Surface Measurement Systems
World Leader in Sorption Science

DVS Application Note 52

Vapour Permeability of Porous Materials using Payne Diffusion Cell

Jiyi Khoo1, Armando R. Garcia1, Dan Burnett1, Haydar Abdalghafor2, Majella E. Lane2, Sandra Van Vlierberghe3, Ana dos Santos3, Veerle Boterberg3 and Peter Dubruel3

1 Surface Measurement Systems Ltd.

2 Department of Pharmaceutics, The School of Pharmacy, University of London, Brunswick Square, London WC1N 1AX, UK.

3 Polymer Chemistry & Biomaterials Group, Department of Organic Chemistry, Ghent University, Krijgslaan 281, S-4, B-9000 Ghent, Belgium.

Vapour permeability in porous materials is of interest to a variety of different industrial sectors including packaging materials, membrane technologies, tissue engineering scaffolds etc. This application note describes the measurement of moisture vapour transmission rates (MVTR) through porous materials (i.e. silicone membranes/human skin and electrospun polymer fibre mats), using a Payne type diffusion cell and DVS instrument.

Introduction

Moisture transport characteristics of porous materials play an important role in many industries. For examples; packaging materials which can be directly related to shelf life and packaged product stability; model membranes which are widely used in in-vitro permeation studies in skin care industry; and electrospun nanofibres for polymeric scaffolds.

Moisture vapour transmission measurements are generally carried out under isothermal conditions. MVTR describes the rate of water permeating through a test specimen into the headspace volume of a container which differs in relative humidity (ΔRH).

Permeability, *P* hence can be represented as:

$$P = \frac{MVTR}{\Delta RH} \qquad (1)$$

with MVTR can be expressed in terms of the mass of moisture transferred, Δm in a unit time, Δt:

$$MVTR = \frac{\Delta m}{\Delta t} \qquad (2)$$

Typically MVTR is determined gravimetrically by two standard dish methods [1], [2], [3]. The dry cup method uses a sealed cup containing drying agent, like zeolite, silica gel or anhydrous calcium chloride. The sealed cup was placed in a controlled climate chamber with constant relative humidity and it is weighed periodically to determine the moisture transport rate of the test specimen. The other wet cup method requires

water in the sealed cup to maintain a 100%RH environment, with a saturated membrane sample. Shortcomings of the wet cup method have previously been recognised, in particular for more permeable films [4]. In addition, these two methods may result in different MVTR values.

Dynamic gravimetric vapour sorption (DVS) is a well-established method for the determination of vapour sorption isotherms. The high mass resolution and excellent baseline stability of DVS allows the fast and accurate determination of water sorption isotherms and diffusion kinetics over a wide range of temperature and humidity. DVS instrument therefore can be used to determine the MVTR of porous materials.

In this application note, the moisture vapour transmission characteristics of porous materials were investigated using a specially designed Payne diffusion cell and DVS instrument.

Method

Payne type Diffusion Cell

A novel diffusion cell: Payne style diffusion cell was designed and developed to measure the permeability/rate of diffusion of a thin film. The design of this cell is shown in Figure 1.

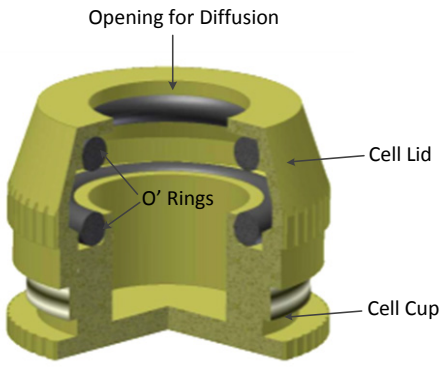

Figure 1. SMS Payne style diffusion cell design.

Sample with a maximum thickness of 1.5mm, and diameter of 7mm can be placed in between the O-rings as shown in Figure 1. However, use of the upper O-ring is optional and can be removed in order to accommodate sample up to 2.4mm in thickness.

