Vapor Permeabilities by Dynamic Sorption

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Synopsis

A new method of measuring the permeability of plastic films to vapors is described. The method is simple and convenient, uses general-purpose equipment, and gives good results in a short time. It is easily adapted to vapors other than water vapor. This method is recommended for measurements of permeability where the expense of specialized equipment is not justified. Further studies on effects of parameters such as temperature, humidity, solvation of polymer, etc., are under way.

INTRODUCTION

The wide use of plastic film for packaging has created the need for measuring vapor transfer rates through film. Fairly sophisticated instruments have been developed for water vapor transfer, but there are many laboratories which cannot afford the necessary investment, particularly if determinations are to be made only occasionally. Also, there are always situations where a rigorously designed instrument does not permit enough flexibility. A simple and convenient method of vapor transfer determination will therefore still be of considerable interest. This is particularly true of a method which is also useful for organic vapor permeability.

In the conventional methods of film testing, such as the ASTM methods for water vapor transfer[1] and for gas transmission,[2] tests are made on a flat piece of film. In the WVT method, a metal container is used, and this introduces somewhat of a weight penalty, because relatively small amounts of water vapor weight have to be measured. If the separate container were to be eliminated, improving weighing accuracy and perhaps greater convenience could be attained.

Moisture permeability by a radioactive tracer technique has been reported.[3] It is precise, sensitive, and rapid, but the use of radioisotopes creates special problems.

Hennessy, Mead, and Stening[4] have made a comprehensive survey of methods for permeability measurements of plastic films. One of the methods described is the "pouch" method developed by K. D. Jeffs and by E. P. Noble and reported in unpublished articles. This method was used to

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measure the permeability of plastic films to oxygen.   Heat-sealed packets containing nitrogen were stored under test conditions, and the oxygen content was measured at intervals by gas chromatography.

Hennessy and co-workers[4] recommend the pouch method for water vapor transmission measurements, and note that standards for the method are under consideration both in England and the United States.

EXPERIMENTAL

Dynamic Sorption Technique

In our adaptation of the pouch method, the pouch is suspended from the arm of a balance.   Either the pouch contains water and the air outside the pouch is dry, or a solid or liquid desiccant is inside the package and the air outside the film is saturated or at a controlled humidity.   Because of the sensitivity of analytical balances, measurements can usually be completed in a relatively short time.
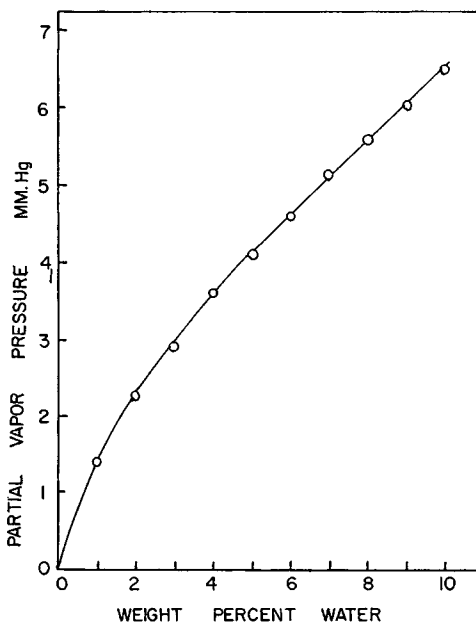

Fig. 1. Partial vapor pressure of water over glycerin solutions at 25°C.

It was shown by Yasuda and Stannett[5] that water vapor diffusion through a polyethylene film is the same whether liquid water is used in contact with the film or if saturated water vapor is used.   This represents the situation where there is no interaction between liquid and film material.   The present method is so versatile that vapor transfer determinations can be made also with solvents which interact with the polymer film, so that the solvent both passes through the film and dissolves in it.

The success of the method depends on two conditions: (1) the air outside the packet is saturated or at a fixed controlled humidity, and (2) the vapor pressure inside the packet is negligible. This applies to operation with desiccant inside the packet. For operation with solvent inside, the locations of saturated and of solvent-free air are interchanged.

Although direct measurement of the vapor pressure was not made, it was observed that condensation took place at a degree or less below room temperature on objects which were suspended in the humidity chamber. This, in effect, measured the dew point and the approach to saturation.

In some cases, glycerin was the water sorbent inside the packet. If there is good mixing of the permeated water, the vapor pressure of the solution can be calculated from the amount of glycerin and permeated water and from the equilibrium partial pressure curve. A plot, from data by Miner,[6] is shown in Figure 1. For all runs using glycerin, the vapor pressure of the solution was less than 1% of the pressure in the humidity chamber.

For most runs, silica gel was the sorbent. The partial pressure was very low until the sorption capacity was reached. There was a color change in the gel at this point.

