply for 10 seconds,
2. Using a hydrogen leak detector, check for leaks between the hydrogen supply and P1,
3. Open the hydrogen gas supply for 15 seconds and set P1 to 5 bar,
4. Using a hydrogen leak detector, check for leaks between P1 and the needle valve,
5. Open the needle valve and using a hydrogen leak detector, check for leaks between the needle valve and V1,
6. Open the hydrogen gas supply and open V1 for 15 seconds, using a hydrogen leak detector check for leaks around the permeation cell and between the connection before V2,
7. Open V1 and V2 for 15 seconds, using a hydrogen leak detector, check for leaks in the connection before P3,
8. Open V2 for 15 seconds, set P3 to 1 bar and using a hydrogen leak detector, check for leaks in the connection after P3 to V6,
9. Open V2 and V6, using a hydrogen leak detector, check for leaks in the connection to the vent,
10. Close V2,
11. Close V1,
12. Open V2 to depressurise system,
13. Close V2,
14. Open V1 for 20 seconds,
15. Open V2 to depressurise system,
16. Close V2,
17. Repeat steps 14 to 16, 20 times to purge the hydrogen side of the permeation cell.

The helium side is also leak checked and purged as well using the steps below.

1. Ensure P2 is closed and open the helium gas supply for 10 seconds,
2. Using a leak detector, check for leaks between the helium supply and P2,
3. Open the helium gas supply for 15 seconds and set P2 to 2 bar,
4. Using a leak detector, check for leaks between P2, the flow controller and V3,
5. Open the helium gas supply and set the mass flow controller to the desired flow rate (20-25 ml/min),
6. Open V3 and V4, using a leak detector, check for leaks around the permeation cell, and the connections after V3, V4 and before V5,
7. Close V3 and V4 and open V5, check for leaks after V5 to P4,
8. Open V3 and set P4 to 1 bar and check for leaks between P4 and the GC,
9. Close V5,
10. Open V3 for 20 seconds,
11. Open V5 to depressurise the cell,
12. Repeat steps 9 – 11, 20 times to purge the material side in the permeation cell,
13. Close V5,
14. Open V4 for 20 seconds,

15. Open V5 to depressurise the cell,
16. Repeat steps 13 – 15, 20 times to purge the helium side of the permeation cell,
17. Close V5.

Blank test and Hydrogen tests

A blank test is carried out by utilising helium alone following the steps as outlined below.

1. Open the helium gas supply
2. Set P2 to 2 bar,
3. Set mass flow controller to 25 ml/min
4. Open V4 and V5
5. Set P4 to 1 bar
6. Monitor the peaks on the GC; an oxygen and nitrogen peak might indicate the presence of air and will indicate a leak in the system or inadequate purging. The presence of a hydrogen peak indicates inadequate purging of the system. It is essential that the system is sufficiently purged before the hydrogen tests.

The hydrogen tests will proceed by opening the hydrogen gas supply, setting the pressure on P1 to the desired pressure (for low pressure tests <20 bar) and opening V1 and the needle valve. The level of hydrogen is monitored through the peak of hydrogen detected by the GC, and this can be quantified using a primary reference standard maintained by NPL. A high peak of hydrogen and increased GC flow rate at the start of the hydrogen experiments might indicate a material with high permeability to hydrogen or a leak within the permeation cell. It is essential that the permeation cell is set up appropriately as depicted in Figure 9.

Initial Test Results

Initial tests were carried out using a blank aluminium disc, and LDPE material within the permeation cell; the test was carried out using hydrogen supplied at 1, 5 and 8 bar. The run time of hydrogen for each test was approximately 3 hours and the set flow of helium utilised was 25 ml/min at 1 bar. The test was carried out using the GC TCD. The results after 3 hours indicate a hydrogen flow below the limit of detection for all samples analysed as indicated in Table 2.

Table 2. Initial test results.

