Spectrophotometric Determination of Water Vapor Permeation through Polymer Films

R. V. HOLLAND and R. A. SANTANGELO, *CSIRO Division of Food Research, North Ryde, N.S.W. Australia*

Synopsis

A novel method for measuring the permeation of water vapor through polymer films is described. A cellulose detector film incorporating cobalt chloride in a blue anhydrous form is sealed between two pieces of test film in a specially designed cell. The cell is placed in a controlled temperature and humidity cabinet, and the disappearance of the blue color of the cobalt chloride is recorded spectrophotometrically as water vapor diffuses through the test film into the detector film. This simple method of determining water-vapor-transmission rates is more rapid than standard gravimetric procedures because of the highly sensitive detection technique.

INTRODUCTION

Polymer films are widely used as barriers to restrict the movement of water vapor. The shelflife of some foods, for example, is determined to a large extent by the water vapor permeability of the packaging film used. Both for quality control and for testing new materials, a rapid and economical procedure for measuring the water vapor transmission rate (WVTR) of simple or laminated films is desirable. A simple gravimetric test is commonly used but it is slow.[1] Procedures involving the use of more elaborate equipment are sometimes used when speed is important, but the results may differ from those obtained with the gravimetric method.[2,3]

In the usual gravimetric method a test film is sealed with wax over a metal cup containing desiccant, the cup is placed in an atmosphere of known humidity and temperature, and the amount of water vapor absorbed through the film is determined by weighing at appropriate intervals, usually over a period of several days.

For the rapid methods, the test film or sheet is clamped between a high humidity chamber and a low-humidity (dry) chamber; water vapor diffusing through the film is continuously monitored by suitable sensitive detection systems, such as infrared or electrolytic detectors.[3,4] Permeation rates can usually be determined within minutes or hours, but according to Winrich,[4] while exposure of the hydrophilic surface of a composite film specimen to the low-humidity side of the test cell leads to reproducible results, these will not correlate with the gravimetric value. The reason for this disparity, according to Winrich, lies in the dynamic or changing rate of transfer and the error can easily be an order of magnitude, i.e., 1.5 instead of 15 $g/m^2/day$.

In this paper a new method of measuring permeabilities is compared with the gravimetric method, which, although not necessarily more accurate than other methods, is highly reproducible and is commonly accepted.

EXPERIMENTAL

The new technique is based on a procedure similar to that described for measuring oxygen permeabilities.[5] A transparent cellulose film containing anhydrous blue cobalt chloride as moisture detector is sandwiched in a brass microcell between two pieces of the film to be tested. The system is held at a known temperature and humidity, and the amount of water vapor permeating through the test film is determined at intervals by measuring the decrease in optical density of the detector film at 690 nm.

Detector Film

Cobalt chloride is blue when dry and pink under humid conditions, both in the solid state and in a number of solvent media. Cellulose films (British Cellophane 30 μm thick) were soaked in 2.6–2.8M aqueous cobalt chloride solutions for about 30 min. The films were removed, wiped on filter paper, dried in a stream of warm air until the color changed from pink to bright blue, and then stored in a desiccator over calcium chloride. The initial absorbance of the resulting detector at 690 nm was optimally between 1.5 and 1.9 for this application, and, as the films absorbed moisture only at high humidities, they could be stored indefinitely under low-humidity conditions ($\leq$20% RH); the films were still pale blue at relative humidities up to about 50%, but rapidly turned pink ($<$ 10 min) at humidities and temperatures normally used for permeability determinations (75% RH at 25°C and 90% RH at 38°C).

As the dry films were rather brittle, they were cut to shape for the cell before drying. Dry detector films remained transparent indefinitely, but if they were exposed for several cycles of moisture absorption and drying, they tended to become clouded because of leaching of salt from the film.

