

Permeability of Polymer Films to Sulfur Dioxide at Low Concentration

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Synopsis

A new apparatus is described for measuring the permeability of polymer films to sulfur dioxide at partial pressures down to 2 Pa. It employs a permeation tube technique for establishing the partial pressure gradient and a detection system based on the absorption of light at 213.8 nm. Data on the permeability to sulfur dioxide of a range of polymer films are presented and discussed.

INTRODUCTION

Previous work¹ has shown that the permeation of sulfur dioxide in films of polyethylene, polycarbonate, and polyamide (nylon 11) is pressure dependent over the partial pressure range of 4.0×10^3 to 100×10^3 Pa. Pressure dependence, therefore, is probably a characteristic of the permeability of other polymer films to sulfur dioxide at these pressures. In such systems, data observed at a specific partial pressure cannot be used to calculate reliable permeabilities at other partial pressures unless the relation between permeability and pressure is known.

Loss of sulfur dioxide by permeation occurs when foods containing this preservative are packaged in polymer films.² However, the partial pressures of sulfur dioxide in the headspace of packages of these foods are less than approximately 20 Pa [200 ppm (v/v)], which is well below the lower limit investigated in the earlier studies.¹ There is a need, therefore, for information on the sulfur dioxide permeability of polymer films at low partial pressures for use in food packaging and in work on atmospheric pollution, where organic polymers are used.

This paper describes a new apparatus for determining the sulfur dioxide permeability of polymer films at partial pressures of the order of 2 Pa and above and presents data observed on a range of film materials.

EXPERIMENTAL

Apparatus

The apparatus is shown diagrammatically in Figure 1. It consists of three main components: a cell in which the test sample was sealed, equipment for

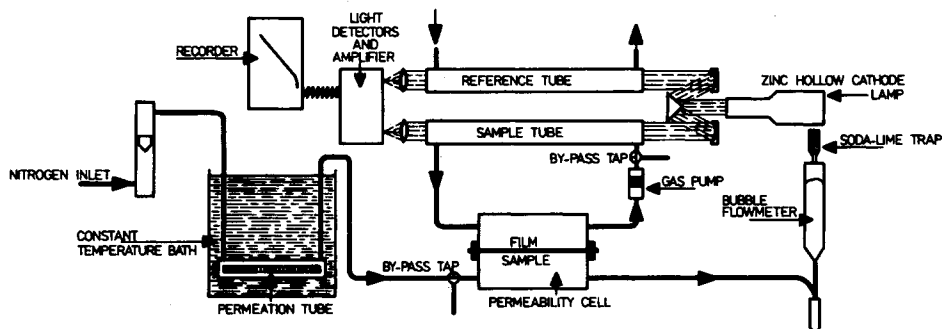


Fig. 1. Schematic diagram of SO_2 permeability apparatus.

establishing a difference in the partial pressure of test gas across the sample, and a detection system for determining the rate of increase in concentration of test gas in the low-pressure side of the cell.

The glass cell was similar to the one described previously,¹ except that it consisted of two compartments and accommodated a single film sample. In operation, the lower compartment was filled with a mixture of sulfur dioxide and inert gas, and the top with inert gas only. Oxygen-free nitrogen was used as the inert gas, and each cell compartment was filled with gas at atmospheric pressure, thus avoiding the necessity for film supports and the possibility of leaks.

The required partial pressures of sulfur dioxide were achieved using the permeation-tube technique described by Scaringelli et al.³ The FEP Teflon tubes (6.35 mm o.d. and 4.76 mm i.d.) were prepared in lengths from 20 to 250 mm and were filled with liquid sulfur dioxide. The tubes were stored over silica gel and anhydrous sodium hydroxide in a desiccator at 5°C until required. In use, the permeation tube was enclosed in a glass tube in a water bath controlled at the required temperature to within $\pm 0.1^\circ\text{C}$. Nitrogen, predried by passing through a column of magnesium perchlorate, was then passed over the permeation tube to produce the required sulfur dioxide-nitrogen mixture. The flow rate of nitrogen was measured by a soap bubble flowmeter.

