

Bending-Beam Study of Water Sorption by Thin Poly(methyl Methacrylate) Films

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Synopsis

A bending-beam technique has been employed to study the effects of film thickness (7–55 μm) and rate of cooling during film preparation ($\sim 6^\circ\text{C}/\text{h}$ to a dry ice quench) on sorption characteristics of water by poly(methyl methacrylate) films coated on thin fused quartz beams ($\sim 84 \mu\text{m}$ thick). In each experiment, the curvature of a polymer coated beam exposed to liquid water was monitored as a function of time by a low power laser pointer. With the use of a transport model which considers the sorption process as the linear superposition of contributions from Fickian diffusion and a first-order polymer molecular relaxation process, the beam curvature data were analyzed to determine the governing transport kinetics and associated transport parameters such as water diffusion coefficient and relaxation rate constant. From curvature analysis for thin films (7–13 μm in thickness), it was found that water diffusion proceeds at early times in a Fickian-like manner with a diffusion constant of $2\text{--}4 \times 10^{-9} \text{ cm}^2/\text{s}$. At later times, significant relaxation contributions lead to non-Fickian diffusion behavior, an effect that is more pronounced as the film thickness or sample cooling rate decreases. In addition, sorption of water was found to reduce the film stress (initially tensile at $\sim 10^8 \text{ dyn}/\text{cm}^2$) at a rate that increases with sample cooling rate. The high initial film stress not present in free-standing films may account for the relatively higher diffusion coefficient ($\sim 2 \times 10^{-8} \text{ cm}^2/\text{s}$) found here for very thick (55 μm) PMMA coatings. Because the bending-beam technique uses coated samples, it is especially well suited for studying penetrant transport into polymer coatings.

INTRODUCTION

Due to their good mechanical properties coupled with relatively low water pickup ($< \sim 2\%$ by weight, see Refs. 1 and 2), poly(methyl methacrylate) (PMMA)-based materials have been widely used in diversified applications involving exposure to water, including photoresist for microfabrication,³ dentistry,⁴ quick road pavement repair,⁵ stone reinforcement,⁶ and aircraft window construction.⁷ Concurrent to these applications are the numerous and on-going studies of water transport kinetics in glassy PMMA—an effort which has spanned across the last two decades.^{8,9} These kinetics studies relied primarily on gravimetric measurements of relatively thick and free (i.e., unsupported) PMMA films (typically, $> 100 \mu\text{m}$ in thickness, see Refs. 1, 2, and 9). In most cases, either the initial and/or later portions of the sample weight vs. time data were analyzed using the classic Fickian diffusion equation characterized by a constant diffusion coefficient. Although the water diffusion coefficient was found to be essentially constant throughout the entire transport experiment at low relative humidities¹⁰ and even in situations involving exposure to liquid water,^{8,11} anomalous behaviors in terms of a dependence of the apparent diffusion coefficient on relative humidity,¹² sample thickness,^{1,9}

and time¹ have also been reported at high relative humidities and during immersion of PMMA in liquid water.

For water transport in PMMA, Turner¹ postulated a "dual-mode" sorption model which consists of (i) filling of microvoids (i.e., of excess free volume frozen in glass) and (ii) a polymer swelling process. Turner's idea is the same as that developed by Paul and Koros¹³ for the sorption of gases in glassy polymers except that Turner emphasized that penetrant dissolution in the Henry's law mode may induce a dilatation of the polymer glass and this can result in non-Fickian effects. Using the dual-mode model, Turner attributed the time dependence of the apparent water diffusion coefficient to the existence of the time-dependent "polymer molecular relaxations" connected with the swelling process. From a more modern viewpoint,¹⁴ the non-Fickian effects can be regarded as resulting from a coupling between molecular diffusion and the rheological response of the polymer glass to penetrant induced dilatation. Based on sorption of organic vapors by poly(vinyl chloride) and polystyrene whose free volumes were varied by prior thermal or vapor treatment, Berens and Hopfenberg¹⁵ proposed that the rates of molecular response in glassy polymers depend both on the free volume deviation from the equilibrium state and alterations of effective free volume by the penetrant. Sorption of penetrant is often manifested by a lowering of the glass transition temperature of the polymer,¹⁶ which reduces the viscosity of the glassy state as well as its resistance to flow. This effect is responsible for the faster decay of stress in relaxation experiments for PMMA films containing water.¹⁷ The plasticization of PMMA by water, which results in an appreciable reduction in craze initiation stress¹⁶ and acceleration of craze and crack growth¹⁸ is another manifestation of the faster rates of molecular response. The contribution of non-Fickian or molecular response effects to the overall sorption process thus varies with the relative humidity (a measure for calculating the diffusional driving force for penetrant transport) and the sample thickness (since it affects the mean rate of diffusion induced deformation of the glass).

