

Measurement of Water Vapor Transmission Rate in Highly Permeable Films

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ABSTRACT: Measurements of water vapor transmission rate (*WVTR*) are often based on the wet cup method described by ASTM E 96-95. In attempting to compare the performance of thin polymer films with moderate to high water vapor permeability, it was observed experimentally that the ASTM method did not give reliable results for highly permeable films. In particular, the *WVTR* depended on film thickness and the ratio of film area to water surface area. It was determined that the high water vapor flux through the more permeable films caused a reduction in the driving force for water vapor transmission, that is, the relative humidity at the inner surface of the film. Consequently, the *WVTR* was underestimated. Comparisons based on a small area ratio and a constant small-flux condition were considered as alternative approaches for evaluating performance using the wet cup method. The constant flux approach produced the best correlation with *WVTR* that was measured with a commercial instrument. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1624–1633, 2001

Key words: water vapor transmission; wet cup test; microlayer coextrusion; Celgard; poly(ethylene oxide); Bionolle

INTRODUCTION

There is a growing need for reliable methods of measuring water vapor transmission rate (*WVTR*) through films that are highly permeable to water vapor. Two standard dish methods are described by ASTM E 96-95.¹ The dry cup method requires a desiccant, usually anhydrous calcium chloride, to maintain the inside of the dish at 0% relative humidity (*RH*). The more commonly used wet cup method specifies distilled water in the dish to maintain 100% *RH*. The prescribed procedure requires the *WVTR* to be taken from the

slope of water loss plotted versus time at steady state.

Shortcomings of the wet cup method have previously been recognized. Sources of resistance to water vapor transmission other than the test film have been considered, and corrections have been proposed for: (1) resistance from the layer of still air in the cup; (2) resistance from the surface of the specimen inside the cup; and (3) resistance from the surface of the specimen outside the cup.² For water vapor-permeable materials, the corrections are significant and cannot be neglected. Indeed, for highly permeable materials the corrections are on the same order of magnitude as the quantity sought.³

We recently encountered some problematic results in attempting to quantitatively compare the

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performances of highly permeable polymeric films on the basis of *WVTR* measured by the wet cup method. This led to an exploration of the test parameters using a range of materials with moderate to high water vapor permeability. Subsequently, alternative approaches to data analysis were considered. Finally, the results were compared with measurements using a commercial instrument designed specifically to determine the *WVTR* of highly permeable films.

EXPERIMENTAL

Materials and Methods

Materials

Materials were provided by Kimberly-Clark Corporation, Neenah, WI. Celgard is a microporous film manufactured by Hoechst Celanese, Summit, NJ. Its porous microstructure and properties are well documented in the literature.^{4,5} Another microporous film was prepared from filled polypropylene with 60 wt % CaCO_3 particles nominally 1 μm in diameter. The as-received pellets were extruded as 3-mil film, and microporosity was created by stretching wide specimens uniaxially to 300% strain at 50%/min and 70°C. Two polypropylene nonwoven webs were identified as NW-0.4 (0.4 oz/sq yd) and NW-0.65 (0.65 oz/sq yd). Regular 75 g m^{-2} Xerographic paper in the as-received condition was included in the study.

Poly(ethylene oxide), PEO, manufactured by Union Carbide (Danbury, CT) with weight average molecular weight of 400,000 and Bionolle 3001 (a butylene succinate adipate random copolyester), manufactured by Showa High Polymer, Japan, were coextruded at 190°C as 1-mil microlayer films with 1024 alternating layers, using methodology described previously.^{6,7} The composition of the microlayer film was varied by altering the feed ratio in the coextrusion process.

Methods

The technique used to measure water vapor transmission rate (*WVTR*) was a modification of the wet cup method described by ASTM E 96-95. In this method the test film covered a Petri dish filled with distilled water, as shown schematically in Figure 1. The mass of water lost from the dish was monitored as a function of time, and the *WVTR* was calculated from the steady-state region. Thickness measurements were obtained

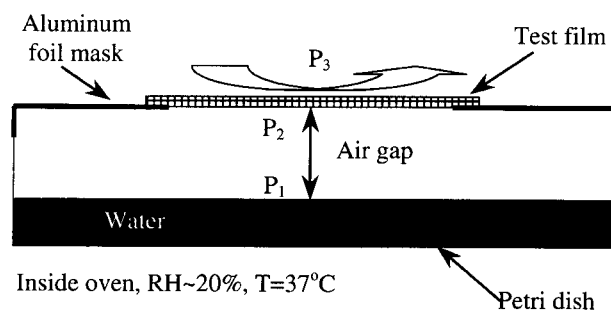


Figure 1 Schematic representation of the wet cup test.