Microcells

Simple microcells were made from two identical brass plates (6 cm × 6 cm × 0.6 cm) with oblong apertures (about 4 cm^2) at the centers.[5] A copper wire gasket of the same shape but slightly larger than the apertures was used as a seal. A strip of detector film (larger than the gasket) was sandwiched between two pieces of test film and laid over the aperture of one of the brass plates. The gasket was placed on top of the film, and the second brass plate was placed on top of the gasket and screwed to the bottom plate with three triangularly placed screws. Hence the gasket sealed the detector film in an airtight envelope and defined the permeation area. The apertures allowed the water vapor from a controlled atmosphere (a constant temperature humidity cabinet) access to the exposed surfaces of the test film. The cell was removed at intervals from the controlled atmosphere and placed in a spectrophotometer, where the change in absorbance of the detector film was monitored through the apertures in the cell. Unless otherwise stated, test films were conditioned before the measurements by holding them overnight in humidity cabinets at the test humidity.

Calibration of Detector Film

The detector film was calibrated by comparing absorbance change with weight change. Samples of detector film were sealed in pouches of low-density polyethylene or nylon 12 and exposed to moisture in a humidity cabinet. A water uptake of 6.48 g/m² of detector film corresponded to unit absorbance change. The maximum absorbance change corresponded to a measured weight increase of 6 mol water/mol cobalt chloride, in harmony with the formula for cobalt chloride hexahydrate. The molar absorbance coefficient (158 at 690 nm) was determined by extraction of cobalt chloride from detector film of known absorbance value.

Because cellulose is itself a desiccant and will compete with the cobalt chloride for available water and because the permeation rate of water vapor in cellulose depends markedly on its moisture content,[6] it is important to determine the relationship between absorbance change and water uptake (Beer's law) over the range of conditions likely to be used, rather than the restricted range of environments provided by the pouches.

A range of humidity conditions (11–90% RH)[7] and two temperatures (25°C and 38°C) were chosen. The moisture uptake rate of dry detector film was measured by continuous weighing of a 10-cm² sample suspended over a constant humidity solution in a sealed jar: the suspension wire for the sample passed through a small hole in the lid of the jar. In a similar way (Fig. 1), the rate at which the absorbed moisture actually combined with the cobalt chloride in the film was measured by recording the absorbance change (at 690 nm) of the film in a sealed cuvette exposed to the same humidity and temperature conditions as the gravimetric experiments.

At relative humidity conditions above about 20%, Beer's law was found to be obeyed in all cases, at least for the first few minutes of water-vapor absorption. Water vapor continued to be absorbed after the blue color had disappeared, presumably due to absorption by the cellulose. The detector film did not absorb appreciable amounts of moisture at relative humidities below about 20% at either 25°C or 38°C, and hence should not be used at low vapor pressures.

Hence in the spectrophotometric method described in this paper, the quantity q of water absorbed by the detector film is given by $q = 6\Delta a \cdot A_0/\epsilon$, where Δa is the change of absorbance of cobalt chloride in the detector film, ϵ is the molar extinction coefficient, A_0 is the area of the detector film, and the factor of 6 corresponds to the ratio of water molecules per molecule of cobalt chloride. This expression of Beer's law may be strictly true only for the initial rate of absorption under some conditions.

