Diffusion of Water Vapor in Plastic Laminates

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PLASTIC laminates are often used as electrical or thermal insulating materials. Because the mechanical, electrical, and thermal properties of these materials are affected by the moisture content, a knowledge of the diffusion properties is valuable for predicting their behavior under various conditions. These materials are anisotropic as has been demonstrated by Freiling, Eckert, and Westwater (*5*) for thermal conductivity. An unsteady-state method was devised for measuring the diffusion coefficient of water in the three principal directions for such materials, and the dependence of the diffusivity on concentration, if any, was determined. The method, not restricted to water, has an advantage of being well adapted for thick specimens.

BACKGROUND

In early work at the University of Illinois attempts were made to determine diffusivities in the three principal directions simultaneously by submitting rectangular parallelepiped specimens of various dimensions to the diffusion medium, and determining weight gain *vs.* time curves. The method of analysis used by Freiling and others (*5*) for anisotropic thermal diffusivity measurements was then applied to determine the three principle mass diffusivities. However, negative diffusivities were found for certain cases. This could be the result of a degree of solubility of the solids or of a dependence of diffusivity on moisture content.

Later, unidirectional tests were developed, which consisted of immersing a specimen in mercury deep enough so that all faces but one were sealed. Tests were made using this technique with diffusion occuring from liquid water and from saturated vapor atmospheres. In many cases diffusivities varied with time. Concentration or some other factor, not time, may have caused the variation. This work was undertaken to determine if any functional relation between diffusivity and concentration really exists. Results with water vapor are shown herein, but not with liquid water because some leaching occurs with the liquid, and this weight loss confounds the weight-gain data.

THEORETICAL CONSIDERATIONS

Because of the slowness of the diffusion process in polymers, an unsteady-state method is attractive for determining diffusivity. Fick's second law may be written:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} \qquad (1)$$

Because undirectional tests were carried out exclusively, two of the terms on the right-hand side of Equation 1 will be zero, depending on the direction of diffusion. Considering diffusion in the x direction, Equation 1 becomes

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} \qquad (2)$$

Equation 2 may be integrated by means of infinite series. However, if the time is relatively small, so that almost no fluid diffuses to the far end of a finite slab, the equation for a semi-infinite slab will be satisfactory. The concentration at any depth x below the surface at any short time is given then by Equation 3.

$$\frac{C - C_s}{C_o - C_s} = \operatorname{erf} \frac{x}{2(D_x t)^{1/2}} \qquad (3)$$

Other major assumptions involved in Equation 3 are that the surface resistance is negligible, the initial concentration is uniform, the surface concentration is constant after time zero, and the diffusivity is constant.

Equation 3 cannot be used unless a good method is available for determining the point concentrations at various times. A sectioning technique, followed by electrical resistivity measurements to indicate the water contents, was investigated experimentally. The electrical method was excellent, but no sectioning technique could be devised which was both rapid and reliable. The use of radioactive water seems promising, but it was not necessary because a direct weighing of the entire solid was feasible.

The total weight at small times of a specimen absorbing from one face can be derived from Equation 3 to give:

$$M_t = 2\, C_s \left(\frac{D_x t}{\pi}\right)^{1/2} \qquad (4)$$

For a solid thickness L in the diffusion direction $C_s = M_s / L$, or the surface concentration is equal to the water uptake at saturation divided by the thickness. Making this substitution, Equation 4 becomes

$$\frac{M_t}{M_s} = \frac{2}{L} \left(\frac{D_x t}{\pi}\right)^{1/2} = \text{fractional uptake} \qquad (5)$$

To estimate the time during which a finite slab may be treated as semi-infinite, assume that the limit occurs when the concentration at the far boundary changes by 1% of its maximum possible change. This is equivalent to stating that $\operatorname{erfc} L/2(D_x t)^{1/2} = 0.01$. Selecting a representative value for L and the maximum value of D, the minimum value for the end of semi-infinite behavior occurs at about 160 hours.

Equation 5 predicts that a plot of M_t/M_s *vs.* $t^{1/2}/L$ should be a straight line for the semi-infinite behavior period, with slope proportional to $D^{1/2}$, if the diffusivity is constant. If diffusivity is distinctly dependent on concentration, data on runs in ambient atmospheres of various humidities should have a different slope for each atmosphere. If there is no dependence, the data for all ambient humidities should fall on the same line.