The purpose of this study was to use the bending-beam technique to (i) see if the thickness dependence of the diffusion coefficient can be explained by a model for non-Fickian effects and (ii) examine the relatively neglected effects of thermal treatment and sample support on water transport characteristics during integral sorption of thin supported PMMA films (7–55 μm) at room temperature. Following the bending-beam technique pioneered by Berry and Pritchett¹⁹ for diffusion studies, the polymer film in this study was coated on one side of a thin fused quartz beam and changes in beam curvature caused by changes in film stress level were monitored during sorption using a low power laser pointer. The curvature data provided a detailed fingerprint of the overall transport process. The bending-beam technique was chosen in this study not only because it used polymer coated beams which were ideal for studying the substrate effect but also because of its high sensitivity (see below), which was crucial for transport studies involving thin films. Aside from their relevance to the electronics industry and short experiment times involved, the small polymer thicknesses adopted in this study were motivated by the study of Berens and Hopfenberg,²⁰ who were able to separate the otherwise similar rates of diffusion and polymer relaxation using polymer microspheres. The effect of thermal treatment was of interest because sorption of organic vapors

by glassy polymers has been found to be significantly affected by prior thermal history.¹⁵ Due to the existence of intrinsic and thermal stress,²¹ a supported polymer film is almost always in a state of higher stress ($\sim 10^8$ dyn/cm² for PMMA, see below) compared to its free film counterpart. The film stress can affect the water sorption rate as has been indicated by Sarser and Kalinin²² in their study of water transport in stressed PMMA films.

To interpret the curvature data collected for the PMMA-water system, the bending-beam theory developed by Berry and Pritchett¹⁹ for Fickian-type penetrant transport has been slightly modified to allow for non-Fickian behaviors caused by polymer molecular relaxations. This was achieved with the incorporation of the empirical non-Fickian transport expression of Berens and Hopfenberg²⁰ but reformulated for thin films. In this expression, the sorption process was considered to be driven by both the concentration gradient induced by classic Fickian diffusion and a first-order relaxation process characterized by a rate constant which presumably represents an average over the entire molecular relaxation spectrum. The physics embodied in this expression is therefore different from prior models which introduced either a time-dependent surface penetrant concentration²³ or a time-dependent diffusion coefficient.²⁴ Using the modified bending-beam theory to analyze the measured curvature data, we have determined water transport kinetics in thin PMMA films prepared with different thermal treatments. To our knowledge, this is the first such study. For the 55 μm thick films, the results were compared with existing literature for free films of similar thickness.

EXPERIMENTAL

Sample Preparation

Quartz Beams. In this study, fused quartz beams (3.8 cm long, 0.3 cm wide, and ~ 0.0084 cm thick) with rectangular cross sections were obtained from the Hibshman Co. (San Luis Obispo, CA). For quartz, the elastic modulus and Poisson's ratio required for curvature analysis are, respectively, 7.3×10^{11} dyn/cm² and 0.16. Prior to use, each quartz beam was cleaned using successively a dilute aqueous solution of DeContam (from Electronic Space Product International, Westlake Village, CA), deionized water and ethanol. The beam was subsequently dried on a hot plate to remove the residual cleaning fluid. To have clearer reflected laser spots on the recording paper during curvature measurements (see below), one end of the quartz beam was coated on one side with a 1000 Å thick layer of chromium over an area of 0.09 cm² ($= 0.3 \times 0.3$ cm). Because of the small thickness and area of coverage, the presence of chromium does not create significant changes in filmstress level and bending stiffness which combine to control the beam curvature.

PMMA. The PMMA used in this study was a proprietary material with a number-average molecular weight of approximately 30,000, an elastic modulus of 2.8×10^{10} dyn/cm², and a Poisson's ratio of 0.34. Its glass transition temperature T_g is about 100°C. After overnight drying at 70–80°C, the powdered material was dissolved in a suitable casting solvent.