The permeability coefficient of a film for water vapor at a fixed temperature is defined by $p = ql/At\,\Delta p$, where q is the quantity (e.g., mL at STP) of vapor permeating through a film of thickness l and area A in time t with a partial pressure difference across the film Δp; the WVTR = q/At. In the gravimetric technique q is found by weighing, and, if an efficient drying agent such as calcium chloride is used, the vapor pressure inside the cup may be assumed to be zero. In practice there may be a static layer of air on one or both sides of the test film[2] which may reduce the effective pressure. Similarly in the spectrophotometric method, as in other nonsteady state techniques,[4] expressing Δp in pressure units corresponding to the nominal vapor pressures may give erroneously large values of Δp and, hence, low values of P. It is, however, simpler to assume (as is done
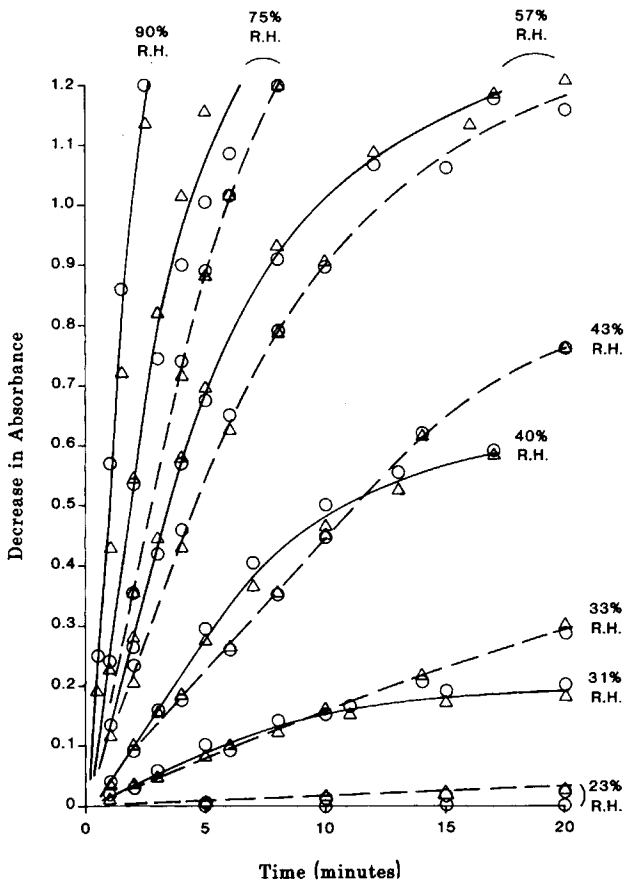
Fig. 1. (——) Detector film absorbance change graphs for 38°C and constant humidities; (-----) detector film absorbance change graphs for 25°C and constant humidities. Two determinations on most films. No detector reponse observed at 11% RH.

in this paper) that Δp equals the test vapor pressure in both procedures, and to calculate the permeabilities of test films on this basis, as the measurement of the true value of Δp is difficult and unnecessary for comparative work.

RESULTS

Figure 1 shows the absorbance change with time of detector films exposed to controlled temperature and humidity conditions. At high humidities the detector film response is linear and remains linear until hydration of the cobalt chloride is almost complete and the blue color has almost disappeared (absorbance difference ~1.2). At lower humidities (<57% RH) the curves flatten out and the detector film remains blue. The time to reach equilibrium is variable, but can take over an hour at lower humidities. At relative humidities of ~23% or lower, there is no change of absorbance (or weight uptake).

In the microcell, where the detector film is sealed within the test film, the detector film response remains linear (Fig. 2) until the absorbance of the film reaches a value of about 0.5, when about 70% of the cobalt chloride has been
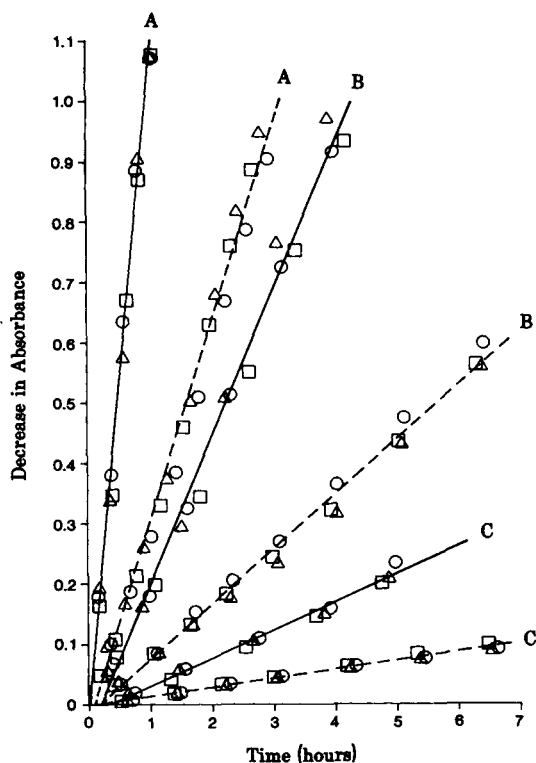
Fig. 2. (—) Absorbance change graphs for 38°C and 90° RH (detector film in microcell); (-----) Absorbance change graphs for 25°C and 75% RH (detector film in microcell). Three determinations on each test film. (A) Nylon 6 film (16 μm); (B) polyethylene terephthalate (13 μm); (C) low-density polyethylene (58 μm)

hydrated (depending on the initial concentration of the desiccant), and the detector film eventually turns pink. Furthermore, the absorbance plots remain linear in some cases for several hours, even though the rates of absorbance change are comparable with the initial rates of the lowest humidity ranges in Fig. 1, which may be linear for only a few minutes.

