Comparing three techniques to determine the water vapour transmission rates of polymers and barrier films

Karyn L. Jarvis[a,†,*], Peter J. Evans[a], Nathan A. Cooling[b], Benjamin Vaughan[b], Jana Habsuda[c], Warwick J. Belcher[b], Chhinder Bilen[b], Grant Griffiths[a], Paul C. Dastoor[b] and Gerry Triani[a]

a. Institute of Materials Engineering, Australian Nuclear Science and Technology Organisation, Lucas Heights, NSW 2232

b. Centre for Organic Electronics, University of Newcastle, Callaghan, NSW 2308

c. Department of Materials Science and Engineering, Monash University, Clayton, Victoria 3800

*Corresponding author: Dr. Karyn Jarvis

ORCID ID: 0000-0003-1370-5045

Phone: +61392143898

Email: kljarvis@swin.edu.au

†Present address: ANFF-Vic Biointerface Engineering Hub

Faculty of Science, Engineering and Technology

Swinburne University of Technology

Hawthorn VIC 3122

Australia

Email: kljarvis@swinburne.edu.au

Abstract

Barrier films are required for a number of applications such as food packaging or organic electronics to prevent product degradation results from exposure to water vapour and oxygen. In order to determine the effectiveness of polymers and deposited barrier films to inhibit water permeation, the water vapour transmission rate (WVTR) needs to be measured. The calcium test, MOCON instrument and tritiated water permeation can all be used to determine the WVTR, but the values produced by these techniques have not been extensively compared. The WVTR of two polymer substrates and two barrier films deposited onto polymer substrates have been measured using these three techniques. For a polyethylene terephthalate substrate and a MOCON reference film, similar WVTR were observed for all three techniques. For two commercially available barrier films, variable WVTRs were observed and attributed to film defects. WVTR measurements play an essential role in the use of polymers and barrier films to retard water permeation, therefore an understanding of the advantages and disadvantages of each technique is of great importance.

Keywords: barrier film, thin films, water permeation, water vapour transmission rate, WVTR

1. Introduction

Polymers films are used in a number of applications such as food packaging [1, 2] and organic electronics [3] that require products to be protected from air and moisture as they are lightweight, cheap, transparent and printable. Polymers typically have water vapour transmission rates (WVTR) in the 0.1 – 100 $g.m^{-2}$/day range [4-8] which is usually sufficient for food packaging but not organic electronic applications [9]. For organic electronics to have sufficient lifetimes for commercial applications, an additional barrier film needs to be deposited onto the polymer to inhibit degradation resulting from exposure to water vapour and oxygen [10]. It has been widely stated that WVTRs in the 10^{-6} $g.m^{-2}$/day range are required to produce organic electronics with a sufficient lifetime [11]. In order to determine the effectiveness of polymers and barrier films to inhibit water permeation, the WVTR needs to be accurately determined. A significant research effort is focused on producing barrier films with the lowest possible WVTRs, with most research groups using one particular measurement technique. But can the effectiveness of two barriers be compared if their WVTRs were measured with different techniques? The calcium (Ca) test, MOCON instrument and tritiated water (HTO) permeation have been used to determine the WVTR of polymers and barrier films, but the values produced by these techniques have not been extensively compared. The Ca test and MOCON instrument are the two most commonly used techniques for determining the WVTR, but both have disadvantages. The lowest detection limit achievable with the most sensitive commercial MOCON instrument is 5 x 10^{-5} $g.m^{-2}$/day [12] while the main disadvantage of the Ca test is lengthy test durations which can be many months for materials with very low WVTRs. A less commonly used method for determining the WVTR is by means of HTO permeation, however only a few studies have used this technique [13-15] as it requires access to radioactive HTO.

MOCON instruments have been used to determine the WVTRs of both polymers [7, 16] and barrier films [17-20]. These instruments use either a modulated infrared sensor (Permatran model with detection limit of 5 x 10^{-3} g.m^{-2}/day [17]) or a coulombmetric sensor (Aquatran with detection limit of 5 x 10^{-4} g.m^{-2}/day [18] and Aquatran Model 2 with detection limit of 5 x 10^{-5} g.m^{-2}/day [12]) to detect water vapour transmission through a flat substrate. Commercial permeation instruments such as the MOCON type or similar, are not capable of measuring the low WVTRs required for organic electronic applications.

The Ca test evaluates the WVTR of a film by in situ monitoring the oxidation of Ca films [21, 22]. The electronic Ca test (e-Ca) measures the decrease in conductivity that occurs due to Ca corrosion resulting from the diffusion of moisture and oxygen through the barrier film [23]. Optical methods have also been used to determine the WVTR [24-26]. This method records images of the deposited Ca pads at regular intervals to monitor the rate of corrosion of the initially highly reflective Ca to almost transparent Ca oxide [24]. WVTR rates as low as 3 x 10^{-7} g.m^{-2}/day have been detected using the Ca test [9]. The accuracy of the Ca test relies on the assumption that Ca oxidation is linear with water exposure. However, previous studies have shown this not to be the case [27, 28]. Ca oxidation kinetics have been investigated using quartz crystal microbalance where they were shown to be non-linear. When the mass gain was plotted against time, three distinct regions were identified; lag region, oxidation region and sensor lifetime. Different WVTR values can be calculated, depending on which region the data was taken from. The non-linearity of Ca oxidation raises doubts about the accuracy of the WVTR determined by the Ca test though it has been proposed that reliable WVTRs can be obtained at short lag times [29].

In the few studies that have used HTO to determine the WVTR of barrier films, the film separates the top and bottom chambers of a stainless steel vessel. HTO, which is placed in the bottom chamber, permeates through the film and is absorbed by hydroscopic lithium chloride (LiCl) in the top chamber. The amount of HTO absorbed by the LiCl is then measured by liquid scintillation counting from which the WVTR can be calculated [14, 15]. The diffusion of HTO through a barrier film has also been determined with an inbuilt β-ray detector. In this method, the HTO that permeated through the membrane was transported by a carrier gas to the detector for quantification [13, 30, 31]. The detection limit of WVTR for HTO permeation is reported to be below 1 x 10^{-6} g.m^{-2}/day [9].