with a digital gauge at a minimum of nine positions on a test specimen. The standard deviation of thickness for each specimen was typically less than 10%. A window of known area was cut into a sheet of aluminum foil, and the film was attached to the aluminum with 5-Minute® epoxy (Devcon). The foil mask without a film covering (open hole) was also studied. The foil mask with (or without) a film was epoxied to the top of a plastic Petri dish that was 57 cm^2 in area. For those tests that followed the ASTM standard, with water surface area the same (within 10%) as the film area, the film was epoxied directly to the Petri dish. Using a syringe, 30 mL of distilled water was added to the Petri dish, and the hole was sealed with epoxy. With 30 mL of water in the dish, the air gap between water surface and film was 6 mm. After allowing the epoxy to cure for 1 h, the sample dish was weighed and placed in a convection oven at $37 \pm 0.5^\circ\text{C}$ and $19 \pm 1.5\%$ RH with air circulation rate of about 0.5 m s^{-1} . The sample dish was periodically removed and weighed. The weight loss as a function of time was recorded. The sample dish was typically removed from the oven for weighing once every hour. To confirm that this procedure did not disturb the weight loss, a sample dish was left in the oven for 15 h before weighing. The weight loss was the same as that in a sample dish removed and weighed every hour. Representative tests of Celgard film and open holes with different areas are shown in Figure 2. The rate of water loss was linear with time after an initial period of about 1 h. This initial period was attributed to temperature equilibration in the sample dish. Although most tests were run for 5–6 h, the tests shown here were extended to 22 h to verify, by the linearity of weight loss with time, that a steady-state water vapor transmission rate was achieved. The slope of the water loss as a function of time normalized to the testing area (*A*)

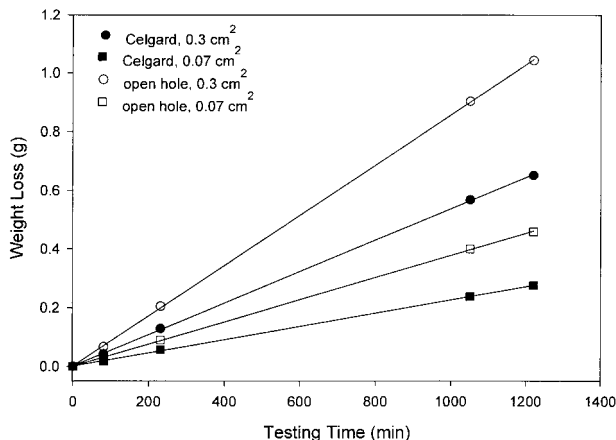


Figure 2 Weight loss as a function of time in the wet cup test.

was taken as the water vapor transmission rate (*WVTR*)

$$WVTR = \frac{\text{mass H}_2\text{O lost}}{\text{time} \times \text{area}} = \frac{\text{flux}}{\text{area}} \quad (1)$$

with units of $\text{g d}^{-1} \text{m}^{-2}$. The standard deviation of the *WVTR* was less than 5%.

The *WVTR* is related to a material characteristic, the water vapor permeability, ϕ , as

$$\phi = WVTR \left(\frac{\ell}{\Delta p} \right) \quad (2)$$

where ℓ is the film thickness and Δp is the pressure difference across the film. Because the thickness of the films varied, the *WVTR* was sometimes normalized to film thickness (\mathfrak{R} = *WVTR* \times ℓ) with units of $\text{g mil d}^{-1} \text{m}^{-2}$.

Several sources of error in the *WVTR* were considered. The following equation has been recom-

mended for the excess water vapor transmission due to edge masking³:

$$\text{excess } WVTR (\%) = \frac{400\ell}{\pi S} \ln \left(\frac{2}{1 + e^{-(2\pi w/\ell)}} \right) \quad (2)$$

where ℓ is the film thickness, w is the width of the masked edge, and S is 4 times the test area divided by the perimeter. The edge effect was negligible because the film thickness ($\ell < 0.1$ mm) was much less than the other two dimensions in all the films tested.

Leakage was also a potential source of error, especially in tests with a very small film area. However, the water loss from a sample dish with no hole in the foil mask was 0.02 g d^{-1} . This corresponded to only about 10% of the flux of the smallest area of Celgard film. Thus, the effect of leakage was neglected. Especially with highly permeable films, there was concern that air circulation in the oven might not be fast enough to maintain the *RH* at the outer surface of the film at the same level as that in the rest of the oven and to prevent formation of a boundary layer at the film surface. This effect would tend to decrease the *WVTR*. This possibility was tested by placing a fan in the oven to blow air directly to the film surface. The fan increased the air circulation rate from 0.5 to 3 m s^{-1} and also decreased the *RH* from 18% to 14%, producing the results shown in Table I. The *WVTR* of a stack of three 1-mil Celgard films increased by about 15% with the fan. The fractional change remained constant as the film area decreased by a factor of 20. This suggested that the *RH* profile on the outside of the film did not depend on water vapor flux through the film. The slight increase in *WVTR* was attributed to the decrease in oven *RH*. Recently, the MOCON Permatran-W 100K (Modern Controls, Inc., Minneapolis, MN) was introduced

Table I Effect of Oven Air Circulation Rate on *WVTR* of 3-mil Celgard Films

Area (cm ²)	Without Fan <i>RH</i> = 18%, <i>T</i> = 37.5°C		With Fan <i>RH</i> = 14%, <i>T</i> = 37.4°C		Increasing
	Flux (g/d)	<i>WVTR</i> (g d ⁻¹ m ⁻²)	Flux (g/d)	<i>WVTR</i> (g d ⁻¹ m ⁻²)	
25	13.91	5570	16.00	6400	15%
10	7.07	7070	8.05	8050	14%
5	4.11	8210	4.76	9530	16%
1.22	1.34	10,970	1.51	12,400	13%