APPARATUS AND PROCEDURE

Diffusivities in each of the three principal directions were determined separately from unidirectional diffusion tests. Initially all specimens were brought to equilibrium with a low humidity atmosphere at 23° C. Specimens were then immersed in mercury so that only the upper face was exposed, then introduced into a higher humidity atmosphere. The diffusion process was then followed by periodic weighing of the specimens. Mercury is an ideal sealant. It permits swelling of the solid. Early tests showed that mercury is relatively impermeable to diffusion of water, and the test materials used do not absorb mercury.

The three different phenol-formaldehyde plastic laminates were supplied by the Continental Diamond Fibre Co., Newark, Del., and are designated as follows: Dilecto X-13 (ASTM specification Grade X), a paper base laminate designed for mechanical usages; Dilecto XXX-13 (ASTM Grade XXX), a paper base laminate designed for electrical uses; and Dilecto C-813 (ASTM Grade C), a cotton canvas base laminate designed for high impact and loading strength. These materials were selected because they are known to be anistropic.

One set of runs was made at 23° C. in a constant tempera-

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ture room. The other set was carried out at 40° C. in a specially constructed constant temperature box and adjoining weighing box. The general procedure was the same at both temperatures, with some modifications being necessary at 40° due to space limitations.

To prevent molds and fungi on the specimens at 40° C. at high humidities, a germicidal ultraviolet lamp was installed in the test chamber. A fan circulated the air in the box over the lamp continuously. This kept the air sterile, and no growths were observed.

Specimens were 1-inch cubes cut from large 1-inch thick slabs of the laminate. These were polished, using metallurgical techniques, with grade 4/0 emery paper. Final polishing scratches on side faces were always parallel to the top (diffusion) face, so as to prevent water from traveling down small capillaries on the specimen sides.

Cut specimens were stored for 2 months or more in desiccators in which the relative humidity was maintained at 31% at 23° C. Selected specimens were weighed periodically to determine when equilibrium with this atmosphere had been established. After equilibrium was established, specimens were introduced into various higher humidity atmospheres with controlled temperature and humidity with only one face exposed to the atmosphere, the other five faces being sealed with mercury.

The apparatus for containing samples, herein called a diffusion unit (Figure 1), consisted of a Lucite plastic box to contain the mercury sealant and sample, a bridge to hold the sample in position, and a glass jar to contain the humidity-controlling solution. The bridge was fastened across the top of the plastic box. In the center of the bridge three holes were drilled in a triangular array. These were tapped, and pointed stainless steel screws were inserted vertically to hold the sample at the desired level in the mercury.

Humidities were controlled by putting various saturated salt solutions in the glass jar around the sample box. Excess salt was present to ensure saturation. An extensive list of salts and the relative humidity above their saturated solutions at various temperatures is available (*7*). The jars were closed with screw caps, so that the humidity in each jar was maintained independent of all the others.

The procedure for all the runs was essentially the same. A specimen was removed from the desiccator, weighed, and properly positioned in its diffusion unit. The time of this weighing was recorded as time zero for that run. After starting, specimens were removed from the diffusion units and weighed at intervals more or less equally spaced on a square root of time scale. To minimize the time out of the diffusion atmosphere for weighing, the weight of each sample was estimated from previous weighings and set up on the balance before the sample was removed for weighing. Ainsworth Chainomatic balances held at the test temperatures of 23° and 40° C. were used exclusively. At 23° weights were recorded to the nearest 0.1 mg. At 40° weights were recorded to the nearest 0.5 mg. The weighing times were less than 1 minute each.

Years would be required to run 1-inch thick specimens with only one face exposed to equilibrium, and even with all six faces exposed the time would be very long. Therefore, equilibrium concentrations were determined by submitting thin specimens (about 0.1 inch thick by 1 inch in cross section) to the same initial and final atmospheres as the run specimens and allowing equilibrium to be established with these. These showed no weight change after about 20 days. A few of the specimens were left in their atmospheres for over 100 days to prove that the equilibrium values were correct. The per cent increase in weight between initial and final conditions found for the thin specimens was assumed to hold for the thicker specimens—i.e., equilibrium concentration is independent of thickness. This assumption is reasonable, but is unproved. In fact, four cloth base specimens, 1 inch thick, run by Chivot (*1*) at 40° C. and 100% relative humidity for approximately 1-1/2 years exceeded the equilibrium weight predicted from 0.1-inch specimens (one by 28%). This could be caused by aging of the material during the long exposure time, thus loosening the structure and permitting the specimens to hold more water.