A measure of the maximum possible rate of moisture transfer was obtained by using a sample of silica gel in a paper tube. When suspended in the humidity flask, it gained weight steadily at the rate of 0.005 g/min for over an hour. This is many times greater than the rate of weight gain in any of the film permeability measurements. It is concluded that all steps in the transfer process are at equilibrium except the permeation through the film.

Materials

Silicone rubber tubing, Silastic medical grade, 0.330 in. inside diameter with a wall thickness of 0.013 in., was obtained from Dow Corning Corp.

Collagen tubing, 0.55 in. in diameter and 0.17 in. thick, was supplied by the Epoxylite Corp.

Epoxy films were made from commercial epoxy glue by casting on glass. After the films hardened, they were stripped from the glass by soaking in water.

Commercial polyethylene, nylon 6, and polystyrene were used.

Packet Construction

Cast epoxy films were formed into a packet by sealing with rubber cement; polyethylene and polystyrene, by heat sealing; nylon, by hot-melt glue or plastic tape.

Silicone rubber and collagen were available in tubular form. A rubber plug was sealed into one end of the tube, using silicone rubber cement. After the tube was filled with sorbent material, the top was closed with a rubber plug and the joint was made tight by wrapping with wire.

Sorbents

These studies were made with water vapor. The sorbent was in the tube to hold the moisture which diffused in and to keep the partial pressure of water vapor inside the tube at a low value. Both liquid and solid sorbents were used. Glycerin was the liquid absorbent. It is quite hygroscopic and can absorb a considerable amount of water before the vapor pressure above the solution becomes appreciable. Glycerin also has the advantage that it is noncorrosive and not hazardous.

However, glycerin softens some films, and for such materials a solid adsorbent is preferred. Molecular sieves, silica gel, or other drying adsorbents can be used. Results reported here were obtained with commercial silica gel.

Procedure

As shown in Figure 2, the packet hung in a glass jar which had a layer of water in the bottom and a strip of filter paper along the sides to act as a wick and keep the air more nearly saturated.
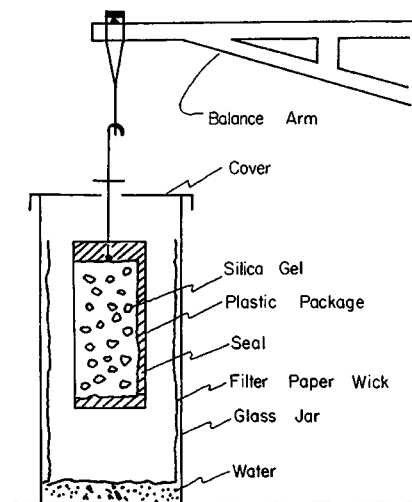

Fig. 2. Diagram of apparatus for dynamic sorption measurements.

The top of the jar was covered and the packet hung from a wire which passed through a small hole in the cover. The gain in weight with time was followed, and the data were used to calculate the permeability coefficient. Experiments were carried out at room temperature, which was 25° ±1°C. A series of measurements were made on polyethylene film at higher temperatures, using a thermostatically controlled air bath.

RESULTS

For polyethylene, all of the weight gain represents permeated water vapor, as a negligible amount of water is dissolved in the plastic at 25°C. The rate of weight increase with desiccant inside the packet is the same as the rate of weight loss with water inside.   This can be seen in Figure 3,
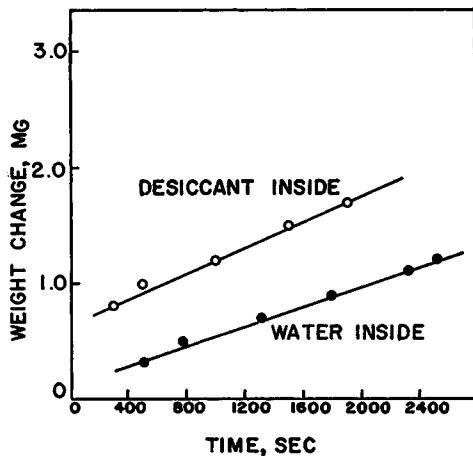

Fig. 3. Weight change for polyethylene pouch, by two different methods.
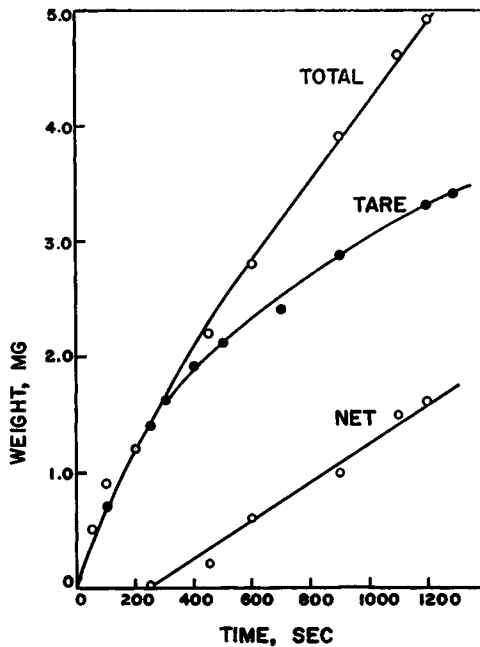