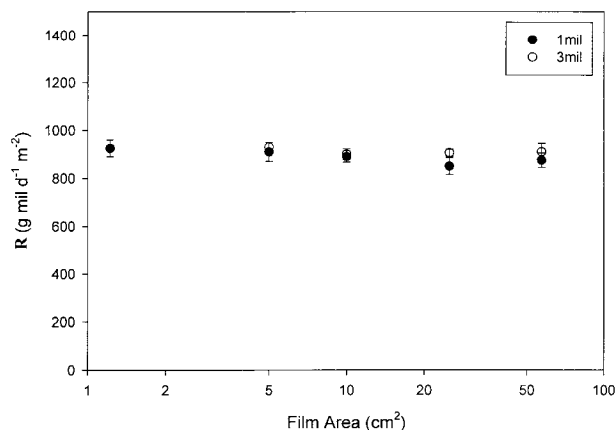


Figure 3 Effect of film thickness and film area on specific WVTR of Bionolle film.

for measuring the water vapor transmission rate of materials with high water-vapor permeability. The test cell is divided into three chambers. The upper chamber contains liquid water and is separated from the center chamber by two Celgard films. Water vapor diffuses through the Celgard films to fill the center chamber with water vapor at 100% *RH*. The center chamber is separated from the lower chamber by the test film. Water vapor that diffuses through the test film into the lower chamber is swept away by a constant flow of dry nitrogen gas and carried to a relative humidity (*RH*) sensor. The WVTR is calculated from the steady-state *RH* reading and the test film area. In order to compare MOCON and cup test results on the same film, test films were epoxied to a 5-cm² aluminum foil mask. Because the cell depends on Celgard film to maintain water vapor in the center chamber at 100% *RH*, Celgard cannot be used as the test film.

RESULTS AND DISCUSSION

Water Vapor Transmission Rate

Among materials used in the study, Bionolle had the lowest water vapor permeability. The specific water vapor transmission rate ($\mathfrak{R} = WVTR \times \ell$) is shown in Figure 3. Within experimental error, $\mathfrak{R} = 950 \text{ g mil d}^{-1} \text{ m}^{-2}$ with no effect of test area or film thickness for 1-mil and 3-mil Bionolle films.

The effect of film area on \mathfrak{R} for PEO, a more highly water permeable polymer than Bionolle, is shown in Figure 4. For thicker PEO films (4.2 mil and 6.5 mil), \mathfrak{R} was independent of film thickness

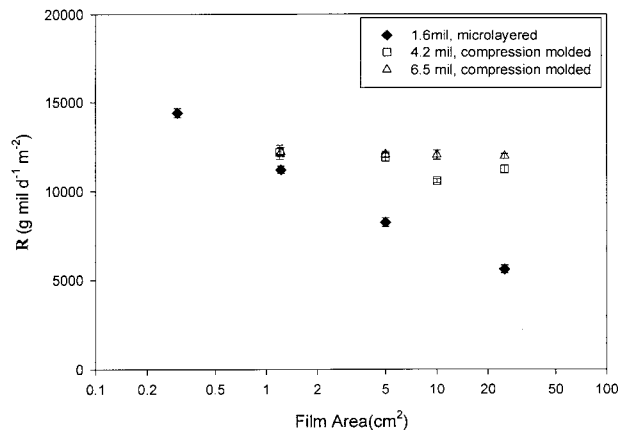


Figure 4 Effect of film thickness and film area on specific WVTR of PEO film.

and film area with $\mathfrak{R} = 12,000 \text{ g mil d}^{-1} \text{ m}^{-2}$. The thin PEO film (1.6 mil) exhibited the same value of \mathfrak{R} as the thicker PEO films if the film area was small. However, increasing the area of the thin film resulted in gradually decreasing \mathfrak{R} values.

The dependence of \mathfrak{R} on the area of Celgard, a film with extremely high permeability, was striking (Fig. 5). When two, three, and four layers of Celgard film were stacked together to examine the effect of thickness, the WVTR changed only slightly. As a consequence, \mathfrak{R} increased dramatically with increasing thickness. The value of \mathfrak{R} for 2-mil Celgard was about 80% higher than that of 1-mil Celgard. Furthermore, \mathfrak{R} decreased with increasing film area in the same manner regardless of thickness. The effect of film area on the water vapor transmission rate of two highly porous nonwoven materials followed the same trend as Celgard.

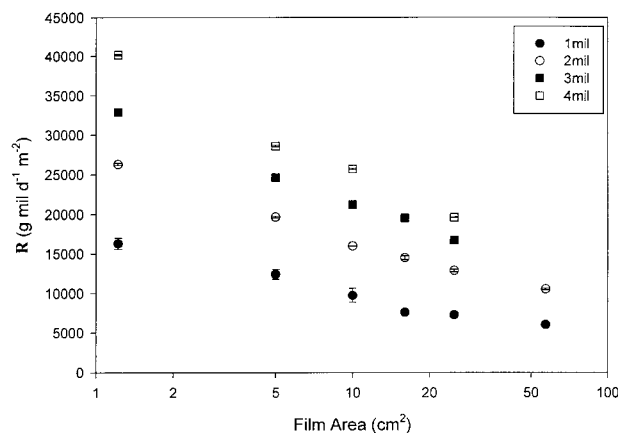


Figure 5 Effect of film thickness and film area on specific WVTR of Celgard film.