Commercial samples of nylon 6, polyethylene terephthalate (Mylar A), and low-density polyethylene were chosen as representative test films for Figure 2. These films were conditioned overnight at the humidity and temperature of the test conditions before assembly in the microcell, but films which had not been conditioned gave identical plots, presumably because conditioning was rapid.

The response of a thick material (plasticized cellulose acetate) is shown in Figures 3(A) and 3(B). In this latter case, there is a lag time for moisture to penetrate the film dried over phosphorus pentoxide, whereas [Fig. 3(A)] film conditioned at 75% RH for a similar time showed no delay and a slightly steeper slope.

Water vapor permeabilities calculated from the gravimetric and spectrophotometric measurements on the above materials are shown in Table I. Regression analysis on the seven permeability measurements done by both methods gave a correlation coefficient of 0.99; the spectrophotometric permeability values appear slightly larger, on average, but a scaling constant does not appear war-
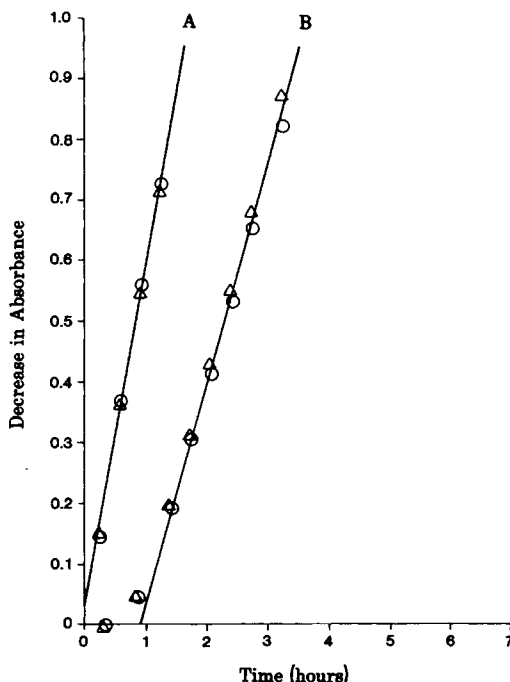
Fig. 3. Absorbance change graphs at 25°C and 75% RH (detector film in microcell). Two determinations on each test film. (A) Plasticized cellulose acetate film (193 μm) conditioned overnight at 75% and 25°C; (B) Plasticized cellulose acetate film (193 μm) dried for 16 h over phosphorus pentoxide.

ranted by the accuracy of the data. Errors are not much larger for the spectrophotometric method, even though the time scale is considerably shorter.

Two gravimetric runs were done on nylon 6 film over a saturated solution of magnesium chloride to assess the effect of a reduced pressure difference across a hydrophilic test film; the results are included in Table I.

TABLE I

Film	Temp and humidity conditions	Assumed partial pressure difference (kPa)	Water Vapor Permeability [(mL H_2O (STP) · μm)/(m^2 · S · kPA)]	
			Gravim. method ± s.d.	Spectrophoto. method ± s.d.
Nylon 6 (16 μm)	38°C, 90% RH	5.96	10.66 ± .03	6.70 ± .05
	25°C, 75% RH	2.38	4.12 ± .12	5.27 ± .25
	38°C, 90% RH	3.91[a]	15.39 ± .13	—
	25°C, 75% RH	1.33[a]	5.89 ± .02	—
Mylar A (13 μm)	38°C, 90% RH	5.96	1.11 ± .01	1.23 ± .08
	25°C, 75% RH	2.38	1.07 ± .03	1.15 ± .05
Low density polyethylene (58 μm)	38°C, 90% RH	5.96	1.01 ± .06	1.06 ± .06
	25°C, 75% RH	2.38	0.63 ± .01	0.84 ± .07
Plasticized cellulose acetate (193 μm)	25°C, 75% RH	2.38	103.8 ± .40	109.8 ± 2.3
	25°C, 75% RH[b]	2.38	—	69.4 ± 3.7

[a] Desiccant: Sat. $MgCl_2$ soln (33% R.H.)