Figure 2 shows how the equilibrium mositure content for thin specimens depends on the ambient humidity.

DISCUSSION OF RESULTS

The experimental diffusivities are summarized in Tables I and II. Detailed data are available (*1, 6, 8*). Figures 3 to 8 give a selection of data for the three materials tested in three directions at two temperatures in three and four ambient humidities.

Duplicate specimens were run in every case. Data for

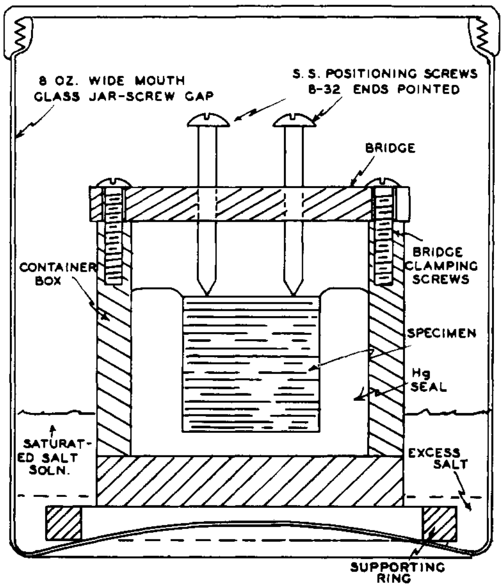

Figure 1. Scale drawing of diffusion unit
Cross-sectional side view, specimen width, 1 inch

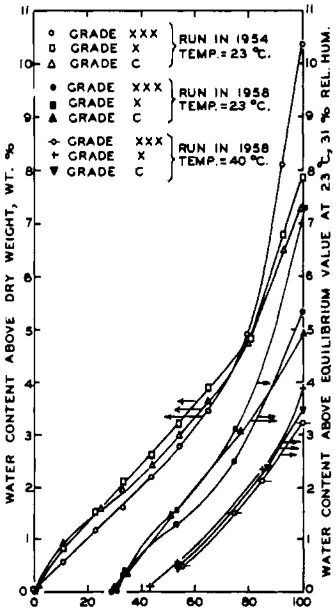

Figure 2. Equilibrium water concentration

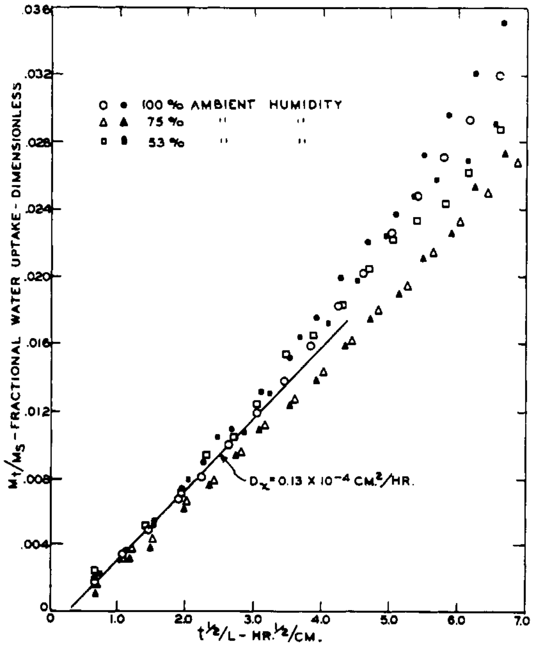

Figure 3. Absorption of water vapor in Grade XXX laminate in x direction at 23° C.

Table I. Summary of Diffusivities at 40° C.

Direction	Ambient % Humidity	D, Diffusivity, Sq. Cm./Hr. × 10^4		
		Grade X	Grade XXX	Grade C
x	100	1.3	2.1	16
	100	1.2	1.7	16
	85	1.4	1.8	12
	85	1.6	1.6	16
	75	No run	0.55	No run
	75	No run	0.86	No run
	54	7.6	0.69	38
	54	10	1.2	30
y	100	1.4	1.1	19
	100	1.7	1.4	17
	85	2.7	1.9	21
	85	2.7	1.9	22
	75	No run	1.0	No run
	75	No run	0.78	No run
	54	15	0.73	53
	54	14	0.91	44
z	100	0.44	0.41	3.2
	100	0.29	0.48	2.6
	85	0.55	0.41	1.5
	85	0.42	0.53	1.4
	75	No run	0.38	No run
	75	No run	0.27	No run
	54	3.4	0.18	2.1
	54	3.1	0.19	1.8

duplicates are shown in the tables and the graphs. The average disagreement between duplicate diffusivities was 18%. Considering the natural variability of the test materials (*10*), this agreement seems good.