The quantity \mathfrak{R} is related to a material characteristic, the water vapor permeability ϕ , as $\mathfrak{R} = \phi \Delta p$ where Δp is the pressure difference across the film. If \mathfrak{R} is found to depend on film area and film thickness, it follows that the pressure difference across the film is not constant. The cup test depends on evaporation of water to maintain 100% RH inside the cup. If the water vapor flux is high, the evaporation rate and the diffusion rate of water vapor through the air gap to the film surface may not be enough to maintain 100% RH within the entire volume of the cup. The resulting gradient from 100% RH at the water surface to a value less than 100% at the film surface effectively reduces the pressure difference Δp .

This effect is shown schematically in Figure 6. If the film has relatively low permeability so that water vapor flux through the film is low, the RH at the inner surface of the film is close to 100% ($P_2 = P_1$), and the pressure difference across the film ($\Delta p = P_2 - P_3$) is the maximum [Fig. 6(a)]. As long as the flux is low enough that 100% RH is maintained at the inner surface of the film, \mathfrak{R} will not depend on film area or thickness. Under this condition, \mathfrak{R} is related directly to the water vapor permeability coefficient, ϕ . This applies to Bionolle films and thicker PEO films.

As the film becomes more permeable, the flux becomes high enough to affect P_2 [Fig. 6(b)]. The RH at the inner side of the film will be less than 100%, with the actual value depending on the flux through the film. Increasing the area of a highly permeable material such as the thin PEO film increases the flux enough to affect the RH at the inner side of the film (P_2). This has the effect of decreasing Δp and accordingly decreasing \mathfrak{R} . Decreasing the thickness of a highly permeable film has the same effect as increasing the area.

An increase in the air gap also reduces P_2 at the inner surface of a highly permeable film. Increasing the air gap from 6 to 8 mm decreased \mathfrak{R} of 1-mil Celgard by about 10% (Fig. 7). Increasing the air gap to the ASTM-recommended standard of 19 mm further reduced \mathfrak{R} to 4700 g mil d⁻¹ m⁻².

Mechanisms of Water Vapor Transmission

For a solid polymer, such as Bionolle or PEO, water vapor permeates the film by sorbing at the entering face, dissolving and rapidly establishing equilibrium, diffusing through the film, and desorbing at the exit face. The mechanism of permeation involves both solution and diffusion. How-

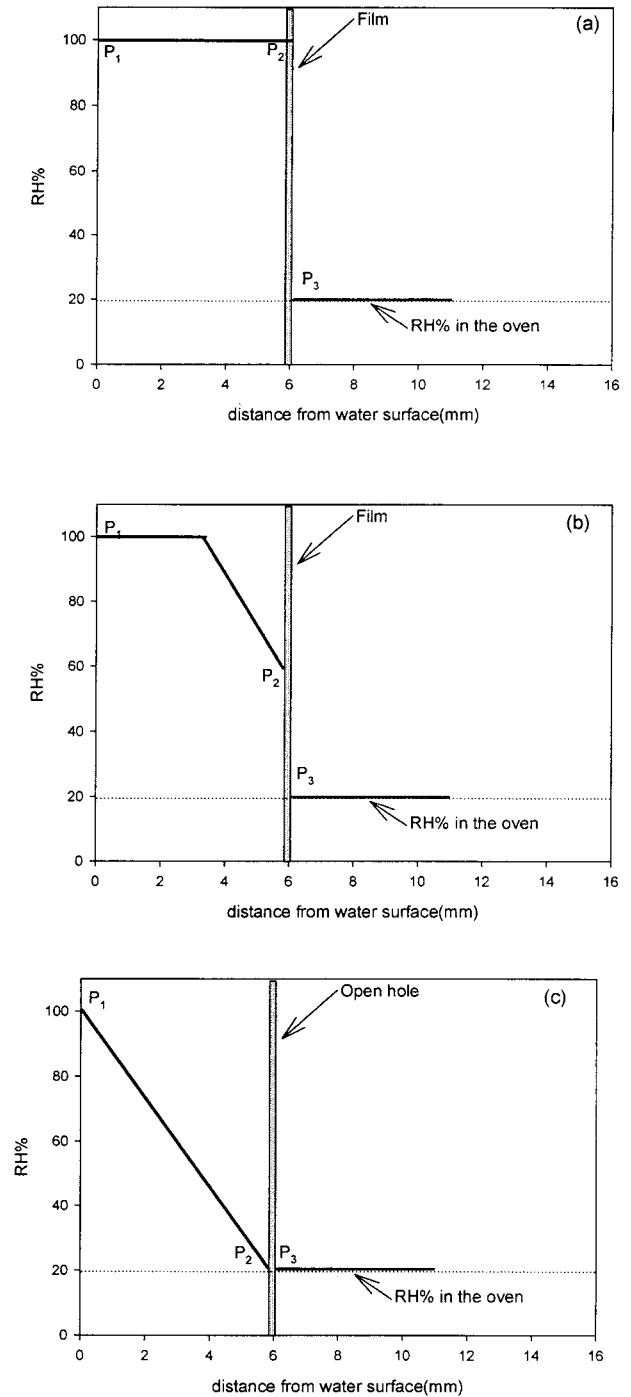


Figure 6 Schematic representations of water vapor pressure in the wet cup test: (a) test film with lower WVTR; (b) test film with higher WVTR; and (c) open cup.