The detection system was similar to a conventional double-beam absorption meter and was operated at a fixed wavelength of 213.8 nm, where sulfur dioxide absorbs strongly.⁴ The light source was a zinc hollow-cathode lamp, which emits a strong resonance line at this wavelength. An interference filter was used to isolate the line at 213.8 nm from other weaker lines. The light beam was split by a prismatic mirror into two beams which were reflected through a pair of glass tubes, 20 mm i.d. and 500 mm long, each fitted with UV-transparent quartz windows. One tube served as a reference and was flushed with dry oxygen-free nitrogen. The second tube was connected to the measuring compartment of the cell through an all-glass, gas-circulating pump similar to that described by Duncan and Lawson.⁵ The light emerging from the optical tubes was detected by a matched pair of solar-blind phototubes (Type R404, Hamamatsu T.V. Co., Japan). The response from the detectors was amplified and fed to a potentiometric recorder.

In addition to the gas lines shown in Figure 1, other all-glass lines and three-way stopcocks were fitted to supply either pure nitrogen or the nitrogen-sulfur dioxide mixture to either compartment of the cell or to the detector tubes.

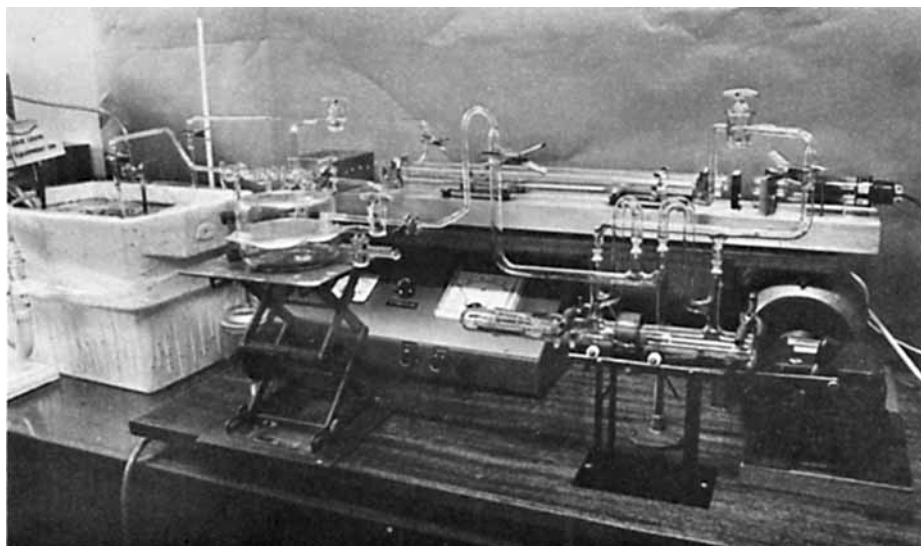


Fig. 2. Apparatus for measuring the SO_2 permeability of polymer films.

Thus, all components could be flushed with nitrogen and the detector set on zero. When the nitrogen stream was directed through the reference tube, the test gas mixture could then be directed into the cell for a permeability determination, or into the measuring tube for a calibration check. Sulfur dioxide was removed from the effluent by absorption in traps containing soda lime or sodium hydroxide solution.

A light application of Apiezon L grease was used on the stopcocks and on the sealing flanges of the cell. This grease was used because measurements using a McBain balance showed that the solubility of sulfur dioxide in the grease at 25°C was low [0.04% (w/w) at a vapor pressure of 3.3×10^3 Pa]. The apparatus was operated in a room controlled at a temperature of $25^\circ \pm 0.5^\circ\text{C}$. The complete apparatus is illustrated in Figure 2.

Calibration

The permeation tubes were separately calibrated in situ by passing nitrogen at a flow rate of 100 ml/min over the tube, bubbling the mixture into a solution of hydrogen peroxide (0.3%) for a known time, and titrating the sulfuric acid formed with sodium hydroxide ($N/100$). The sulfur dioxide trap used was similar to that described by Shipton⁶ and was attached to the first by-pass shown in Figure 1.

Permeation tubes were also used to supply gas mixtures to calibrate the detection system. This was done by flushing the apparatus with nitrogen and adjusting the detector to zero. Nitrogen containing sulfur dioxide was then passed through the sample tube, and the flow rate at the exit end of the tube was measured by a soap bubble flowmeter. The recorder response was noted as a function of the sulfur dioxide concentration calculated from the known tube output and nitrogen flow rate.

