The Adsorption and Absorption of Water Vapor by Polyethylene Terephthalate

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Synopsis

An experimental technique for the simultaneous determination of the amount of gas or vapor absorbed and adsorbed by a film of material is given. For Mylar film at 40°C it was found that the amount of water at an activity of 0.9 that was adsorbed was about 1×10^{-7} g/cm². Assuming that a water molecule is cubical in shape and 3.26 Å on an edge and the surface is geometrically flat, this amounts to several layers of water molecules on the surface for any thickness.

INTRODUCTION

Absorption and desorption kinetics are often studied by following the change in weight of a film of material exposed to vapor at constant temperature and pressure. The results are usually plotted as curves showing the ratio of the amount MT absorbed or desorbed at time T to the amount $M\text{-}INF$ absorbed or desorbed at equilibrium versus $T^{1/2}$. Theoretically, the plot should be a straight line up to about $MT/M\text{-}INF = 0.6$ and then should rise to unity asymptotically. In addition to absorption, however, adsorption of the permeant on the surface of the material can also occur simultaneously and contribute to the gain in weight. To decide whether or not adsorption is a significant factor, a method is needed for the determination of the amounts of permeant adsorbed and absorbed.

There are various and sundry indications that the adsorption of water vapor on polymer films may be appreciable. Zettlemoyer et al.[1] determined the adsorption isotherms of nitrogen and krypton on polyethylene, nylon, and collagen. Their isotherms yielded to BET analysis and gave surface areas of reasonable magnitude which for the same sample agreed very well for the two gases at different temperatures. These authors concluded that the BET theory provides a satisfactory method for investigating the surface areas of organic solids with nonpolar gases. The point is that organic solids can show "normal" adsorption behavior, i.e., adsorption behavior similar to that of inorganics.

Adsorption of water vapor on the quartz spring alone (description and conditions given below) was found to be 0.03 mm or 0.012 mg. Since the area of some of our sample films was much larger than that of the quartz

spring, the gain in weight due to adsorption of water vapor on the polymer might be significant.

During the course of this research it was found that when a Pyrex glass flask connected to a pressure transducer-recorder combination was charged with about 1 mm water vapor quickly and the source was shut off, the pressure proceeded to fall, quite steeply at first, then asymptotically to about $1/4$ of the original pressure. Polydimethylsiloxane was then applied to the inner surface of one Pyrex flask and a fluorotelomer, Vydax 525, to another. Both were applied and cured according to the procedures given by their respective suppliers, Dow Chemical Company and du Pont Corporation. The sorption experiment was then repeated using the coated flasks. The extent of sorption of water vapor on these two thin polymer coatings was about $3/4$ of that for the Pyrex glass. These experiments were run at 30.0°C. It appears that water vapor adsorbs on all solids at this temperature, at least there are no widely known exceptions. Water vapor will, therefore, adsorb on these two films. Of course, some water vapor dissolved in the film. Since the solubility of water vapor in these polymers is quite low, the films are very thin, and the vapor pressure is low, it was felt that the amount absorbed is negligible. Because adsorption is primarily a function of the adsorbate, if adsorption dominates over absorption in these experiments, then the sorption curves of water vapor pressure versus time for both polymer films should be of the same general shape as for the Pyrex glass. Since the sorption curves of water vapor on glass are adsorption and the sorption curves were all similar, then one would surmise that the sorption curves of water vapor on polydimethylsiloxane and the fluorotelomer are also adsorption curves.

The adsorption isotherm of water vapor on glass shows hysteresis.[2] If some polymers actually do adsorb significant amounts of water vapor, one would expect that one of them might also show hysteresis, especially one in which the solubility of water is low. This is the case for poly(methyl methacrylate).[4] One would again surmise that water vapor does adsorb on poly(methyl methacrylate) and other polymers in significant amounts and is responsible for the hysteresis.