Material	**H2 Pressure (bar)**	**H2 Flow (ml/min)**	**Amount (%mol/mol)**
Aluminium disc	1	5	< 0.4
		25	< 0.4
		100	< 0.4
LDPE	1	25	< 0.4
	1	200	< 0.4
	5	25	< 0.4
	5	200	< 0.4
	8	25	< 0.4
	8	200	< 0.4

The result of the initial testing indicates that permeation across the LDPE material occurred at a concentration below the limit of detection of the GC TCD; this indicates that an instrument more sensitive to hydrogen like the GC PDHID would need to be utilised for subsequent testing. Testing would also need to be carried out for a longer run time, using other materials and increasing hydrogen pressures to effectively help in ascertaining and comparing the permeation rate of hydrogen through different materials at different pressures.

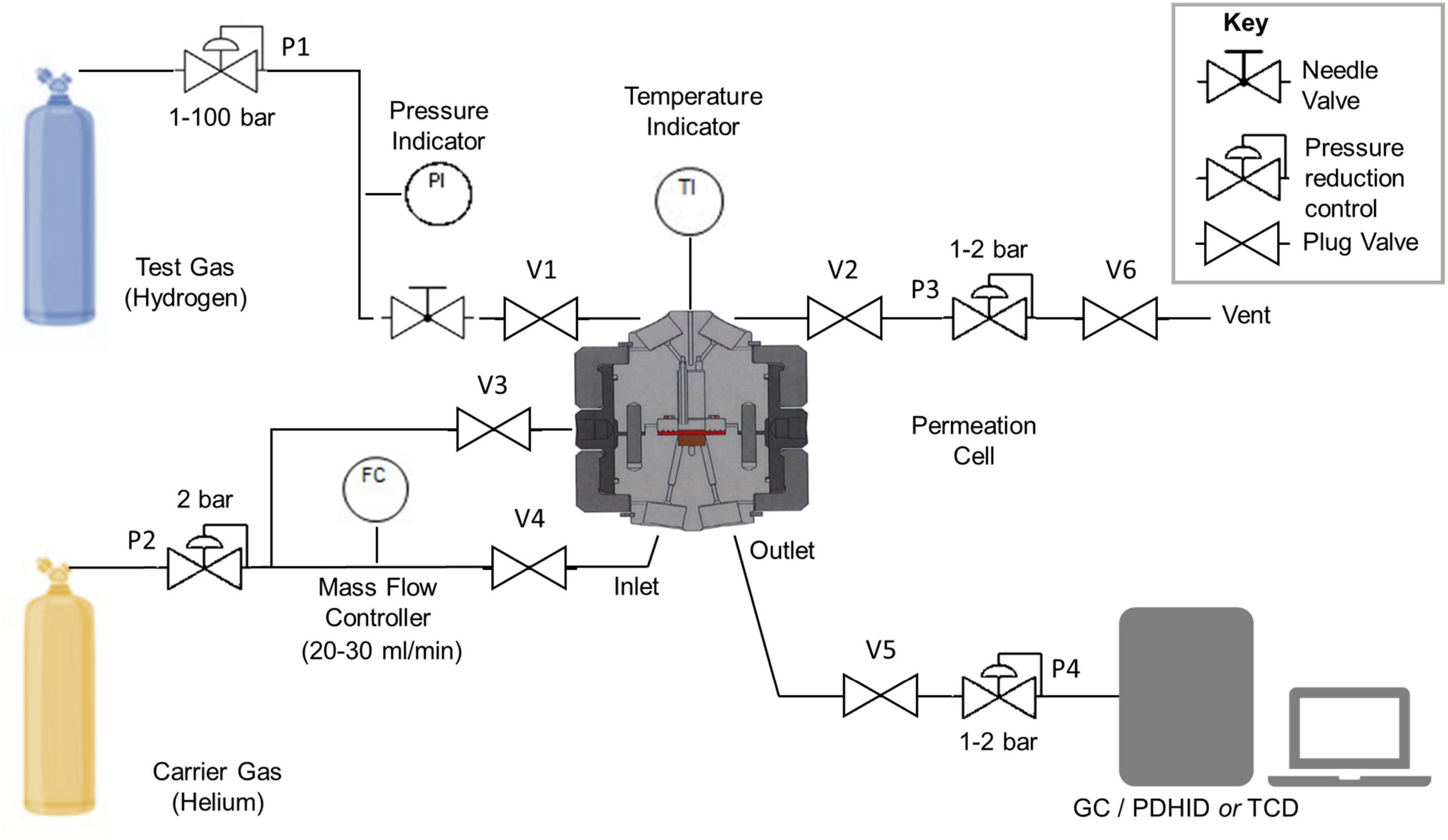

Figure 9 Schematic representation of the experimental set-up for hydrogen gas permeability measurement using a Gas Chromatograph