Few studies have used more than one technique to measure the WVTR of the same film. Seo and co-workers [32] used MOCON to determine the WVTR of the PET substrate and the more sensitive Ca-test to measure the WVTR of barrier films. The Catest has also been used when the WVTR of an alumina barrier film determined by MOCON was lower than the detection limit [16]. A combination of MOCON and the Ca test has also been used by Carcia et al. [18], however only barrier layers with thicknesses less than 7.5 nm could be analysed by MOCON as thicker layers were below the MOCON detection limit. Although both techniques were used, direct comparisons between the two techniques were restricted by the MOCON detection limit. Only one study has directly compared the WVTRs measured using HTO permeation and the optical Ca test. Both WVTRs were determined under ambient conditions for a 10 nm alumina film and resulted in similar values of 2 x 10^{-3} g.m^{-2}/day with HTO permeation and 1.5 x 10^{-3} g.m^{-2}/day with the optical Ca test [15]. In a recent multi-laboratory study, WVTRs of a multilayer barrier film measured using the calcium test were compared with those obtained from cavity ringdown spectroscopy, tuneable diode laser absorption spectroscopy, isotope marking mass spectrometry and MOCON [33]. In this study, the WVTR was determined under

two conditions (20 °C, 50% relative humidity (RH) and 38 °C, 90% RH), though not every technique could determine the WVTR at each condition. At 20 °C, 50% RH, the WVTR was below the detection limit for MOCON. Reasonable agreement in WVTRs was reported across the range of techniques, however outliers were observed which were attributed to film defects.

In the present study, we have used the e-Ca, MOCON and HTO permeation techniques to investigate the WVTRs of two polymer substrates and two commercially sourced barrier films. These materials were chosen for study as they possess a variety of the characteristics featured in barrier film research. A 75 μm PET substrate was chosen as it is a commonly used substrate for organic electronics due to its low cost. The 127 μm thick MOCON reference material was selected as it was accompanied by a reference sheet which specifies its WVTRs, as determined by MOCON, at several of relative humidities. The two barrier films were chosen as typical examples of commercially available products, with one possessing a single barrier film and the other having a multilayer structure. Of particular interest in the present study is an assessment of the HTO based method relative to the other two techniques, which are more frequently used to assess barrier performance. Direct comparison of the WVTRs obtained from the selected methods has been made where possible. This analysis highlighted some of the strengths and limitations of the various methods chosen for the present study. In addition, it clearly showed the variability in WVTRs of samples selected from the same batch of substrate material or barrier film. The aim of this study is to demonstrate that there are many factors to consider in WVTR measurement and due to this, caution needs to be taken when comparing barrier films whose WVTRs have measured by different techniques.

2. Materials and Methods

2.1. Materials

Two polymer substrates were selected for water permeation tests. These comprised 75 μm thick polyethylene terephthalate (PET) (Multaplex EMCL) and the MOCON 127 μm thick PET reference material (MOCON, Inc.). Two commercially available films based on PET substrates with additional barrier layers, designated A (50 μm) and B (200 μm), were obtained from their manufacturers. Liquid scintillation cocktail (Ultima Gold™ uLLT) and tritiated water (37 MBq/mL) were purchased from Perkin-Elmer. Lithium chloride (99%) was purchased from Sigma Aldrich.

2.2. HTO permeation

The HTO permeation rig is shown in Fig. 1. Determination of the WVTR by HTO permeation assumes that the tritium atoms diffuse as molecular HTO [14] and that the permeation rates of water and HTO are the same. A 10 MBq/mL HTO working solution was made by dilution of the 37 MBq/mL HTO stock. For the polymer substrates and barrier film A, 5 μL of 10 MBq/mL HTO working solution and 45 μL of Milli-Q water were combined in the hollow of the stainless steel base resulting in a total droplet activity of 50 kBq. For barrier film B, 50 μL of 10 MBq/mL HTO was pipetted directly into the hollow, resulting in a total droplet activity of 500 kBq. A circular test piece with a diameter of 150 mm was placed over the base followed by a Teflon seal, resulting in available film area of 0.009 m^2. A vial containing 3 g of LiCl was inserted into the vial holder of the glass vessel. The glass vessel was then bolted onto the stainless steel base. A RH of ~95% was measured in the lower part of the chamber during each experiment with an average ambient temperature of 25 °C. After the desired test duration of 1 to 3 days for polymer substrates and 7 days for barrier films, the LiCl vial was removed. In

addition, the inside of the glass vessel and the top surface of the substrate were each rinsed with 50 mL of Milli-Q water to capture any HTO which may have permeated through the film but not absorbed by the LiCl. To determine the total mass of HTO passing through the substrate, the three separate samples were analysed using a liquid scintillation counter: glass rinse, substrate rinse and the LiCl from the vessel. 8 mL of Milli-Q was added to the vial containing LiCl. In two other vials, 3 g of LiCl was added to 8 mL aliquots of the glass rinse and substrate rinse solutions. All three vials were then shaken vigorously and left overnight to ensure the LiCl was completely dissolved. 12 mL of scintillation cocktail was then added to each, followed once again by vigorous shaking and left overnight. Samples were then placed in the liquid scintillation counter and the counts per minute (CPM) for each was determined. The beta decay energy of tritium is transferred to the phosphors in the liquid scintillation cocktail which in turn emit photons in the range of 0 – 18.6 keV that are detected by the liquid scintillation counter. The CPM of each sample was measured at least 20 times using a Packard Tri-Carb 2900 TR liquid scintillation analyser and the results averaged. The counts per minute were then used to calculate the WVTR using a linear regression equation determined from a calibration plot for total activities of 0.005 to 50 kBq. The WVTR ($g.m^{-2}$/day) was then calculated from the following equation:

$$WVTR = \frac{Dv(CPM + c)}{1000mADiAc}$$

Where Dv = droplet volume (µL), CPM = counts per minute, c = y-axis intercept of linear regression, m = slope of linear regression, A = surface area of film (m^2), D = experiment duration (days) and iAc = Initial total activity of droplet (KBq).

