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Development of cost effective facility for measurment of gas permeability of silicone membrane for its sutability for modified atmospheric storage

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ABSTRACT

The silicone membrane consists of a fine nylon fabric covered with a thin and uniform layer of silicone rubber compound: dimethyl – polysiloxane. They have extremely good thermal stability, excellent electric insulating properties, outstanding water repellency, good chemical resistance but very weak strength and often need to be reinforced. The manometric gas exchange with the atmosphere surrounding the packaged material takes place due to various properties of the membrane. Various parameters like areal weight, tearing resistance, water absorbance, bursting strength, tensile properties should be determined before considering the design procedure.

Manometric gas transmission equipment was fabricated to study the gas permeability of the silicone membrane. The silicone film sample is mounted in a gas transmission cell, so as to form a sealed semi- barrier between two chambers. One chamber contains the test gas at a specific high pressure and the other chamber at a lower pressure, receives the permeating gas. The lower pressure chamber is initially evacuated and the transmission of the gas through the test specimen is indicated by the increased pressure.The gas transmission equipment consisted of a manometric gas transmission cell vacuum pump, vacuum gauge, test gas cylinder, mercury manometer and needle valves. The manometric gas transmission cell consisted of a lower plate, made of electroplated mild steel. A vacuum pump capable of reducing the pressure in the system to 26 Pa or less was connected to register the vacuum during evacuation of the system. Just before the upper plate, a mercury manometer was provided for measuring upstream gas pressure to a maximum of 70 kpa. Travelling microscope was used to measure the height of the mercury in the cell manometer leg accurately. The test gases used were dry and pure CO_2 (98.98% CO_2, 0.38% O_2, 0.43% N_2 and 0.21% other gases) and O_2 (99.1% O_2, 0.72% CO_2 and 0.18% other gases).

Key words: Silicone membrane, Manometric gas transmission equipment, Membrane permeability, Modified atmosphere pressure

The silicone membrane consists of a fine nylon fabric (52 to 54 g/m^2) covered with a thin and uniform layer (about 90 (micron); 80 g/m^2) of silicone rubber compound : dimethyl - polysiloxane (Marcellin, 1972 and 1974). The nylon net enhances the mechanical properties of the membrane, while the silicone coating regulates the gas exchange.

Silicone rubbers are unique among the many types of natural and synthetic rubbers available in the sense that instead of the usual chain of carbon atoms, the 'backbone' of their molecules is made of alternate atoms of silicones (Si) and oxygen (O_2) (Roff et al., 1971; Harper, 1975; Yescombe, 1976; Ravindra Naik and Kailappan, 2007; Ravindra Naik et al., 2014). Various organic side groups can be attached to the chain to modify the characteristics. In dimethyl silicone rubber, the organic side groups are CH_3.They have extremely good thermal stability, excellent electric insulating properties, outstanding water repellency, good chemical resistance but very weak strength and often need to be reinforced. For

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coating purpose, dimethyl polysiloxane, a highly viscous liquid is used (Ash and Ash, 1983, Roff et al., 1971).

Mathematics of gas permeability

The mechanism of gas permeation through non porous polymeric films was first elucidated by Stern et al. (1965). This permeation process by which a small molecule permeates through a polymeric film involves four stages (Ashley, 1985; Rogers, 1985).

The mechanism of gas permeation through a non-porous plastic membrane is fundamentally different from the one involved in the diffusion of gases through porous barriers. In the later case, the diameter of the pore is smaller when compared to the mean free path of the gas in the former. The diffusion flux through the barrier will be approximately inversely proportional to the square root of the molecular weight of the gas. Permeability, however, is a resultant of two phenomena, solution and activated diffusion (Rogers, 1985).

Measurement of gas permeability and gas transmission rate

Under steady state conditions, the gas transmission rate (GTR) is defined as the volume of gas permeating through a membrane of unit area, under unit pressure difference (ASTM, 1978).

