

Permeability of Deuterium and Helium in Poly(vinyl Alcohol)

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Synopsis

We report the permeabilities of deuterium and helium-4 through poly(vinyl alcohol) (PVA) over the temperature range of 25–125°C. For deuterium, permeabilities ranged from 0.5×10^{-18} to 50×10^{-18} mol·m/m²·s·Pa at these two extreme temperatures. Helium permeabilities were roughly five times higher. We also studied the effects of different curing temperatures and time on the deuterium permeability and found that, to within experimental error, results were the same for samples heat treated at any temperature between 100°C and 140°C. Aluminizing the samples using a special process decreased the permeabilities by a factor of at least 5. A sensitive apparatus constructed around a quadrupole spectrometer was used to measure the very low permeabilities. The apparatus is described in detail.

INTRODUCTION

Several of the new alternative energy concepts which are presently under study, particularly fusion, rely on hydrogen or its isotopes as a source of energy. Thus, in the last decade there has been increased interest in the development of technology related to hydrogen or hydrogen handling. Poly(vinyl alcohol) (PVA) is of interest as a hydrogen barrier or container material because of its relatively low permeability to hydrogen and because it can be readily fabricated into various shapes. For example, Henderson et al.¹ used fabricated PVA microspheres filled with deuterium–tritium gas as targets in laser-fusion experiments.

Unfortunately, there is little information available on the permeability of hydrogen or its isotopes in polymer materials such as PVA. Steinmeyer and Braun² investigated the hydrogen, deuterium, and tritium permeabilities of several elastomer materials but did not look at PVA. Pye, Hoehn, and Panar³ measured the permeability of PVA at 30°C, but their apparatus required a high backing pressure (1000 psi) to produce a measurable permeability. We were interested in values under more reasonable pressures.

In this report we present experimental results on the permeability of deuterium and helium-4 through thin films of PVA over the 25–125°C range. The thin films were cast on stronger Mylar backing sheets to simplify handling problems and, for completeness, we measured the permeability of deuterium through this material. We also briefly studied PVA sheets coated with 6- μ m layers of Al prepared by a special pulsed gas coating process.⁴

The primary purpose of this study was to determine the effects of various production parameters on the PVA permeability. Once the PVA layer is cast, it must be heat-treated to obtain the low permeabilities and to harden the coat; several different curing times and temperatures were tried to determine the

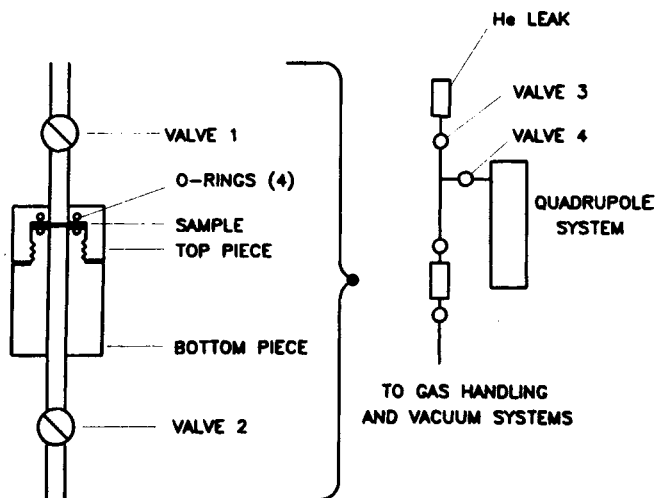


Fig. 1. Permeation cell (on the left) and gas measuring system (on the right) for the apparatus used for these experiments.

optimum conditions. Other things studied were the effects of a dimethylol urea, $(\text{HOCH}_2\text{NH})_2\text{CO}$, treatment (used as a cross linker) and the effects of the aluminum layer.

