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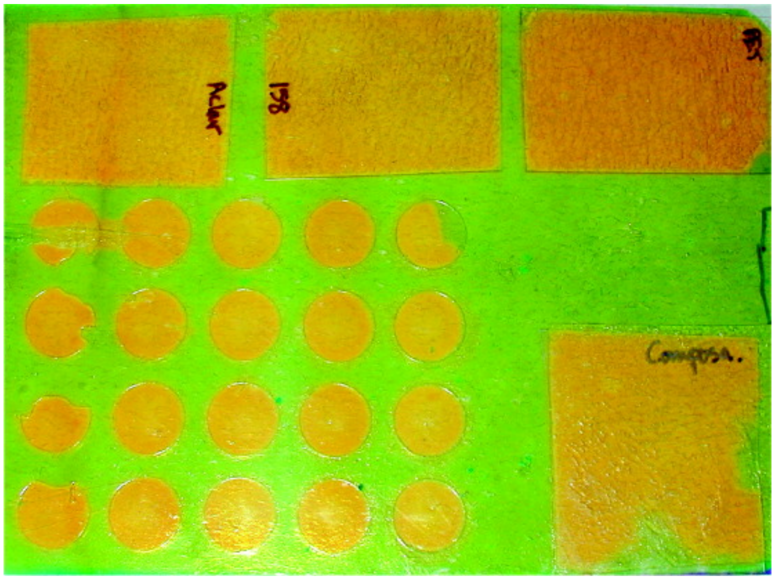

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# Method for Combinatorial Screening of Moisture Vapor Transmission Rate

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A high-throughput method for screening the moisture vapor transmission rate of barrier films was developed. This moisture high-throughput screening (MHTS) technique is based upon a Nafion−crystal violet (CVN) sensor that changes color from yellow to green upon absorption of water. Using an appropriate set of known standards, the slope of absorbance (at 630 nm) as a function of time can be converted into moisture vapor transmission rate (MVTR) values that agree with those obtained using ASTM F1290. High-throughput screening was demonstrated by depositing 20 emulsion-based poly(vinylidene chloride) films, using a 48-well template, of varying thicknesses onto the CVN sensor film and aging at 40 °C and 90% relative humidity for 72 h. MVTR values were accurately determined to a level of 0.9 g/m$^2$·day, at which point side-diffusion of moisture between the barrier and sensor films prevented observation of lower values. Larger sample size and edge-sealing are two proposed methods for improving the sensitivity of MHTS.

## Introduction

The combinatorial study of materials has already proven its value in the areas of biotechnology[1] and the discovery of medicinal compounds.[2,3] More recently, this methodology has moved into applications such as discovery of hydrogen-producing catalysts,[4] optimization of polymer processing,[5] and composite design.[6] The primary advantage of the combinatorial technique is the speed at which different materials can be synthesized, formulated, and tested for a particular application (sometimes referred to as high-throughput screening or HTS). In addition to speed, the amount of material needed for a combinatorial study is far less than that required for conventional methods, which makes combinatorial materials discovery more affordable when the materials are expensive. The need for speed in the combinatorial science magnifies the necessity for automation of different steps in the material discovery process. Consequently, a tremendous effort is focused on automating the formulation, synthesis, and screening steps in discovering new materials. Many of these methods are applicable to the screening of any type of functional material, whereas others are targeted for specific functionality in a particular area of application.

Materials with varying levels of gas or moisture barrier are used in a wide range of packaging applications from food[7] and medical packaging[8] to the protection of electronic materials.[9] Significant research and development effort has focused on the discovery of inorganic and polymeric materials for barrier applications over the past several decades.[10−12] In the present study, a combinatorial approach for the evaluation of moisture barrier is demonstrated. This study is part of a broader effort focused on the development of new tools and methods for the entire combinatorial process, such as formulation, coating, and screening in a high-throughput manner. HTS methods for the determination of oxygen transmission rate (OTR) and haze have also been developed,[13] but the methodology shown here for determination of moisture vapor transmission rate (MVTR) is the most quantitative and robust.[14,15] This method relies on a change in the optical absorbance of a sensor film that occurs as the result of a simple acid−base reaction (see Figure 1). Depositing barrier films of interest as "spots" on a glass plate covered with sensor film allows 20 or more MVTR values to be measured simultaneously by one spectrometer. In this fashion, the effects of a variety of parameters that may affect barrier performance (e.g., film thickness, additives, etc.) can be quickly screened to determine an optimal barrier. This technique has been termed moisture high-throughput screening (MHTS).