ever, the high water vapor permeability of Celgard results from a microporous morphology comprised of crazes and fibrils (Fig. 8). The primary mechanism of water vapor transmission is

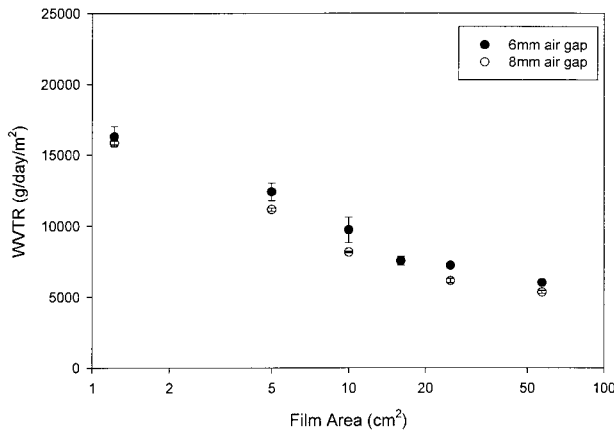


Figure 7 Effect of film area on WVTR of Celgard film for different air gaps.

assumed to be free-particle diffusion through large, nonadsorbing pores (Knudsen diffusion) under a partial pressure gradient.

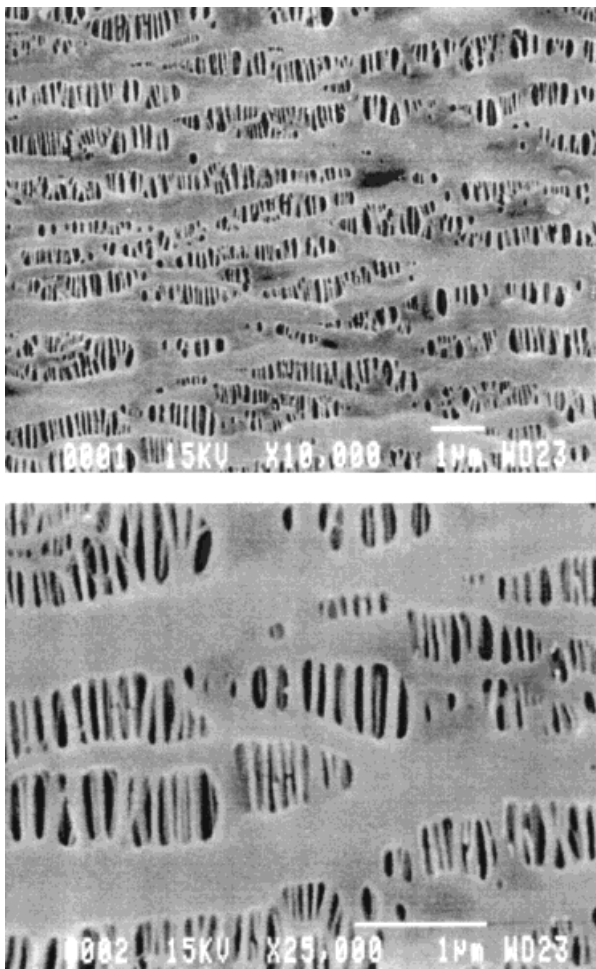


Figure 8 Scanning electron micrographs of Celgard film showing microporous morphology.

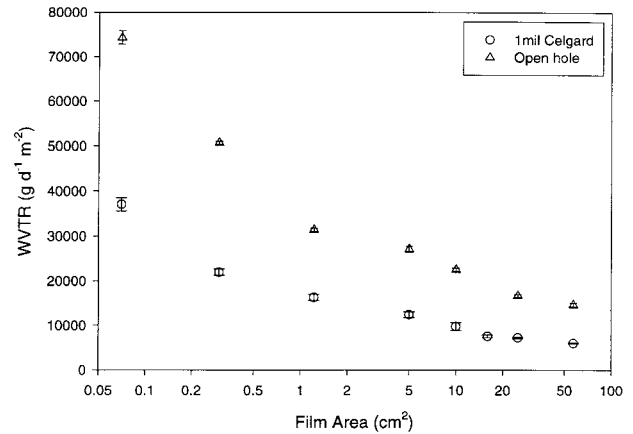


Figure 9 Effect of film area on WVTR through 1-mil Celgard film compared with WVTR through an open hole.

Because water vapor transmission through Celgard film occurred by Knudsen diffusion, a test dish that is covered with Celgard film could be considered as an open cup that is masked to reduce the area for transmission of water vapor. In Figure 9 the WVTR through 1-mil Celgard film is compared with WVTR through an open hole. The WVTR increased from 6,000 to 37,000 g d⁻¹ m⁻² as the area of 1-mil Celgard film decreased from 57 cm² to 7 mm². In comparison, the WVTR through an open hole increased from 14,700 to 74,060 g d⁻¹ m⁻². The WVTR through the open hole was only a factor of 2 larger than the WVTR through Celgard. Moreover, the proportionality did not change with area (Table II).

The area of an open hole with the same WVTR as Celgard film is included in Table III. Regardless of the Celgard film area, the flux through 1-mil Celgard was equivalent to the flux through a hole of about a third the area. The continuous microporous structure responsible for the high WVTR of Celgard also explained the small thickness dependence of WVTR. The pores were sufficiently large and numerous that stacking several 1-mil films did not seriously disrupt the continuity of the porous pathways, and hence the effective hole area was only slightly reduced.