Figure 2 depicts a typical experimental set-up for MVTR measurements. It clearly shows that the cell has two main components: cell lid which holds the test specimen and cell cup with a small reservoir to hold the moisture scavenger/drying agent.

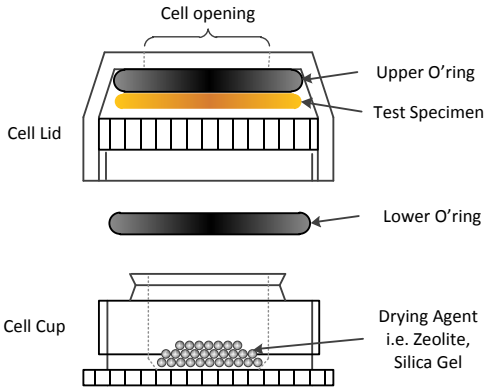

Figure 2. Experimental set-up for moisture vapour transmission rate measurement.

Once the test specimen is fitted on the lid, the bottom cell cup can be screwed into the upper cell lid, before placing on a DVS metal sample pan for measurement in the DVS instrument (Figure 3). The cell has an opening diameter of 4.4 mm on the top, providing an area of 15.54 mm^2. for moisture transport.

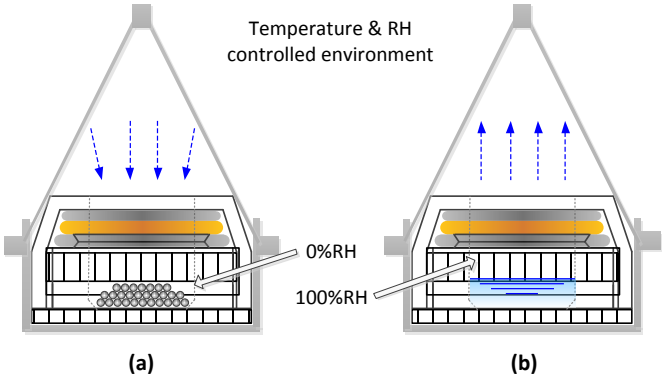

Figure 3. Payne type diffusion cell with DVS metal sample pan (C-WM-017) for (a) dry cup method and (b) wet cup method.

Results

Example 1: Synthetic Model Membranes and Skin

Synthetic model membranes are commonly used in the Franz cell chamber – an in-vitro skin permeation assay frequently used for evaluating the release actives from topical formulations or the penetration of drug across skin in formulation development. However, such in-vitro permeation test always face with a challenge about the validity and representability of the testing membranes, whether it should be a synthetic model membrane or excised human skin.

Three model membranes, namely CarboSil® membrane (100µm thickness), Polyurethane membrane (40µm thickness) and Silicone membrane (82µm thickness) were used in this work. Moisture vapour flux obtained from these model membranes were subsequently compared to that of a human trypsinized stratum corneum. Zeolite was employed as moisture scavenger for this example.

Payne diffusion cell loaded with membrane sample was subjected to two humidity stages. Initial drying step was at 0% RH for two hours, followed by a high humidity step at 90% RH for 3 hours. All experiments were measured at 32°C, and the data were collected in triplicate.

Change in mass of zeolite[1] at 90%RH refers to the diffusion of water vapour through the membrane via the cell opening. Therefore, in-vitro trans-membrane water vapour diffusion rate can be calculated from the slope of the moisture uptake by zeolite. Subsequently the water vapour flux was determined by taking into account the area of the cell opening, i.e. 15.54 mm^2. Water vapour flux is presented in the unit of $mg.min^{-1}.mm^{-2}$ (SI unit in $g.hr^{-1}.m^{-2}$).