In many cases, both in our work and in the literature, unsteady-state sorption plots of $MT/M\text{-}INF$ versus $T^{1/2}$ using water vapor as the permeant do not rise linearly from the origin as they should, but generally intercept the abscissa on the positive side giving the impression that there is a short time lag before the start of sorption. This delay is usually attributed to the time required for the admission of the water vapor, but this may not be entirely the case. In order to give the appearance that the sorption curve rises linearly from the origin as it theoretically should, the curve would have to be raised on the graph paper. This implies that the individual weight readings, MT, are lower than they should be and that a buoyant effect is involved. Calculations show that the buoyant effect of water vapor at low pressures can be ignored. However, the actual curve would fall below the position theoretically expected if the denominator of

the fraction, $MT/M\text{-}INF$, were larger than it should be. One would again surmise that adsorption of water vapor by the polymer film may be a factor.

Since glass and silica are reported to adsorb as many as 250 layers of water molecules,[2,3] adsorption by polymers may be appreciable. Adsorption of water vapor by polymers may not manifest itself in the plot of $MT/M\text{-}INF$ versus $T^{1/2}$, however, Theoretically, a plot of $MT/M\text{-}INF$ versus $T^{1/2}$ (for absorption) should be linear up to about 0.6 and then asymptotically tend toward unity. Rand[5] has shown that the fractional amount of water vapor adsorbed on glass is initially a linear function of $T^{1/2}$ and thereafter tends toward unity. Again, since adsorption is primarily a function of the adsorbate, adsorption of water vapor on some polymers could be initially linear and then asymptotically tend to unity. Even if adsorption exceeds absorption for these polymers, the resultant combined plot would still be initially a straight line and subsequently monotonically tend to unity and could easily be construed entirely as an absorption curve.

Although the above are merely indications, there are enough of them to warrant serious consideration of the possibility that adsorption may be a significant factor.

The object of this report is (1) to submit a method whereby the amount of gas or vapor absorbed and the amount simultaneously adsorbed by many materials can be determined, (2) to show, where the amount adsorbed is not negligible compared with the amount absorbed, that the resulting plot of $MT/M\text{-}INF$ versus $T^{1/2}$ need not rise linearly from the origin or will differ elsewhere from the theoretical absorption curve, (3) that diffusivity values can be affected, and (4) that the mechanism of sorption as now postulated may be affected when polar permeants are used.

EXPERIMENTAL

Material

Poly(ethylene terephthalate) film (Mylar) was selected for this investigation primarily because it could be obtained commercially in a variety of thicknesses, with each film of highly uniform thickness. Mylar polyester films, type A, were donated by the du Pont Corporation and were outgassed at 1×10^{-5} mm Hg for about one week. The density values of samples taken from the same sheet of Mylar film and adjacent to the samples used in this work were 1.3900 and 1.3906 g/cc for the 0.5-mil film and 1.3956 and 1.3965 g/cc for the 5-mil film. The respective crystallinities are 47.1% and 46.7% for the 0.5-mil film and 51.3% and 52.0% for the 5-mil film. The amorphous contents would therefore be 52.9% and 53.3% and 48.7% and 48.0%, respectively. The values which will be used in this report are 53.1% amorphous content for the 0.5-mil film and 48.3% amorphous content for the 5.0-mil film. The density (and crystallinity) values were kindly furnished by Dr. C. J. Hefflefinger of the du Pont Mylar Laboratories, Circleville, Ohio, using a density gradient column. The surfaces

of the films were wiped clean with distilled water. The water used as the permeant source was purified by alternately freezing and thawing it under vacuum.

Apparatus and Procedure

The apparatus consisted of a cylindrical glass enclosure containing two similar quartz spring balances hung side by side and connected by suitable valving to a thermostated water reservoir, a mercury manometer, and a mechanical vacuum pump. The enclosure, manometer, and reservoir and the connections between them were housed in a thermostated cabinet.

The quartz springs were obtained from the Worden Quartz Products Corp., Houston, Texas. They had a capacity of 100 mg, a maximum extension of 200 mm, and spring constants of 0.4017 and 0.4000 mg/mm.