High accuracy in determining diffusion coefficients for variable materials with extremely low diffusivities is not practical. Results are ordinarily given to one or two significant figures only (*4*). Great care was taken with the present tests, so two significant figures seem warranted. Superimposed on the variations inherent in the test materials are errors due to experimental difficulties. The worst experimental error is roughly estimated by assuming additive weighing errors of 0.5 mg. at the original and final times for the thin saturation specimens and at the original and individual times for the thick test specimens. Errors due to measurements of time and of thickness are neligible, and for short times swelling is not detectable. The worst errors are as low as 12% for the diffusivity of the Grade C material run at 100% ambient humidity and as high as 169% for the Grade X material run at 54% humidity. The greatest weight gains, and therefore the best accuracy, occurred at the high humidities; the worst occurred at low humidities. Figure 4 illustrates maximum error limits for one set of conditions.

Temperature Effect. As expected, temperature is an important variable for all three test materials at all humidities. The diffusivities at 40° C. were as much as 25 times the values observed at 23° C. The usual increase was a factor in the order of 5 to 10. This factor is much greater than the possible experimental errors. Figures 3 and 4 contrast data obtained at the two temperatures.

The use of two temperatures permits an estimate of the activation energy for diffusion. The resulting values of E, based on the usual relationship,

$$D = D_o \exp. - \frac{E}{RT} \tag{6}$$

are shown in Table III. The values are approximate only; they are based on assumptions that diffusivity is independent of the state of stress, the concentration of the diffusing medium, and time, and that there is no absorption, surface diffusion, or capillary flow. The average value of the activation energy is about 22,000 cal. per gram mole. This is about double the latent heat of vaporization and indicates that it is difficult for the water molecules to acquire suffi-

Table II. Summary of Diffusivities at 23° C.

Direction	Ambient % Humidity	D, Diffusivity, Sq. Cm./Hr. × 10^4		
		Grade X	Grade XXX	Grade C
x	100	0.23	0.14	3.2
	100	0.19	0.19	3.1
	75	0.41	0.09	3.7
	75	0.34	0.10	3.7
	54	0.43	0.11	5.3
	54	0.60	0.17	4.6
y	100	0.33	0.12	3.8
	100	0.27	0.14	4.2
	75	0.51	0.16	4.7
	75	0.41	0.16	4.5
	54	0.58	0.14	6.1
	54	0.48	0.17	5.3
z	100	0.030	0.032	0.12
	100	0.033	0.043	0.11
	75	0.052	0.057	0.20
	75	0.071	0.046	0.21
	54	0.068	0.11	0.31
	54	0.19	0.12	0.29

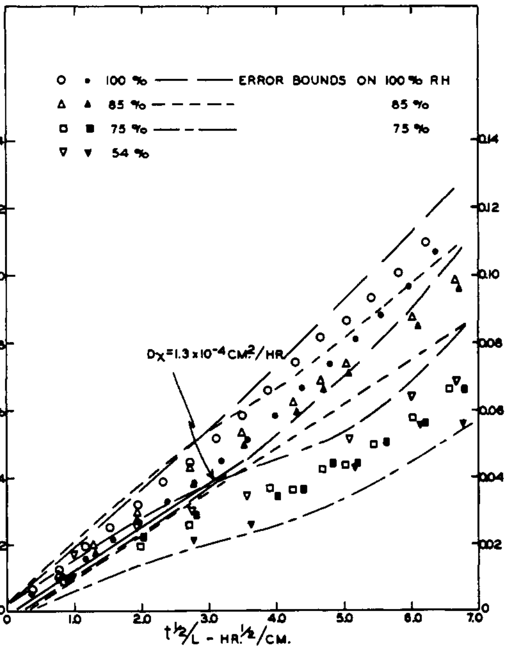

Figure 4. Effect of temperature

Same as in Figure 3, Grade XXX, x direction, but tested at 40° C. Dotted line, estimates of maximum error in observations