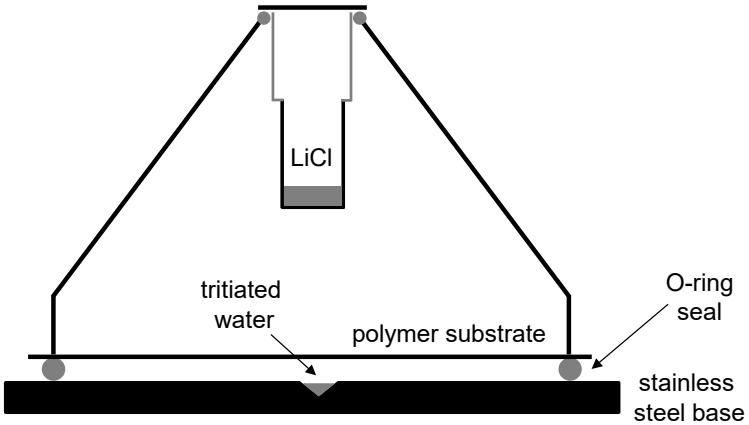


Fig. 1 Schematic diagram of HTO permeation rig

2.3. MOCON permeation testing

The MOCON Permatran instrument was used to measure water permeation where the test cell is divided into two chambers by the film under investigation (Fig. 2). Humidified nitrogen enters the outer part of the cell and exits via an exhaust port. Pre-dried, moisture-free nitrogen is continuously admitted to the inner half of the test cell to transfer the water vapour that permeates through the film to the sensor. For the MOCON reference film, the WVTR was measured at 23 °C/50 % RH and 23 °C/100 % RH, to enable comparison to HTO permeation. For the 75 μm PET substrate, the WVTR was measured at 23 °C/50 % RH. The WVTRs of the two barrier films were determined under three conditions: 23 °C/50 % RH, 38 °C/50% RH and 38 °C/85% RH. The substrate was placed in the instrument and the conditions were initially set at 23 °C/50% RH. The humidified nitrogen was allowed to flow until the WVTR reached equilibrium, which was typically around 40 hours, for both uncoated and coated substrates. The substrate was kept in the instrument and the conditions were then changed to 38 °C/50% RH and then 38° C/85% RH. In each case, conditions were maintained until WVTR equilibrium was achieved. A constant humidified nitrogen flow rate of 10 mL/min was used in all experiments.

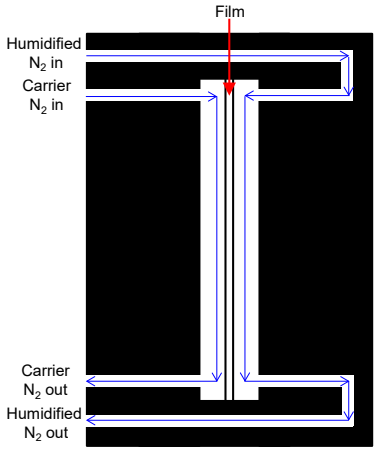


Fig. 2 Schematic diagram of MOCON permeation testing instrument

2.4. Calcium testing

The electrical calcium (e-Ca) testing system used in the present study is shown in Fig. 3. This system is based on the system developed at the U.S. Department of Energy's National Renewable Energy Laboratory (NREL), Golden, Colorado, USA, which has been previously described [34]. The e-Ca system consists of a Ca sensor on a test card, which is separated from the barrier film to be tested by a metal spacer block. As water vapour diffuses through the barrier film into the cavity created by the spacer it reacts with the Ca sensor, converting the Ca to $Ca(OH)_2$. This reaction is monitored as an increase in resistivity as the Ca is oxidised. From the stoichiometry of the reaction and the dimensions of the Ca sensor, spacer, and the area of exposed barrier film, the measured resistivity of the Ca sensor (once a steady vapour transmission rate has been reached) can be converted into a measure of WVTR by the following formula [1]:

$$WVTR = n\delta\rho_{Ca}\left(\frac{l_{eff}}{w}\right)\left(\frac{A_{Ca}}{A_B}\right)\left(\frac{M_w}{M_{Ca}}\right)\left[\frac{d\left({}^{1}/_{R}\right)}{dt}\right]$$

where

$A_B = barrier\ aperture$

228 $A_{Ca} = total\ Ca\ sensor\ area$

229 $\delta = density\ of\ Ca\ \left(1.55 \frac{g}{cm^3}\right)$

230 $l_{eff} = sensor\ effective\ length$

231 $M_{Ca} = atomic\ mass\ of\ calcium$

232 $M_w = molecular\ weight\ of\ water$

233 $n = 2\ (Reaction\ ratio\ of\ calcium\ to\ permeate)$

234 $\rho_{Ca} = thin\ film\ calcium\ volume\ resistivity$

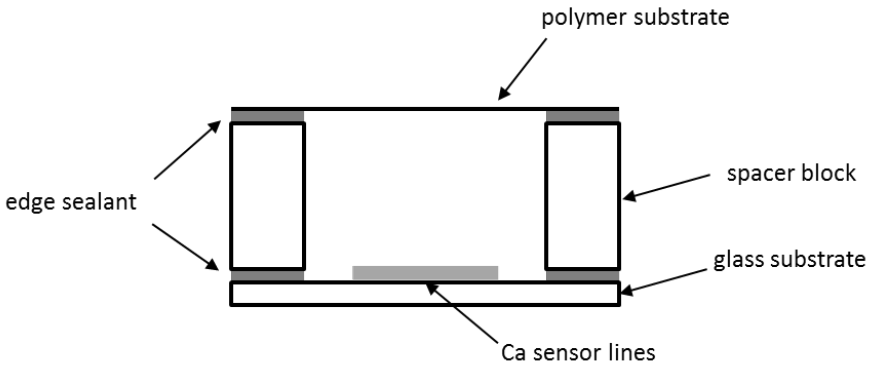
235 $R = calcium\ resistance$

236 $w = line\ width$

237 $WVTR\ = water\ Vapour\ Transmission\ Rate$

238

239 Test durations of the uncoated polymer substrates were less than 2 days. Barrier films A and B
240 had test periods of 1 and 9 months respectively. Ca test card fabrication and assembly was
241 performed in a dry nitrogen atmosphere glove box (<1 ppm water and <1 ppm oxygen). Ca test
242 cards are fabricated by thermally evaporating, through a patterned shadow mask, a 100 nm
243 gold layer (with 20 nm titanium under layer) onto a glass substrate for the electrical
244 connections, followed by a 1000 nm calcium layer for the sensor lines. The Ca test card, metal
245 spacer block, and polymer barrier film were then assembled using a commercial edge seal tape
246 (ADCO HelioSeal PVS 101). Testing was performed with the samples in an environmental
247 chamber set to a temperature of 25 ± 2 °C and RH between 40-55%. A Keithley 2400
248 Sourcemeter together with a custom switching system and software were used to monitor the
249 change in resistance of the Ca sensor lines over time. The WVTR is then determined from the
250 above equation. The WVTR was calculated once the system reached steady state conditions.
251