Many types of instruments have been developed to measure the permeability of gases through polymeric membrane (ASTM, 1978; Ashley, 1985; Griffin et al., 1985 Bosco, 1997; Ravindra Naik et al., 2014). They all have a gas transmission cell in which the membrane sample is mounted to form a sealed barrier between two chambers. One chamber contains the test gas and the other receives the permeant. A pressure or concentration gradient between the two chambers drives the gas from one chamber to the other. The GTR could be determined from changes in gas concentration (Sweep gas technique), from changes in volume (volumetric technique) or from changes in pressure (manometric technique). In the present study manometric technique was used to develop the gas measurement set up.

Manometric technique

The equipment involved in the manometric technique is very similar to that of the volumetric technique. For measurement of GTR, chamber - 1 is pressurized to P_1 with the test gas while chamber - 2 is evacuated to P_2. Here again, the gas flows through the membrane sample under the pressure gradient. When a steady state is reached (i.e., change of pressure as a function of time becomes constant), the GTR is calculated using this technique offers advantages similar to the volumetric method (Edmond et al., 1991; Christie et al., 1995, Bosco 1997).

MATERIALS AND METHODS

Description of the equipment

The gas transmission equipment (Fig. 1) consisted of a manometric gas transmission cell (A), vacuum pump (B), vacuum gauge (C), test gas cylinder (D), mercury manometer (E) and needle valves (F_1,F_2 and F_3). The manometric gas transmission cell (Fig. 2) A_1 consisted of a lower plate (G), made of electro-plated mild steel. On one side of the plate, steps (H) and (I) were provided to place the filter paper and the film to be tested, respectively. The steps were made in such a way that on the film (at the circumference) an 'O' ring could be placed. At the center of the plate, a hollow space (J) was provided to collect the transmitted gas. This hollow space was connected to a calibrated 'U'-shaped cell manometer leg (K) to indicate the pressure of transmitted gas. It was made of precision bore capillary tube of 133 mm long with a bore 5 mm dia. At the other end of this cell manometer leg (K), a cell mercury reservoir (L) was provided which can hold all the mercury (Hz) in the manometer leg. Above the lower plate (G), an upper plate (M) was placed. The upper plate was also made of electro-plated mild steel. A cavity of 90 mm dia size (N) was provided to fill the