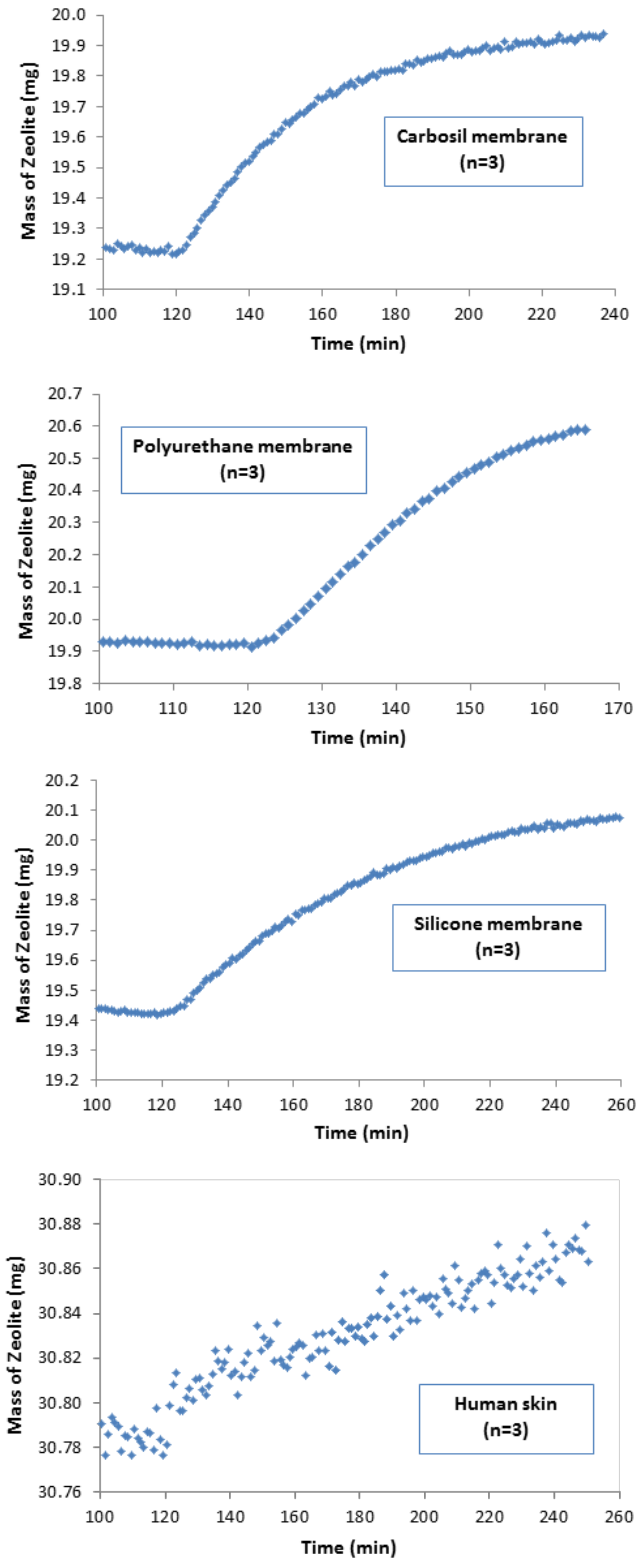

Figure 4. Change in mass of zeolite in response to 90%RH (at 120th minute), for CarboSil®, Polyurethane and Silicone membranes, and human skin.

[1] Δmass of zeolite was determined by subtracting the Δmass of membrane from Δmass of zeolite + membrane, in response to 90%RH.

Figure 4 depicts the change in mass of zeolite in a function of experimental time, in response to humidity change from 0%RH to 90%RH at the 120th minute.

Among the tested membranes, Polyurethane was the most permeable barrier to water vapour, with faster kinetics and much higher moisture uptake. This was followed by CarboSil® membrane meanwhile, Silicone membrane was the least permeable. Comparing to the human skin measurement, it can be clearly observed that the data points of human skin became more scattered, which could be attributed to the variability of skin thickness and extremely low moisture diffusion rate.

Table 1: Water vapour flux through membrane and human skin samples

Samples	Diffusion rate [mg/min]	Water vapour flux [g/(hr.m^2)]
CarboSil®	0.0150 ± 0.0046	57.36 ± 18.70
Polyurethane	0.0220 ± 0.0026	84.14 ± 11.16
Silicone	0.0093 ± 0.0012	35.71 ± 3.76
Human Skin	0.0012 ± 0.0004	4.63 ± 1.71

Water vapour flux results (Table 1) determined from the study show that human skin was the least permeable among all tested samples. Even though Silicone membrane has the closest flux value to that of human skin, it was still 7-times higher than human skin sample.