[b] Assembled cell stored for 16 h over P_2O_5 desiccant before permeability measurement.

DISCUSSION

The absorption of water vapor by the detector film is clearly a fairly complex matter, depending on the permeability of cellulose and the degree of hydration of cobalt chloride at each humidity. The detector film is capable of much faster absorbance changes than are shown in Figure 2 (cf. Fig. 1), but measuring considerably faster permeation rates would require corrections for detector response time and continuous rather than intermittent recording of absorbance change.

The most surprising difference between Figures 1 and 2 is the prolonged linear absorbance change with time observed in Figure 2 in spite of low water uptake rates. An explanation of these results is as follows: in the controlled humidity environments of Figure 1, no response is observed at 11% RH, a small amount of water vapour is slowly absorbed at about 23% RH, and at higher humidities the cellulose becomes increasingly more permeable and an increasing proportion of the cobalt chloride becomes hydrated. At the test RH values of 90% and 75%, the decrease in absorbance is seen to be rapid and linear until at least 50% of the cobalt chloride (starting absorbance 1.5–1.9) has reacted.

In the enclosed environment of the microcell under test conditions, the internal vapor pressure increases until it is equal to the external vapor pressure and the detector film becomes pink. Once absorption of the water vapor starts (presumably at a relative humidity of about 23%) the rate of pressure increase inside the microcell may diminish, but there is no possibility of the reaction ceasing at a lower vapor pressure than the test RH. Furthermore, the water vapor absorption remains linear, as in the highest humidity curves in Figure 1, until at least 50% of the cobalt chloride has reacted. An increase in the initial absorption rate is not likely, as this would imply that the test film permeability was increasing. On the other hand, a decrease in the initial rate of absorption because of slow equilibration or depletion of anhydrous cobalt chloride (as in Fig. 1) is opposed successfully for a considerable time by the increasing pressure in the microcell; as the internal pressure approaches the test conditions the linearity can no longer be sustained.

The upper limits for water vapor transmission rates are given by the detector response curves at 90% and 75% RH in Figure 1. Water vapor transmission rates of nylon 6 (the most permeable of the test films) is at least 20 times slower than this rate. There appears to be no minimum response rate (the slowest rates in Fig. 2 are considerabley slower than the RH 23% rates of Fig. 1), but a lag time before reaction starts might occur. Since a linear response occurs at all permeation rates tested in Figure 2, it might be possible to estimate the initial pressure over the detector film, and hence the initial pressure difference across a test film, by calibrating the slope of the detector response in the microcell against slopes obtained at known vapor pressures, such as in Figure 1. In practice, this calibration may not be necessary, for direct scaling to results obtained by gravimetric or other methods (as is done in this paper) is likely to be more convenient and accurate. Since the absorbance change gradient is linear, and the slope of this line is all that is required for permeability calculations, it is a simple matter to collect sufficient data for an accurate determination of the slope; for a satisfactory measurement the consumption of cobalt chloride may be over 50% (nylon 6) or a few percent (polyethylene).

Within the wide range of permeability values measured under the different

conditions shown in Figure 2, the correlation between the gravimetric and spectrophotometric permeabilities is good. Hence for films which have been conditioned for a sufficient time, equivalent results can be obtained by the two methods, over a permeability range of most practical interest.

The absorbance/time plots in Figure 2 and also 3(A) are all linear and pass through or close to the origin. Plots from conditioned films are expected to pass thorugh the origin, as little delay occurs before the steady state transfer of water vapor begins.