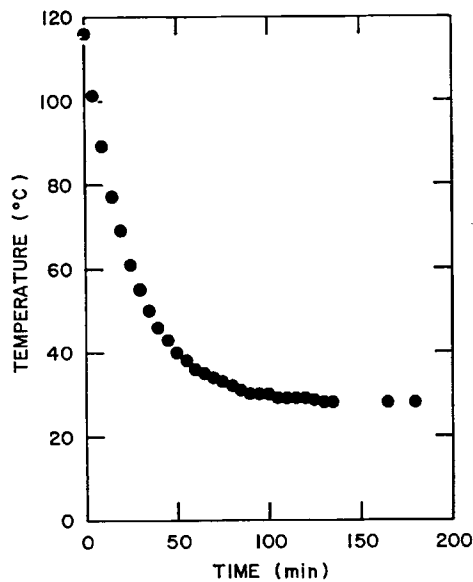


Fig. 1. One of the three cooling schedules used during PMMA film preparation.

Beam Coating. The PMMA solution was spun onto quartz beams and dried sequentially at 85°C for up to 1 h for slow evaporation of the casting solvent and then at 120°C ($> T_g$) for up to several days to drive off the residual volatiles. Following drying, the PMMA samples (7–13 μm in thickness as measured by a stylus profilometer) were either (i) quenched to dry ice (sublimation temperature = -78.5°C) and then warmed up to room temperature, (ii) cooled at a rate $< 4^\circ\text{C}/\text{min}$ to room temperature (see Fig. 1 for the temperature schedule), or (iii) slowly annealed at a rate of $\sim 6^\circ\text{C}/\text{h}$ to room temperature. A few thick samples (55 μm thick) were prepared by quenching to room temperature from 120°C to study the substrate effect. The quenched samples were left in a vacuum desiccator with the vacuum on overnight prior to the bending-beam experiment to remove any residual moisture. The other samples were either used immediately or kept in a vacuum desiccator until use.

Bending-Beam Experiment. The setup used for the bending-beam experiment is shown in Figure 2. It consists of a low power laser (i.e., ~ 1 mW He-Ne laser at 6328 Å), a beaker containing an optical-grade quartz window, a fixture for holding the quartz beams, and, mounted vertically about a meter away, a plexiglass board with a piece of form paper for recording the positions of laser spots reflected from the quartz beam. Compared to a microscope,¹⁹ the laser pointer used here offers two advantages: (i) correction for the refractive index difference between water (1.33) and air (1.00) is straightforward, and (ii) sensitivity to small angular deflections of the quartz beam can easily be increased by increasing the distance between the sample and the form paper. When necessary, other detection techniques such as the highly sensitive capacitance-change method²⁵ capable of detecting movements as small as 3×10^{-10} cm can be used.

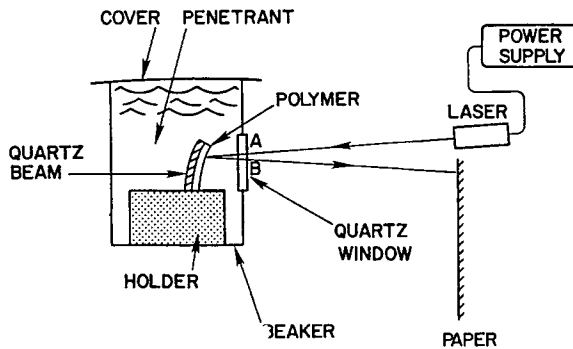


Fig. 2. Schematic drawing of the setup used for the bending-beam experiment.

In the bending-beam experiment, the quartz beam with its one end clamped on the holder was first placed in the beaker in the absence of water. For the purpose of increased accuracy in data analysis, the laser was then guided through the window at normal incidence to hit the free (chromium-coated) end of the beam and the position of the quartz beam adjusted so that the incident (point A in Fig. 2) and reflected (point B in Fig. 2) laser beams were in the same vertical plane. After marking the position of the reflected laser spot on the paper, deionized water was carefully poured into the beaker (the whole process took less than 5 s). This was followed immediately by marking of the laser position until it no longer changed with time, indicating saturation of PMMA with water. With the use of simple geometry and refractive index considerations, the deflection of the free end of the beam and the beam curvature were derived from the position of the reflected laser spot. All sorption experiments were performed at room temperature (22°C).

TRANSPORT MODEL

In the absence of film thickness changes upon Fickian sorption characterized by a constant diffusion coefficient, Berry and Pritchett¹⁹ have derived the general expression relating the beam curvature ($1/R$ with R being the beam's radius of curvature) to the penetrant concentration C , which is both time- and position-dependent:

$$\psi \left[\frac{1}{R} \right] = \int_{-0.5}^{+0.5} \left(\frac{C}{C_{\infty}} \right) (1 + Ku) du \quad (1)$$