6.3 EXPERIMENTAL SET-UP – PRESSURE GAUGES

The use of gas chromatography has been problematic, and the experimental set-up has therefore been modified to replace the gas chromatography with pressure gauges. The reasons for these modifications are two-fold. First, the gas chromatography instrument is in high demand which causes delays in testing and due to their expense, purchasing a dedicated instrument was beyond the means of this project. The gas chromatography also requires a continuous flow of helium carrier gas which if there is a leak in the system could become a safety risk. Consequently, using the gas chromatography system overnight was prohibited limiting the length of tests that could be conducted.

Principle

The modified experimental set-up to measure permeability using pressure gauges is shown schematically in Figure 10. As in the previous set-up, this consists of a test specimen mounted so that it forms a barrier to the flow of gas through the cell forming an upstream and downstream chamber. The upstream chamber contains high-pressure hydrogen gas that is allowed to slowly permeate through the specimen. The downstream chamber is the receiver chamber containing inert gas (either nitrogen or helium) at ambient pressure into which the hydrogen gas permeates. The amount of hydrogen gas that permeates through the specimen is determined by the increase in the pressure of the downstream chamber. Pressure in the upstream and downstream chambers are measured using 100 bar WIKA Precision digital pressure gauges model CPG1500. The gauges are accurate to a 0.05% full scale reading and capable of wirelessly downloading the data digitally to a laptop.

Test conditions

Specimens should be conditioned by exposing the specimens to laboratory conditions for 48 hours prior to testing (23±2 °C and 50 %Rh). The tests were conducted under the same conditions.

Procedure

1. Place a permeable support in the downstream chamber, this is essential to prevent the specimen from bulging or bursting,
2. Coat the flat edges of the specimen thinly and uniformly with vacuum grease to hermetically seal the two chambers from each other. Ensure none of the grease touches the centre of the specimen that is to be tested,
3. Place the specimen on to the sealing O-ring, followed by the upper part of the cell,
4. Clamp the two halves of the cell together using a torque wrench and ensure that the specimen is completely sealed against the O-ring,
5. Connect the pressure gauges and gas supplies as shown in Figure 10,
6. Conduct leak checks on the cell and the connection lines, using hydrogen and helium leak detectors, on the upstream and downstream sides of the cell, respectively,
7. Check the upstream side of the cell first. Close valve P1 and open the hydrogen gas supply for 10 seconds. Using a hydrogen leak detector, check for leaks between the hydrogen supply and P1. Pressurise the system by opening the hydrogen gas supply for 15 seconds and set P1 to 5 bars, then close valve P1. Using the hydrogen leak detector, gradually open the valves leading to the cell, checking for leaks in the gas-line and the upstream chamber of the cell,
8. Conduct a similar leak check on the helium side. Close valve P2 and open the helium gas supply for 10 seconds. Using a helium leak detector, check for leaks between the gas supply and P2. Pressurise the system by opening the gas supply for 15 seconds and set P2 to 2 bars, then close valve P2. Using the helium leak detector, gradually open the valves leading to the cell checking for leaks in the gas-line and the downstream chamber of the cell,

Note: When leaks are detected the gas supply must be switched off and experiments stopped till the source of the leak is identified.

9. Purge both the upstream and downstream sides of the cell by repeatedly pressurising and venting the system (20 times),
10. The hydrogen permeability test is conducted by opening the hydrogen gas supply, setting the pressure on P1 to the desired pressure (< 70 bar) and opening V1 and the needle valve. An increase in pressure in the downstream chamber will confirm transmission of hydrogen gas through the specimen,
11. Record the time at which the test is started and record the pressure from both the upstream and downstream pressure gauges on the laptop,
12. Plot a curve of the pressure in the downstream chamber versus time, continuing until steady state has been reached as indicated by a straight line.