Table III. Activation Energy for Diffusion

Direction	Ambient % Humidity[a]	E, Activation Energy, Cal./G. Mole		
		Grade X	Grade XXX	Grade C
x	100	19,000	27,000	18,000
y	100	18,000	24,000	16,000
z	100	26,000	27,000	10,000
x	75	. . .	21,000	. . .
y	75	. . .	18,000	. . .
z	75	. . .	20,000	. . .
x	54	31,000	21,000	21,000
y	54	35,000	18,000	23,000
z	54	33,000	5,000[a]	20,000
Recommended Values for E and D_o				
x or y, E		26,000	22,000	19,000
x or y, D_o		3.3×10^{14}	2.3×10^{11}	3.3×10^{10}
z, E		30,000	24,000	20,000
z, D_o		3.9×10^{16}	2.0×10^{12}	1.2×10^{10}

[a] Doubtful.

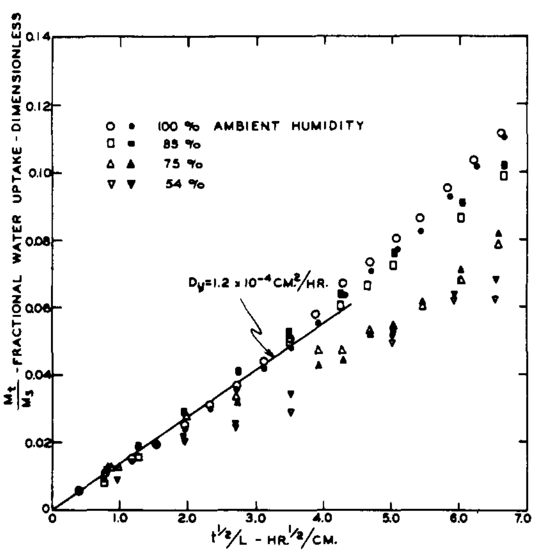

Figure 5. Grade XXX laminate absorbing in *y* direction at 40° C.

Effect of direction

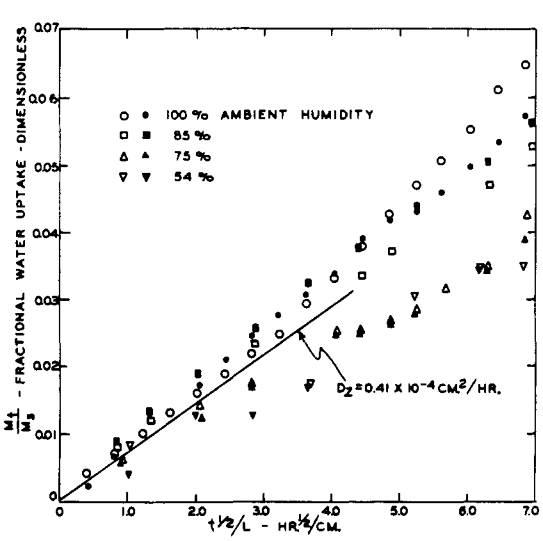

Figure 6. Grade XXX laminate absorbing in *z* direction at 40° C.

cient energy to progress into the solid. No consistent effect of humidity is apparent. However, the activation energy for the Grade C material is somewhat less than the energy for the other two materials, and the value for the *z* direction is a little larger than that for the *x* and *y* directions. Recommended equations are included in Table III.

Anisotropic Behavior. Diffusivities in the *x* and *y* directions (parallel to the laminations) were similar for any one material. However, in the *z* direction (perpendicular to the laminations) the diffusion was slower, in several cases the diffusivity being only a few per cent of the values for the other principal directions. Tables I and II show that in no case was D_z greater than D_x or D_y. Figures 4, 5, and 6 illustrate short-time diffusion in the three principal directions for the Grade XXX material at 40° C. In this example D_z is about one fourth of D_x or D_y. It is usually to be expected that solids having a laminated structure will exhibit a smaller diffusivity perpendicular to the layers than parallel to them.

Different Materials. Among the three test materials, the most obvious fact is that the cloth-base laminate (Grade C) is significantly more permeable than the two paper-base laminates. The effect is most pronounced for the directions parallel to the laminations.

