Vapor Permeation in Polymer Films

INTRODUCTION

In the course of work on thermotropism,[1] we performed control experiments in water baths to obtain constant stress baselines. (Thermotropism is temperature-induced dimension changes other than normal expansion or contraction.) These results indicated effects more complex than simple creep, the major effect being the diffusion of water into the film and the consequent swelling and change in dimensions and creep. We thus have a simple way to measure permeation in laboratory film samples where there is appreciable interaction between the polymer and diffusing liquid. An absorption-desorption weight measurement[2] could give the same information but the procedure is more tedious.

The following describes a simple, optically amplified length change measurement to determine diffusion coefficients. When coupled with a rapid TGA weight loss measurement for solubility, the permeability is obtained.

EXPERIMENTAL

Figure 1 is a schematic diagram of our apparatus. The sample (0.6 × 10 cm) is first clamped in place and held taut by slight tensile stresses (ca. 6×10^6 dynes/cm^2) supplied by small weights (ca. 10–20 g) on the balance arm. With a 2.5-cm balance arm and a mirror–scale distance of about 1.5 meters, one can easily detect a 0.05% sample length change.

A run is made by immersing the sample in the test fluid and measuring the length change as a function of time. Typical data for water permeation in poly(1,4-benzamide) film are shown in Figure 2. The S-shaped curve has a characteristic half-time of 17 min. Also shown in Figure 2 are weight gain data gathered on a second specimen of the same sample in 100% R.H. air. The half-time in the weight gain experiment is 15 min, illustrating the equivalence of these measurements. For thin film samples (thickness, Δ) the half-times can be converted into diffusion coefficients, D, by use of the expression[2]

$$D = 0.04919 \ \Delta^2/t_{1/2} \qquad (1)$$

Following the length change measurement, the sample is cut from the clamps and the equilibrium solvent concentration determined by heating in a TGA apparatus (du Pont 900 Thermoanalyzer with the du Pont 950 thermogravimetric analysis attachment).
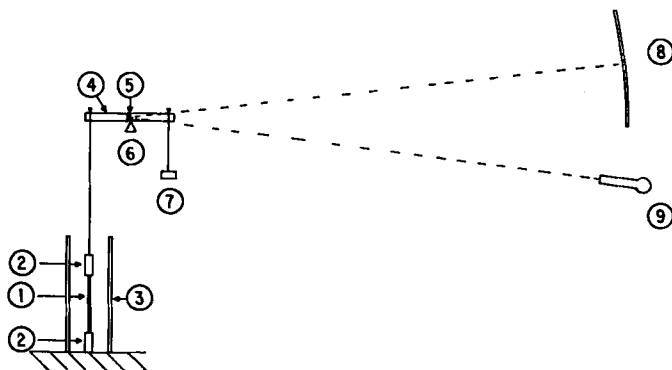

Fig. 1. Apparatus schematic. ① Sample; ② clamps; ③ fluid container, ④ balance beam; ⑤ mirror; ⑥ knife edge; ⑦ counter weight; ⑧ galvanometer scale; ⑨ light source.
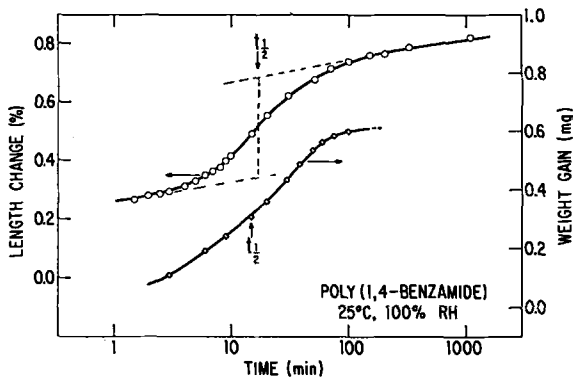
Fig. 2. Poly(1,4-benzamide) at 25°C, 100% R.H.

We can thus determine Henry's law coefficient S and hence the permeability coefficient P:

$$P = S \times D \tag{2}$$

RESULTS

To show that the experiments are reversible, we present Figure 3. Curve 1 was initially obtained with a poly(1,4-benzamide) film. After soaking in water for 23 hr, the sample was dried by exposure to an IR lamp (ca. 150°C) for 5 hr and then the experiment was repeated—curve 2. The half-lives are similar and illustrate the degree of reproducibility obtained by this technique.

To help illustrate the equivalence of these measurements to the more conventional permeation measurements, we present data for five different films encompassing a spread of water permeabilities (Table I). The water permeabilities were first determined by the standard cup method (ASTM-E96-66) and reported as IPV's. The water solubilities were determined by soaking the samples in water for one week and then measuring their weight loss as they were heated to 200°C in our TGA apparatus. From this information we then computed the diffusion coefficients and the half-times. These are shown compared to the measured values from our length change experiments. The agreement is fair (factor of 2) throughout the range.

TABLE I
Measurements on Five Different Films

Film	Thickness, mils	IPV[a]	Wt-% H_2O[b]	D, cm^2/sec	$t_{1/2}$, min calcd.	$t_{1/2}$, min exp.
Poly(*m*-phenyleneiso-terephthalamide)	3.35	58.7	10.2	0.0604	98	270
Nylon 66	2.03	305.5	9.54	0.239	9.6	4.9
Polycarbonate	5.48	105.5	0.378	5.30	3.0	2.9
Cellulose acetate	1.07	808	7.57	1.23	0.49	0.73
Poly(ethylene terephthalate)	1.00	115	1.1	0.254	2.1	1.2

[a] In g H_2O/100 m²-hr-4.4 cm Hg (H_2O).
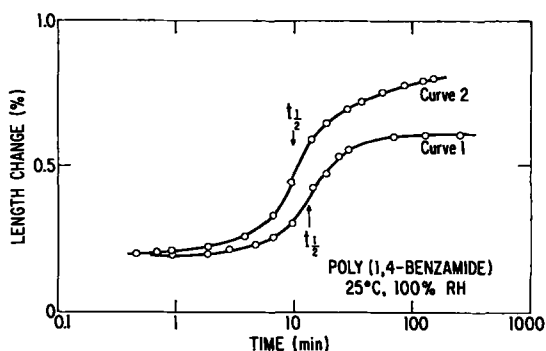
[b] At 25°C, 2.38 cm Hg (H_2O).

Fig. 3. Poly(1,4-benzamide) at 25°C, 100% R.H.

The response of polymers with relatively low water pickup is at first surprising. However, in earlier work, one of us (R.M.I.) observed similar water effects on the limits of Hookean elasticity. Dry poly(ethylene terephthalate) films show an elastic strain limit of ~1.5%, while wetting the same films changes this to 0.5%.

The effect is not limited to water. Other experiments have shown that polyimides and polyamides exhibit similar length changes-versus-log time curves in ethanol, and we conclude that the phenomenon will be general where diffusant–polymer interaction (i.e., solubility) is of a reasonable magnitude.

References

1. F. Agolini and F. P. Gay, *Macromolecules*, **3**, 349 (1970).

2. J. Crank and G. S. Park, *Diffusion in Polymers*, Academic Press, New York, 1968, pp. 15–16.

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