where

$$K = \frac{2m(1 + mn)}{1 + m}$$

$$m = \frac{h_f}{h_b}$$

$$n = \frac{E_f(1 - \nu_b)}{E_b(1 - \nu_f)}$$

with the parameters h , E , and ν denoting, respectively, the thickness, elastic modulus, and Poisson's ratio, the subscripts f and b , film and beam properties, and C_∞ the equilibrium penetrant concentration. In eq. (1),

$$\psi = \frac{1/R - 1/R_i}{1/R_\infty - 1/R_i}$$

where the subscripts i and ∞ indicate initial and equilibrium properties. The concentration distribution which produces curvature changes can be established by considering the transport process, whether Fickian or non-Fickian, as the linear superposition of contributions from Fickian diffusion [the first-term on the right-hand side of eq. (2)] and a first-order molecular relaxation process [the non-Fickian contribution, i.e., the second term on the right-hand side of eq. (2)]:

$$C/C_\infty = \lambda F[D] + (1 - \lambda)[1 - \exp(-kt)] \quad (2)$$

where λ is the fraction of C_∞ due to Fickian diffusion, k is a first-order relaxation rate constant, t is the time, and the parameter F is a function of the constant diffusion coefficient D :

$$F = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \times \exp\left[\frac{-D(2n+1)^2\pi^2t}{4h_f^2}\right] \times \cos\left[\frac{(2n+1)(u+0.5)\pi}{2}\right]$$

Equation (2) is the thin-film analogue of an expression proposed by Berens and Hopfenberg²⁰ for solvent transport into polymer spheres. The relaxation process prescribed in eq. (2) is independent of the concentration gradient driving Fickian diffusion, and thus is compatible with the case of Case II transport. This model is, admittedly, empirical but provides a reasonable framework for data analysis.

In arriving at eq. (1), the following assumptions have been made: (i) both polymer and beam behave elastically, (ii) D , E_f , and ν_f are independent of concentration, and (iii) the polymer's volumetric swelling is linearly proportional to the penetrant concentration.

Elastic behaviors were assumed due to the small strains encountered during the bending-beam experiment and that the temperature of the sorption experiment (22°C) was far below the glass transition temperature of the water saturated PMMA.^{16,26,27}

The assumption that D is independent of concentration might at first seem contradictory, since, as mentioned earlier, the water diffusion coefficient during sorption of water by PMMA has been found to depend both on time

and relative humidity (and therefore on water concentration). This conclusion was reached, however, using a transport model which assumed the concentration gradient induced by Fickian diffusion as the sole driving force^{23, 24} and in which the diffusion coefficient was allowed to depend on penetrant concentration or time. An alternative approach utilizes the transport model embodied in eq. (2) for data analysis (see, for example, Refs. 15 and 20), where the transport process is assumed to be governed both by Fickian diffusion characterized by a constant diffusion coefficient and by a time-dependent (non-Fickian) molecular relaxation process initiated by the plasticizing penetrant. The latter approach was adopted in this study for it allows for easier data interpretation.

The slope or modulus of PMMA can decrease with increasing water content by up to $\sim 30\%$ according to the tensile stress-strain data obtained by Shen et al. (Fig. 2 in Ref. 26). Such changes in modulus do not significantly affect the value of $1 + mn$ and therefore K , the only polymer modulus dependent term in eq. (1), because $mn \ll 1$ in this study. By eq. (1), the assumption of constant PMMA modulus is thus not expected to significantly alter the results shown below.

To our knowledge, data concerning the concentration dependence of ν_f are not available. The effect, however, should be small based on the same argument above for the polymer modulus.

Upon exposure to water, the density of PMMA is known to increase in a nonlinear fashion with increasing water uptake.^{1, 2} Turner¹ was able to obtain an approximate fit to the reported experimental data using an empirical expression which assumed a constant fraction of sorbed water participating in volume swelling with the remaining water filling the preexisting microvoids. Based on this empirical expression, the law of mass conservation and low water pickup by PMMA ($< \sim 2\%$ by weight), it can be easily shown that the volume swelling of PMMA is approximately proportional to the water concentration during sorption.

As indicated previously, one approach adopted in this study to resolve the complex transport process into separate contributions of Fickian diffusion and polymer relaxation is to accelerate the diffusion process by reducing the diffusion distance, e.g., the film thickness. This does not affect the relaxation rate, which is independent of sample dimensions [right-hand term of eq. (2)].

