Bending-cantilever method for the study of moisture swelling in polymers

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Self-induced bending of a bilayer strip is shown to be a simple but sensitive method for the study of water absorption and swelling in polymers. Expressions for both the time-dependent and equilibrium curvature of the strip have been derived, enabling both diffusional and dilatational parameters to be extracted from experimental data. To illustrate the technique, it is shown that a vacuum-dried epoxy swells linearly with water content, at a rate of 0.93% in volume per weight percent of water. Desorption into vacuum has been observed under diffusion-controlled conditions and the diffusion coefficient for water in the epoxy found to be 2.5 × 10^{-9} cm^2/s at 295 K.

Introduction

Water absorption by polymers is a common phenomenon, to which epoxies are no exception [1]. Investigations of the sorption of water by an epoxy used in laminated circuit boards have been pursued by a variety of techniques, some of which are described elsewhere in this issue [2, 3]. From gravimetric measurements [2], it has been found that below about 360 K the sorption and desorption of water are essentially reversible processes. In this regime, absorption of water involves a relatively simple solution process, which can be described thermodynamically in terms of an equilibrium between water in the vapor phase and water as an interstitial solute in the polymeric host.

This paper is concerned with one of the most direct consequences of water absorption, namely the tendency of the host to undergo swelling or dilatation [4]. In the context of circuit board technology, this tendency is inevitably opposed by constraints which lead to the generation of internal stress. Modeling calculations of such stresses require a knowledge of the swelling parameter specifying the fractional volume change associated under free-expansion conditions with unit concentration of absorbed water. The present paper shows how this parameter can be determined by a simple bending-cantilever method. In addition, it is shown that the method can also be used to obtain the diffusion coefficient of water in the polymeric host.

Theory

As shown in **Figure 1**, the method makes use of the bending of a bilayer strip consisting of the polymer layer attached to an inert (nonabsorbing) elastic backing. The behavior of this composite sample is similar to that of a bimetallic thermostat element except that the effect of principal interest is now the bending caused by changes in humidity rather than temperature. In response to a stepwise change in ambient humidity, a previously equilibrated sample will gradually bend because of the swelling (shrinkage) caused by absorption (desorption) of water. After re-equilibration, the change in the curvature of the bilayer is a measure of the change in the volume of the polymer. Moreover, if exchange with the surroundings is rate-limited by the diffusion of water within the polymer layer, the kinetics of bending can be used to obtain the diffusion coefficient for water in the polymeric host.

In this section we derive an expression for the curvature of the bilayer using an approach similar to that employed by Timoshenko in his work on bimetallic strips [5]. The present calculation, however, is further complicated by the inclusion of kinetic considerations, which necessitate a generalization of Timoshenko's equilibrium analysis to include the bending produced by an inhomogeneous distribution of moisture through the thickness of the polymer layer. As a step towards the analysis of the bilayer, it is useful to consider first the polymer layer by itself, when imagined to be momentarily detached from the elastic backing. We assume that the polymer is isotropic and swells in volume V proportionally to a uniform water concentration C_0. Thus, we may write

$$\varepsilon_H = SC_0 , \tag{1}$$

where ε_H is a hygroscopic strain analogous to a thermal expansion strain, and S is a linear swelling parameter equal to one-third of the volumetric swelling factor:

$$S = \Delta V/3VC_0 . \tag{2}$$

Although a uniform concentration of water produces a simple swelling (pure dilatation) without internal stress, a nonuniform concentration profile $C(z, t)$ at instant t through the thickness (z-coordinate) of the strip will in general produce elongation, bending, and internal stress. With the usual assumption that plane cross sections remain plane, the stress $\sigma(z, t)$ is given by

$$\sigma(z, t)/E_1' = SC(z, t) - \varepsilon_D(t) - z/R_D(t), \tag{3}$$

where E_1' denotes $E_1/(1 - \nu_1)$, E_1 and ν_1 are Young's modulus and Poisson's ratio of the polymer layer, $\varepsilon_D(t)$ is the strain at the midplane (chosen as origin, $z = 0$), and $R_D(t)$ is the radius of curvature. Since the detached layer is under no external forces, we find by integrating Eq. (3) over the thickness a_1 of the layer that

$$\varepsilon_D(t) = S \int_{-1/2}^{+1/2} C(u, t)du \equiv S\overline{C}(t), \tag{4}$$