A rectangular sample weighing 92.94 mg with an average thickness of 0.543 mil was hung on one spring and another weighing 92.35 mg with an average thickness of 5.00 mils was hung on the other spring. The air was pumped from the system, the temperature of the cabinet was set to 40.0°C, and the temperature of the water reservoir was so set that the resulting vapor pressure of the water would provide a relative humidity surrounding the Mylar films of about 0.9. After the system reached equilibrium, the vacuum line was closed and water vapor admitted. As the samples increased in weight, the elongation of the quartz springs was followed with a Gaertner Cathetometer which could be read to ±0.02 mm. Only a few early readings could be obtained because the films sorbed water so rapidly. While the system was allowed about 50 hr to reach equilibrium, it was almost at equilibrium at the end of 24 hr. A more precise value cannot be given because fluctuations of the room temperature from day to night caused both the temperature of the cabinet and water reservoir and consequently the weight of water vapor sorbed and cathetometer readings to oscillate. Because of this behavior, the experiment was repeated. The results were almost the same. Figure 1 shows plots of $MT/M\text{-}INF$ versus $T^{1/2}$ for both samples. Since the ambient conditions for the two runs are practically the same, and also to avoid confusion, only one curve is drawn through the data for the thin film and only one for the thick film. The irregularities in the plots after 400 min were observed to follow slow cabinet temperature changes over the range $40.0 \pm 0.3°C$. Equipment with numerous microbalances which will give much more accurate results is needed.

DISCUSSION AND RESULTS

Let S be the concentration of the sorbate on the surface of the polymer films, and let C_a be the concentration in the amorphous phase of the films. Now, if two samples of the same material with different ratios of surface area to weight are exposed to a sorbate simultaneously, as described above, the surface concentrations and the concentrations in the amorphous phase must be the same at equilibrium conditions. It is assumed that the solu-

bility of water vapor in the crystalline phase is negligible and that the amorphous regions of the two films and the solubilities of water vapor therein are the same. Since the relative amounts of water vapor adsorbed by the amorphous phase (when saturated) and the crystalline phase are unknown and may be different, correction cannot be made for any difference in the amount of water vapor adsorbed by the crystalline phase on the surface (or in the interior) due to the difference in crystallinity. It will therefore be assumed that the actual surfaces of the two films are essentially the same. An effort was made to avoid this situation by obtaining films with precisely the same per cent crystallinity, but it was not quite successful. The total weight, W_1, sorbed by the first film is given by

$(S \times$ area of film #1)

$$+ (C_a \times \text{wt of film #1} \times \% \text{ amorphous content of film #1}) = W_1$$

and for the second film

$(S \times$ area of film #2)

$$+ (C_a \times \text{wt of film #2} \times \% \text{ amorphous content of film #2}) = W_2.$$

Substituting the results for the first experiment (cabinet temperature = 40.2°C and water vapor activity = 0.894) for the Mylar film of average thickness 0.543 mils, and correcting for the weight of water vapor adsorbed by the quartz springs (0.012 mg each) gives

$$S \times 102.62 \text{ cm}^2 + C_a (92.94 \times 0.531) \text{ mg} = (0.672 - 0.012) \text{ mg}$$

and for the second film of average thickness 5.00 mils

$$S \times 10.79 \text{ cm}^2 + C_a (92.35 \times 0.483) \text{ mg} = (0.595 - 0.012) \text{ mg.}$$

Solving gives

$$S = 0.000165 \text{ mg/cm}^2,$$

$$C_a = 0.0130 \text{ mg/mg.}$$

For the second experiment, $T = 40.1°C$ and vapor activity = 0.911 Using the same samples the equations are

$$S \times 102.62 \text{ cm}^2 + C_a (92.94 \times 0.531) \text{ mg} = (0.660 - 0.012) \text{ mg,}$$

$$S \times 10.79 \text{ cm}^2 + C_a (92.35 \times 0.483) \text{ mg} = (0.591 - 0.012) \text{ mg.}$$