During penetrant transport, the stress level relative to that at equilibrium, $\Delta\sigma$, can be calculated using

$$\Delta\sigma = \left[\frac{E_b h_b^2}{3(1 - \nu_b)L^2 h_f} \right] \Delta\delta \quad (3)$$

where L is the unclamped length of the beam and $\Delta\delta$ is the deflection of the free end of the beam relative to that at equilibrium.²¹ The end deflection is related to the beam curvature R via

$$\delta = L^2/2R$$

Given C/C_∞ , one can calculate the fractional penetrant uptake:

$$\frac{M_t}{M_\infty} = \int_{-0.5}^{0.5} \frac{C}{C_\infty} du \quad (4)$$

where M_t is the mass of the penetrant in the film at time t and M_∞ is the value of M_t at equilibrium.

DATA ANALYSIS

Using eqs. (1) and (2), one can first vary the diffusion coefficient D , assuming Fickian transport ($\lambda = 1$) to see if good match in ψ vs. $\sqrt{Dt/h_i^2}$ data can be obtained between the model and the data throughout the sorption experiment. In the event of a poor match which often occurs during later stages of sorption (i.e., non-Fickian transport), the value of D is varied until the Fickian model predicts the experimental ψ data up to $\psi = 0.5$. Because the time at $\psi = 0.5$ coincides closely with that at $M_t/M_\infty = 0.5$, this diffusion coefficient would be similar to that based on the initial portion of the M_t/M_∞ data—a common practice in the area of diffusion. With the diffusion coefficient fixed, one can then vary λ ($= 0-1$) and k ($\geq 10^{-8} \text{ s}^{-1}$) until the experimental ψ data are predicted by the non-Fickian model. Values of k smaller than 10^{-8} s^{-1} have negligible effect on water transport since they correspond to relaxation times greatly exceeding the time scale of the experiment. Knowing transport parameters, one can then calculate the values of M_t/M_∞ at all times for both Fickian and non-Fickian transport.

RESULTS AND DISCUSSION

Effect of PMMA Cooling Rate

Figure 3 plots the experimental ψ vs. $\sqrt{Dt/h_i^2}$ data (●) during sorption of a PMMA film (11.3 μm thick) which was slowly annealed to room temperature at a rate of $\sim 6^\circ\text{C}/\text{h}$. The Fickian model ($\lambda = 1$, solid line) predicts the initial experimental data up to $\psi = 0.5$ at a diffusion coefficient of $1.8 \times 10^{-9} \text{ cm}^2/\text{s}$. With the use of the non-Fickian model at $D = 1.8 \times 10^{-9} \text{ cm}^2/\text{s}$, $\lambda = 0.82$, and k (first-order relaxation rate constant) = $3 \times 10^{-4} \text{ s}^{-1}$ (-----), good agreement between experiment and model is obtained up to $\psi = 1$. Because the characteristic diffusion time θ ($= h_i^2/D = 710 \text{ s}$), is smaller than the mean relaxation time η ($= 1/k = 3300 \text{ s}$), the Fickian diffusion process initially proceeds at a faster rate compared to the process of molecular relaxation. From Figure 3, it is clear that water sorption continues beyond the Fickian equilibrium time ($\sqrt{Dt/h_i^2} \sim 1.5$). In this regime, the relaxation-controlled mechanism dominates, with the water concentration in the film remaining essentially uniform (i.e., position-independent) but increasing with time towards saturation. This relaxation contribution can lead to film swelling.¹

For a sample with a faster cooling rate ($< 4^\circ\text{C}/\text{min}$, shown in Fig. 1) and similar thickness, the relaxation contribution disappears. Figure 4 shows the experimental ψ vs. $\sqrt{Dt/h_i^2}$ data (●) which compare well with predictions

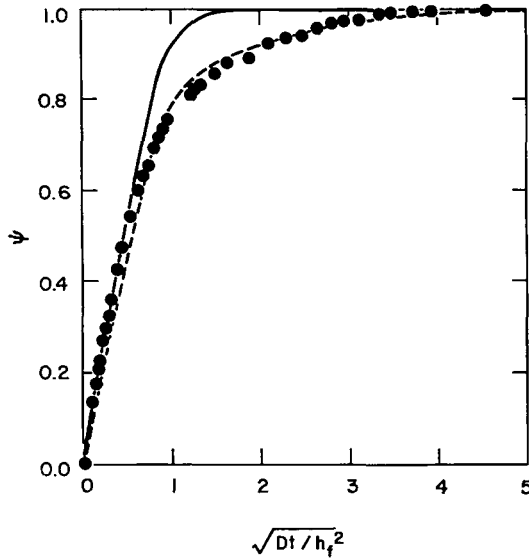


Fig. 3. $\psi - \sqrt{Dt/h_f^2}$ data from experiment (●), the Fickian model (—) and the non-Fickian model (-----) during sorption of water by a slowly annealed PMMA film of 11.3 μm thick.

provided by the Fickian model (—) at a diffusion coefficient (1.8×10^{-9} cm^2/s) identical to that obtained for the slowly annealed sample (Fig. 3). As the cooling rate increases even further to that corresponding to quenching to dry ice, water transport remains Fickian for a film 12.7 μm thick, although the diffusion coefficient (3.7×10^{-9} cm^2/s) becomes about twice that for the samples prepared under smaller cooling rates (Figs. 3 and 4).