In addition, the flux value of 4.63 ± 1.73 g/(hr.m^2) was found to be relatively lower than the reported value from *in-vivo* measurement [5]. This may be related to different skin sites used, sex of donor, area of skin harvested, and even the skin preparation method. In this study, information about the donor of the skin is protected by the ethical agreement.

This study has demonstrated that Payne diffusion cell coupled with DVS instrument can be very useful tool in measuring the in-vitro trans-membrane water vapour flux.

Example 2: Electrospun Polymers

In recent years, electrospun polymers have shown great potential in fabricating novel scaffolds used for various tissue engineering applications. These bioscaffolds are produced by spinning the polymeric fibres onto a support. The electrospun polymer has a high porosity which can vary from microscale to nanoscale range. Such porous structure is very effective for fast and homogeneous tissue ingrowth [6].

Materials used in this study were extruded from a solution of Poly ε-caprolactone (PCL) for a final thickness of 300µm. SEM image of the membrane structure of the electrospun PCL is shown in Figure 5. In this example, silica gel was employed as moisture scavenger.

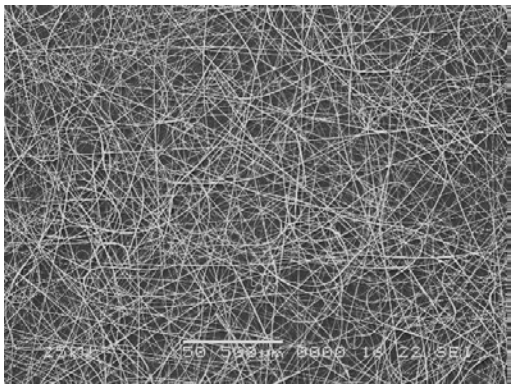

Figure 5. SEM image of an electrospun structure of PCL used in this study.

Electrospun PCL membrane was carefully trimmed and loaded into the Payne diffusion cell. Initial drying step was at 0%RH for one hour, and the sample was subjected to different humidity environments, e.g. 30%RH, 50%RH and 80%RH. All measurements were conducted at 35°C, unless otherwise stated.

Influence of relative humidity

Water vapour flux results show very high moisture vapour permeability of electrospun PCL membrane, as summarised in Table 2.

The diffusion rate is significantly influenced by the change in humidity. This is due to the fact that a higher humidity corresponds to a higher gradient between the two sides of the PCL membrane. Water diffusion kinetics were relatively fast and the moisture uptake of the silica gel increased up to 12% w/w (at 100%RH), when exposed to the humidified environment during 10 minutes.

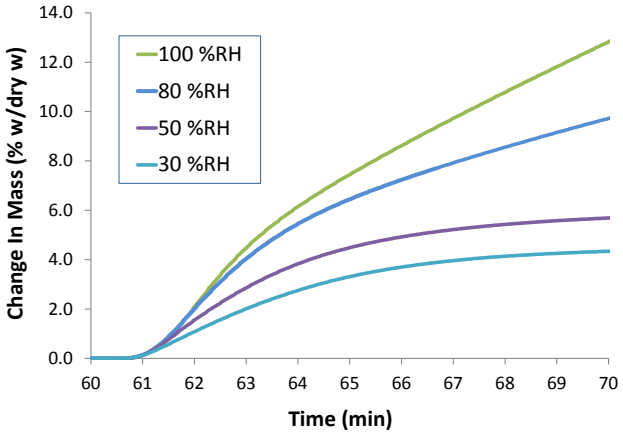

Figure 6. Change in mass of silica gel in response to varying relative humidity for the electrospun PCL membrane.