In the following sections, the formulation, manufacture, calibration, and use of MHTS sensor film for combinatorial screening of MVTR is described. An initial experiment demonstrates the quantitative agreement between MVTR values obtained using MHTS and those obtained using a more accepted technique (i.e., ASTM F1249). Next, with the accuracy of MHTS proven, a combinatorial plate containing 20 barrier film spots with varying thicknesses is tested. Finally, the ongoing challenge of side diffusion is discussed, which sets the lower limit of MVTR that can be assessed. Barrier levels below 0.9 g/m$^2$·day (at 40 °C and 90%RH) are difficult to measure for this reason, although potential improvements are suggested.

## Sensor Manufacture, Operation, and Usage

**Sensor Solution and Film Preparation.** Reagent grade crystal violet from Aldrich (Milwaukee, WI) is dissolved in methanol to create a 0.61 wt % solution. Dissolution of CV takes ∼1 h using a magnetic stirrer. This CV solution is then

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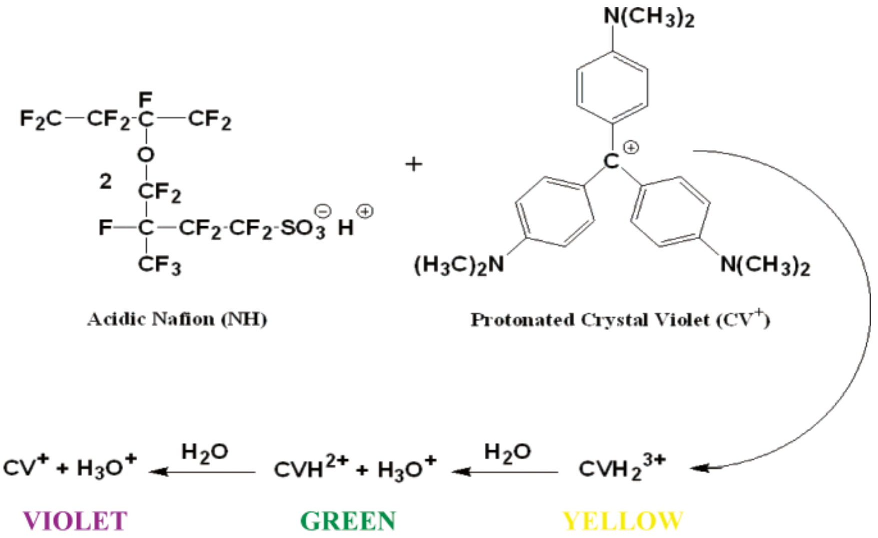


**Figure 1.** Proposed scheme for color change that occurs during water uptake by CVN sensor film.

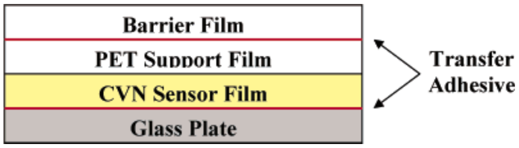


**Figure 2.** Schematic cross section of the layers on a combinatorial test plate. The barrier film may be coated directly onto the PET support film, thereby eliminating the upper layer of transfer adhesive (as in Figure 7). If the barrier film were laminated, there would actually be a second PET support film between the upper layer of transfer adhesive and the actual barrier film (as in Figure 5).

combined with a 5 wt % Nafion solution, tradename Liquion 1100, from Ion Power (Bear, DE) to yield a dry Nafion/CV weight ratio of 12. The crystal violet/Nafion (CVN) solution is typically stirred for 15 min to achieve homogeneity of components. The supported CVN sensor film is then prepared by coating the CVN solution onto 2-mil (~50 $\mu$m)-thick PET film, Mylar D from GE (Charlotte, NC), using the 4-mil opening (~100 $\mu$m) on a blade-coating bar (also known as a Byrd bar). The dry sensor thickness resulting from this procedure is ~1.5 $\mu$m. After drying in a hood for 1 h, the visible spectrum of this solid CVN film is measured using a $\mu$Quant spectrometer from Bio-Tek Instruments, Inc. (Winooski, VT). The sensor films absorbance is measured at 435, 630, and 800 nm to determine the net absorbance ratio using

$$\text{Ratio} = \frac{A_{630} - A_{800}}{A_{435} - A_{800}} \qquad (1)$$

This ratio should be 19.6 ± 5.0. When the ratio is too low, indicated by a greenish film color, a small amount of Nafion solution (around 5% of total CVN solution volume) is added and the solution is stirred for 15 min. The newly diluted solution is again coated onto PET and dried, and the absorbance ratio is retested. This procedure is repeated until the appropriate absorbance ratio is achieved. The final adjusted sensor solution is then filtered through a G6 glass filter from Fisher Scientific, Inc. (Hampton, NH). Both sides of the supported CVN sensor film are then laminated with 467 transfer adhesive from 3M (St. Paul, MN). Finally, the supported sensor film is laminated to a plate of window glass measuring 3.375 × 5 × 0.125 in.