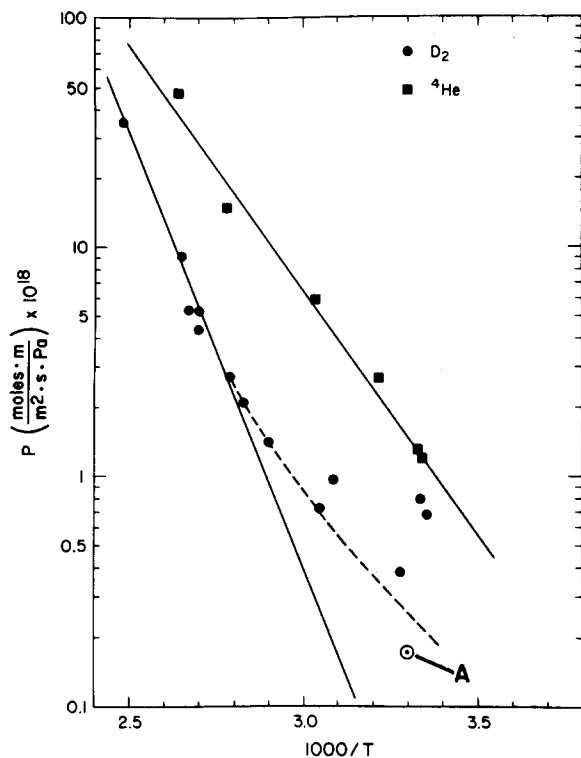
Because of the low permeabilities found, it was necessary to design a new instrument for these measurements. The permeating gas was collected in an evacuated volume for 10 min and then released into a sensitive quadrupole for measurement. This equipment, which operated automatically under computer control, is also described in detail in this report. It was capable of measuring permeabilities down to the 10^{-20} mol·m/m²·s·Pa range.

EXPERIMENTAL

We used a sensitive mass quadrupole apparatus to measure the low hydrogen and helium permeability rates encountered in this study. In these experiments we wished to rapidly measure many samples and the apparatus and technique were developed for small (1-in.) diameter sample sheets. Because of the small sample sheet area, the experimental error was high, but the results were comparable to those found by other authors for similar low permeability rates. With the method used, it was necessary to collect the permeating gas over a period of time to obtain a measurable signal. Because of the minute amounts of gas passing through the film, the method was essentially a constant pressure technique since the backing pressure remained constant and the internal pressure remained in the high vacuum range. The apparatus and experimental method will now be discussed.

Apparatus

The apparatus used for these experiments is depicted schematically on the left side of Figure 1. As indicated in the figure, the sample was held between



gave a measurable mass-4 signal which decayed from, typically, 10^{-5} torr to background (10^{-7} torr) over about 20 sec. During this period the decreasing quadrupole signal was sampled 1000 times with the computer. The computer then summed the stored values minus the above background. Since the decay rate was determined by the pumping characteristics of the system and was thus the same for all samples; the corrected signal summation was proportional to the amount of gas initially collected. The entire measurement process was repeated six times for each experiment, and the experiment was then repeated two to three times for each sample to obtain consistent results.

Before and after each run the response of the quadrupole and vacuum system was calibrated by repeating the sequence with the standard helium leak (valve 3 open, valve 1 closed). For a given sample, each series of experiments took at least 1 working day to complete. Because of the long periods of time required and a significant drift in the quadrupole, there was a relatively large error associated with this type of measurement (estimated at about 50%).

After the bulk of these experiments was concluded, we found it necessary to replace the electron-multiplier detector of the quadrupole. Unexpectedly, the new detector was a factor of over a 100 times more sensitive than the old, and because of this it was possible to measure the permeating gas directly without the long collection periods needed previously. This resulted in far better reproducibility, primarily because of the short time periods between measurements and calibrations. This method was used to measure the temperature dependence of the deuterium and helium-4 permeabilities through one of the sample sheets. With similar samples and temperatures, the results measured with the two techniques agreed to within a factor of about 2. Thus, we have confidence in the less accurate procedure used for most of the experiments.

Instrumentation

We used a digital Inficon IQ-200 quadrupole coupled to a Hewlett-Packard 9815 desktop computer via a parallel interface for these experiments. The computer was used to collect, store, and reduce the data from the quadrupole electronics and, as mentioned, it also controlled the operation of valve 4 during the experiments.

The quadrupole was housed in an all-metal apparatus and could be baked out at 200°C as needed. The quadrupole housing was pumped by a conventional mercury diffusion pump with a liquid-nitrogen cooled trap. Background pressures were typically 10^{-7} torr.