When a thick film not at equilibrium with the test conditions [e.g., a dried film, in the most extreme case, as in Fig. 3(B)] is tested by the spectrophotometric method, the time for moisture to pass into the detector depends on the water vapor diffusion coefficient of the test film.

Of course, the present procedure leads to a holdup time, as the moisture is detected not when it first penetrates the test film, but when the RH exceeds 23% in the dead space (~0.1 mL) between the films. Since the amount of water required for this purpose is extremely small (a few nanomoles) the detector response time should compare very favorably with that found in other techniques.

It should be noted that the permeability obtained from the dried film [Fig. 3(B)] is significantly smaller than that obtained from a thoroughly conditioned film [Fig. 3(A) and Table I], presumably because some time is necessary for the film to relax to a more plasticized state. If such data have to be used for rapid permeability determinations, they can be empirically calibrated against the steady state permeability obtained from conditioned film, as is done with any rapid method.

Laminated films have not been considered in this comparison between gravimetric and spectrophotometric procedures, because in many cases conditioning times may be too long[8] to allow a rapid determination of transmission rates (a problem shared by all rapid methods) and in some cases the transmission rates are different if the hydrophilic or hydrophobic side faces the detector. In spite of these complexities, rapid nonequilibrated transmission rates may often be readily measured, and calibrated against steady-state values as for thick films; in many cases too, rapid equilibration can be expected, as with thin single web films.

While the correlation between the gravimetric and spectrophotometric methods is in general good, there are some discrepancies. Except for nylon 6 at 38°C and 90% RH, the spectrophotometric permeabilities appear slightly higher than the gravimetric. As calcium chloride is a more efficient desiccant than the detector film (which does not absorb moisture at RH values below about 20%), such a trend seems surprising. On the other hand, the close contact between the drying surface (the detector film) and the inside surface of the test film in the microcell essentially eliminates the possibility of a static air layer between the two surfaces, which is characteristic of the gravimetric method.[2] Except at high internal humidities, the balance of these effects appears to give slightly larger permeabilities by the spectrophotometric method.

For nylon 6 at 90% RH and 38°C, the gravimetric method appears to give much higher values than the spectrophotometric method (Table I). Similar results were obtained for thin films of cellulose where high WVTRs were experienced. The relationship between permeability and vapor pressure breaks down for such

films,[6] due to the hydrophilic nature of the polymer. When saturated magnesium chloride solution (33% RH), instead of calcium chloride, was used as a desiccant with nylon 6 in the gravimetric method, the film became considerably more permeable (Table I). Presumably, this was because of the plasticizing effect of water vapor on the film. Direct comparison of two methods, using nylon films as test material, requires that the vapor pressure be controlled on both sides of the film, which is usually not possible.

In any case, according to Newns,[2] the simple gravimetric method is entirely unsuited to materials with a very high permeability to water vapor, such as regenerated cellulose; consequently, some other method should be used if calibration of spectrophotometric permeabilities at very high vapor transfer rates is required.

CONCLUSION

The spectrophotometric technique described in this paper is simple and precise, and does not require elaborate detection systems. An advantage of the new method is the possibility of more rapid (by an order of magnitude) permeability determinations. If proper precautions are taken to standardize the method against other procedures, reliable permeability values can be obtained; faster or slower permeation rates than those considered here should be measurable with suitable modifications and calibrations of the method.

References

1. British Standard 3177, 1959.
2. A. C. Newns, *J. Text. Inst.*, **41**, 269 (1950).
3. R. M. Husband and P. J. Petter, *Tappi*, **49**, 565 (1966).
4. K. M. Winrich, *Tappi*, **54**, 1302 (1971).
5. R. V. Holland, M. L. Rooney, and R. A. Santangelo, *Angew. Makromol. Chem.*, **88**, 209 (1980).
6. J. Crank and G. S. Park, *Diffusion in Polymers*, Academic, London, 1968, pp. 259–313.
7. L. B. Rockland, *Anal. Chem.*, **32**, 1375 (1960).
8. E. G. Davis, *Food Technol. Austr.*, **22**, 62 (1967).