The complex geometry of the masked cup precluded precise calculation of the RH at the inner film surface (P₂). However it was possible to demonstrate a significant reduction in P₂ in the unmasked cup under test conditions of high water vapor flux. The water vapor permeability of stagnant air has not yet been precisely determined. Permeability is defined as the time rate of water

Table II Comparison of Area Effect on WVTR Measurement Between Open Hole and Celgard

Area (cm ²)	Open Hole		1-mil Celgard		$WVTR_{\text{hole}}/WVTR_{\text{Celgard}}$
	Flux (g/d)	$WVTR$ (g d ⁻¹ m ⁻²)	Flux (g/d)	$WVTR$ (g d ⁻¹ m ⁻²)	
57 (ASTM)	83.8	14,700 ± 410	34.3	6020 ± 80	2.4
25	41.8	16,700 ± 300	18.1	7230 ± 150	2.3
10	22.5	22,500 ± 380	9.7	9720 ± 900	2.3
5	13.6	27,100 ± 700	6.2	12,400 ± 620	2.2
1.22	3.8	31,400 ± 400	2.0	16,300 ± 710	1.9
0.3	1.5	50,700 ± 300	0.66	21,940 ± 700	2.3
0.07	0.52	74,060 ± 1500	0.26	37,030 ± 400	2.0
No hole	0.020				

vapor transmission through unit area of unit thickness induced by unit vapor pressure difference between two specific surfaces. Currently, many European standards use Schirmer's equation to calculate the water vapor permeability of the still air layer in the cup:

$$\phi_{\text{air}} = \left[\frac{2.306 \times 10^{-5} P_o}{R_v T P} \right] \left[\frac{T}{273.15} \right]^{1.81} \quad (3)$$

where T is the temperature (K), P is the ambient pressure (Pa), P_o is the standard atmospheric pressure (101,325 Pa), and R_v is the ideal gas constant (461.5 J K⁻¹ kg⁻¹ for water). The water vapor transmission rate is obtained from the permeability as

$$WVTR = \frac{\phi_{\text{air}} \Delta P}{W} \quad (4)$$

where W is the thickness of the air layer and ΔP is the pressure difference between the two surfaces.

In the present study ($T = 37^\circ\text{C}$), the ϕ_{air} obtained from eq. (3) was 2.0×10^{-10} kg m⁻¹ s⁻¹

Pa⁻¹. The air-layer thickness in the open cup [Fig. 6(c)] was 6 mm, and the RH difference ($\Delta P = P_1 - P_3$) was 80% (from 100% to 20%). The saturation vapor pressure of water at 37°C and 1 atm was 6265 Pa. Using eq. (4), the $WVTR$ in the uncovered cup was 14,500 g d⁻¹ m⁻², which corresponds closely to the experimental value of 14,700 g d⁻¹ m⁻². On increasing the air-layer thickness in the open cup to the ASTM-recommended 19 mm, the $WVTR$, calculated from eq. (4), was 4670 g d⁻¹ m⁻². This coincides with the measured $WVTR$ of 1-mil Celgard with a 19-mm air gap, suggesting that under these conditions the test measured the rate at which water evaporated and diffused through the air layer. In the present study, utilizing a 6-mm air gap, most tests were performed under conditions of P_2 intermediate between 100% RH and 20% RH .

Comparison of WVTR for Various Materials in the Cup Test

The procedure recommended by ASTM E 96-95 requires the $WVTR$ to be measured on a film area comparable to the water surface area. In the present study the largest test area (57 cm²) was

Table III Area of Open Hole Required to Achieve Same Water Vapor Flux as Celgard Film

Area (cm ²)	Flux of 1-mil Celgard (g/d)	Area of Open Hole to Achieve Same Flux as Celgard (cm ²)	$\text{Area}_{\text{Celgard}}/\text{Area}_{\text{open hole}}$ for Same Flux
57 (ASTM)	34.3	18.4	3.0
25	18.1	7.9	2.8
10	9.7	3.5	2.6
5	6.2	1.9	2.9
1.22	2.0	0.4	3.1
0.3	0.66	0.1	3.1
0.07	0.26	0.03	2.4

Table IV Approaches for Comparing WVTR of Different Materials

	<i>a</i>	<i>b</i>	$WVTR_{\text{film}}/$ $WVTR_{3\text{-mil Bionolle}}$ as ASTM (57 cm ²)	$WVTR_{\text{film}}/$ $WVTR_{3\text{-mil Bionolle}}$ at Small Area (1 cm ²)	$WVTR_{\text{film}}/$ $WVTR_{3\text{-mil Bionolle}}$ at Constant Flux (1 g/d)
Open air	3.75	0.76	49	125	197
Nonwoven 0.4	1.94	0.75	25	65	83
Nonwoven 0.65	1.93	0.76	25	64	82
1-mil Celgard	1.73	0.73	20	58	73
Paper	1.51	0.76	19	50	57
2-mil Celgard	1.40	0.76	18	47	54
3-mil Celgard	1.16	0.78	17	39	42
4-mil Celgard	1.05	0.77	14	35	37
1.6-mil PEO	0.71	0.79	11	24	22
4.2-mil PEO	0.29	0.96	8	10	9
6.5-mil PEO	0.19	0.99	6	6	6
B/PEO 90/10	0.15	0.95	5	5	5
1-mil Bionolle	0.09	0.98	3	3	3
3-mil Bionolle	0.03	0.99	1	1	1

the same as the water surface area and therefore met this ASTM condition. The $WVTR$ of 57-cm² films was compared to the $WVTR$ of the material with the lowest permeability (3-mil Bionolle), listed in Table IV. In this comparison the most permeable film, a nonwoven material (NW-0.4), was 25 times more permeable than Bionolle.