Table 2: *Water vapour flux through electrospun PCL membrane at varying relative humidity values*

% Relative Humidity	Diffusion rate [mg/min]	Water vapour flux [g/(hr.m^2)]
100	0.1152	444.82
80	0.1109	428.28
50	0.0751	289.94
30	0.0432	166.90

Influence of sample thickness

In order to investigate the effect of sample thickness, two PCL membranes (300µm thick each) were placed together resulting in an overall thickness of 600µm. As anticipated (Figure 7), the permeability rate (*dm/dt*) was reduced with increased thickness, when comparing the moisture uptake of two different sample thicknesses at 80%RH.

However, the reduction of the permeability rate for the thicker sample was minor (water vapour flux at 424.32 g.hr^{-1}.m^{-2}, which is less than 1% in reduction). Therefore, it can be concluded that the moisture permeability is not strongly dependent on the sample thickness of PCL membrane. This may be due to the high porosity of the PCL membrane.

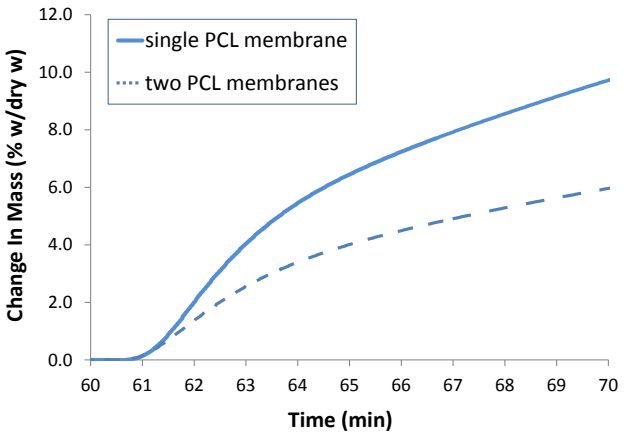

Figure 7. Change in mass of silica gel in response to different sample thickness of PCL membrane at 80%RH.

Influence of temperature at high humidity

On the other hand, increasing the temperature (up to 45°C) has accelerated the vapour permeability rate, possibly due to the rearrangement/ expansion of the PCL fibres at elevated temperatures. The water vapour flux through the PCL membrane was significantly increased by nearly 50% (637.84 g.hr^{-1}.m^{-2}).

Conclusion

This application note has shown that Payne diffusion cell, coupled with DVS instrument can be used to determine the moisture permeability properties of membrane samples. DVS can be employed to reliably and rapidly assess the diffusion of moisture and organic solvent vapours under controlled environment. Similar experiments could also be performed on other thin polymer films such as those found in packaging industry, and membrane in filtration applications.

References

1 United States Pharmacopeial (2007) USP 30–NF 25, Containers—Permeation h671i. Rockville, MD: USP; 267–269.
2 ASTM E 96 (1996) Standard Test Methods for Water Vapor Transmission of Materials.
3 ASTM F1249 – 06 (2011) Standard Test Method for Water Vapor Transmission Rate Through Plastic Film and Sheeting Using a Modulated Infrared Sensor.
4 Hu, Y., Topolkaraev, V., Hiltner, A. and Baer, E. (2001) Measurement of water vapor transmission rate in highly permeable films. Journal of Applied Polymer Science, 81(7), p1624-1633.
5 Bronaugh, R. L. and Maibach, H. I. (2001). Topical Absorption of Dermatological Products. New York.
6 Moroni, L., Licht, R., de Boer, J., de Wijn, J. R. and van Blitterswijk, C. A. (2006) Fiber diameter and texture of electrospun PEOT/PBT scaffolds influence human mesenchymal stem cell proliferation and morphology, and the release of incorporated compounds. Biomaterials, 27(28), p4911-4922.

Head Office:
Surface Measurement Systems, Ltd
5 Wharfside, Rosemont Road
LondonHA0 4PE, UK
Tel: +44 (0)20 8795 9400
Fax: +44 (0)20 8795 9401
Email: science@surfacemeasurementsystems.com

United States Office:
Surface Measurement Systems, Ltd, NA
2125 28th Street SW, Suite I
Allentown PA, 18103, USA
Tel: +1 610 798 8299
Fax: +1 610 798 0334