Calculations

The gas permeability of hydrogen through the specimen is calculated from the gradient of the straight-line, $\frac{dp}{dt}$, obtained once steady state conditions have been reached.

The permeability, P, (*mol.m/(m*^{2}*.s.Pa*) is obtained using the following equation:

$$P = \frac{V_c \times d}{R \times T \times A \times p_h} \times \frac{dp}{dt} \qquad \textbf{21}$$

where,

$\frac{dp}{dt}$	change in pressure per unit time during steady state diffusion (*Pa* s^{-1})
V_c	volume of the downstream chamber (m^3)
T	test temperature (*K*)
p_h	pressure of gas in the upstream, high-pressure chamber (*Pa*)
A	area of specimen (m^2)
R	gas constant (8.31×10^3 $J\ mol^{-1}\ K^{-1}$)

The diffusion coefficient, *D*, is calculated from the time lag, t', which is the intercept of the slope of the diffusion curve in the steady state on the time axis (see section 3.2 and Eqn. 14).

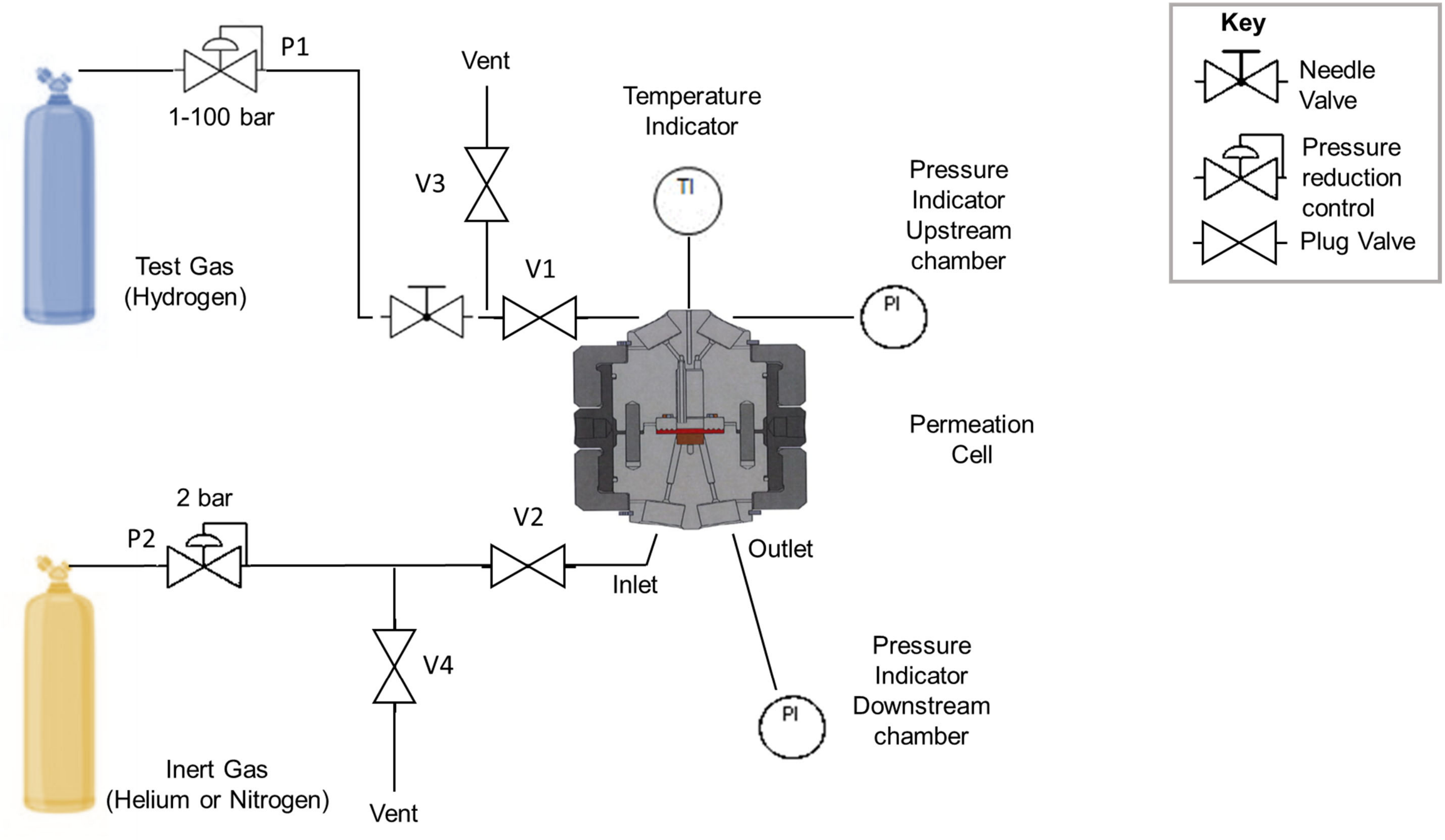

Figure 10 Schematic representation of the experimental set-up for hydrogen gas permeability measurement using pressure gauges.

Experimental results