Solving gives

$$S = 0.0000815 \text{ mg/cm}^2,$$

$$C_a = 0.0129 \text{ mg/mg.}$$

Although the values of S are quite small, which is to be expected from a hydrophobic material such as Mylar, from the known propensity of water vapor to adsorb on practically everything it is highly unlikely that the sur-

face is entirely devoid of water, i.e., that $S = 0$.   The differences in the
values of S and the values of C can be attributed to a small difference in the
final temperatures and relative humidities between the two experiments.
In fact, it was observed that fluctuations in W_1 relative to W_2 could arise at
the end of an experiment because the samples did not gain and lose weight
in phase.   That is, as the temperature cycled $\pm 0.3°C$, the thinner film
changed weight much faster then the thick film—demonstrating the need
for very tight temperature control.

The value of S for the first experiment is 0.000165 mg/cm². This
amounts to

$$\frac{1.65 \times 10^{-7} \text{ g/cm}^2 \cdot 6.023 \times 10^{23} \text{ molecules/mole}}{18.016 \text{ g/mole}} = 5.5 \times 10^{15} \text{ molecules/cm}^2$$

or since one molecule of water vapor covers 10.6 Å², the area covered would
be

$$5.5 \times 10^{15} \text{ molecules/cm}^2 \cdot 10.6 \times 10^{-16} \text{ cm}^2/\text{molecule} = 5.8 \text{ cm}^2/\text{cm}^2.$$

For the second experiment, the area covered would be

$$2.9 \text{ cm}^2/\text{cm}^2.$$

Once the amorphous regions of the surface become saturated, adsorption
could proceed there also so that at the end of the experiment, at equi-
librium, both the amorphous and crystalline areas may be covered with
water.   If the actual and geometric surface areas of the films are the same
and the adsorbed layer is uniformly thick, there must be about 3 to 6
layers of water molecules on any thickness of Mylar at an activity of 0.9
and a temperature of 40°C.   Of course, the adsorbed water could be
held entirely or partly as a uniform layer, entirely or partly in capillaries,
etc.   For purposes of illustration, a situation where the adsorbed water
vapor is a significant amount (about 20%) of the absorbed water will be
discussed.

It appears reasonable to postulate that the water vapor initially adsorbed
by the amorphous regions is immediately absorbed.   Eventually, the rates
of adsorption and absorption at the surface of the film become equal and
thereafter adsorption as a layer or in capillaries, etc., proceeds rather
rapidly.   Figures 2 and 3 show adsorption curves, both labeled AD of the
above description assuming that the sorbent is a hydrophyllic material.
The curves labeled AB on Figures 2 and 3 are the same and are freehand
approximations to a theoretical absorption plot (use of exact theoretical
plots will not alter anything).   They are linear up to $MT/M\text{-}INF = 0.6$
and then asymptotically reach unity.   The resultant curves, RE, of Figures
2 and 3 were obtained by adding ordinates and dividing by the total weight
of sorbate.   The ordinates of the AB and AD curves are the weights sorbed,
and for the RE curves the ordinate is the fractional weight sorbed, $MT/M\text{-}$
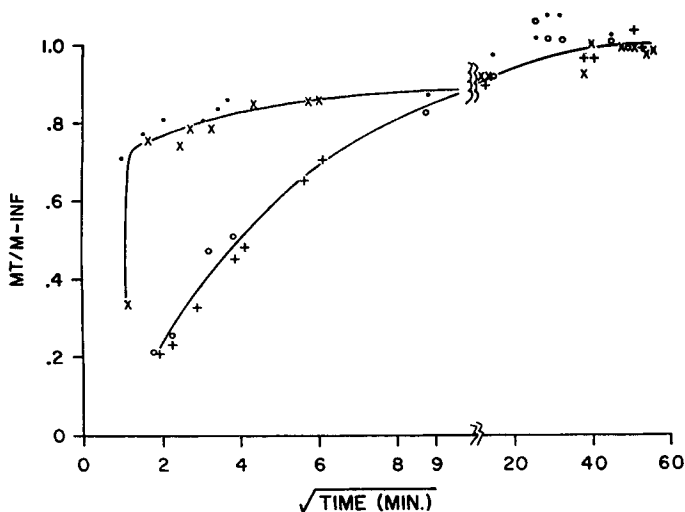INF, where $M\text{-}INF = 1.2$.