252

253

254 **Fig. 3** Schematic diagram of calcium testing setup

255

3. Results and Discussion

3.1. WVTR of MOCON and PET substrates

The WVTR of the MOCON reference film was investigated using the e-Ca test, MOCON and HTO permeation. The WVTR values determined at room temperature (23-25 °C) are listed in Table 1. Very similar WVTR values were obtained using the e-Ca test and MOCON when evaluated at similar RH. Increasing the RH from 50 to 100 %, on the same piece of film, increased the WVTR measured by the MOCON instrument from 1.22 to 2.26 $g.m^{-2}$/day, similar to the trend previously observed for polyethylene napthalate films [4]. The MOCON reference film is accompanied by a list of reference WVTRs for temperatures of 5 – 50 °C at 100% RH. At 23 °C, the film has a listed WVTR of 2.1 $g.m^{-2}$/day which is close to the value of 2.26 $g.m^{-2}$/day measured by the MOCON instrument. For RH of 95-100%, slight differences were observed when the WVTR was measured using MOCON in comparison to HTO permeation. The WVTR obtained at a RH of 95% with HTO permeation is lower than that measured with the MOCON instrument at 23 °C/100% RH. This difference will be discussed below.

Table 1 WVTRs of 127 μm MOCON reference film

Technique	Test period (days)	Temperature (°C)	Relative humidity (%)	WVTR ($g.m^{-2}$/day)
HTO	1	25	95	1.27
e-Ca	N/A	25	40-55	1.28
MOCON	N/A	23	50	1.22
		23	100	2.26

HTO permeation of the 75 μm thick PET film was undertaken for test durations of 1, 2 and 3 days to monitor the transmission kinetics. As shown in Table 2, WVTR values of approximately 1.6 $g.m^{-2}$/day were observed for all test durations. These results showed that water permeation was linear for test durations up to 3 days and that 1 day is sufficient for the system to reach steady state conditions and thus allowing an accurate WVTR of this material to be determined. Measurements were undertaken of two different PET pieces using the e-Ca test which yielded WVTRs of 1.20 and 1.95 $g.m^{-2}$/day. A similar WVTR of 1.88 $g.m^{-2}$/day was obtained by the MOCON instrument. All three techniques yield comparable values in the range 1-2 $g.m^{-2}$/day. WVTRs of PET in the range from 3-17 $g.m^{-2}$/day have been reported in the literature [32, 35, 36]. This wide range in values is mostly due to variations in RH, temperature and substrate thickness. In particular, higher WVTRs have been shown to result from increases in temperature and RH [37, 38]. The experimental conditions therefore need to be taken into account when comparing the WVTR of the same polymers and barrier films. Previously it has been shown that when the measurement conditions are identical between the Ca-test and HTO permeation, very similar WVTRs are produced [15]. All three techniques used herein yielded similar WVTRs at room temperature (23 – 25 °C). However, the e-Ca and MOCON tests were carried out at similar RHs (40-55%) while HTO permeation was undertaken at 95% RH. For materials that obey Fick's law, it is generally accepted that permeation is linear with water concentration [38]. Therefore, a higher WVTR would be expected for the HTO measurement since the mass of water vapour per unit volume of air at a RH of 95% will be almost double that at the 40-55% conditions used for the e-Ca and MOCON analyses. The absence of a significant differences between the three techniques for both the MOCON reference film and the 75 μm PET substrate suggests that the HTO method may be underestimating the WVTR. Such behaviour suggests that the assumption that the rates of H_2O and HTO permeation are the same, may not be valid. Unfortunately, the validity of the equal rate assumption, on which the

301 HTO method is based, remains unresolved at the present time due to an apparent lack of
302 reported studies on the relative permeabilities of the two species in polymeric materials. While
303 higher WVTRs might be expected for the HTO measurements in Tables 1 and 2, it is worth
304 noting that variability in values obtained with the same or similar techniques is not uncommon
305 in moisture permeation studies. For instance, in the multi-laboratory study of a multilayer
306 barrier film carried out by Nisato et al. [33], the results at 20 °C/50% RH varied by a factor of
307 2-3. It is also worth noting that HTO permeation is not affected by residual water that may be
308 trapped within the substrate or barrier layers. Water from this source, has previously shown to
309 influence the measured WVTR in H_2O based techniques [39]. Although for both the 75 μm
310 PET and 127 μm MOCON reference films HTO permeation produced a lower than expected
311 WVTR based on RH, the differences are only slight thus suggesting that these three techniques
312 are comparable under these conditions.
313
314 **Table 2** WVTRs of 75 μm PET film

Technique	Test period (days)	Temperature (°C)	Relative humidity (%)	WVTR ($g.m^{-2}$/day)
HTO	1	25	95	1.56
	2	25	95	1.59
	3	25	95	1.60
e-Ca	N/A	25	40-55	1.20
	N/A	25	40-55	1.95
MOCON	N/A	23	50	1.88