Deuterium and helium test gases were 99.9% pure or better and were used from the cylinders without further purification. The relative quadrupole responses of deuterium and helium were assumed to be proportional to their published cross sections: the relative response of helium to deuterium was taken as 0.4.⁵

Preparation of Plastic Samples

All of our samples for this work were prepared from a poly(vinyl alcohol) (Aldrich Chemical Co.) which was 98% hydrolyzed with an average molecular weight of about 126,000. The degree of polymerization, percent hydrolysis, and viscosity of the PVA are all important parameters in choosing the proper solvent

for preparing the films. Although completely hydrolyzed PVA is soluble in cold water, only addition of an alcohol will prevent precipitation of PVA at elevated temperatures. PVA materials having a lower percentage of hydrolysis can be dissolved in mixtures of 40–85% methanol or isopropanol in water. Permeability characteristics of the cast PVA film should be dependent upon the degree of polymerization, percent hydrolysis, and viscosity to some extent, although we did not study these effects. These three parameters undoubtedly effect other physical properties such as tensile strength, elongation, moisture resistance, and others.

For this work we used a mixture of 10% methanol in distilled water as solvent. The PVA was ground to a very fine powder to help speed dissolution. Five parts (by weight) of the powder was slowly added to 100 parts (by weight) of the solvent at room temperature while maintaining vigorous high shear mixing. When the powder was all added, the mixture temperature was slowly raised to about 75°C and held there for 90 min before slow cooling to room temperature. The vigorous stirring must be maintained at all times.

Prior to forming the laminate, the Mylar film (0.010 in. thick) was sandblasted on the surface on which the PVA was to be cast. This surface was then washed with distilled water followed by methanol. The proper amount of PVA mixture, calculated to give the required final thickness, was poured onto the Mylar and the solvent slowly evaporated open to air.

After the solvent was evaporated, the laminates were treated at 100°C, 120°C, or 140°C (see the next section for temperatures and times used). This heat treatment increases the crystallinity of the PVA and reduces the hydrogen permeability and absorption of water. We found that the heat treatment was necessary to obtain the low permeabilities we observed.

To maintain minimum permeability, it is essential to keep the heat-treated samples in a dry atmosphere. If necessary, redrying can be accomplished at 100°C for 16–24 h, although this must be done with care to prevent delamination of the PVA film from the Mylar backing.

The bond between the two plastic films appears to be mechanical and is not very strong. The sheets can be easily pulled apart by hand; thus handling of the final laminate requires some care.

The aluminum layer was prepared using a pulsed gas process which periodically added oxygen to the coating apparatus. The process, developed by Springer et al., is described in detail elsewhere.⁴ This tended to break up the aluminum layer forming laminar, rather than columnar growth. Our experiments indicated that the permeabilities of the sample sheets were not decreased by aluminized layers produced with more standard techniques and that this process was essential for decreasing the deuterium and helium permeabilities.

RESULTS AND DISCUSSION

Major results for this work are shown in Table I. The errors shown in the table are the standard deviation for the results for three different samples prepared from the same sheet and heat treated similarly. Where no numbers are shown only one sample was measured.

In the last column of the table we list results from Ref. 3 for hydrogen permeating through PVA. In view of the different samples and gases used (the

TABLE I
Summary of Permeability Results for Deuterium Gas at 0.8 atm

Layers	Heat treatment (°C h)	Permeability ^a (mol·m/m ² ·s·Pa × 10 ¹⁹)	
		This work (deuterium)	Ref. 3 (hydrogen)
Mylar	—	330	2000
Mylar/PVA	100 24	1.1 ± 0.3	2.3
	120 24	1.3 ± 0.5	
	140 2	1.3 ± 0.2	
Mylar/PVA/Al	120 24	0.2	
Mylar/PVA (DMU)	120 24	2	

^a The Mylar used in all experiments was 0.010 in. thick while the PVA layers were 0.003 ± 10% in. The aluminum layer was approximately 6 μm. All measurements were done at room temperature.

isotope effect is discussed below), the agreement for PVA is quite good. The discrepancy for Mylar can be explained as due to the use of different materials and different sample histories.

We made one measurement of the permeability of the Mylar backing sheet to make sure it was not limiting the permeability of the laminates. Because of the much higher permeability of Mylar compared to the PVA, it was obvious that the latter was controlling the permeability of the layers, but, to be sure, in several runs we repeated the measurements twice, both with and without the Mylar layer. In all cases where this was done the results were, within the experimental error, the same. Thus most of the samples were measured with the Mylar backing in place. Some of the results under the lines labeled "Mylar/PVA" in the table are for the separated PVA layer, but for simplicity this is not indicated in the table.