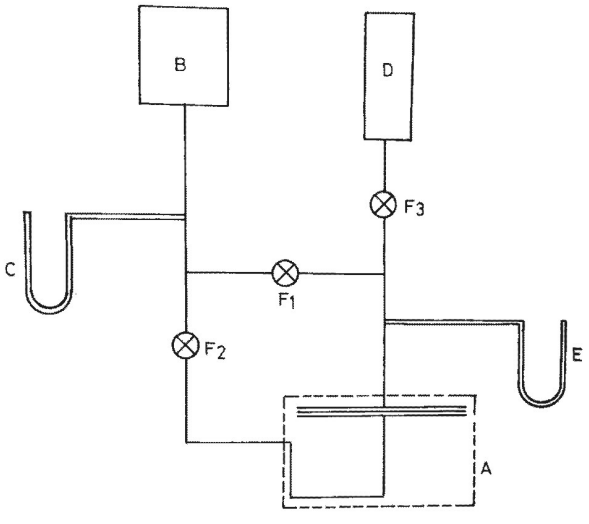
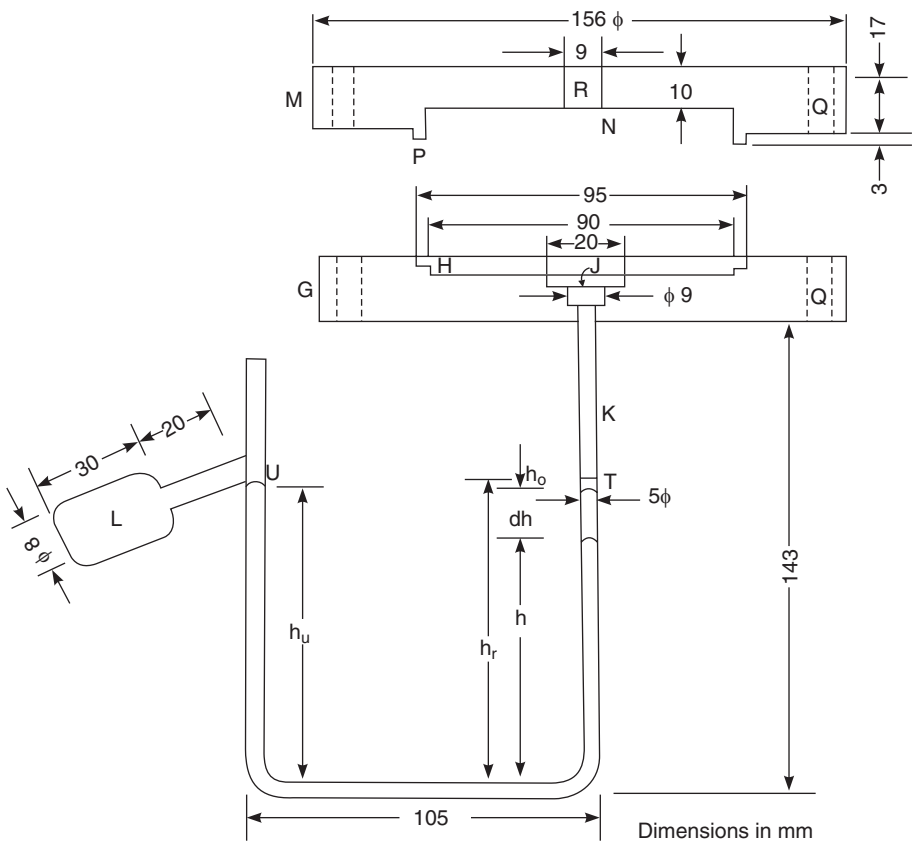


Fig. 1. Gas transmission equipment component arrangement



G. LOWER PLATE
H. STEP FOR FILTER PAPER
I. STEP FOR O RING
J. STEP FOR GAS COLLECTION
K. MANOMETER LEG
L. MERCURY COLLECTING BULB
M. UPPER PLATE
N. SPACE FOR GAS TO BE TRANSMITTER
P. PROJECTION FOR PRESSING THE O RING
Q. HOLE TO INSERT BOLT
R. GAS INLET

Fig. 2. Manometric gas transmission cell

test gas which is to be transmitted through the film. A projection (P) was provided in the upper plate which compressed the 'O' ring placed on the lower plate and made the chamber air tight using bolts and nuts (Q). The cavity of the upper plate was connected to the test gas inlet pipe (R). Vacuum pump (B) capable of reducing the pressure in the system to 26 Pa or less was connected to both upper and lower plates through two needle valves F_1 and F_2 and vacuum gauge (c) to register the vacuum during evacuation of the system. These two needle valves were provided to maintain a vacuum in both upstream and downstream gas lines. The upper plate was connected to the test gas cylinder (D) through a needle valve (F_3). This needle valve was provided for admitting and adjusting the pressure of the test gas slowly. Just before the upper plate, a mercury manometer (E) was provided for measuring upstream gas pressure to a maximum of 70 kpa.

A travelling microscope having a lowest measurement of 0.01 mm was used to measure the height of the mercury in the cell manometer leg accurately. The test gases used were dry and pure CO_2 (98.98% CO_2, 0.38% O_2, 0.43% N_2 and 0.21% other gases) and O_2 (99.1% O_2, 0.72% CO_2 and 0.18% other gases). The ratio of the volume of gas available for transmission to the volume of gas transmitted at the completion of the test was approximately 100:1.