where for convenience the sample is taken to be of unit width, and we have introduced the dimensionless coordinate $u \equiv z/a_1$ and the average concentration $\overline{C}(t)$. Since the detached layer is under no external moment, we also find that

$$1/R_D(t) = (12S/a_1) \int_{-1/2}^{+1/2} C(u, t)udu. \tag{5}$$

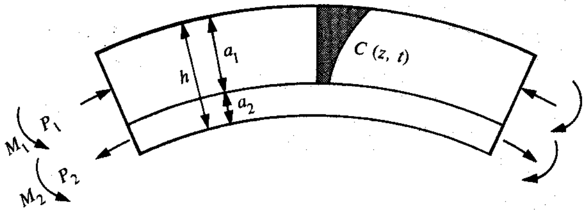

Figure 1

Self-induced bending of a bilayer strip caused by swelling associated with the moisture concentration profile $C(z, t)$ through the polymer layer.

It will be noted from Eq. (5) that the curvature of the detached layer vanishes for the uniform distribution $C(u, t) = C_0$, or indeed for any distribution that is symmetrical about the midplane.

With these results for the detached layer, we now return to the bilayer of Fig. 1. We again assume that plane cross sections remain plane on bending, and seek the curvature $1/R(t)$ which produces mutual accommodation of the two layers, while also satisfying the requirements that no external forces or moments act on the bilayer. As indicated in Fig. 1, accommodation is achieved by subjecting the polymer layer to a couple M_1 and a uniformly distributed compressive force P_1, while bending the backing layer with couple M_2 and extending it with force P_2. The equilibrium conditions require that the magnitudes of P_1 and P_2 be equal ($P_1 = P_2 = P$) and furthermore that the couple $Ph/2$ balance the couples M_1 and M_2. We thus obtain

$$Ph/2 = [(E_1'I_1 + E_2'I_2)/R(t)] - E_1'I_1/R_D(t), \tag{6}$$

where $E_2' = E_2/(1 - \nu_2)$, E_2 and ν_2 are Young's modulus and Poisson's ratio of the backing, $I_1 = a_1^3/12$ and $I_2 = a_2^3/12$. A second relation involving P is provided by the requirement of dimensional matching at the interface, which leads to

$$P\left(\frac{1}{a_1E_1'} + \frac{1}{a_2E_2'}\right) + \frac{h}{2R(t)} = \varepsilon_D(t). \tag{7}$$

Upon eliminating P from Eqs. (6) and (7), we find with the help of Eq. (4):

$$A/R(t) = S\overline{C}(t) + [B/R_D(t)], \tag{8}$$

where

$$A \equiv (h/2)\{[m^2(1+mn)(1+(1/nm^3))/3(1+m)^2]+1\}, \tag{9}$$

$$B \equiv hm^2(1 + mn)/6(1 + m)^2, \tag{10}$$

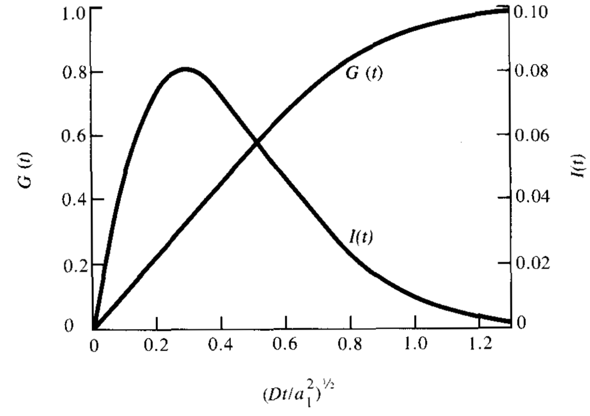

Figure 2

The functions $G(t)$ and $I(t)$, as determined by numerical integration for the case of diffusion-controlled bending in response to a stepwise humidity change.

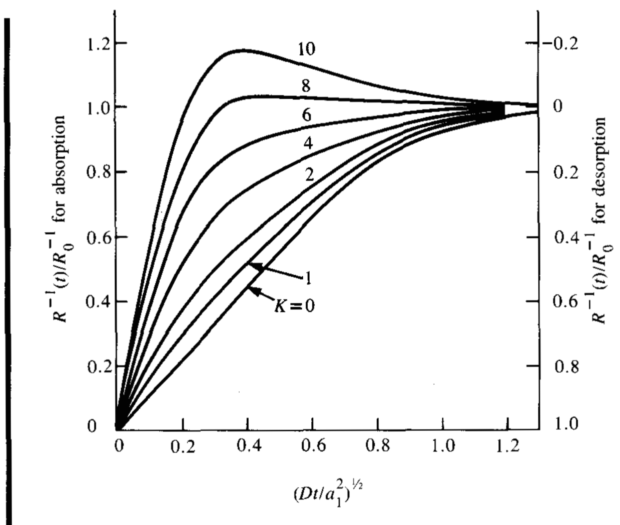

Figure 3

Diffusion-controlled bending of a bilayer, for various values of the parameter K defined by Eq. (14).