Effect of Ambient Humidity. The starting conditions for all specimens were the same—namely, at a uniform temperature of 23° C. and at equilibrium with air at 31% relative humidity. Diffusion runs consisted of suddenly changing the relative humidity to a new value. For half the runs a simultaneous change in temperature to 40° C. was imposed also. However, the time required for thermal equilibrium is so short (about 10 minutes) that all the diffusion for the high temperature runs may be assumed to occur at 40° C.

When a specimen is placed in a new ambient humidity, its surface concentration changes to a new level, assumed to be the new equilibrium value. The change is imagined to be instantaneous. Any lag will be evidenced by the sorption curves missing the origin as in Figure 3. On the remaining figures, the curves were translated to pass through the origin. This translation was always less than 1 hour. A moving concentration profile quickly comes into existence, the point values depending on the surface concentration. Thus, if the diffusivity is concentration-dependent, its values calculated from runs made at different ambient humidities should be different.

Some change in *D* with varying humidities was detected, but the variation was neither large nor systematic. If concentration-dependence does exist for these materials, it is weak.

The diffusivities listed in Tables I and II were calculated from the slope of the early straight-line portion of the graphs of fractional weight gain *vs.* the square root of time. A single line gives an adequate fit for each material in each direction, at each temperature, at all humidities, for short times, as shown in Figure 3. A single line signifies a diffusion coefficient which is independent of concentration, position, and time. As the time becomes intermediate (more than a few days, but far short of the years needed for a close approach to saturation) the data diverge, and a single line is no longer suitable. However, if no significant dependence of diffusivity on concentration exists for short times, then none should exist for longer times. In Figures 7 and 8, an apparent deviation from a single diffusivity seems to exist at short times for runs made at 54% relative humidity. However, this cannot be accepted as significant, because the runs at 54% humidity have possible errors of about 100%. Runs at higher humidities are much more reliable.

An alternative procedure of testing for concentration-dependence is to obtain absorption data for long times, such as shown in Figure 9. A functionality between *D* and *C* is then assumed—for example, $D = aC^b$, $D = ae^{bC}$, etc., where *a* and *b* are empirical constants. Then a numerical or graphical technique is applied to solve Equation 2, treating *D* as a variable. Arbitrary values of *a* and *b* are then investigated to see if a predicted weight *vs.* times relationship agrees with the experimental one. Chivot worked with this approach (*1*) and concluded that no direct, continuous function exists between *D* and *C*. He showed that a more promising approach is to assume step changes in *D* with concentration. This makes sense if stress relief occurs at specific concentrations. Experimental proof of this relief hypothesis is not available.

Crank (*3*) presents an exact procedure for finding the constants such as *a* and *b* above when the functionality is linear or exponential. His method is recommended for future experimenters who encounter a variable diffusivity.

The state of stress in solids undergoing absorption is not constant. During early times swelling occurs only in the wet portion of the solid. The dry portions tend to resist the expansion. The result is that the dry portions are in tension and the wet portions in compression. As time passes the two portions change in size; thus, the strain in each part changes. Eventually all stress disappears as saturation is approached. A detailed discussion of stress-dependent diffusivity is given by Crank (*2*).

At present the best explanation for the divergence of the data obtained at different humidities after short times—e.g.,

Effect of material

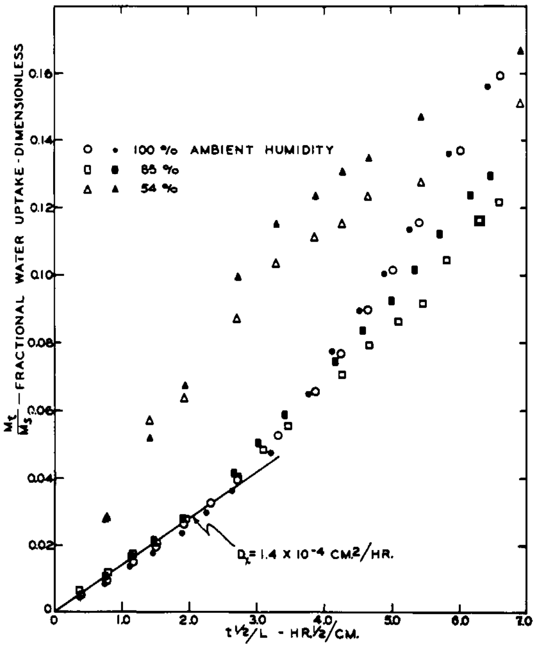

Figure 7. Grade X laminate absorbing in x direction at 40° C.
Compare to Figures 4 and 8