Calibration of gas transmission cell

The void volume of the filter paper was determined from the absolute density of its fiber content, the weight of the filter paper and its apparent volume. High grade, medium retention qualitative non-ashing cellulosic filter paper of 1.45 g/ml cellulose fiber density and 90 mm dia was used. The apparent volume was calculated from the thickness and diameter of filter paper. The void volume was expressed in microlitres (µl) and designated as Vs.

The volume of the cell manometer leg from S to T was determined by mercury displacement. The volume was obtained by dividing the weight of the mercury displaced by its density (13.54 g/cc) and was expressed in microlitres (µl), designated as V_{st}. Similarly, the volume of the cell manometer leg from T to U was determined. The average cross sectional area of the capillary was determined by dividing this volume by the length of capillary from T to U. The area in mm^2 to an accuracy of $0.01mm^2$ was determined and was designated as 'a'. The area of transmission, ie. the area of filter paper was designated as A.

The top surface of the horizontal capillary tube was taken as datum plane. The mercury was poured from the reservoir into the cell manometer carefully by tipping the cell. The distance from the datum plane to the upper calibration line 'T' in the capillary leg was recorded as h_T. The distance from the datum plane to the top of the mercury meniscus (U) in the reservoir leg was recorded as h_u.

Silicone membrane permeability

All the mercury from the capillary was transferred into the reservoir of the cell manometer system by

carefully tipping the cell. The filter paper was centered in the lower plate cavity. A light coating of vacuum grease was applied on the metal surface on which the membrane was seated. The 'O' ring was placed on the membrane at its circumference. The two plates were tightened uniformly using bolts and nuts to ensure air tightness.

The needle valves F_1, F_2 and F_3 were opened. By using a vacuum pump, the bottom of the cell was evacuated. The needle valves F_1 and F_2 were closed. The test gas was allowed to flush the connecting line and the top of the chamber. Again the system was re-evacuated. The mercury was poured from the reservoir into the manometer system of the cell by carefully tipping the cell. The height of the mercury in the capillary leg was recorded just before the release of the test gas into the top of the cell. After a suitable estimated time for attaining a steady state condition, the height of the mercury, h in the capillary tube and the corresponding time, t were recorded at 15 min interval.

For each 't' the function g (h) was calculated using the following equation as defined by ASTM (1978).

$$g(h) = \frac{-1}{ART}\left[(V_f + aC_2\, p_g - h_u + h_T) \times \ln\left(1 \frac{h_o - h}{p_g - h_u} + h_o\right)\right] + 2a\,(h_o - h) \quad (1)$$

where,

A, Area of gas transmission, 6361.72 mm^2; R, Universal gas constant, 8.314x103, l.Pa/ (mol.°K); T, Absolute temperature, 298.15°K; V_f, $(V_s + V_{st})$ = 672.3 + 2932.44 = 3604.74 µl; a, Area of capillary, T_U, 19.635 mm^2; P_g, Pressure of the gas to be transmitted 67 kpa for O_2 and 53 kpa for CO_2; h_u, Height of mercury in cell reservoir leg from datum plane to top of mercury meniscus to 105 mm; h_T, Maximum height of mercury in the cell manometer leg from the datum plane to upper calibration line T, 102mm; h_o, Initial height of mercury in the capillary leg at the start of the actual transmission run after steady state conditions attained, mm; h, Height of mercury in the cell capillary leg at any given time t_1, mm.

The time interval for each observation of permeance measurement was 2 to 5 min and 5 to 15 min for CO_2 and O_2 respectively. Permeance (P) was calculated as,

$$P = \frac{g(h)}{t\text{-}to} \quad (2)$$

where,

P, Permeance of the membrane, mol m^{-2}, s^{-1}, Pa^{-1}; g(h), Calculated value from equation; t, Time at which `h' was measured from capillary cell leg, seconds, and t_0, Time of start of the actual transmission run after the reach of steady state conditions, seconds.

Permeability of the film was calculated

$$P_r = P \times X \quad (3)$$

where,

P_r, Permeability of the membrane, mol. m^{-1} s^{-1} pa^{-1}; P, Permeance of the membrane, mol m^{-2} s^{-1} pa^{-1}; and X, Thickness of the membrane, m.