For the calculation of the permeation rate the volume of the downstream chamber and associated tubing needs to be accurately measured. This was achieved by sealing an aluminium specimen in place and filing the downstream chamber with argon (molar mass 39.948 g mol^{-1}) pressurised at 97.5 bar at 21.3 °C. Fillings were performed three times and the cell was weighed before and after each filling (see Table 3). Using ideal gas law, the volume of the downstream chamber was calculated to be equal to 19.421 ml (1.942×10^{-5} m^3).

Table 3. Weight of permeation cell, empty and filled with argon gas.

Weight of empty cell (g)	Weight of filled cell (g)	Mass of Ar (g)
4743.156	4746.255	3.099
4743.156	4746.248	3.092
4743.155	4746.238	3.083
4743.156	4746.247	3.091
4743.156	**4746.247**	**3.091**

The experimental results for the different materials are presented in Figure 11 and Figure 12, and the calculated permeability and diffusivity for four materials provided by the National Composites Centre in Table 4. In Table 5, permeability and diffusivity values of various materials at ambient temperature collected from various sources in the literature are presented. The measured values reported here are in good agreement with values from the literature for similar materials.

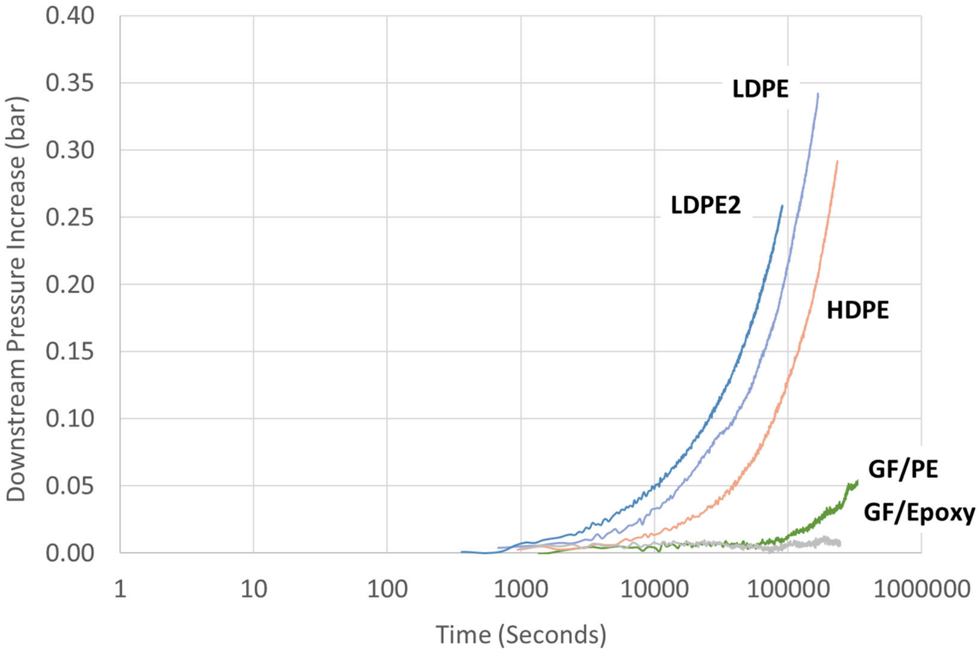

Figure 11. Increase of pressure in the downstream cell due to diffusion of hydrogen gas.