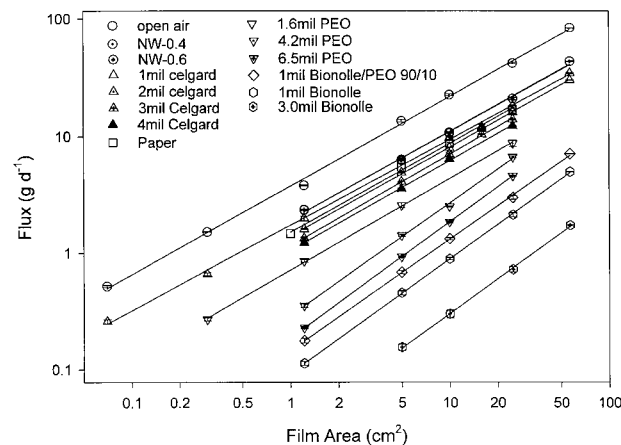
As the present study demonstrated, the driving force for water vapor transport through a film (P_2) is considerably reduced if the flux through the film is high. Accordingly, the measured $WVTR$ is lower than it would be if $P_2 = P_1$. A larger film area, which increases the flux, magnifies the effect. By requiring the largest film area, the ASTM condition is the most likely to give misleading results, especially in comparing the $WVTR$ of materials with vastly different water vapor permeabilities. Decreasing the film area relative to the water surface area lessens the effect. In a comparison of the $WVTR$ for 1-cm² films (Table IV) the permeability of the nonwoven material (NW-0.4) increased to 65 times that of 3-mil Bionolle because of the increase in P_2 for the smaller film area.

For the most permeable materials the flux through even a 1-cm² film was high enough to affect P_2 . That with decreasing film area the \mathfrak{R} for Celgard films did not converge to a limiting value (Fig. 5) means that even the smallest area used in the study did not produce a low-enough flux to meet the condition $P_2 = 100\% RH$. Rather than base comparisons on a constant-area $WVTR$

value, a more satisfactory approach is to compare materials under conditions of constant flux. Empirically, the flux, F , exhibited a power law dependence on the film area, A :

$$F = a \times A^b \quad (5)$$

where flux is expressed in g d⁻¹, A is expressed in cm², and a and b are constants. Values of a and b from the plots in Figure 10 are included in Table IV. The parameter b reflects the effect of film area and thickness on ΔP . If b is unity, then \mathfrak{R} , the specific $WVTR$, is independent of film area and


Figure 10 Logarithmic plot of water vapor flux (F) versus film area (A) for various films.

thickness. In this case, a is the $WVTR$. Only the least permeable films met the condition of b equal to unity. Although the parameter b must approach unity at low flux, the data for the more permeable films fit eq. (5), with b values of 0.73–0.79.

The film area required to achieve a low flux of 1 g d^{-1} (A_{film}) was calculated from eq. (5) using the parameters in Table IV, and the films were compared as:

$$\frac{WVTR_{\text{film}}}{WVTR_{3\text{-mil Bionolle}}} = \left(\frac{A_{\text{film}}}{A_{3\text{-mil Bionolle}}} \right)^{-1} \quad (6)$$

In this comparison the nonwoven material (NW-0.4) was 83 times more permeable to water vapor than 3-mil Bionolle. Of the three methods for comparing the $WVTR$, the constant flux approach came closest to achieving conditions of comparable P_2 . The result for a small area (1 cm^2) was close to the constant flux approach, although for the highly permeable Celgard and for nonwoven materials, the $WVTR$ from the two methods differed significantly. The deviation of ASTM E 96-95 from the constant flux result was significant even for 1.6-mil PEO film, and the deviation became very large as the permeability increased. The three methods gave essentially the same results only if the permeability was relatively low (Bionolle and thick PEO films.)

Decreasing the film area is one method for approaching the condition $P_2 = P_1$. However, as demonstrated in Table IV, decreasing the film area to less than 2% of the water surface area is not sufficient among the materials compared to eliminate differences in driving force, although the comparison based on a small area produced a much better correlation with the constant flux result than the ASTM condition did.

Decreasing the air gap in the cup is another approach to increasing P_2 at the inner surface of a film with a high $WVTR$. The ASTM E 96-95 standard suggests an air gap of $19 \pm 6 \text{ mm}$ to avoid contact between water and specimen. This is considerably larger than the 6-mm air gap used in this study. Even carrying out the experiment very carefully with a small air gap was not satisfactory for comparing materials with large differences in $WVTR$, especially when using a film area equal to the water surface area, as required by the ASTM method.