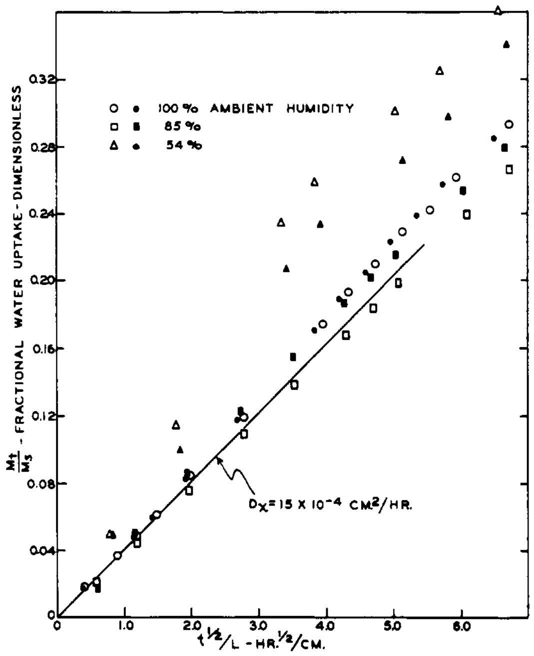

Figure 8. Grade C laminate absorbing in x direction at 40° C.
Compare to Figures 4 and 7

in Figure 4—is that diffusivity is stress-dependent. This seems consistent with the sigmoid curves in Figure 9. It would be valuable to have measurements of diffusivity for specimens under external tension or compression. Such tests would show conclusively whether the state of stress is important.

Considerable stress definitely does develop during absorption. For some specimens in this research, visible cracks appeared after 10 days or so. Data taking was terminated at such time.

Osmotic Pressure Theory. An interesting theory described by Tester (*9*) considers diffusion to result from osmotic pressure of water solubles inside the solid. The theory predicts that inflection points in the weight *vs.* square root of time curve are not possible. The theory is not applicable to the present materials because inflection points are observed as illustrated in Figure 9.

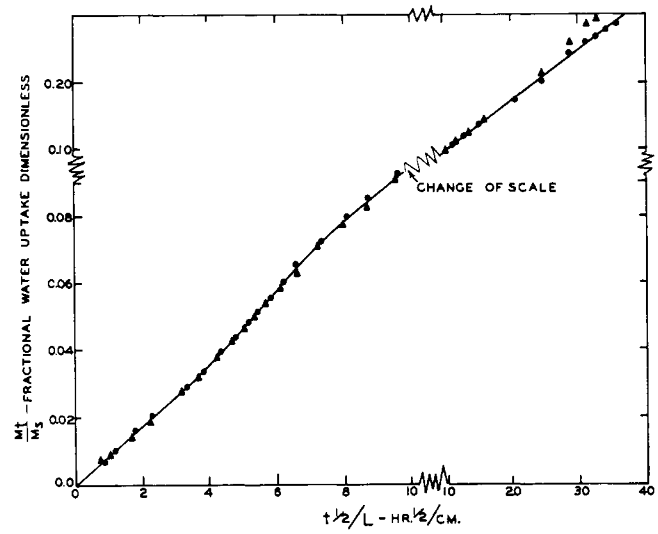

Figure 9. Water uptake at long times
Grade XXX laminate absorbing in z direction at 40° C.

NOMENCLATURE

C = concentration at a point at time t, g. per cu. cm.
C_o = initial uniform concentration at zero time, g. per cu. cm.
C_s = concentration at equilibrium, g. per cu. cm.
D = diffusivity, sq. cm. per hr.
D_o = coefficient defined by Equation 6, sq. cm. per hr.
D_x, D_y, D_z = diffusivity in the x, y, and z directions, sq. cm. per hr.
E = activation energy for diffusion, cal. per g. mole x ° K.
L = thickness of specimen in direction of diffusion, cm.
M_s = total water uptake from time zero to saturation, g. per sq. cm. of exposed surface.
M_t = total water uptake during time t, g. per sq. cm. of exposed surface.
t = time, hr.
T = absolute temperature, ° K.
x = distance along one principal axis parallel to laminations, cm.
y = distance along second principal axis parallel to laminations, cm.
z = distance along principal axis perpendicular to laminations, cm.

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