$$m \equiv a_1/a_2\,, \tag{11}$$

and

$$n \equiv E_1'/E_2'\,. \tag{12}$$

Equation (8) shows that the curvature of the bilayer is in general given by the sum of two terms. However, for the uniform distribution $C(u, t) = C_0$, the second term vanishes [cf. Eq. (5)] and Eq. (8) reduces to

$$A/R_0 = SC_0\,. \tag{13}$$

Equation (13) is used for the evaluation of the parameter S from the curvature obtained under equilibrium conditions. It should be noted that this equation is identical to Timoshenko's result for the uniformly heated bimetallic strip if the hygroscopic strain SC_0 is replaced by the differential thermal strain $(\alpha_1 - \alpha_2)\Delta T$, where α_1 and α_2 denote the linear expansion coefficients of the two layers, and ΔT is the temperature change from the reference state.

To pursue the determination of the diffusion coefficient from the kinetics of bending, we combine Eqs. (4), (5), (8), and (13) to obtain the dimensionless form

$$R^{-1}(t)/R_0^{-1} = G(t) + KI(t), \tag{14}$$

where

$$K \equiv 2m(1 + mn)/(1 + m), \tag{15}$$

$$G(t) \equiv (1/C_0)\int_{-1/2}^{+1/2} C(u, t)du, \tag{16}$$

and

$$I(t) \equiv (1/C_0)\int_{-1/2}^{+1/2} C(u, t)udu. \tag{17}$$

The evaluation of the integrals $G(t)$ and $I(t)$ is complicated by the fact that under the diffusion-controlled conditions of present interest, the concentration profile $C(u, t)$ is represented by an infinite series [6, 7]. By numerical integration, we have obtained $G(t)$ and $I(t)$ for the case where the diffusion coefficient is independent of concentration and sorption or desorption occur in response to a stepwise change in the concentration at the free surface. These functions are shown in **Figure 2**, plotted against the dimensionless variable $(Dt/a_1^2)^{1/2}$, where D is the diffusion coefficient of interest. Using Fig. 2, we have evaluated Eq. (14) for a range of values of the parameter K, with the results shown in **Figure 3.** The case $K = 0$ represents the limiting extreme where the kinetics of bending simply follow the same curve $G(t)$ as that for gravimetric measurements. For $K > 0$, the bending curves lead the gravimetric curve, owing to the greater effect of near-surface layers on the curvature of the bilayer. One striking result evident from Fig. 3 is that for large K-values, the bending curves for sorption (desorption) are predicted to develop a maximum (minimum). The experiments described in the following section do not, however, provide a test of this prediction, since the K-values of our samples were too small. For the determination of the diffusion coefficient D, Fig. 3 was used to construct **Figure 4,** which provides the value of the parameter $(Dt_{0.5}/a_1^2)^{1/2}$ at which bending is half complete $[R^{-1}(t)/R_0^{-1} = 0.5]$. Final acceptance of the D-value obtained by this procedure requires some assurance that the kinetics of bending were in fact diffusion-controlled. One step in this direction is to check that the shape of the experimental curve is consistent with that predicted theoretically. In addition, it is also highly desirable to check that consistent results are obtained with samples of substantially different thickness.

Experimental results

Test samples were obtained from composite sheets prepared from available circuit board materials. These sheets consisted of cured epoxy-glass laminate on a backing sheet of copper. To provide samples of epoxy-copper without glass reinforcement, these sheets contained areas where pieces had been cut out of the glass fabric. Bilayer strips approximately 2.5 cm long and 0.2 cm wide were cut from the glass-free areas with a small shear. For some bilayer samples, the epoxy thickness was reduced to approximately one-third of its initial value by grinding on 600-grit silicon carbide paper. Other samples were prepared for gravimetric measurements of the water content in the epoxy by etching away the copper backing. Test strips were mounted in a simple fixture which could be quickly transferred between a vacuum chamber and chambers held at various fixed humidities. Following transfer from one chamber to another, changes in the curvature of the bilayer were observed as a function of time via the deflection measured with a low-power microscope fitted with a graduated eyepiece.

