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

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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.

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 5×10^{-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 5×10^{-3} g m^{-2}/day [17]) or a coulombmetric sensor (Aquatran with detection limit of 5×10^{-4} g m^{-2}/day [18] and Aquatran Model 2 with detection limit of 5×10^{-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

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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 3×10^{-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 1×10^{-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 2×10^{-3} g m^{-2}/day with HTO permeation and 1.5×10^{-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

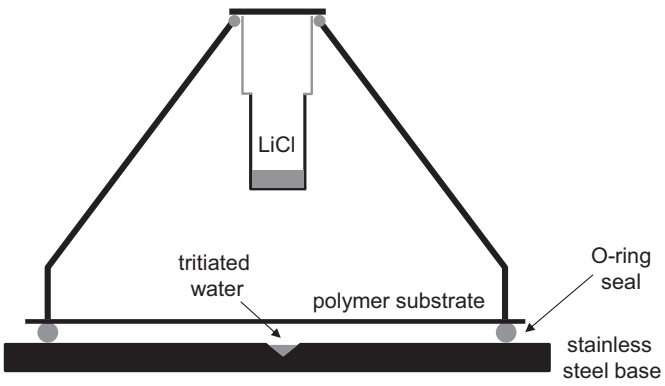

Fig. 1. Schematic diagram of HTO permeation rig.