

Measuring Diffusion Coefficients by Hydroelasticity

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Synopsis

A new method for obtaining diffusion coefficients of polymers and composites by measuring relative length changes is proposed. The method is based on interrelating diffusivity and hydroelasticity, and it is applicable to materials whose dynamic and equilibrium stage coefficients of hydroelasticity are equal.

INTRODUCTION

Hydroelasticity of polymers or composites is defined as the reversible dimensional change (swelling) of the material exposed to liquid or vapor penetration. In essence, hydroelasticity is analogous to thermoelasticity: the first is approached by examining the strain against the relative weight change caused by liquid or vapor absorption, and in the latter the strain is linked to a temperature interval ΔT . Hence, the coefficient of hydroelasticity may be expressed by¹

$$\mu = \frac{\Delta L/L_0}{\Delta W/W_0} \quad (1)$$

where $\Delta L/L_0$ is the relative length change and $\Delta W/W_0$ is the relative weight gain.

To determine μ , both the relative length change and the relative weight gain of the material are recorded at different exposure periods and μ is obtained from the slope of the curve relating length change to weight change. Such a procedure for the transverse coefficient of a unidirectional composite immersed in water at 98°C is described in ref. 2.

The diffusivity of the material in the direction normal to the surface is described by the Fickian equation resulting in³

$$D = \left(\frac{hM}{4M_m} \right)^2 \frac{\pi}{t} = \pi \left(\frac{hk_W}{4M_m} \right)^2 \quad (2)$$

where h is the thickness of the material, M is its percent penetrant content, t is the exposure time, the subscript m denotes a maximum value, and k_W is the slope of the linear portion of the plot of M vs. $t^{1/2}$.

A common experiment for the measurement of D is to expose the material to the penetrant and to weigh the specimen at specified time intervals to determine its weight gain. Both k_W and M_m are thereafter determined from a plot of the penetrant content versus square root of time, and D is calculated by eq. (2). A detailed example applied to composite materials can be found in ref. 3.

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INTERRELATING DIFFUSIVITY AND HYGROELASTICITY

The diffusivity and hygroelasticity are interrelated as derived from eqs. (1) and (2) considering that $M = (\Delta W/W_0) \times 100$. This results in eq. (3), where L is the percent dimensional increase $(\Delta L/L_0) \times 100$ and k_L is the slope of the linear portion of the plot of L vs. $t^{1/2}$:

$$D = \left(\frac{h\mu L}{4\mu_m L_m} \right)^2 \frac{\pi}{t} = \pi \left(\frac{h\mu k_L}{4\mu_m L_m} \right)^2 \quad (3)$$

where μ and μ_m are the initial and equilibrium values, respectively, of the coefficient of hygroelasticity.

The coefficient of thermal expansion often exhibits a temperature dependence, and in view of the analogy between thermoelasticity and hygroelasticity, the question of the dependence of the coefficient of hygroelasticity on $\Delta W/W_0$ should be considered. A recent article⁴ suggested that if such dependence indeed existed, it could result from a specimen geometry effect. For example, the geometry (thickness) can affect the diffusion mechanism resulting in a Fickian, modified Fickian, or Case II mechanism for the same polymer as the thickness is increased (see, for example, ref. 5). The change to Case II in the diffusion mechanism can affect μ due to the constraint between the less swollen material in the core and the outer swollen envelope. Under such conditions, swelling is also accompanied by a specimen shape change. In addition to this, anisotropic hygroelastic behavior may also result from the polymer morphology, e.g., its molecular orientation.⁶ Consequently, μ exhibits a function in $\mu W/W_0$, and the discrete values of μ and μ_m as in eq. (3) are meaningless.

For many composite materials however, this is not the case, and substantial data gathered recently indicate that for many epoxy and polyester composites μ is constant throughout. Moreover, these data provide significant evidence indicating that as long as μ_m is calculated before the swelling process creates major damage (viz., distortion or cracking) to the specimen,

$$\mu = \mu_m \quad (4)$$

This situation is likely in composite materials where the reinforcement tends to restrain dimensional damage in the matrix. For cases where eq. (4) is applicable, eq. (3) reduces to

$$D = \pi \left(\frac{hk_L}{4L_m} \right)^2 \quad (5)$$

Some of the already existing data which support the above observation expressed by eq. (4) are summarized below. An extensive work by Ishai⁷ shows linear relationships between $\Delta L/L_0$ and $\Delta W/W_0$ up to equilibrium for pure epoxy resins and for longitudinal and transverse glass fiber composites exposed to hot and cold water cycles. The exceptions are a slight deviation from linearity at the very initial stage of the water take-up process (also observed by others) and another possible deviation at equilibrium corresponding to the onset of leaching damage. Similar observations were made on transverse glass fiber-reinforced epoxies exposed to water at 97°C² and on longitudinal and transverse glass-reinforced composites exposed to various humidity levels.⁸ Examinations of graphite fiber-reinforced epoxy data^{9,10} and pure epoxy resin data¹¹ also indicate that $\mu = \mu_m$.

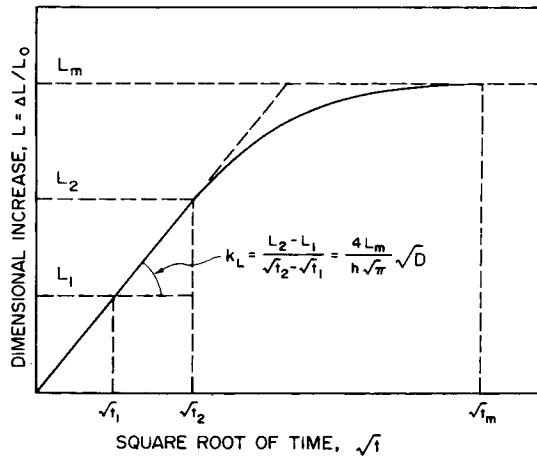


Fig. 1. Illustration of the relative length change as function of the relative weight gain. Coefficient of diffusion is calculated from the slope of the linear portion of the curve and from the maximum relative length change.

IMPLICATIONS AND CONCLUSIONS

It is obvious that eq. (5) suggests a new technique for measuring the coefficient of diffusion. By this technique the relative length change of the specimen is plotted against the square root of time, and the coefficient of diffusion is calculated as illustrated in Figure 1.

The dimensional change technique for measuring diffusion coefficients for composites is advantageous over the weight change technique. First, readings can be taken continuously by using various length change measuring methods and devices such as transducers, strain gauges, light diffraction, etc., while the specimen is continuously exposed to the test environment. Second, the technique of weighing is carried out periodically, and in most cases the specimen has to be removed from the test environment and transferred to the balance. Moreover, the results are always sensitive to the method employed for drying the specimen surface.

It is, therefore, concluded that the dimensional change technique—although of particular applicability—provides a very convenient method for measuring the diffusion coefficient. This technique is applicable to the many material-liquid/vapor systems whose coefficients of hygroelasticity are independent of the absorbed penetrant level.

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