The equilibrium measurements of **Figure 5** were performed on a bilayer consisting of 0.009 cm of epoxy on 0.00356 cm of copper. From these thicknesses and the values 4.5 GPa for E_1' and 197 GPa for E_2', the parameter A in Eq. (13) has the value 0.0105. The results of Fig. 5 were obtained by exposure of the bilayer and its companion gravimetric samples to various humidities, starting from the vacuum-dried state. At the completion of these measurements it was found that the initial curvature was recovered within 3% on re-drying, confirming that bending occurred elastically as assumed by the theory. The slope of the line drawn in Fig. 5 corresponds to a swelling factor S of 0.31% linear strain (0.93% volumetric strain) per weight percent of water. Alternatively stated, the swelling amounts to 0.55% linear strain (1.65% volumetric strain) on exposure of the dried epoxy to air at 100% relative humidity. Although the plot shown in Fig. 5 is linear, it will be noticed that the line shows a small offset from the origin. At present, it is not known whether this is caused by an intrinsic nonideality in the dilatation behavior of the material, or whether some other factor, such as excess water absorption at free surfaces, may be involved.

Turning to kinetics, it is apparent from the theory section that in principle, at least, the diffusion coefficient may be determined equally well from the bending observed during either sorption or desorption. Previous experience with the diffusion of sulfur in various polymers had, however, alerted us to the difficulties which may arise in sorption experiments from a source-limited absorption rate [8]. For this reason, vacuum desorption was adopted as the preferred

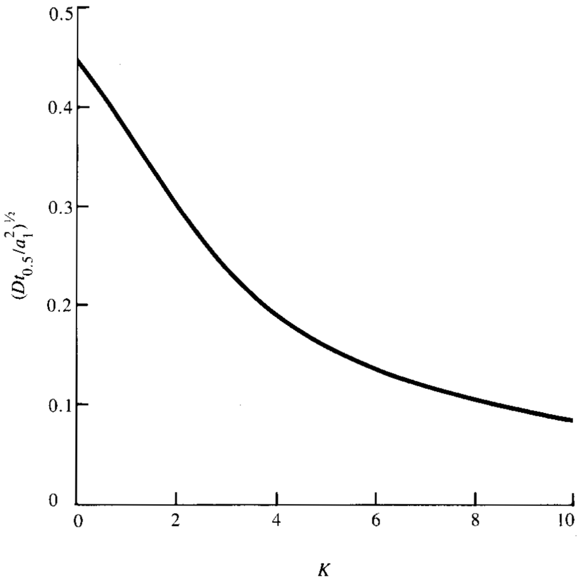

Figure 4

The dimensionless parameter $(Dt_{0.5}/a_1^2)^{1/2}$ plotted as a function of K.

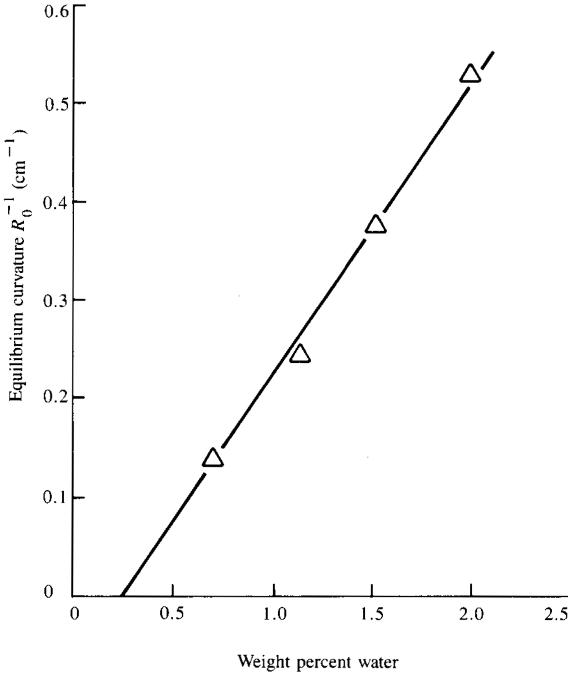

Figure 5

Equilibrium measurements at 295 K of the moisture-induced curvature of a bilayer consisting of 0.009 cm of epoxy on 0.00356 cm of copper.