**Moisture Sensor Chemistry and Mechanism.** Optochemical sensors for humidity have been widely studied in a variety of applications and conditions.[16−21] In particular, sensors based on a mixture of Nafion and crystal violet have shown promise.[16,20,21] This system changes color from yellow to green to dark blue (or violet), depending on the ambient humidity (or moisture uptake). The mechanism of the Nafion−crystal violet sensor appears to be a simple acid−base reaction, as proposed in Figure 1. Nafion (a sulfonic acid-substituted fluoropolymer) protonates the crystal violet (a pH indicator), turning it yellow. Protonated crystal violet is a stronger acid than water, which causes protons to be transferred from crystal violet (CV) to form $H_3O^+$. As the CV deprotonates, the color turns from yellow to green and eventually to violet. In a Nafion−crystal violet sensor film, green is observed prior to blue because of the presence of fully ($CVH_2^{3+}$) and partially ($CVH^{2+}$) protonated species. The speed and extent of color change depends on the thickness of the sensor material and the ratio of the components (i.e., Nafion to crystal violet).[16]

This material can be used as a moisture sensor when a thin sensor film attached to a substrate is covered with a barrier film of interest (e.g., poly(vinylidene chloride) (PVdC) latex).[22] Figure 2 shows a schematic cross section of the layers present in a typical test plate. By placing this construction into a temperature/humidity-controlled chamber and measuring its absorbance at 630 nm as a function of time, a slope that correlates to moisture uptake is obtained. Absorbance in the yellow region of the visible light spectrum increases with time as a result of the color change in the sensor film as the CV becomes deprotonated (see Figure 1). The absorbance−time curve can then be further processed using calibration standards to obtain the moisture transmission through the sample.

**MHTS Sensor Calibration.** Slopes of absorbance as a function of time are converted to MVTR values using a series of known reference films that are attached to each plate. References are established using a Permatran-W 3/31 (MG)

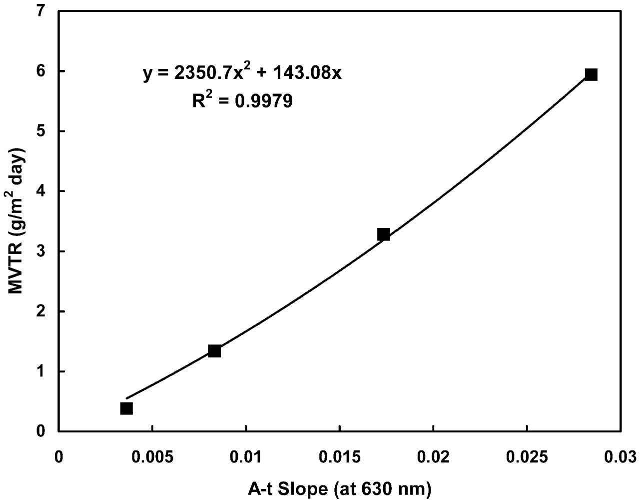


**Figure 3.** Calibration curve for CVN sensor film that correlates the MVTR of four standards (Table 1 provides more detail), measured using ASTM F1249, with the slope of absorbance as a function of time at 630 nm. These data were gathered at 40 °C in a 90% RH controlled environment.

**Table 1.** MHTS Reference Materials

| material | form | manufacturer | thickness ($\mu$m) | MVTR[a] | $A-t$ slope |
|---|---|---|---|---|---|
| PVdC latex | coating[b] | W. R. Grace | 22 | 1.34 | 0.0083 |
| Mylar PET | film | General Electric | 127 | 5.94 | 0.0284 |
| Composaclean | film | Cleanfilm | 110 | 3.28 | 0.0173 |
| Aclar | film | Honeywell | 38 | 0.38 | 0.0036 |

[a] MVTR, in units of g/m$^2$•day, is performed using a Mocon Permatran-W 3/31 operated at 40 °C and 90% RH. [b] Daran SL158 latex is made into a coating by blade-coating onto 50-$\mu$m PET.

instrument, made by Mocon (Minneapolis, MN), that conforms to ASTM F1249. Figure 3 shows a typical calibration curve, fit with a second-order polynomial, used to convert unknown absorbance−time slopes to MVTR values. The reference films shown in Figure 3 are summarized in Table 1 with respect to absorbance−time ($A-t$) slope, MVTR, and manufacturer. Accuracy of this technique can be further improved by adding more reference films, especially ones that are close to the MVTR range of interest. The MHTS test method can produce MVTR values that quantitatively agree with the Permatran instrument.