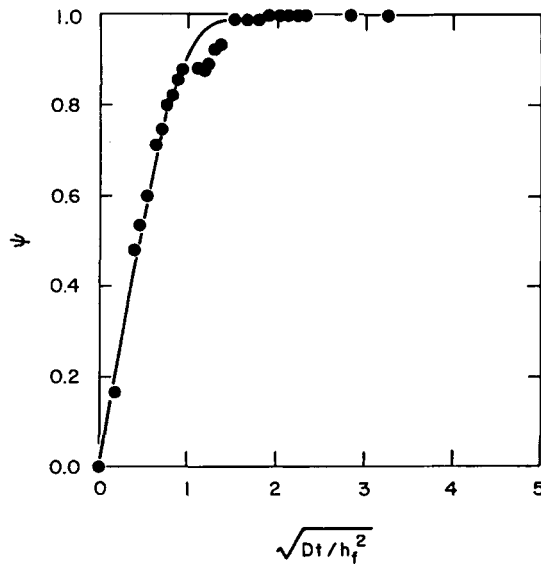


Fig. 4. $\psi - \sqrt{Dt/h_f^2}$ data from experiment (●) and the Fickian model (—) during sorption of water by a PMMA film of 11.3 μm thick which was prepared under the cooling schedule in Figure 1.

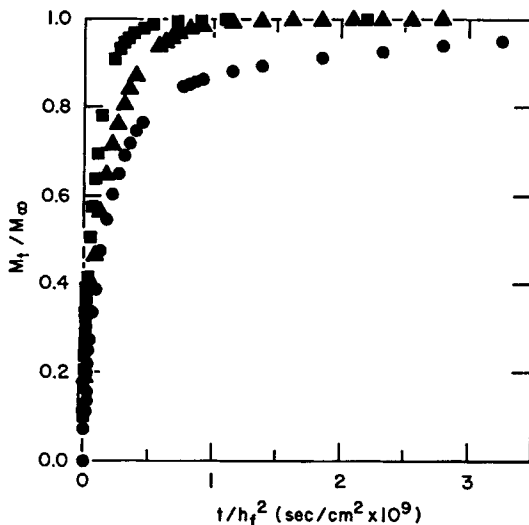


Fig. 5. $M_t/M_\infty - t/h_i^2$ relationships for the PMMA samples which were slowly annealed (\bullet), cooled under the schedule in Figure 1 (\blacktriangle), and quenched to dry ice (\blacksquare).

Shown in Figure 5 are the corresponding fractional water uptake (M_t/M_∞) data for all the samples as a function of the time parameter, t/h_i^2 , which was chosen to account for the small difference in sample thickness. For the slowly annealed sample (\bullet), M_t continues to increase almost linearly with t beyond the Fickian equilibrium time ($t/h_i^2 = 1.3 \times 10^9$ s/cm²), a behavior characteristic of the relaxation controlled mechanism.²⁸ From Figure 5, it can be seen that the time to saturation (τ) increases with decreasing cooling rate. This finding runs parallel to the observation of Ensore et al.²⁹ concerning the reduced sorption rate of *n*-hexane in thermally annealed polystyrene microspheres compared to that in the as-received samples.

For the PMMA-water system, sorption reduces the film stress. In all cases, the room-temperature stress level prior to the sorption experiment is tensile and is of the order of 10^8 dyn/cm². The initial rate of stress reduction, $\Delta\sigma/t$, increases with increasing cooling rates, from 4×10^5 dyn/cm²/s for the slowly annealed sample to 1.5×10^6 dyn/cm²/s for the quenched sample. A similar effect of cooling rate on stress reduction rate has also been observed in stress relaxation experiments using free PMMA films.¹⁷

Effect of PMMA Thickness

With a thickness decrease from 11.3 to 7.4 μm for the samples cooled under the temperature schedule in Figure 1, water sorption becomes non-Fickian with a significant relaxation contribution. Figure 6 shows the experimental ψ data for the 7.4 μm sample and model predictions with $D = 1.4 \times 10^{-9}$ cm²/s, $\lambda = 0.83$, and $k = 9.4 \times 10^{-4}$ s⁻¹. For quenched samples, a similar thickness decrease (from 12.7 to 7 μm) does not result in the appearance of the relaxation contribution, although it does significantly reduce the diffusion coefficient from 3.7×10^{-9} to 1.8×10^{-9} cm²/s. The decrease in diffusion coefficient with decreasing film thickness is in good accord with the trend