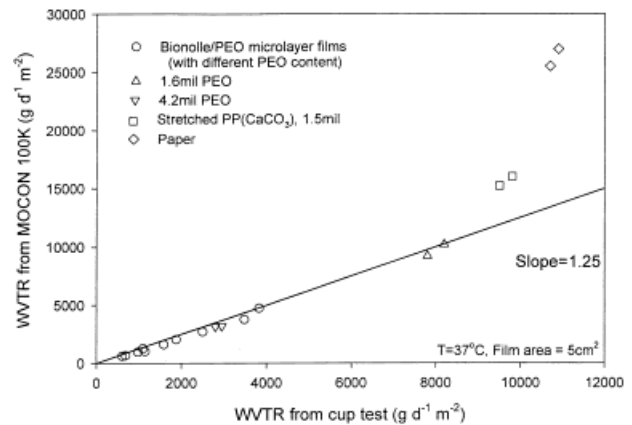


Figure 11 Comparison between $WVTR$ obtained from the wet cup test and $WVTR$ measured with MOCON 100K for a 5-cm^2 film area.

Comparison of $WVTR$ by Different Tests

The cup tests were compared with results from a commercial instrument that was recently introduced to test the $WVTR$ of highly permeable films. In the comparison experiments the $WVTR$ of 5-cm^2 films was measured with the wet cup method at 37°C , and the same films were tested in the MOCON Permatran-W 100K at 37°C . For this study a series of films with different water vapor permeabilities was prepared by varying the ratio of Bionolle to PEO in coextruded microlayer films. The design of the MOCON test cell precludes a meaningful test of Celgard film. A CaCO_3 -filled polypropylene (PP) film, stretched to create porosity, and regular copy paper replaced Celgard as materials with high water vapor permeability. The 5-cm^2 stretched polypropylene film and the paper were somewhat less permeable than Celgard with $WVTR$ in the cup test of about 9600 and 10,900 $\text{g d}^{-1} \text{ m}^{-2}$, respectively, compared to 12,400 $\text{g d}^{-1} \text{ m}^{-2}$ for a 5-cm^2 area of Celgard film. The MOCON results and the cup test of 5-cm^2 films correlated well if the $WVTR$ was less than about 10,000 $\text{g d}^{-1} \text{ m}^{-2}$ (Fig. 11). The higher driving force ($P_2 - P_3$ in Figure 6) of the MOCON, 100% RH compared to 80% RH in the wet cup test, required the correlation to have a slope of 1.25. If the $WVTR$ were higher than 10,000 $\text{g d}^{-1} \text{ m}^{-2}$, the MOCON produced higher values of $WVTR$ than the cup method with a 5-cm^2 test area. This was anticipated from the previous demonstration that P_2 in the cup test decreases as the film becomes more permeable. For example, the $WVTR$ of stretched PP and paper was 15,600 and 26,000 $\text{g d}^{-1} \text{ m}^{-2}$ from the MOCON, as com-

Table V Comparison of WVTR ($\text{g d}^{-1} \text{m}^{-2}$) Measurements of Highly Permeable Films

	Constant Flux (1 g/d) ^a	MOCON 100K
Stretched PP	18,100	15,600
Paper	21,400	26,000
Celgard	26,500	Not measurable

^a Corrected for 100% RH.

pared to 12,000 and 13,600 $\text{g d}^{-1} \text{m}^{-2}$ (after correction to 100% RH) from the 5-cm² cup test. The WVTR for the same area of 1-mil Celgard, corrected to 100% RH, would have been 15,500.

The MOCON results were also compared with the constant flux method (Table V). A value of 18,100 $\text{g d}^{-1} \text{m}^{-2}$ for the constant flux (1 g d^{-1}) WVTR, corrected to 100% RH, was estimated for stretched PP film using the WVTR of a 5-cm² film and eq. (5) with $b = 0.79$. This was in fairly good agreement with the MOCON result of 15,600 $\text{g d}^{-1} \text{m}^{-2}$. The MOCON result for paper of 26,000 $\text{g d}^{-1} \text{m}^{-2}$ exceeded the constant flux value of 21,400 $\text{g d}^{-1} \text{m}^{-2}$. It has already been noted that the MOCON design precludes meaningful WVTR measurements of Celgard, a film with a higher WVTR than paper. Attempts to measure the WVTR of Celgard with the MOCON gave irreproducible and improbably high values. Celgard would have a constant flux (1 g d^{-1}) WVTR of 28,300 $\text{g d}^{-1} \text{m}^{-2}$ (corrected to 100% RH). It was concluded that the MOCON results correlate well with the constant flux method for materials with moderate to high WVTR, up to about 20,000 $\text{g d}^{-1} \text{m}^{-2}$. However, the MOCON appears to give erroneously high results for very permeable films, that is, those with a WVTR approaching that of Celgard.

CONCLUSIONS

This study, motivated by the growing demand for polymeric films with high water vapor permeabil-

ity and the consequent requirement for reliable evaluation of water vapor transmission rate, has exposed inaccuracies possible with an uncritical application of the wet cup method described by ASTM E 96-95. It was determined that the high water vapor flux through the more permeable films caused a reduction in the driving force for water vapor transmission. Consequently, the WVTR was underestimated. Thus, alternative approaches to data analysis have been formulated that would permit meaningful comparisons among thin films with moderate to high water vapor permeability. Comparisons based on a constant flux condition were considered more reliable than those based on a small test area. The study has established the upper limit in the WVTR for validation of a commercial instrument specifically designed to measure water vapor transmission of highly permeable films.

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