**Calculation Procedure.** A one-dimensional model for diffusion of water through a barrier film is considered in order to interpret the experimental data. The concentration of water in the barrier film (versus the location $z$ and time $t$) is given by

$$\frac{c}{c_0} = 1 - 2\sum_{n=0}^{\infty}\frac{(-1)^n}{\left(n+\frac{1}{2}\right)\pi}\exp\left[-\left(n+\frac{1}{2}\right)^2\pi^2\frac{D}{L^2}t\right]\cos\left(n+\frac{1}{2}\right)\frac{\pi z}{L} \tag{2}$$

where $D$ is the diffusion coefficient of water in the barrier material, $L$ is the thickness of the barrier layer, and $c_0$ is the concentration of water in the barrier material at the surface exposed to humid environment. The concentration of water at the sensor layer ($z = 0$) is

$$\frac{c}{c_0} = 1 - 2\sum_{n=0}^{\infty}\frac{(-1)^n}{\left(n+\frac{1}{2}\right)\pi}\exp\left[-\left(n+\frac{1}{2}\right)^2\pi^2\frac{D}{L^2}t\right] \tag{3}$$

Assuming $\alpha = D/L^2$ and taking into account that the absorbance of the sensor dye is proportional to the concentration of water, the following relationship is obtained,

$$\varphi(t) = \frac{A}{A_0} = 1 - 2\sum_{n=0}^{\infty}\frac{(-1)^n}{\left(n+\frac{1}{2}\right)\pi}\exp\left[-\left(n+\frac{1}{2}\right)^2\pi^2\alpha t\right] \tag{4}$$

where $A$ is the absorbance of the sensor material at a specific wavelength. The absorbance value for the dye at the equilibrium with moisture ($A_0$) is read from the asymptotic value of the background absorption in the sensor plate. The value for $\alpha$ is estimated by a nonlinear fit of eq 4 to the experimental absorbance values. Figure 4 shows typical fits to the experimental data for three different types of barrier materials (PET, Aclar, and emulsion-based PVdC (film 7 from Figure 7)). The inflection point for the absorbance curve can be calculated approximately by keeping only two terms in eq 4. Therefore, the value for the slope at the inflection point is given by

$$\text{slope} = \pi\alpha C_1 \tag{5}$$

with $C_1 \cong 0.5887$. The value for the slopes obtained by this method are subsequently converted to the moisture vapor transmission rates using a calibration curve that relates MVTR to absorbance slope (see Figure 3).

## Results and Discussion

Recent improvements in barrier film preparation, handling, and storage, along with improvements in sensor film design, have allowed the MHTS test method to provide quantitative agreement with MVTR values that are obtained using ASTM F1249. Poly(vinylidene chloride) latex-based barrier films are used to demonstrate the effectiveness of the MHTS technique. PVdC is well-known for its low permeability to water.[23,24] An initial validation experiment, carried out at 40 °C and 90% relative humidity (RH), compares MVTR values obtained using the MHTS sensor film to those obtained using ASTM F1249. Higher testing temperatures and humidity will increase the slope of absorbance as a function of time, thereby decreasing the time required to obtain a reliable MVTR value. Next, with the accuracy of the MHTS technique proven, the MHTS results from a combinatorial array of PVdC latex-based films of varying thicknesses is shown. A clear trend of decreasing MVTR with increasing film thickness is established, although this trend appears to plateau for films with thicknesses >40 $\mu$m as a result of side-diffusion of moisture into the sensor film. In the final portion of this section, the consequences and prevention of side-diffusion is addressed.

**Validation of Sensor.** A series of PVdC latex-based films of increasing thicknesses were cast on 50-$\mu$m PET film, using Daran SL 158 (see Table 1 for more information). Figure 5 shows these films laminated to an MHTS test plate. Table 1