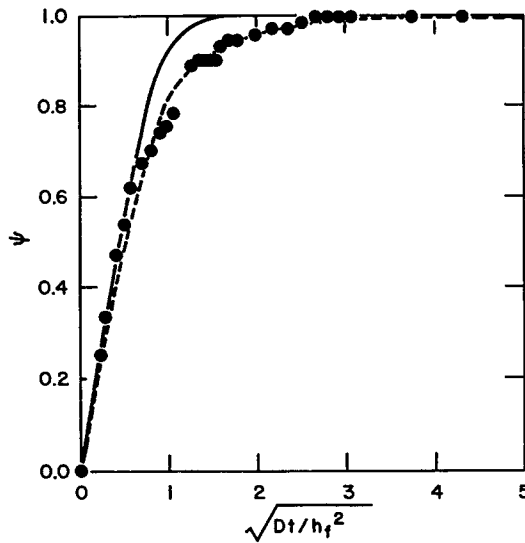


Fig. 6. $\psi - \sqrt{Dt/h_f^2}$ data from experiment (●), the Fickian model (____), and the non-Fickian model (-----) during sorption of water by a PMMA film of $7.4 \mu\text{m}$ thick which was cooled under the schedule in Figure 1.

obtained by Turner¹ during liquid water immersion of PMMA. Shown in Figure 7 are the corresponding M_t/M_∞ vs. t/h_f^2 curves for the two thicknesses of quenched samples. It is clear that the two curves are not superimposable. Similar behavior was also found for the samples annealed under the temperature schedule in Figure 1. This thickness dependence indicates that the initial Fickian portion observed for the PMMA-water system is not Fickian in the classic sense, for if it were, the two M_t/M_∞ curves would have

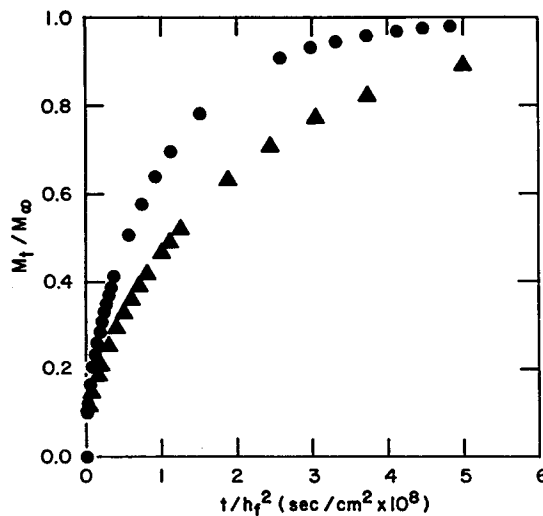


Fig. 7. $M_t/M_\infty - t/h_f^2$ relationships for quenched samples of $12.7 \mu\text{m}$ (●) and $7 \mu\text{m}$ (▲) in thickness.

been superimposable [see eqs. (2) and (4) with $\lambda = 1$]. Roussis⁹ has also observed the thickness dependence of the M_t/M_∞ data based on gravimetric measurements of free films and termed the initial Fickian-like behavior as pseudo-Fickian.

Vrentas et al.³⁰ have proposed the Deborah number De for determining the relative contributions of Fickian diffusion and polymer relaxation:

$$De = \eta/\theta$$

where the parameters η ($\sim 1/k$) and θ ($= h_f^2/D$) have been defined earlier as, respectively, the relaxation and diffusion times. According to them, anomalous transport behavior involving both Fickian and relaxation processes is probable when $De \sim 1$. It is interesting to note that for the samples in Figures 3 and 6, where the relaxation contribution is important, $De = 4.7$ and 2.7 , respectively, i.e., of the order of unity.

