Permeation of Tritiated Water through Polypropylene

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The permeability of water through the polypropylene film was studied using tritiated water. Experiments were carried out in a flow type vessel designed for the determination of the permeability of water. All permeated water was captured by a water bubbler. The permeability was evaluated from the amount of tritiated water permeated through the polymer. The obtained apparent permeability increased with increasing temperature. The temperature dependence was governed by the water vapor pressure. The permeability of water through polypropylene normalized by water vapor pressure was found to be

1.9×10^{-13} g cm cm^{-2} s^{-1} Torr^{-1} at 296 K.

Keywords: tritiated water, permeation, polypropylene

I. Introduction

Hydrophobic polymers are used to package foods and medicines in order to isolate them from air and moisture. However, polymers may absorb and permeate some water. It causes to damp the packed material and reduction of their quality. Therefore, the barrier properties of polymer films against water vapor are a particularly important criterion in the development of package material.

Hydrophobic polymers are widely used as a barrier material for handling radioactive materials. In case of tritium handling the possible conversion of molecular HT into HTO demands special precautions. For instance, HTO absorbed in polymer gloves constitutes an enhanced radiological hazard due to the associated proximity to the skin of workers and the more prolonged exposure time.

To understand the barrier properties of polymer materials against water, the permeation of tritiated water needs to be accurately evaluated. In this works the permeation of tritiated water through polypropylene was measured at ambient near temperatures.

II. Experimental
II. A. Theory

In general, the amount of the water permeated through hydrophobic polymers, like polyethylene or polypropylene, is given by the expression

$$q = \frac{D(C_{up,H_2O} - C_{down,H_2O})}{L} a \cdot t, \qquad (1)$$

where D denotes the diffusion coefficient of water through the polymer, C_{up,H_2O} and C_{down,H_2O} are the surface concentrations of water at the upstream and downstream sides respectively, a is the permeation area of the polymer, L is the thickness of the polymer and t the time. The water concentration at the surface of the polymer can be considered proportional to the product of the solubility constant and the vapor pressure. Hence,

equation can be rewritten as

$$q = \frac{D \cdot S (P_{up,H_2O} - P_{down,H_2O})}{L} a \cdot t, \quad (2)$$

where S stands for the solubility constant and P_{up,H_2O} and P_{down,H_2O} are the water vapor pressures of the upstream and downstream sides, respectively. If it is assumed that $P_{up,H_2O} = const.$ and $P_{down,H_2O} \approx 0$, the amount of permeated water is given by

$$q = \frac{D \cdot S \cdot P_{up,H_2O}}{L} a \cdot t. \quad (3)$$

The $D \cdot S$ term is actually the permeability coefficient of water through the hydrophobic polymer. Equation 3 indicates that the permeability ($D \cdot S$) is evaluated from the cumulative amount of water permeated (q).

II. B. Apparatus

The experimental apparatus was designed following Eq. 3 and it was assumed that some of radiological isotope exchange reactions of HTO absorbed in polymer with structural C-H bonds in the polymer can be ignore. Figure 1 shows a simple schematic diagram of the experimental setup. The measurement vessel consists of an upper and a lower vessel separated by the sample polymer film. Both the upper and the lower vessel are made of stainless steel where inside surface are coated by gold. The size of the vessels determine the permeation area of 28.3 cm^2. The lower vessel stored tritiated water (10 cm^3). To estimate the humidity of the lower vessel, the dummy vessel equipped a hygrometer was also placed. Since the humidity in the dummy vessel was close to 100 % at the various temperature of the experiments, the humidity in the lower vessel was considered achieving saturation. To transport the water permeated through the polymer to the
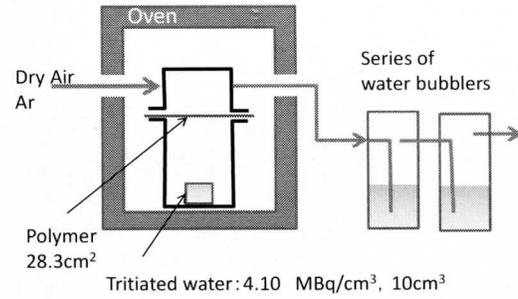

Fig. 1. Schematic diagram of experimental setup.

series of bubblers, the upper volume was swept by argon gas. Permeated water, i.e. H_2O and HTO, was mainly captured by the first bubbler. Consequently, the tritium concentration in the first bubbler increased with time.

II. C. Procedures

The plastic cup was filled with 10 cm^3 tritiated water and placed into the lower vessel. The concentration of the tritiated water was assayed to be 4.10 ± 0.09 MBq/cm^3 ($HTO/H_2O = 6.91 \times 10^{-8}$) with a liquid scintillation counter. Polypropylene film (Omega data systems in the Netherlands) was selected as sample, its thickness was 6 m. Viton O-rings were used to fix the polypropylene film between the lower and the upper vessel. During an experiment the vessels were kept on a thermostat at a given temperature. Temperature were selected in the range of 278 K - 413 K. The gas inlet and outlet of the upper vessel were connected with the carrier gas supplier and the water bubblers, respectively. The water bubblers contained 100 cm^3 of Millipore water. The high purity argon as the carrier gas flowed through the upper vessel to carry tritiated water permeated to the water bubbler. The flow rate of argon gas was maintained constant at 30 sccm.