315
316

3.2. WVTR of barrier films

WVTRs were determined for the two barrier films designated A and B. Film A was 50 μm thick and comprised of an approximately 100 nm thick single metal oxide barrier layer deposited on PET. For all three techniques, the WVTRs were measured with the barrier film surface facing the high humidity environment. At room temperature, the WVTR determined by the three techniques ranged from 2.0 x 10^{-1} g.m^{-2}/day for the e-Ca test to 4.5 x 10^{-2} g.m^{-2}/day for HTO permeation, as shown in Table 3. A decrease in the WVTR of approximately one to two orders of magnitude compared with uncoated PET demonstrates the effectiveness of a metal oxide layer as a barrier film. Similar WVTR values were observed for the MOCON (0.90 x 10^{-1} g.m^{-2}/day) and the e-Ca test (2.0 x 10^{-1} g.m^{-2}/day). As these measurements were undertaken under similar conditions, these values once again suggest reasonable agreement between the two techniques. As found previously, the HTO technique yielded a lower WVTR value (4.5 x 10^{-2} g.m^{-2}/day) than either the MOCON or e-Ca test despite being carried out at a higher humidity. The origin of such behaviour is at this stage unknown, but possible causes could be unequal HTO/H_2O permeation or that residual water does not influence HTO measurements, as previously mentioned. Very little information is available on the transmission rates of HTO compared to H_2O through polymeric substrates and barrier films. Previous experiments have been conducted to gain insight if tritium diffuses through a polymer substrate and barrier film as molecular HTO or atomic tritium [14], but did not compare HTO to H_2O. It would be advantageous if the rates of HTO and H_2O diffusion had been experimentally determined as this would shed light on the validity of the assumption that the two rates are similar. In the absence of such confirmation, an explanation of the lower WVTRs obtained with HTO permeation remains in abeyance.

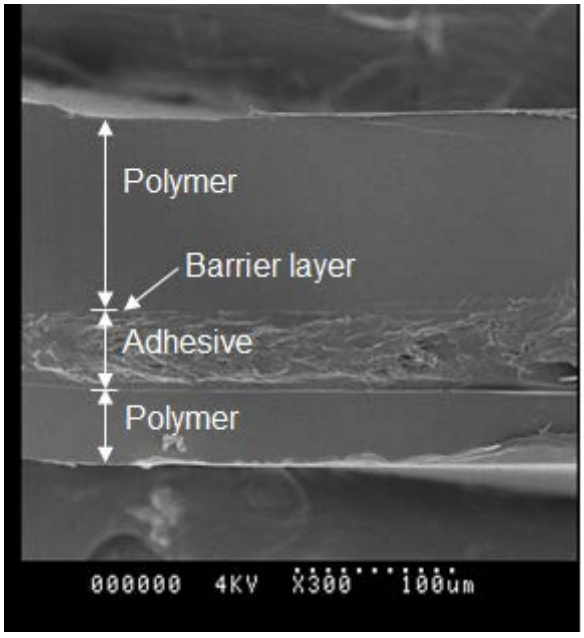
To demonstrate the effect of increasing temperature and/or RH on WVTR, barrier film A was also measured using MOCON at 38 °C/50% RH and 38 °C/85% RH for 3 separate pieces of film. As expected, increases in WVTR were observed by increasing the temperature and RH. The temperature and RH at which the WVTR is measured, has shown to have a significant effect on the calculated values. The WVTR increases as the temperature increases due to the kinetic theory of gas. As the temperature is increased, the velocity of the water vapour molecules also increases thus resulting in greater diffusion [40]. The WVTR also increases as the RH increases at a constant temperature, as the mass of water per unit of volume of air increases. The greater mass of water vapour on one side of the film has a greater driving force on the film, thus accelerating water permeation. It has previously been shown that increasing the RH and temperature increased the WVTR of polypropylene and polyvinyl alcohol films [38]. To investigate sample to sample differences, the WVTRs of three pieces of barrier film A were measured using MOCON. Two of the three pieces had WVTRs that were significantly higher than the first sample tested, as shown in Table 3. The observed differences were attributed to defects in the barrier layer in the WVTR, which were not detected by the visual inspection carried out on all samples prior to testing. Such defects, formed during the handling or processing of barrier films, have previously shown to have a significant effect on permeation performance [39].

Table 3 WVTR of 50 μm thick barrier film A

Technique	Test period (days)	Piece number	Temperature (°C)	Relative humidity (%)	WVTR ($g.m^{-2}/day$)
HTO	7	N/A	25	95	4.5×10^{-2}
e-Ca	N/A	N/A	25	40-55	2.0×10^{-1}
MOCON	N/A	1	23	50	9.04×10^{-2}
			38	50	4.78×10^{-1}
			38	85	9.66×10^{-1}
		2	23	50	4.96×10^{-1}
			38	50	1.31
			38	85	2.82
		3	23	50	4.95×10^{-1}
			38	50	1.52
			38	85	3.08

Barrier film B was a multilayer film on PET with a total thickness of 200 μm, as shown in Fig. 4. For all three techniques, the WVTR measurements were undertaken with the more hydrophobic side of film facing the high humidity environment. The WVTRs of 5 different pieces of the barrier film were prepared for HTO permeation tests and 9 different pieces for MOCON analysis. Only a single measurement was made using the e-Ca test due to the long equilibration time required. The results of all measurements are shown in Table 4. The WVTRs obtained from HTO permeation ranged 8.4×10^{-3} – 5.5×10^{-5} $g.m^{-2}/day$ across the 5 different pieces. These values are significantly lower than for barrier film A which demonstrates the effectiveness of multilayer structures over a single barrier layer in reducing the WVTR, which is in agreement with previous studies [32, 41-43]. In addition, the greater thickness of barrier film B (200 μm) compared with barrier film A (50 μm) is also likely to contribute to its lower WVTR. The single measurement with the e-Ca method yielded a WVTR of 3.6×10^{-5} $g.m^{-2}/day$, which is comparable with the lowest value obtained from HTO permeation. However, averaging the WVTRs determined via HTO permeation results an average WVTR of 2.58 x

383 10^{-3} g.m^{-2}/day, which is two orders of magnitude greater than the WVTR determined by the
384 single Ca test. A previous study observed lower WVTRs determined by the Ca test in
385 comparison to HTO permeation [14]. Calculating the average WVTR however, does not taken
386 into account any differences in the WVTR due to defects in different pieces of the film but not
387 others. It is therefore difficult to ascertain if the difference in the WVTRs determined by HTO
388 permeation and Ca test are due to instrument or experimental differences. All the MOCON
389 measurements on film B at 23 °C/50% RH were found to be below the Permatran detection
390 limit of 5 x 10^{-3} g.m^{-2}/day. This limitation prevents a direct comparison with the HTO and e-
391 Ca methods, though there is consistency in the fact that the WVTRs measured with HTO
392 permeation and the e-Ca test all fall below this MOCON detection limit.
393