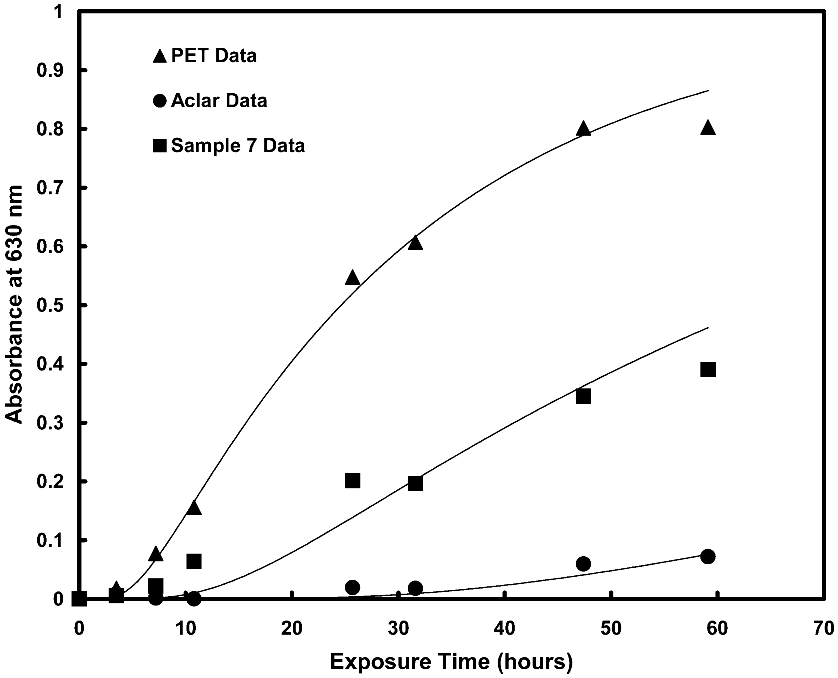
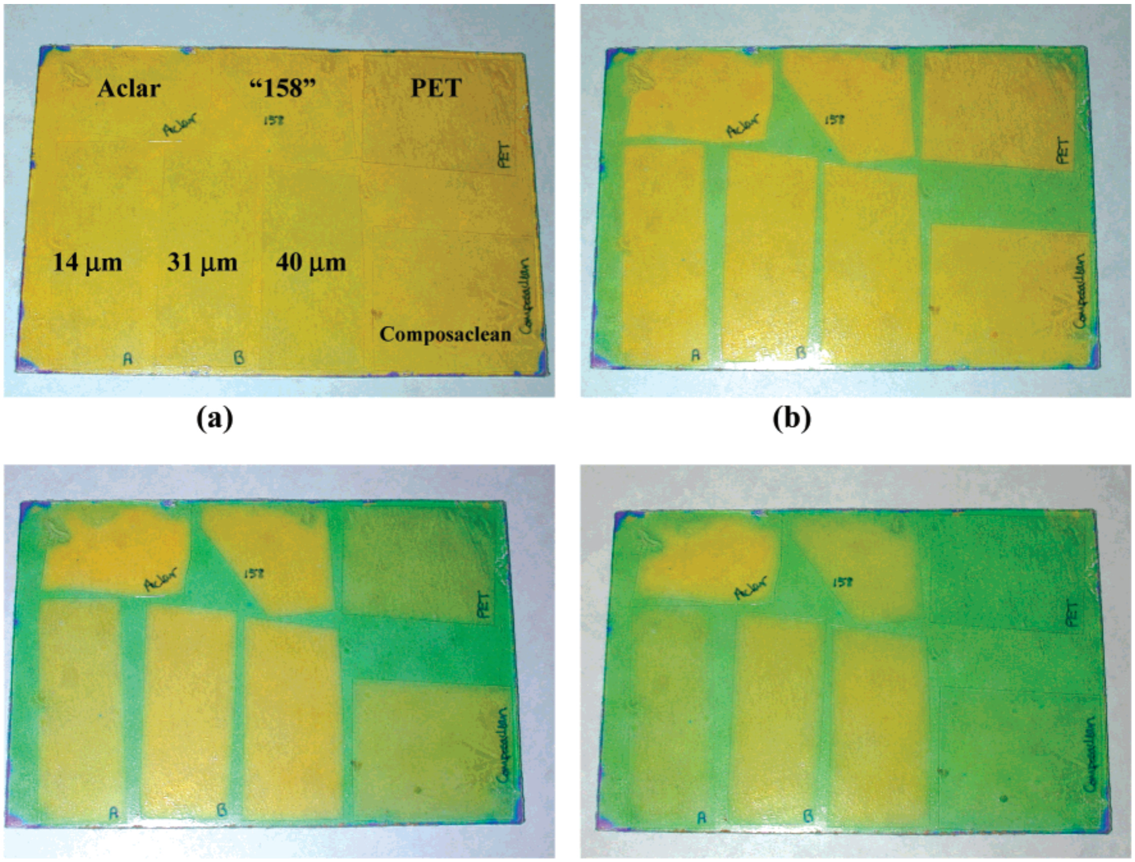


**Figure 4.** Plot of absorbance (at 630 nm) as a function of time, illustrating the fit of the one-dimensional diffusion model (eq 4) to experimental data obtained for 125-$\mu$m PET (▲), Aclar (●), and PVdC (film 7 from Figure 7) (■).