The dew point of argon gas was determined to be less than 223K. It is mentioned that the atmosphere of both lower and upper vessel should be air and argon, respectively. The tritium concentration in the bubbler was routinely assayed with a liquid scintillation counter to determine the cumulative amount of tritiated water. On this study, the same film was used for all permeability measurements without replacement.

III. Results and Discussion

Figure 2 shows the increase in tritium concentration of the water in the bubbler as a function of time at four temperature. The amount of tritium in the bubbler increased linearly with time, which should be expected from Eq. 3. However, the slopes would be the apparent permeability $\left(D \cdot S \cdot P_{up,H_2O} \cdot a \cdot t \middle/ L \right)$ except when it is normalized from the water vapor pressure of the lower vessel and the permeation area. As apparent permeability from Fig. 2 the slopes increase with increasing temperature. The apparent permeability plotted as a function of the reciprocal temperature in Fig. 3, follows an Arrhenius type line. The permeability at 308 K is 5 times larger than that at 288 K. Therefore, a reduction of permeability can effectively be accomplished by decreasing the ambient temperature.

The apparent permeability contains a vapor pressure of water term, which depends on ambient temperature. To obtain the permeability ($D \cdot S$), the apparent permeability was normalized by the vapor pressure of water, the thickness of the polymer and the effective area of the polymer. The result is shown in Fig. 4. The obtained permeability followed an Arrhenius type equation. It is assumed that the temperature dependence on water solubility into
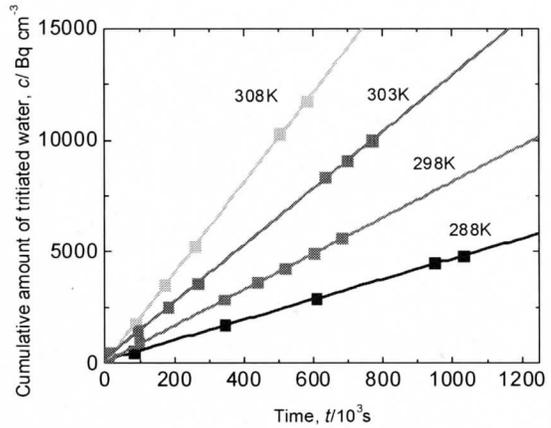

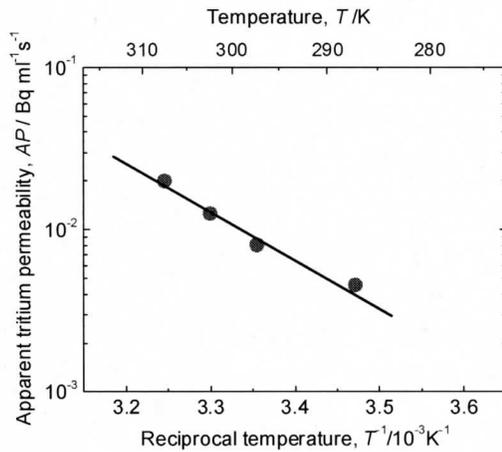Fig. 2. Time-dependence of the amount of tritiated water permeated through polypropylene.

Fig. 3. Apparent permeability of tritiated water.

polypropylene obeys van't Hoff law and then the diffusion follows Arrhenius law. Therefore, the temperature dependence of the permeability at the narrow temperature range of this investigation can be represented by an Arrhenius type equation [1].
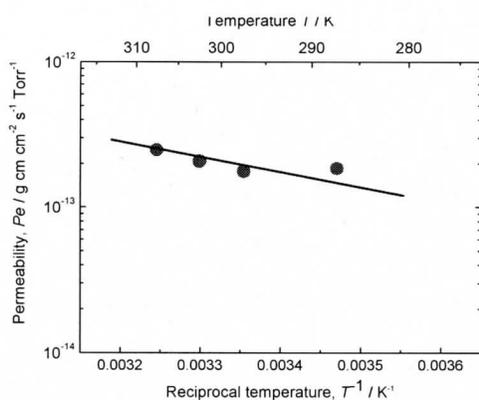
Fig. 4. Permeability of tritiated water through polypropylene.

The slope for the temperature dependence in Fig. 4 was reduced by the normalization of water vapor pressure. It means that the temperature dependence of the apparent permeability (see Fig. 3) was governed by the water vapor pressure on the experimental conditions.

The permeability of water through polypropylene was found to be 1.9×10^{-13} g cm cm^{-2} s^{-1} Torr^{-1} at 296 K (see Fig. 4). The permeability cited in the literature is 3.7×10^{-13} g cm cm^{-2} s^{-1} Torr^{-1} at 296 K [2]. Possible reasons for this difference are (1) the degree of polymerization of the sample [3], (2) the history of the polymer or (3) the different atmosphere. Additional work is necessary to clarify this discrepancy.

IV. Summary

The permeability of water through polypropylene was measured using tritiated water. The permeability of water normalized by water vapor pressure was found to be 1.9×10^{-13} g cm cm^{-2} s^{-1} Torr^{-1} at 296 K.

Acknowledgments

References

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