394

395 **Fig. 4** Cross sectional SEM of barrier film B

396

397 In order to determine the effect of temperature and RH on the WVTR of barrier film B, these
398 parameters were increased for two pieces to 38 °C/50% RH and then 38 °C/85% RH. While
399 the WVTRs for one piece was both below the aforementioned MOCON detection limit at 38

400 °C, the other piece returned significantly higher values of 1.94 x 10^{-2} and 3.33 x 10^{-2} g.m^{-2}/day
401 for 50% and 80% RH respectively. This significant increase prompted further measurements
402 at 38 °C/85% RH on additional pieces of barrier film B. These values are listed in Table 4 and
403 ranged from < 5 x 10^{-3} - 1.02 x 10^{-1} g.m^{-2}/day. A variation of this magnitude, which was also
404 present to a lesser extent in the HTO measurements at 25 °C, highlights the influence of defects
405 in determining the permeability of barrier materials even in the case of samples from the same
406 sheet of barrier film. This in turn implies significant inhomogeneity in the barrier layers due to
407 defects that were introduced during manufacture or subsequent handling. A similar finding has
408 been reported by Fahlteich et al. [39] who found the presence of such defects in several
409 multilayer barrier systems and studied their effect under different test conditions.
410

411 **Table 4** WVTR of 200 µm thick barrier film B

Technique	Test period (days)	Piece number	Temperature (°C)	Relative humidity (%)	WVTR ($g.m^{-2}/day$)
HTO	7	1	25	95	8.4×10^{-3}
		2	25	95	3.5×10^{-3}
		3	25	95	4.5×10^{-4}
		4	25	95	2.2×10^{-4}
		5	25	95	5.5×10^{-5}
e-Ca	N/A		25	40-55	3.6×10^{-5}
MOCON	N/A	1	23	50	$< 5 \times 10^{-3}$
			38	50	$< 5 \times 10^{-3}$
			38	85	$< 5 \times 10^{-3}$
		2	23	50	$< 5 \times 10^{-3}$
			38	50	1.94×10^{-2}
			38	85	3.33×10^{-2}
		3	38	85	1.02×10^{-1}
		4	38	85	1.19×10^{-2}
		5	38	85	8.65×10^{-2}
		6	38	85	8.28×10^{-2}
		7	38	85	4.26×10^{-2}
		8	38	85	4.76×10^{-3}
		9	38	85	$< 5 \times 10^{-3}$

412

413

414 # 4. Conclusions

415

416 The WVTRs of polymers and barrier films have been determined using HTO permeation,
417 MOCON and the e-Ca test. A comparison of the three techniques was made using two PET
418 substrates and two commercial barrier films in order to assess their suitability under different
419 conditions. For both the 75 µm PET and MOCON reference films, similar WVTRs were

420 measured with all three techniques. This similarity occurred even though a higher humidity
421 was used in the HTO tests. Therefore, it is possible that HTO permeation may underestimate
422 the WVTR However, previous work by Nisato et al using a number of test methods found a
423 factor of ~ 3 difference in the WVTRs measured under the same conditions. Thus, in this
424 context, the lack of a difference due to the higher RH is unlikely to be significant. It is also
425 worth noting that the WVTR determined by HTO permeation cannot be impacted by residual
426 water in the film unlike the Ca test and MOCON. For the two barrier films, a comparison
427 between the three techniques proved more difficult due to variations in the defect densities
428 present in different test samples. The results for barrier film A at 23-25 °C ranged from 4.96 x
429 10^{-1} to 4.5 x 10^{-2} g.m^{-2}/day with a similar spread observed at 38 °C. The problem of sample
430 variability was also encountered with barrier film B. In addition, room temperature WVTRs
431 could not be obtained with the MOCON Permatran due to its detection limit. HTO permeation
432 at 25 °C yielded values that varied by two orders of magnitude with only the lowest recorded
433 of these agreeing closely with the single e-Ca measurement. MOCON was the only technique
434 used to measure samples at the higher temperature of 38 °C. Once again, considerable sample
435 to sample variability was observed with WVTRs ranging from 1.02 x 10^{-2} to < 5 x 10^{-3} g.m^{-}
436 ^{2}/day. The results obtained for this barrier film showed that only the HTO and e-Ca methods
437 are capable of determining the performance of barrier materials with WVTRs below 1 x 10^{-4}
438 g.m^{-2}/day.
439
440 The biggest challenges when comparing WVTR are the measurement conditions and the
441 presence of film defects. The WVTR is significantly affected by temperature and RH and
442 therefore these conditions need to be closely matched to accurately compare the WVTRs of
443 two samples. However, a previous study by Nisato et al. has shown that even when the material
444 and conditions are identical, different WVTRs were observed, thus suggesting inherent

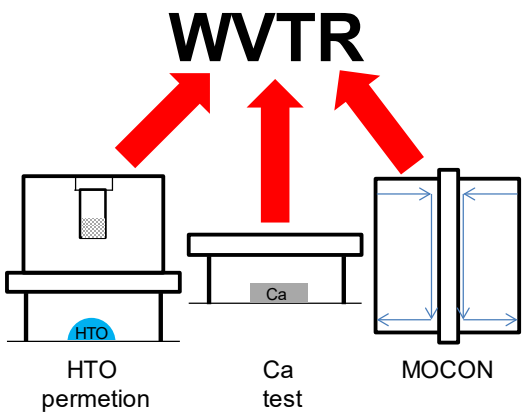
instrument to instrument variabilities. It appears to be necessary to conduct multiple WVTR measurements of different pieces of the barrier film, to ascertain if any differences in the WVTR are due to film defects or the actual barrier properties. Each measurement technique examined in this study has shown to have its own advantages and disadvantages for determining WVTR. MOCON can determine WVTR at a broad range of temperatures and RH due to having precise control over both of these parameters but the detection limit of MOCON is however relatively high, at 5×10^{-3} to 5×10^{-5} $g.m^{-2}$/day, depending on the model. In cases where barrier materials contain defects and hence, do not meet specification, the WVTRs can be evaluated by means of the MOCON method as shown in the present study. For this reason, the MOCON instruments offer a viable and quicker means of initially assessing the barrier properties of a material followed by one of the other techniques when the WVTR is found to fall below the MOCON detection limit. HTO permeation is very sensitive, with a detection limit as low as 10^{-6} $g.m^{-2}$/day, but the RH cannot be easily varied in this static system. The e-Ca test can also be used to determine WVTR over a range of temperatures and RH if placed under a controlled atmosphere. The duration of the e-Ca test can also be considerably longer than either of the other two techniques due to the potentially long lag times, which are dependent on the WVTR of the film. The present study demonstrates that the strengths and limitations of available WVTR measurement techniques need to be considered in order to determine which is most appropriate for the barrier film under investigation.