Fig. 1. Sorption of water vapor by Mylar films: (●) 0.543 mil, run #1; (O) 5 mil, run #1 (X) 0.543 mil, run #2; (+) 5 mil, run #2.

Figure 2 shows that if a straight line is put through the initial points of the resultant curve, a reasonable fit is obtained and the straight line when extrapolated intercepts the abscissa on the positive side. Figure 3 shows that if the bulk of the adsorption takes place at a later period, the effect on the resultant curve will be different. Inspection of Figure 1 shows that the curves for the thinner film in the interval from $T^{1/2} = 2$ to $T^{1/2} = 4$ are irregular and could be construed to be convex toward the abscissa in this region. In this respect the curve resembles the resultant curve of Figure 3. The irregularity of the points is not entirely due to reading errors. Irregular points were too often observed in prior work. During the second run all points were carefully determined to minimize reading errors. Despite this, the thinner film was observed to lose weight in the above interval, as the plot in Figure 1 shows. The reason for this may again be adsorption. As the water vapor adsorbs on the surface of the polymer, heat is released and the surface of the polymer film is warmed. However, since the surface of the polymer is saturated with water vapor, some water is driven out. This behavior may account in part for many of the sigmoidal curves shown in the literature. At this time one cannot say that adsorption is the factor responsible for the behavior of some of the experimental curves; all that can be done is to point out the possibility that adsorption may be involved.

Generally, unsteady-state sorption experiments are carried out in steps. The first step could cover the range from vacuum conditions to $^1/_5$ the saturated vapor pressure of the sorbate; the second step from $^1/_5$ to $^2/_5$ the saturated vapor pressure of the sorbate, etc. Diffusivity and concentration values can be computed for each step. However, both values could be in error due to adsorption, depending on the geometry, nature of the material,
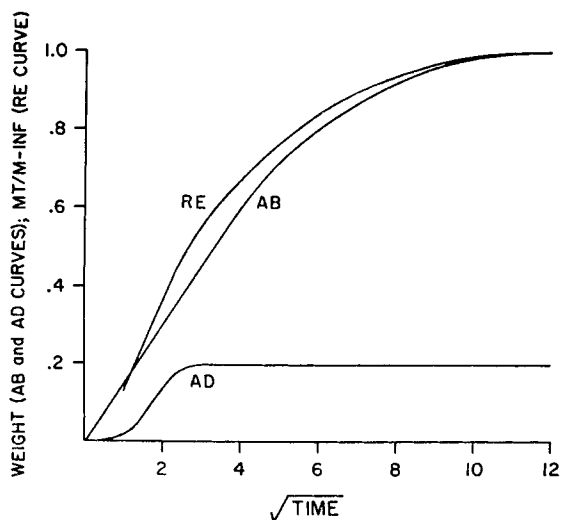
Fig. 2. Combination of an absorption and a selected adsorption curve to show resultant curve as a normal absorption curve: AB, absorption curve; AD, adsorption curve; RE, resultant.

and nature of the sorbate. Suppose that the correct diffusivities determined only by the absorption curve, e.g., AB in Figure 2, were obtained and were substantially the same for each step, and that adsorption was significant and varied for each step not only in amount but location of the maximum rate of increase relative to the absorption curve, as shown by the AD curves in Figures 2 and 3. Figures 2 and 3 show that the diffusivities computed from the straight line portion of the resultant curves RE will not be the correct values. The point here is that a plot of $\bar{D}$ versus C could be seriously affected by the shape of the adsorption curve for each step.