Fig. 4. Permeation of water vapor through silicone rubber, showing correction for adsorption by the film.
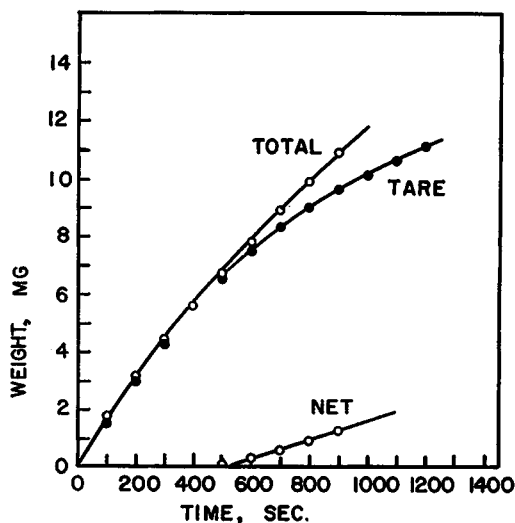
Fig. 5. Permeation of water vapor through nylon 6, which has high absorptivity for water vapor.

which shows the weight changes at steady state for this film. The slopes of the two curves are about the same, indicating agreement in the calculated permeabilities. At higher temperatures, the solubility is not negligible, but the correction is easily made. The transient portion of the curves is not well understood and is still under study.

For many other materials, adsorption of water vapor is significant. For example, Figure 4 shows the weight gain for silicone rubber. The upper curve is the total weight gain, and the middle curve is that for an empty tube of the same dimensions. The lower curve is the difference, which is the weight of permeated moisture. The permeability is calculated from this curve.

With water inside the tube, a similar phenomenon does not take place. All of the weight change represents permeation, and permeabilities calculated in this way agree with those obtained from the runs with desiccant inside.

A typical run for nylon 6 is shown in Figure 5. The permeation is quite small compared to the adsorption, and a run of at least 20 min is necessary to detect and measure the permeation. Usually, an induction period is observed for permeation during which time no moisture permeates the film. This induction period is of the order of 500 sec.

Permeabilities measured by this method are listed in Table I. The standard error, when given, was calculated from replicate measurements on different samples of the same film. The precision of the method is seen to be about ±20%. In some cases for thin films, about 20 min were required for a measurement after the packet was prepared. Less permeable films took somewhat longer, up to 3 hr for reliable results.

TABLE I
Permeabilities of Plastic Film

	Thickness, mils	$P \times 10^9$, std cc-cm/cm²-sec-cm Hg	
		Experimental	Literature values
Collagen	1.7	2170 ± 800	
Silicone rubber	13	1830 ± 210	
Epoxy	4.0	1480 ± 113	
Nylon 6	1.0	94	50[7]
Polystyrene	1.0	65 ± 12	108 to 127[8]
Polyethylene	1.0	11.3 ± 1.6	10[8]; 20[7]; 8.3[5]

Results of measurements on three samples of polyethylene at higher temperatures are shown in Figure 6. The effect of film density, indicative of differing degrees of crystallinity, is evident. The activation energies, proportional to the slope of the lines plotted as log P versus $1/T$, are quite close for the three samples.

ORGANIC VAPORS

Conventional methods of measuring the permeability of plastic films to water vapor are very difficult to use for other vapors. For the ASTM method, it would be necessary to maintain an atmosphere of potentially explosive vapor in an oven. For the Honeywell apparatus, a different
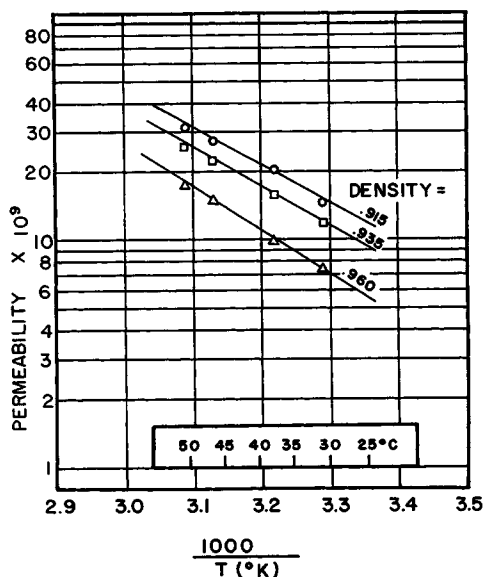

Fig. 6. Permeability of three different polyethylenes as a function of temperature.

sensor as well as considerable redesign to accommodate the organic vapor would be needed.

The method described in this article can be used as easily for organic vapors as for water vapor. This has been described elsewhere.[8]

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