Membrane permeability depends on many factors like gas solubility, temperature, microporosity and pressure difference between the two surfaces of the membrane. Permeability of the film was measured during the day time and the variation of the temperature during measurement was observed to be 28 ± 3°C. Gillbert (1972) reported that a small change in room temperature did not affect the permeability significantly. However, to overcome the effect of temperature on volume and pressure of test gas, the pressure was maintained constant throughout the experiment.

RESULTS AND DISCUSSION

Gas permeability of the membrane

The permeance and permeability of the membrane to different components of the air are the basic parameter required to design the modified atmosphere storage using the silicone membrane. The permeance and

Table 1 Effect of pressure on the permeability of the silicone membrane to different storage gas components

Pressure (atm)	CO_2 (m^3 cm^{-2} h^{-1})	O_2 (m^3 cm^{-2} h^{-1})	N_2 (m^3 cm^{-2} h^{-1})
0.25	6.960[a]	1.150[a]	0.537[a]
	(21.623)	(3.573)	(1.668)
0.50	7.033[c]	1.150[a]	0.533[a]
	(21.850)	(3.573)	(1.656)
0.75	6.990[ab]	1.153[a]	0.537[a]
	(21.716)	(3.582)	(1.668)
1.00	7.033[bc]	1.170[b]	0.533[a]
	(21.85)	(3.635)	(1.656)
1.25	7.020[bc]	1.1770[b]	0.537[a]
	(21.810)	(3.657)	(1.668)
1.50	6.987[ab]	1.150[a]	0.537[a]
	(21.707)	(3.573)	(1.668)
1.75	7.010[bc]	1.147[a]	0.537[a]
	(21.779)	(3.563)	(1.668)
Mean	7.005[bc]	1.157	0.536
	(21.762)	(3.594)	(1.665)
	SEd	CD (0.05)	CD (0.01)
CO_2	0.0183	0.0392	0.0543
O_2	0.0069	0.0148	0.0205
N_2	0.0047	0.0101	0.0140

Values in paranthesis is permeability × 10^{-14} (mol m^{-1} s^{-1} Pa^{-1})