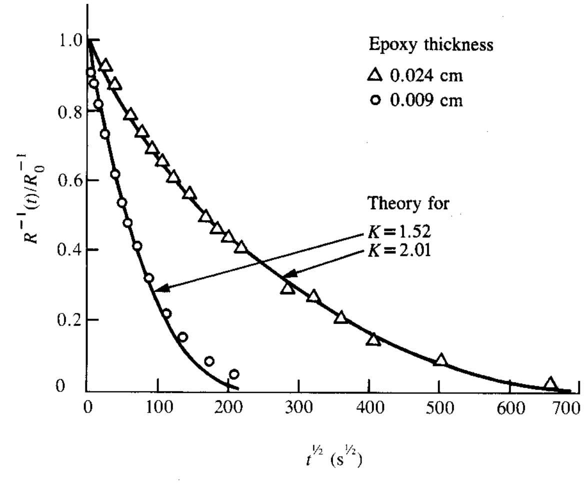

Figure 6

Bending kinetics at 295 K for moisture desorption into vacuum. The data points are for the two thicknesses of epoxy indicated, each on 0.00356 cm of copper. The solid lines are the theoretical curves for the appropriate K-value, pinned to the data at the $t_{0.5}$ point.

experimental approach after preliminary measurements on sorption from a stagnant atmosphere had indicated a somewhat delayed response. Vacuum desorption results are shown in **Figure 6** for two different epoxy thicknesses for which the times $t_{0.5}$ differed by almost an order of magnitude. Using the D-values obtained from Fig. 4, the theoretical desorption curves appropriate to the K-values of these samples have been calculated from Eq. (14) and are shown by the solid lines of Fig. 6. From the satisfactory agreement obtained, we conclude that desorption had occurred under the Fickian conditions assumed by the theory, and that the diffusion coefficient D for water in the epoxy is 2.5×10^{-9} cm^2/s at 295 K. This value is approximately twice that obtained by extrapolation of the results of Marsh et al. [2] to room temperature. Allowing for the scatter in their data, however, the agreement is reasonable. It is also of interest to note that the single-stage reversible sorption-desorption behavior observed in the present work is associated with concentration-independent diffusion, in contrast to the more complicated behavior reported for higher temperatures [2].

Concluding remarks

Since internal stresses may be generated in circuit boards by moisture swelling and by thermal expansion, it is of interest to compare the magnitude of these two effects. Taking a typical value of 60×10^{-6}/K for the expansion coefficient of the epoxy, we find that a temperature excursion of roughly 90 K is required to produce a strain equal to that produced by exposure of the dried epoxy to air at 100% relative humidity. We conclude that under service conditions, stresses induced by changes in humidity can thus be comparable to or even exceed those associated with temperature fluctuations. This conclusion only applies within a relatively shallow distance of an unsealed surface, since the diffusion coefficient reported above is small enough to ensure that regions more than a few millimeters away from an exposed surface are essentially isolated from the ambient humidity. We also note that during the manufacture of circuit boards, immersion in hot aqueous solutions may produce near-surface stresses that are approximately double those due to the temperature differential alone.

From a general perspective, the principal significance of the present work is the demonstration of a simple, sensitive, and convenient method for the study of moisture in polymers. The method appears to be readily adaptable for use over a range of temperatures, for the investigation of the heat of solution and the activation energy for diffusion. Other advantages are that only small samples are required, and that the bilayer geometry is naturally compatible with the investigation of a coating or film prepared on a supporting substrate. For these reasons, it is believed that the method may find further use for the characterization of polymers for packaging or other applications. In addition to metals, it would seem that substrates of glass, silica, silicon, or sapphire are also suitable, provided they are thin enough to provide adequate sensitivity. We should also mention that the bending-cantilever method has application for sorption studies outside the present area of moisture in polymers. For example, we have used the method to study the sorption of hydrogen and deuterium by an amorphous palladium-silicon alloy [9]. However, the present work is the first in which we have analyzed the kinetics of diffusion-controlled bending and obtained a diffusion coefficient by application of the method. The analysis given here involves the assumptions that the dilatation is proportional to the concentration, and that the diffusion coefficient is concentration-independent. In addition, it is also assumed that the bilayer behaves elastically. This implies the virtual absence of viscoelastic stress relaxation in the polymer layer, and hence confines use of the method to the relatively rigid regime below the glass transition temperature. Fortunately, these limitations do not appear to be serious for the hydrophobic polymers of principal interest for microelectronic applications.

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