Now the accepted mechanism of absorption for gases such as He, N_2, O_2, etc., requires that the gas or vapor dissolve directly into the surface of the sorbent and follow Henry's Law.   If the sorbent is completely covered by multiple layers of water molecules, how can this be true for water vapor? One could conjecture that the adsorbed water is in the form of isolated clusters or mounds which cover only a fraction of the surface.   This situation could arise in the case of crystalline polymers.   The crystals on the surface present polar sites for adsorption and are highly impermeable to water.   Hence a mound of water might form on each crystalline area, leaving the amorphous regions relatively bare so that the usual mechanism of absorption will function.   It may be possible to investigate this situation by using another quartz spring and a sample whose surface was treated with a solvent to remove surface crystallinity.

The actual surface area of the Mylar film is undoubtedly larger, perhaps many times larger than the geometric area.   Surface irregularities could arise during crystal formation because the crystalline regions have a higher
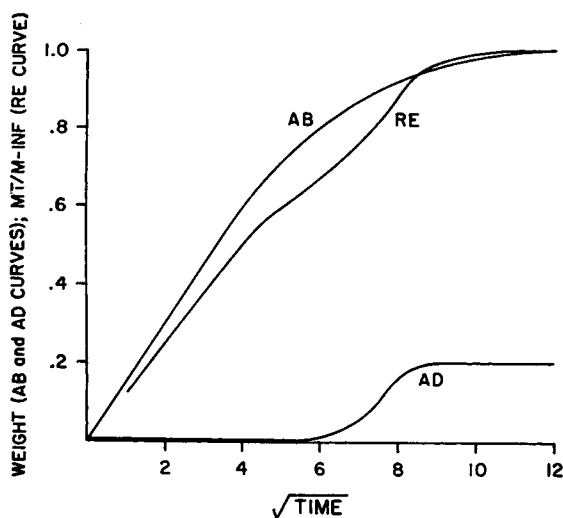
Fig. 3. Combination of an absorption curve and a selected adsorption curve to show resultant curve as a normal absorption curve with several points out of position: AB, absorption curve; AD, adsorption curve; RE, resultant.

density than the amorphous regions. Assuming a uniform thickness during film formation, as the film cools the crystalline regions at or near the surface will contract more than the amorphous regions, producing indentations and perhaps, either alone or in combination, capillaries in the surface. On exposure to vapor at a pressure below the saturated vapor pressure, these depressions and capillaries will tend to fill with water. Due to the concavity of the surface of the condensed liquid, the vapor pressure exerted will not be the saturated vapor pressure but will be in equilibrium with the ambient vapor pressure,[6] a well-known fact. Thus liquid water could be present at vapor pressures below the saturated vapor pressure not only in the adsorbed layer but also in depressions and capillaries. Since the weight of the adsorbed layer should be directly and roughly linearly proportional to the vapor pressure of the permeant in the intermediate relative humidity range (where adsorbing molecules see primarily multiple, uniform layers of adsorbed sorbate), departures therefrom could be construed to indicate the presence of depressions, capillaries, and/or other surface irregularities.

There is the possibility that the per cent crystallinity in the 0.5- and 5-mil samples is the same and the difference in density is due to structural differences in the amorphous phases. (This possibility was suggested by Dr. C. F. Heffelfinger, Film Dept., E. I. du Pont de Nemours and Co., Circleville, Ohio.) Without a knowledge of the solubility of water vapor in these two different amorphous phases, the amount of water adsorbed cannot be ascertained. There is also the possibility that the test material has a "skin" of small but finite thickness with a different structure from that of the interior and in which the solubility of the sorbate is different

(probably) from that in the interior.   No references showing that films of poly(ethylene terephthalate) possess such a skin were found.   For the general case it may be possible to enlarge the system of simultaneous equations to include other effects such as capillary condensation and skin formation.

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