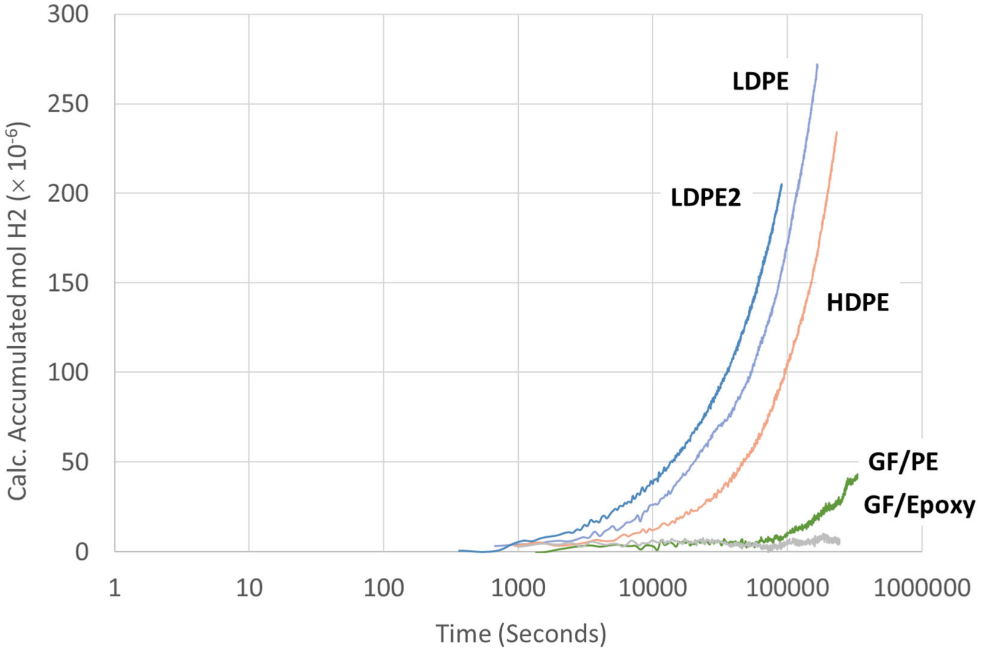

Figure 12. Accumulated hydrogen gas in the downstream cell due to diffusion.

Table 4. Calculated permeability and diffusivity.

Material	**Materials Index Register**	**Thickness** (mm)	**Upstream pressure** (bar)	**Permeability** $\left(\frac{\mathrm{mol\ H_2\ \ m}}{\mathrm{m^2\ s\ MPa}}\right) \times 10^{-9}$	**Diffusivity** $\left(\frac{\mathrm{m^2}}{\mathrm{s}}\right) \times 10^{-10}$
LDPE	AJPD	1.031	51.6	1.94	---
LDPE2	AJPD	1.070	50.9	2.65	---
HDPE	AJPC	1.071	50.4	1.35	---
GF/PE	AIUR	1.937	47.9	0.37	0.20
GF/Epoxy	AJPF	1.070	50.5	0.06	---

Table 5. Permeability and diffusivity of various materials at ambient temperature from various sources in the literature.

Material	Grade	Upstream Pressure (bar)	Permeability $\left(\frac{\text{mol H}_2\ \text{m}}{\text{m}^2\ \text{s MPa}}\right) \times 10^{-9}$	Diffusivity $\left(\frac{\text{m}^2}{\text{s}}\right) \times 10^{-10}$
LDPE [6]	LD ZE41K	100	2.84	3.18
HDPE [7]	HD HB111R	100	0.93	1.35
HDPE [8]		---	0.89	---
PE [9]		---	2.40	3.90
Epoxy [9, 10]	LY556/HY917	---	0.57	---
GF/Epoxy [9, 10]	E-glass V_f=56%	---	0.13	---
CF/Epoxy [9, 10]	Toho HTA7 V_f=60%	---	0.18	---

7 OBSERVATIONS AND NEXT STEPS

Values for the permeability of hydrogen through specimens of LDPE, HDPE, GF/PE and GF/Epoxy are in good agreement with literature values for similar materials. Values for the permeability of hydrogen have been obtained from thermoplastic specimens within a day and from glass fibre-reinforced thermoplastics within 3 days. Permeability of hydrogen through glass fibre-reinforced epoxy composites is significantly slower than through thermoplastic composites and will require longer test times to determine accurate permeability values.