(a) (b)

(c) (d)

**Figure 5.** Effect of time on color of MHTS plate in 40 °C and 90% RH environment: (a) 0, (b) 4, (c) 24, and (d) 72 h. Thicknesses of test films shown on second plate image (b) and information pertaining to standards provided in Table 1.

provides pertinent information on the standard films used on this plate, and the thickness of each of the test films is shown in Figure 5a. Prior to testing the plate, it is completely dry and is, therefore, yellow (Figure 5a). After 4 h of testing (Figure 5b), the unprotected areas of the sensor film have turned green, allowing the standard and test films to be clearly seen. Over time, the plate becomes progressively greener as moisture infiltrates the sensor film. From these images alone, the MVTR of the various films could be qualitatively ranked upon the basis of the rate at which the

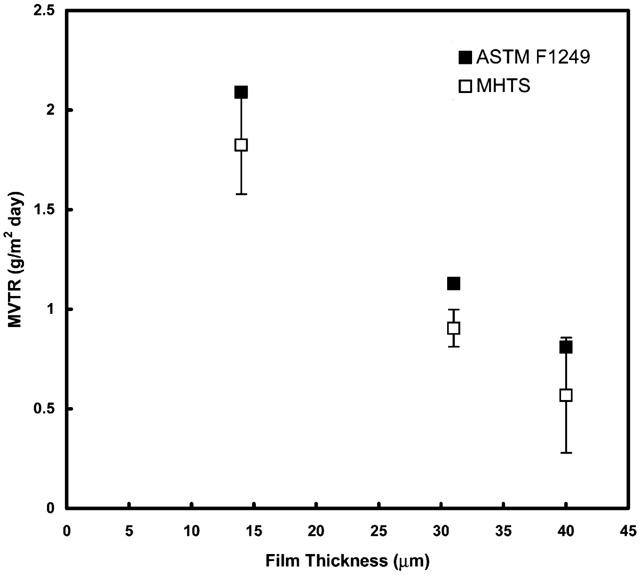


**Figure 6.** Comparison of MVTR values obtained using ASTM F1249 and MHTS techniques. All measurements were obtained using 40 °C and 90% RH environment.

underlying sensor turns green. In the case of the standard films, the PET would presumably have the highest MVTR value (i.e., it offers the least resistance to moisture transmission and quickly turns green), and Aclar should have the lowest MVTR, which is confirmed by the data shown in Table 1. Furthermore, it is apparent that the thinnest of the test films has a higher MVTR than the thicker versions and is somewhere between that of Composaclean and the Daran SL 158 standards (shown in Figure 5 as "158"). These assertions are confirmed by the actual measured and calculated MVTR values.

Figure 6 shows the comparison between the MVTR values measured using ASTM F1249 and those calculated using MHTS slopes. The error bars on the MHTS data represent one standard deviation. The ASTM F1249 values, measured with the Permatran instrument, have a reported error of 15%. Considering the relatively large error associated with each of these techniques, the agreement between them is believed to be quantitative, although the techniques themselves may be thought of as semiquantitative. The use of additional standards on the MHTS plate would presumably improve the accuracy of MVTR values obtained from $A-t$ slopes, although more standards will reduce the number of samples that can be simultaneously tested in a combinatorial array.

**Combinatorial MVTR Assessment.** A combinatorial array of 20 PVdC latex-based films were cast on 50-$\mu$m PET film using a centrifugation process that dries all of the films simultaneously.[25] This array was then laminated to a glass plate that had already been covered with MHTS sensor film. When creating the circular barrier films, the latex volume was varied to produce columns of increasing thickness, moving from left to right across the plate. Figure 7 shows the aging of the combinatorial MHTS plate at 40 °C and 90% RH. The reference films on this plate are identical to those used in the previous validation experiment (see Figure 5). After aging for 72 h (Figure 7d), the increasing film thickness, moving from left to right across the plate, is