Acknowledgements

The Cooperative Research Centre for Polymers (CRC-P) is gratefully acknowledged for their funding (Application No: 20110054). The work was also performed in part at the Materials node of the Australian National Fabrication Facility, a company established under the National

Collaborative Research Infrastructure Strategy, to provide nano and microfabrication facilities for Australia's researchers. Dr. Jaleh Mansouri is acknowledged for providing the SEM image.

Graphical Abstract



Highlights

- Ca test, MOCON and HTO permeation measured WVTR of 4 films
- Similar WVTR were observed for two polymer substrates with all 3 techniques
- Film inhomogeneities resulted in different WVTR for two barrier films
- Different experimental conditions make direct comparisons challenging

References

[1] I. D. Rosca, J.-M. Vergnaud, Approach for a testing system to evaluate food safety with polymer packages, Polym. Test. 25 (2006) 532-543.

[2] U. Moosheimer, C. Bichler, Plasma pretreatment of polymer films as a key issue for high barrier food packagings, Surf. Coat. Tech. 116–119 (1999) 812-819.

[3] J. Ahmad, K. Bazaka, L. J. Anderson, R. D. White, M. V. Jacob, Materials and methods for encapsulation of OPV: A review, Renew. Sust. Energ. Rev. 27 (2013) 104-117.

[4] J. A. Bertrand, D. J. Higgs, M. J. Young, S. M. George, H2O Vapor Transmission Rate through Polyethylene Naphthalate Polymer Using the Electrical Ca Test, J. Phys. Chem. A 117 (2013) 12026-12034.

[5] S.-H. K. Park, J. Oh, C.-S. Hwang, J.-I. Lee, Y. S. Yang, H. Y. Chu Ultrathin Film Encapsulation of an OLED by ALD, Electrochem. Solid St. 8 (2005) H21-H23.

[6] M. Vähä-Nissi, P. Sundberg, E. Kauppi, T. Hirvikorpi, J. Sievänen, A. Sood, M. Karppinen, A. Harlin, Barrier properties of Al_2O_3 and alucone coatings and nanolaminates on flexible biopolymer films, Thin Solid Films 520 (2012) 6780-6785.

[7] T. Ahmadzada, D. R. McKenzie, N. L. James, Y. Yin, Q. Li, Atomic layer deposition of Al_2O_3 and Al_2O_3/TiO_2 barrier coatings to reduce the water vapour permeability of polyetheretherketone, Thin Solid Films 591, Part A (2015) 131-136.

[8] R. Paetzold, A. Winnacker, D. Henseler, V. Cesari, K. Heuser, Permeation rate measurements by electrical analysis of calcium corrosion, Rev. Sci. Instrum. 74 (2003) 5147-5150.

[9] J.-S. Park, H. Chae, H. K. Chung, S. I. Lee, Thin film encapsulation for flexible AM-OLED: a review, Semicond. Sci. Tech. 26 (2011) 034001.

[10] H. Klumbies, P. Schmidt, M. Hähnel, A. Singh, U. Schroeder, C. Richter, T. Mikolajick, C. Hoßbach, M. Albert, J. W. Bartha, K. Leo, L. Müller-Meskamp, Thickness dependent barrier performance of permeation barriers made from atomic layer deposited alumina for organic devices, Org. Electron. 17 (2015) 138-143.

[11] G. Dennler, C. Lungenschmied, H. Neugebauer, N. S. Sariciftci, A. Labouret, Flexible, conjugated polymer-fullerene-based bulk-heterojunction solar cells: Basics, encapsulation, and integration, J. Mater. Res. 20 (2005) 3224-3233.

[12] J. G. Lee, H. G. Kim, S. S. Kim, Defect-sealing of Al_2O_3/ZrO_2 multilayer for barrier coating by plasma-enhanced atomic layer deposition process, Thin Solid Films 577 (2015) 143-148.

[13] B. I. Choi, H. S. Nham, S. B. Woo, J. C. Kim, Ultralow water vapor permeation measurement using tritium for OLED displays, J. Korean Phys. Soc. 53 (2008) 2179-2184.

[14] A. A. Dameron, S. D. Davidson, B. B. Burton, P. F. Carcia, R. S. McLean, S. M. George, Gas Diffusion Barriers on Polymers Using Multilayers Fabricated by Al_2O_3 and Rapid SiO_2 Atomic Layer Deposition, J. Phys. Chem. C 112 (2008) 4573-4580.

[15] M. D. Groner, S. M. George, R. S. McLean, P. F. Carcia, Gas diffusion barriers on polymers using Al_2O_3 atomic layer deposition, Appl. Phys. Lett. 88 (2006) 051907-051903.

[16] P. S. Maydannik, T. O. Kääriäinen, K. Lahtinen, D. C. Cameron, M. Söderlund, P. Soininen, P. Johansson, J. Kuusipalo, L. Moro, X. Zeng, Roll-to-roll atomic layer deposition process for flexible electronics encapsulation applications, J. Vac. Sci. Technol. A 32 (2014) 051603.

[17] T.-S. Kwon, D.-Y. Moon, Y.-K. Moon, W.-S. Kim, J.-W. Park, Al_2O_3/TiO_2 Multilayer Passivation Layers Grown at Low Temperature for Flexible Organic Devices, J. Nanosci. Nanotechno. 12 (2012) 3696-3700.

[18] P. F. Carcia, R. S. McLean, M. H. Reilly, Permeation measurements and modeling of highly defective Al_2O_3 thin films grown by atomic layer deposition on polymers, Appl. Phys. Lett. 97 (2010) 221901-221903.