In an attempt to understand the effects of different curing conditions on the films, we did a differential thermal analysis (DTA) of the granular PVA starting material and an untreated cast film. With this experimental technique, the heat generated or absorbed by the sample (compared to a standard) is measured as the temperature is increased. The plots for the two were similar, showing a melting point of about 220°C and marked thermal decomposition above 160°C. These results indicated that 140°C is about the maximum temperature for safe heat treatment of the samples. Further, as can be seen from the table, there is no measurable difference between the permeabilities of the samples heat treated under the different conditions. Thus, an intermediate temperature (120°C) is suggested for this application. We also found no significant change for the sample which was treated with the chemical crosslinker (DMU). Although the crosslinker did not lower the permeability as we had hoped, it did tend to make a smoother coat.

One very gratifying result is the large decrease in the permeability of the aluminized sample. As can be seen this resulted in a four- to ninefold decrease (based on the errors) in the deuterium flow rate through the material. The measured permeability through the aluminized sample was near or below the limit of sensitivity of the apparatus; thus the decrease could be even greater than this.

With the techniques we used to prepare the films, one would expect an occasional pinhole to form in the PVA film; but, of the samples studied, there was only one occurrence of such a defect. Here the pinhole was obvious: on addition of the test gas, the leak rate jumped immediately to a value at least a factor of 1000 greater than those observed for the other samples. We tried several non-destructive methods, such as penetrants and low energy radiography, to prove the quality of the films and look for pinholes. None proved successful. This was not surprising as the methods were limited to detections of pinholes with diameters greater than 0.001 in.

There was a noticeable difference on switching from deuterium to helium-4 gas. In the former case the equilibration times were longer, on the order of 4 h; with helium-4, however, the signal reached steady state in about 0.5 h. This effect indicated to us that the process was indeed a permeation process rather than mere leakage through defects.

The results of the temperature dependence experiments for one sample heat treated at 120°C are shown in Figure 2 for both deuterium and helium gas. The single point labeled A in the figure is the result found for the same sample using the more sensitive collection technique. As can be seen, the results with the two techniques are in good agreement.

For the deuterium case the data at high temperatures appears to fit a straight line (on the semilog plot) at temperatures above about 85°C. But the data points tends to fall more and more away from the line as the temperature is decreased below this point. The effect may be due to some physical change in the structure of the PVA polymer. This hypothesis is not unreasonable since this is near the temperature needed to cure the layers.

The solid line fitting the data at high temperatures can be represented by the equation

$$\ln(P \times 10^{18}) = -8680/T + 25.1 \quad (1)$$

where T is the absolute temperature (K) and the permeability P has the units shown in the figure. The data for the helium-4 case appears to fit a single straight line with the equation

$$\ln(P \times 10^{18}) = -4900/T + 16.6 \quad (2)$$

Note, however, that a similar line and curved section as for deuterium could also be fit to this series of data. Thus, one should probably not extrapolate the helium data to much higher or lower temperatures.

In both of the DTA curves discussed above, there was a slight but noticeable change in slope in the 50–100°C range which might correspond to the process causing the effects seen in Figure 2.

The isotope effect on the hydrogen permeabilities in polymers is not well understood. In general, from theoretical considerations, one expects the diffusion to be inversely proportional to the square root of the mass of the permeating atoms. However, the permeability constant P is equal to the product of the diffusion coefficient D and the solubility S and in most cases the latter is not known. Steinmeyer and Braun² looked at the isotope effect in several cases and found that the relative permeability could go either way depending on the material. In comparing our data to that of Pye, Hoehn, and Panar³ we could conclude that the permeability decreases on going from hydrogen to deuterium, but

the large experimental error associated with these experiments does not warrant this conclusion.

Thus, it would be difficult to extrapolate the results to the third isotope, tritium. To a fairly good approximation (at least to a factor of 2) one could assume that the permeabilities of deuterium and tritium are the same. To this approximation, one could use eq. (2) for the tritium case.

We would like to thank J. T. Rowen for helping to cast and cure the PVA sheets, A. T. Young for performing and interpreting the DTA experiments, W. R. David for helping with some of the permeability experiments, R. W. Springer and G. A. Reeves for aluminizing the samples, and D. E. Elliott and T. H. Feiertag for the nondestructive tests. All are workers at Los Alamos National Laboratory.

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Received May 24, 1983

Accepted June 29, 1983