The internal volume of the measuring circuit and of the sample tube was required for the permeability calculations. The circuit volume was determined

by sealing a sample of 0.05 mm aluminium foil in the cell and injecting a known volume of carbon dioxide into the nitrogen-filled circuit through a sampling port fitted to the cell. The gas was then mixed by the circulating pump and the concentration of carbon dioxide estimated by gas chromatography. The volume of the sample tube was determined by sweeping the gas mixture from the tube with nitrogen, reconnecting the circuit, and measuring the decrease in carbon dioxide concentration. The estimated volumes of the total circuit and sample tube were 740 ml and 150 ml, respectively.

Operation

Two procedures, a slope method and a concentration increase method, were used for the permeability measurements. The choice of method depended on the rate at which the partial pressure of sulfur dioxide increased in the measuring circuit. Under conditions where the rate was higher than approximately 0.2 Pa per working day, the gas pump and detection system were operated continuously and the permeability calculated from the slope of the recorder trace. With lower rates of permeation, nitrogen was circulated in the measuring circuit until the partial pressure of sulfur dioxide had increased to 0.5 to 1.0 Pa, and the detection system was used to determine the increase over the known time interval. In this method, the sample tube was flushed with nitrogen at the end of the measurement and the instrument zero checked.

RESULTS AND DISCUSSION

By varying the length of the permeation tubes, their temperature, and the flow rate of the carrier gas, a wide range of concentrations of sulfur dioxide may be obtained (Table I).

Figure 3 is an Arrhenius plot of the permeability coefficient versus temperature for a typical Teflon permeation tube. The plot is linear over the 20–45°C range. The activation energy for the permeation process, calculated from the slope of the line, is 4770 J/mole, which is similar to the value of 4520 J/mole reported by Lucero.⁷

The UV detection system was calibrated using partial pressures of sulfur dioxide in nitrogen from 0 to 1.2 Pa. Over this range, the calibration plot was linear, and at maximum sensitivity the calibration factor was 164.2 ± 3 mm/Pa. Based on a signal-to-noise ratio of 2:1, the detection limit of the unit was 0.05 Pa. Although not required in the present work, other observations showed that the response of the detection system is linear up to partial pressures of approximately 5 Pa.

TABLE I
Output Range of SO₂ Permeation Tubes

Tube length, mm	Tube temperature, °C	Carrier gas flow rate, ml/min	SO ₂ partial pressure, Pa
20	20	500	0.049
20	20	25	0.98
20	45	25	6.5
200	45	25	65

TABLE II
Permeability of Polymer Films at 25°C to SO₂ at Partial Pressures from 2.4 to 60 Pa

Material	Thickness, mm × 10 ²	SO ₂ Permeability × 10 ¹⁰ , ml (S.T.P.) × mm × cm ⁻² × sec ⁻¹ × cm ⁻¹ Hg
Polyethylene (low density)	3.8	193
Polyethylene (low density)	6.4	223
Polyethylene (high density)	2.1	56.8
Polycarbonate (Lexan)	2.5	210
Polystyrene	3.8	220
Polyamide (nylon 11)	4.1	21.6
Polypropylene (Propafilm O)	2.5	7.13
PVDC/polypropylene/PVDC (Propafilm C)	2.8	0.103
Poly(vinyl chloride) (rigid)	14.5	1.16
PVDC/regenerated cellulose/PVDC	2.6	0.374
Polyester (Mylar A)	1.3	2.01

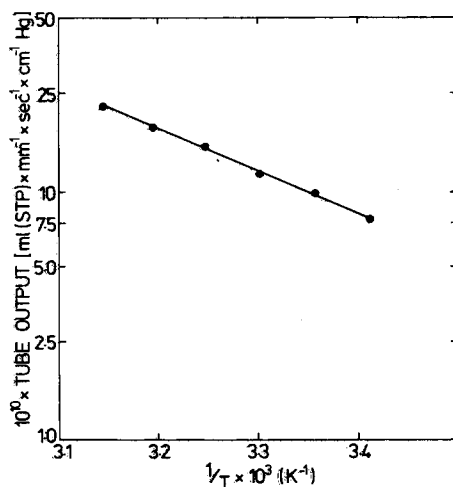


Fig. 3. Effect of temperature on output of SO₂ permeation tube.