The next step in the hydrogen permeability work will be to assess the repeatability of the measurements. It can already be seen that it is possible to distinguish between the different materials, so the next step will be to assess the uncertainty of the permeability values. Further work is also required to obtain repeatable values for the diffusion coefficients. Variables that must be assessed are the effects that the temperature has on the system and the effect that the initial pressure of the upstream and downstream chambers has on the measurements.

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[10] Humpenoder J., Gas permeation of fibre reinforced plastics. Cryogenics, 1998. 38: p. 143-147.

8 APPENDIX 1

ASTM D1434-82(2015) - Standard Test Method for Determining Gas Permeability Characteristics of Plastic Film and Sheeting
ISO 15105-1:2007 Plastics - Film and sheeting - Determination of gas-transmission rate - Differential-pressure methods
ISO 15105-2:2003 Plastics - Film and sheeting - Determination of gas-transmission rate - Equal-pressure method

Oxygen Transmission Rate
ASTM D3985 (17) - Standard Test Method for Oxygen Gas Transmission Rate Through Plastic Film and Sheeting Using a Coulometric Sensor
ASTM F1307 (20) - Standard Test Method for Oxygen Transmission Rate Through Dry Packages Using a Coulometric Sensor
ASTM F1927 (20) - Standard Test Method for Determination of Oxygen Gas Transmission Rate, Permeability and Permeance at Controlled Relative Humidity Through Barrier Materials Using a Coulometric Detector
ASTM F2622 (20) - Standard Test Method for Oxygen Gas Transmission Rate Through Plastic Film and Sheeting Using Various Sensors
DIN 53380-3: Determining the gas transmission rate of plastic film, sheeting and mouldings by the carrier gas method

Carbon Dioxide Transmission Rate
ASTM F2476 (20) - Standard Test Method for the Determination of Carbon Dioxide Gas Transmission Rate (CO2TR) Through Barrier Materials Using an Infrared Detector
DIN 53380-4: Testing of plastics - Determination of gas transmission rate - Part 4: Carbon dioxide specific infrared absorption method for testing of plastic films and plastic mouldings

Water Vapour Transmission Rate
ASTM F1249 (20) - Standard Test Method for Water Vapor Transmission Rate Through Plastic Film and Sheeting Using a Modulated Infrared Sensor
ASTM E398 (20) - Standard Test Method for Water Vapor Transmission Rate of Sheet Materials Using Dynamic Relative Humidity Measurement
ASTM E96/E96M (22) - Standard Test Methods for Gravimetric Determination of Water Vapor Transmission Rate of Materials
DIN 53122-1: Determination of the water vapour transmission rate of plastic film, rubber sheeting, paper, board, and other sheet materials by gravimetry
ISO 15106-1: 2003 Plastics - Film and sheeting - Determination of water vapour transmission rate Part 1: Humidity detection sensor method
ISO 15106-2: 2003 Plastics - Film and sheeting - Determination of water vapour transmission rate Part 2: Infrared detection sensor method
ISO 15106-3: 2003 Plastics - Film and sheeting - Determination of water vapour transmission rate Part 3: Electrolytic detection sensor method
ISO 15106-4: 2008 Plastics - Film and sheeting - Determination of water vapour transmission rate Part 4: Gas-chromatographic detection sensor method
ISO 15106-5: 2015 Plastics - Film and sheeting - Determination of water vapour transmission rate Part 5: Pressure sensor method
ISO 15106-6: 2015 Plastics - Film and sheeting - Determination of water vapour transmission rate Part 6: Atmospheric pressure ionization mass spectrometer method
ISO 15106-7: 2015 Plastics - Film and sheeting - Determination of water vapour transmission rate Part 7: Calcium corrosion method