Substrate Effect

To investigate into the substrate effect, it was necessary to study films thicker than those used in Figures 3–7 because of the availability of literature data for thick free films. For $55 \mu\text{m}$ thick PMMA coatings prepared by quenching to room temperature, we found water transport to be Fickian with $D = 1.5 \times 10^{-8} \text{ cm}^2/\text{s}$. This is in sharp contrast to the much smaller D value of $5\text{--}7 \times 10^{-9} \text{ cm}^2/\text{s}$ obtained^{1,2} for free films of $100 \mu\text{m}$ – 0.5 cm in thickness, which are equivalent to $50 \mu\text{m}$ – 0.25 cm for coated films due to the symmetry in water penetration in free films. Although this discrepancy may be explained in terms of differences in factors such as molecular weight, thermal history, and residual monomer content, the high stress level in the PMMA coating might have played an important role. Based on the mass uptake data of Sarser and Kalinin,²² an increase by more than a factor of 10 in water diffusion coefficient can occur in going from unstressed films to films which have been stressed at $1.5 \times 10^8 \text{ dyn/cm}^2$.

WATER SORPTION MECHANISM

In an attempt to explain the observed non-Fickian behavior dominated by molecular relaxations and the higher diffusion coefficient observed for PMMA coatings relative to free-standing films, consider water sorption in the initial Fickian-like stage to be governed by both filling the free volume in PMMA via a Fickian diffusion-driven concentration gradient, and by swelling involving large-scale segmental motions to accommodate more water. The existence of molecular relaxations in this stage of transport is supported by the observed reduction in the film stress with time and by the thickness dependence of the M_t/M_∞ vs. t/h_f^2 data discussed previously. Because of the slow rates of molecular relaxations in relatively dry PMMA, sorption is initially dominated by Fickian diffusion. As the water front moves through the film, the water concentration in the penetrated layer increases with time. This results in increased rates of molecular relaxation behind the front, leading to the acceleration of water sorption [eq. (2)] and the observed Fickian-like behavior in which Fickian diffusion and polymer relaxation contributions are superim-

posed upon each other. While the relaxation contribution becomes more important due to increasing water concentration as sorption proceeds further, the Fickian contribution decreases as a result of decreasing concentration gradient.

For the relaxation contribution to be clearly separable from the Fickian contribution, the rates of Fickian diffusion and molecular relaxation must be made dissimilar. One way to achieve this is to shorten the Fickian saturation time by decreasing, for instance, the film thickness or the diffusion distance under the same sample preparation conditions as has been demonstrated in Figures 4 and 6. This can be achieved without affecting molecular relaxation rates which are thickness-independent. Alternatively, one can decrease the rates of molecular relaxations by reducing the rate of cooling, i.e., by increasing the sample annealing time (while keeping the film thickness constant) to obtain a more relaxed or ordered PMMA structure containing a smaller preexisting free volume. Alfrey et al.³¹ have shown that polystyrene samples cooled more slowly have a smaller specific volume at any temperature below the glass transition temperature. Higher ordering with a smaller free volume would cause both a smaller diffusion coefficient and slower molecular relaxations. This can account for the data of Figures 3–5 in which the water diffusion coefficient (and presumably the fraction of the preexisting free volume) is higher for the quenched sample than for the sample annealed under the schedule in Figure 1. Although slow annealing may reduce the free volume further from that obtained under the cooling schedule in Figure 1, the difference is not sufficient to cause a difference in the diffusion coefficient which dominates the Fickian-like transport. The smaller free volume obtained for the slowly annealed PMMA, however, might have significantly slowed down the rates of molecular relaxations from those corresponding to the sample cooled under the schedule in Figure 1. This may be why molecular relaxations were found to dominate water transport beyond the Fickian saturation time in the case of slowly annealed PMMA (Fig. 3). Because polymer relaxation is independent of film thickness, a more ordered structure for the sample in Figure 3 compared to that in Figure 6 may also account for the smaller relaxation rate constant (k) obtained for the sample in Figure 3. The above discussion is not meant to preclude the possible contributions of other effects (e.g., plasticization) to the process of molecular relaxations.

During cooling, the film coated on a beam is not allowed to contract or relax to a length corresponding to its free-standing state due, for instance, to the thermal expansion mismatch between the polymer and the beam. This creates a high film stress or preexisting free volume which may partly account for the higher diffusion coefficients obtained for PMMA coatings compared to those for free films prepared under otherwise similar conditions.

SUMMARY

Using the bending-beam technique, it has been demonstrated that the film thickness, the thermal treatment, and, possibly, the stress level in the film play an important role on water sorption by thin PMMA films. Water sorption was found to be at least initially dominated by Fickian-like transport with Fickian and polymer relaxation contributions superimposed upon each

other. Non-Fickian behavior dominated by molecular relaxations is more pronounced as the film thickness decreases and/or as the rate of cooling through the glass transition temperature decreases. The bending-beam technique described herein allows transport studies of penetrant into ultra-thin polymer films which are not easily amenable to conventional gravimetric techniques.

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