Table II shows the data observed on permeability to sulfur dioxide on a range of commercially available polymer films at vapor pressures ranging from 2.4 to 60 Pa. The two PVDC-coated materials, polypropylene and regenerated cellulose, showed lower permeabilities to sulfur dioxide than the remaining homogeneous materials. It is well known that PVDC coatings have good barrier properties to a wide range of gases and vapors. The data observed on the two polypropylene materials show that this applies also with sulfur dioxide. The material coated on each side with PVDC at a nominal thickness of 1.5×10^{-3} mm was approximately 70 times less permeable than the uncoated polypropylene of about the same thickness.

The values shown in Table II for polyamide, polycarbonate, and the two batches of polyethylene agree to within approximately 25% with the values, extrapolated from 4.0×10^3 Pa to near-zero partial pressure, published previously¹ for these types of material. This agreement is reasonable since the tests were made on different batches and thicknesses of material using different methods. Of greater interest, however, is whether the pressure dependence

observed previously with these materials over the range of 4.0×10^3 to 100×10^3 Pa exists within the much lower pressure range used in the present work. Polycarbonate was included in this study since it showed a sulfur dioxide permeability which was highly dependent on pressure. The reason for this behavior has been attributed^{8,9} to structural changes within the polymer arising from the formation of molecular complexes between the penetrant and carbonate groups. Measurements were made at seven partial pressures of sulfur dioxide ranging from 2.3 to 60 Pa. A mean value of $(197 \pm 8.5) \times 10^{-10}$ ml (S.T.P.) \times mm \times cm⁻² \times sec⁻¹ \times cm⁻¹ Hg was observed, but there was no evidence of pressure dependence.

Thus, although the pressure range differed by a factor of more than 25, the concentrations of vapor sorbed were evidently too small to produce sufficient structural change within the polymer to have any measurable effect on the permeation process. A similar study on polyethylene in this low pressure range showed no evidence of pressure dependence.

In the absence of highly anomalous effects, it is clear that pressure dependence is not likely to cause errors of practical importance in estimating gas and vapor permeabilities at the low concentrations used in the present work. For instance, the data for polycarbonate show that the sulfur dioxide permeability increases by 50% from 140×10^{-10} to 210×10^{-10} ml (S.T.P.) \times mm \times cm⁻² \times sec⁻¹ \times cm⁻¹ Hg as the partial pressure is reduced from 4.0×10^3 Pa to near zero. Assuming that the increase is linear, the change in permeability over a partial pressure range from 100 Pa to near zero corresponds to 1.6 permeability units. Thus, even with this highly pressure-dependent system, the difference in permeability is well within the experimental error of the method, and comparable results, therefore, may be obtained at any known partial pressure within this range.

The apparatus described has a number of features which are important in studying the transport of penetrants at low partial pressures in polymer films:

1. Three materials only are in contact with the penetrant in the measuring circuit and in the high-pressure side of the cell and its inlet lines. These are glass, grease on the stopcocks and cell flanges, and the polymer film under test. The silicone rubber septum in the sampling port is faced with a piece of poly(vinylidene chloride) film during the permeability runs to reduce loss of penetrant in the measuring circuit. Since the covered septum has an exposed area of less than 0.01 cm², losses by absorption in, or permeation through, these materials are negligible.

2. The total pressure of gases on each side of the film sample is 1 atmosphere, so the possibilities of leaks and of mechanical damage to the sample are minimized.

3. The gases in each cell compartment are dynamic, so the formation of localized concentration gradients of test vapor is averted.

4. The detection system is nondestructive and may be used to measure the cumulative rate of increase in penetrant concentration. This feature extends the range of permeabilities that may be measured and provides a convenient means for determining when steady-state conditions have been reached.

5. The permeation tube technique represents a convenient means for achieving accurately known, low concentrations of penetrant in the high-pressure side of the cell.

6. Although outside the scope of the present work, the apparatus could be modified to measure diffusion coefficients of sulfur dioxide in polymer films by the time lag method. The major modification required would be a reduction in the internal volume of the glass components so that the gas mixing time is negligible compared with the diffusion time lag.

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