[19] H. G. Kim, S. S. Kim, Aluminum oxide barrier coating on polyethersulfone substrate by atomic layer deposition for barrier property enhancement, Thin Solid Films 520 (2011) 481-485.
[20] K. Lahtinen, P. Maydannik, P. Johansson, T. Kääriäinen, D. C. Cameron, J. Kuusipalo, Utilisation of continuous atomic layer deposition process for barrier enhancement of extrusion-coated paper, Surf. Coat. Tech. 205 (2011) 3916-3922.
[21] S. Schubert, H. Klumbies, L. Muller-Meskamp, K. Leo, Electrical calcium test for moisture barrier evaluation for organic devices, Rev. Sci. Instrum. 82 (2011) 094101-094108.
[22] J. H. Choi, Y. M. Kim, Y. W. Park, J. W. Huh, B. K. Ju, I. S. Kim, H. N. Hwang, Evaluation of gas permeation barrier properties using electrical measurements of calcium degradation, Rev. Sci. Instrum. 78 (2007) 064701-064705.
[23] J. Meyer, P. Görrn, F. Bertram, S. Hamwi, T. Winkler, H.-H. Johannes, T. Weimann, P. Hinze, T. Riedl, W. Kowalsky, Al_2O_3/ZrO_2 Nanolaminates as Ultrahigh Gas-Diffusion Barriers—A Strategy for Reliable Encapsulation of Organic Electronics, Adv. Mater. 21 (2009) 1845-1849.
[24] G. Nisato, M. Kuilder, P. Bouten, L. Moro, O. Philips, N. Rutherford, P-88: Thin Film Encapsulation for OLEDs: Evaluation of Multi-layer Barriers using the Ca Test, SID Symposium Digest of Technical Papers 34 (2003) 550-553.
[25] P. F. Carcia, R. S. McLean, M. H. Reilly, M. D. Groner, S. M. George, Ca test of Al_2O_3 gas diffusion barriers grown by atomic layer deposition on polymers, Appl. Phys. Lett. 89 (2006) 031915-031913.
[26] J. Greener, K. C. Ng, K. M. Vaeth, T. M. Smith, Moisture permeability through multilayered barrier films as applied to flexible OLED display, J. Appl. Polym. Sci. 106 (2007) 3534-3542.
[27] S. J. Gregg, W. B. Jepson, 186. The oxidation of calcium in moist oxygen, J. Chem. Soc. (Resumed) (1961) 884-888.
[28] D. A. Nissen, The low-temperature oxidation of calcium by water vapor, Oxid. Met. 11 (1977) 241-261.
[29] D. J. Higgs, M. J. Young, J. A. Bertrand, S. M. George, Oxidation kinetics of calcium films by water vapor and their effect on water vapor transmission rate masurements, J. Phys. Chem. C 118 (2014) 29322-29332.
[30] R. S. Bujas, R. Dunkel, Method and apparatus for measuring ultralow water permeation, US 6804989 B2, 2004.
[31] R. Dunkel, R. Bujas, A. Klein, V. Horndt, A new method for measuring ultra-low water-vapor permeation for OLED displays, J. Soc. Inf. Display 13 (2005) 569-573.
[32] S.-W. Seo, E. Jung, C. Lim, H. Chae, S. M. Cho, Water permeation through organic–inorganic multilayer thin films, Thin Solid Films 520 (2012) 6690-6694.
[33] G. Nisato, H. Klumbies, J. Fahlteich, L. Muller-Meskamp, P. van de Weijer, P. Bouten, C. Boeffel, D. Leunberger, W. Graehlert, S. Edge, S. Cros, P. Brewer, E. Kucukpinar, J. de Girolamo, P. Srinivasan, Experimental comparison of high-performance water vapor permeation measurement methods, Org. Electron. 15 (2014) 3746-3755.
[34] M. O. Reese, A. A. Dameron, M. D. Kempe, Quantitative calcium resistivity based method for accurate and scalable water vapor transmission rate measurement, Rev. Sci. Instrum. 82 (2011) 085101.
[35] J. Fahlteich, M. Fahland, W. Schönberger, N. Schiller, Permeation barrier properties of thin oxide films on flexible polymer substrates, Thin Solid Films 517 (2009) 3075-3080.
[36] J. S. Lewis, M. S. Weaver, Thin-film permeation-barrier technology for flexible organic light-emitting devices, IEEE J. Sel. Topics Quantum Electron. 10 (2004) 45-57.
[37] Z. Zhang, I. J. Britt, M. A. Tung, Permeation of oxygen and water vapor through EVOH films as influenced by relative humidity, J. Appl. Polym. Sci. 82 (2001) 1866-1872.
[38] C. Mo, W. Yuan, W. Lei, Y. Shijiu, Effects of temperature and humidity on the barrier properties of biaxially-oriented polypropylene and polyvinyl alcohol films, J. Appl. Packag. Res. 6 (2014) 40-46.

583 [39] J. Fahlteich, S. Mogck, T. Wanski, N. Schiller, S. Amberg-Schwab, U. Weber, O. Miesbauer, E.
584 Kucukpinar-Niarchos, K. Noller, C. Boeffel, The role of defects in single- and multi-layer
585 barriers for flexible electronics, SVC Bulletin Fall 2014 (2014) 36-43.
586 [40] J. Huang, Y. Chen, Effects of Air Temperature, Relative Humidity, and Wind Speed on Water
587 Vapor Transmission Rate of Fabrics, Text. Res. J. 80 (2010) 422-428.
588 [41] P. F. Carcia, R. S. McLean, M. D. Groner, A. A. Dameron, S. M. George, Gas diffusion ultrabarriers
589 on polymer substrates using Al_2O_3 atomic layer deposition and SiN plasma-enhanced
590 chemical vapor deposition, J. Appl. Phys. 106 (2009) 023533-023536.
591 [42] S. Lee, H. Choi, S. Shin, J. Park, G. Ham, H. Jung, H. Jeon, Permeation barrier properties of an
592 Al_2O_3/ZrO_2 multilayer deposited by remote plasma atomic layer deposition, Curr. Appl. Phys.
593 14 (2014) 552-557.
594 [43] D.-S. Han, D.-K. Choi, J.-W. Park, Al_2O_3/TiO_2 multilayer thin films grown by plasma enhanced
595 atomic layer deposition for organic light-emitting diode passivation, Thin Solid Films 552
596 (2014) 155-158.

597