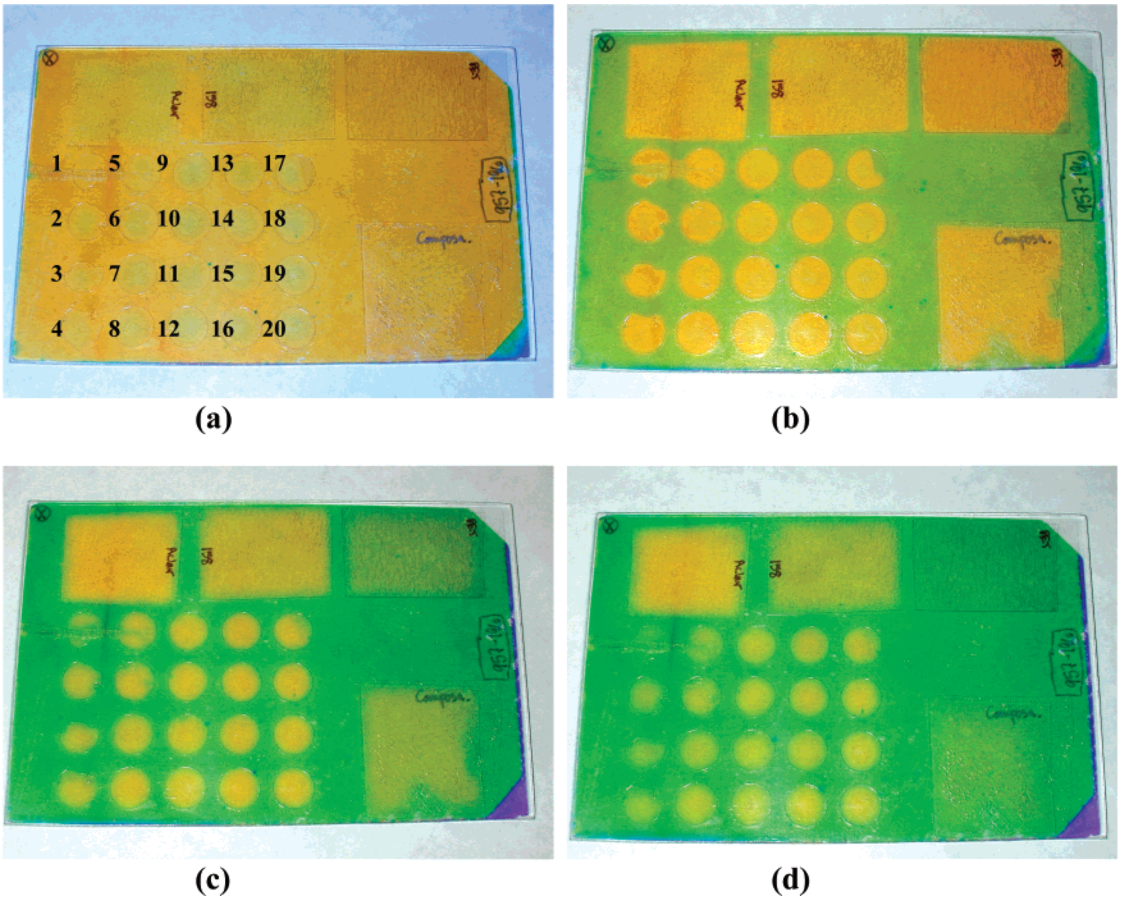


**Figure 7.** Aging of combinatorial MHTS plate in 40 °C and 90% RH environment: (a) 0, (b) 3, (c) 26, and (d) 72h.

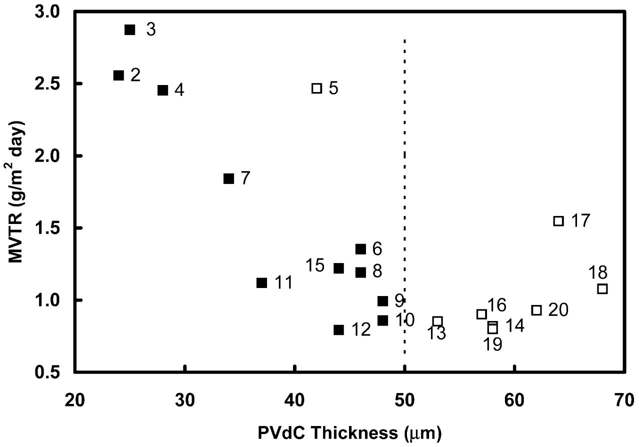


**Figure 8.** Plot of calculated MVTR values, from combinatorial MHTS plate (Figure 6), as a function of circular test film thickness. Data points have been separated into those without defects (■) and those having defects or experiencing side-diffusion (□). Numbers next to the data points correspond to the numbered films on the combinatorial MHTS plate (Figure 6a).

apparent because of the decreasing amount of green color observed. Just as in Figure 5, the films with the higher MVTR turn green more rapidly. Visual defects in some of the barrier films can be observed after only 3 h of aging (Figure 7b). On the basis of their appearance in this image, films 1, 5, and 17 would be expected to have an abnormally high MVTR.