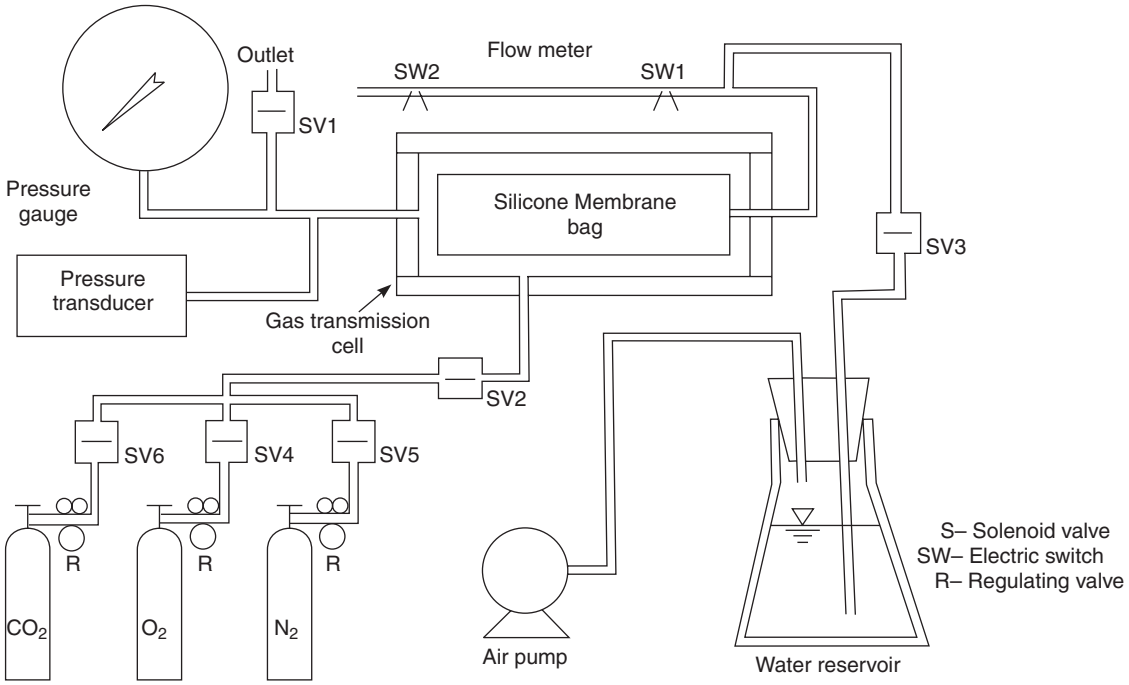


Fig. 3. Gas transmission cell utilized to measure permeability of silicone membrane

permeability of the membrane were calculated by the function g(h) with the value of 'h' at time 't' using the gas permeability apparatus.

The silicone membrane was more permeable to CO_2 (22.921×10^{-14} mol $m^{-1}s^{-1}$ Pa^{-1}) than O_2 (3.845×10^{-14} mol m^{-1} s^{-1} Pa^{-1}) and N_2 (1.755×10^{-14} mol.m^{-1} s^{-1} Pa^{-1}). The ratio of permeability of CO_2 : O_2; CO_2 : N_2 and O_2 : N_2 was 5.97, 13.06 and 2.19, respectively.

To confirm the suitability of the apparatus developed at the laboratory and to know the effect of pressure (from 0.25 to 1.75 atm) on the permeability of the silicone membrane to the different components of the gases, the experimental membrane sample was sent to McGill University, Canada. The permeability rate for different components of gases obtained is presented in Table 1. The interaction study showed that there is no significant difference in the permeability rate at the various applied pressure. The average permeability was 7.005 cm^3 / cm^2 /h (21.762×10^{-14} mol m^{-1} s^{-1} Pa^{-1}) for CO_2, 1.157 cm^3 /cm^2 /h (3.594×10^{-14} mol m^{-1} s^{-1} Pa^{-3}) for O_2 and 0.536 cm^3 / cm^2/h (1.665×10^{-14} mol m^{-1} s^{-1} Pa^{-1}) for N_2.The experimental setup used is given in Fig. 3.

For the design of the modified atmosphere storage for the experiment, the permeability of the membrane as measured by the permeability apparatus developed in the laboratory was considered. The permeability was 1770.67, 296.98 and 135.62 L m^{-2} day^{-1} for CO_2, O_2 and N_2, respectively. Normally, the CO_2 permeates four to six times faster than O_2 and O_2 four to six times faster than N_2 (Exama et al., 1993). Since CO_2 is the largest of the three gas molecules, its diffusion coefficient is the lowest. Its permeability coefficient however, is the highest, because its solubility in polymers is much greater than the other gases (Marcus Karel et al., 1975). The difference in the ability of different polymer films to transmit gases arise in part from the differences in crystalinity, in part from mobility differences between different types of polymeric chains and finally from specific influences of functional groups of the polymers on the solubility of gases and vapours in amorphous portion of the polymer.

CONCLUSION

Manometric gas transmission equipment was fabricated to study the gas permeability of the silicone membrane. The gas transmission equipment consisted of a manometric gas transmission cell vacuum pump, vacuum gauge, test gas cylinder, mercury manometer and needle valves. The manometric gas transmission cell consisted of a lower plate, made of electroplated mild steel. Vacuum pump (B) capable of reducing the pressure in the system to 26 Pa or less was connected to register the vacuum during evacuation of the system. Just before the upper plate, a mercury manometer was provided for measuring upstream gas pressure to a maximum of 70 kpa. It was observed that the membrane permeability depends on many factors like gas solubility, temperature, microporosity and pressure difference between the two surfaces of the membrane.

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