Figure 8 shows MVTR values, calculated using the $A-t$ slopes from the combinatorial MHTS plate (Figure 7), as a function of barrier film thickness. The data points are numbered to correspond to those shown in Figure 7a. Films with a thickness of $<50$ $\mu$m show the anticipated linear trend of decreasing MVTR with increasing thickness. As expected, films 1, 5, and 17 exhibited an abnormally high MVTR value relative to the rest of the data. Film 1 actually had an MVTR so large (~8 g/m$^2$·day) that it had to be left out of Figure 8 to preserve the scale for the rest of the data. Beyond a thickness of 50 $\mu$m, all of the films appear to have the same MVTR (0.9 ± 0.1 g/m$^2$·day). This leveling of the data is primarily attributed to the phenomenon of side-diffusion, in which moisture penetrates the interface between the barrier and sensor film rather than permeating directly through the barrier film.

**Side-Diffusion.** Side-diffusion is the major factor limiting the sensitivity of the MHTS technique. Figure 9a illustrates the effects of side-diffusion during the aging of a barrier film. After only 26 h of aging, dark green around the edges of the barrier film can be observed, and this effect becomes very pronounced at 52 h. When performing MHTS measurements, absorbance is nominally measured at the center of a film, and the level of side diffusion observed after 52 h of aging is likely to increase the measured absorbance. Beyond 73 h of aging, the sensor film is completely saturated by side-diffusion moisture. Any barrier film requiring longer than 3 days to establish an MHTS slope will simply register the value associated with the side-diffusion limit (i.e., MVTR ≈ 0.9 g/m$^2$·day for the case shown here).

There are at least two methods that can be used to diminish the effect of side diffusion and improve the sensitivity of MHTS-based measurements. Increasing sample size, which will extend the time needed for moisture to reach the center of the film where absorbance measurements are taken, is the simplest technique to enhance MHTS sensitivity. An example of this was shown in Figure 5, where side-diffusion was unable to reach the center of the barrier films after 72 h of aging (Figure 5d). Another option for limiting side-diffusion is the use of a sealant. In Figure 9b, the aging of a barrier film of thickness identical to that shown in Figure 9a is shown. The edge of this film has been sealed with poly(isobutylene) (PIB) deposited from a 10 wt % solution in toluene. After 99 h of aging, the color of this film is still very homogeneous, suggesting that moisture has permeated only directly through the film rather than from the side. Quantitative evaluation of these techniques and evaluation of other methods that limit side-diffusion are currently underway and will be the topic of a future report.

## Conclusions

A method for high-throughput screening of moisture vapor transmission rate has been developed on the basis of a Nafion–crystal violet sensor film. As the sensor film absorbs water, its color changes from yellow to green (and eventually to blue-violet). Using known references, the slope of optical absorbance (at 630 nm) as a function of time can be converted to MVTR values with accuracy comparable to ASTM F1249. The MVTR of at least 20 films can be tested simultaneously by depositing them in a standard 48-well array as circles, with a diameter of 1 cm. Currently, this technique can measure MVTR only down to 0.9 g/m$^2$·day at 40 °C and 90% RH because of side-diffusion of moisture between the barrier and sensor films. Lower MVTR values can be measured at lower temperatures (e.g., the limit is ~0.1 g/m$^2$·day at 23 °C). Greater MHTS sensitivity can likely be achieved by using larger sample sizes or by edge-sealing

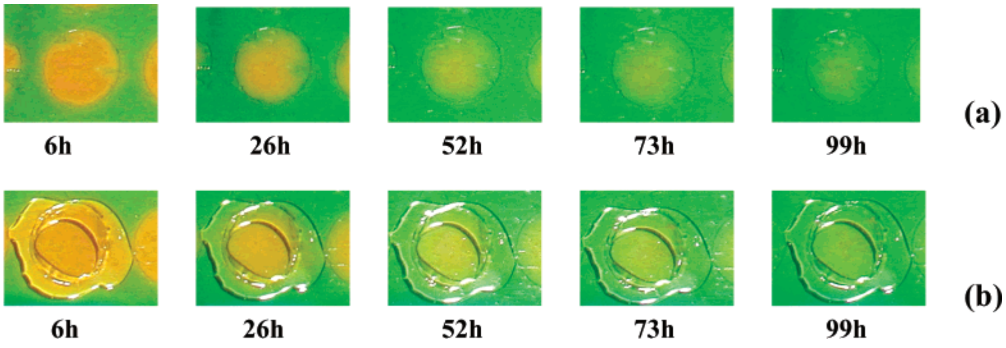


**Figure 9.** Comparison of side-diffusion in unsealed (a) and sealed (b) barrier films. Both of the films shown have a thickness of 46 $\mu$m.

sample films in an effort to slow the process of side-diffusion. Further optimization of the MHTS method is ongoing, and quantitative analysis of improvements will be the subject of future work.

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