

General Formula for Bending Beam Determination of Case II Diffusion in Polymer-Containing Bilayer Structures

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SYNOPSIS

An exact formula has been presented to correlate the bending curvature variation ratio, Ω , of any given bilayer structure comprising a solvent-swellable polymer layer with diffusion time, t , under case II diffusion. The formula can be used to determine the diffusion front velocity, v , for layered structures comprising a thick polymer film on a thin substrate or vice versa when subjected to solvent diffusion. According to this formula, there is little effect from plasticization or swelling in the transverse direction on the diffusion curve of Ω vs. t if the polymer layer to be investigated is relatively thin and its intrinsic hygroscopic strain ratio is less than unity. By using this model, the diffusion of *N*-methyl pyrrolidinone (NMP) in a 18- μm rodlike pyromellitic dianhydride *p*-phenylene-diamine (PMDA-PDA) polyimide film, coated on a 75- μm silicon substrate, is found to be case II with a diffusion front velocity of 1.84×10^{-7} cm/s. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Many techniques have been applied to study the transport of solvents in polymers. They include using a piezoelectric quartz microbalance, digi-bridge capacitor, interferometer, forward recoil spectrometer, bending beam apparatus, etc.¹⁻⁵ Among these, the bending beam technique is a relatively convenient method. Many devices may comprise layered structures with a polymer overcoat or substrate. With the application of the technique, one may be able to investigate *in situ* the diffusion behavior of a given solvent in the supported or constrained polymer layer. The technique has, actually, been successfully applied in the measurements of the diffusions of water in epoxy coatings on copper sheets and polyimide films on silicon substrates by Berry et al.⁵ and Jou et al.,⁶ respectively. However, complicated numerical computations must be employed in order to calculate the desired diffusion coefficient. This would consequently greatly limit the usage of

the technique. To make it more convenient to apply, a simplified model has been developed.⁷

However, all the models in the above studies concern only case I diffusion. The diffusions of many solvents in polymers may belong to case II or anomalous. It seems necessary to extend the technique for case II diffusion. In a previous study, a thin-film approach has been presented regarding, mainly theoretically, the application of the technique on case II diffusion.⁸ The model has reached a very simple formula, which is only a function of diffusion front velocity and time. With the development of the case II diffusion model, the application of the bending beam technique seems to be widened. However, the model is only valid for bilayered structures comprising a thin polymer or solvent-swellable film. One may frequently encounter layered structures comprising a thick polymer overcoat or substrate. In flexible printed circuit boards, for example, the polymer layers may be as thick as the copper foils. Therefore, it seems necessary to further extend the technique for structures comprising a thick polymer or solvent-swellable layer.

In this study, an exact formula is presented to correlate the bending curvature variation ratio of a

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bilayer structure caused by solvent-induced swelling in its polymer or solvent-swallowable layer with diffusion time under case II diffusion. This model is valid for layered structures comprising a thick polymer or solvent-swallowable film on a thin substrate or vice versa. It has taken into account the effects of solvent plasticization, swelling in the thickness direction, the preexisting intrinsic strain, and hygroscopic strain. At the end of this study, the theoretical model has been applied to calculate the diffusion front velocity of *N*-methyl pyrrolidinone (NMP) diffusion in a rodlike polyimide thick film coated on a silicon substrate. Comparison is made between the theoretical and experimental diffusion curves.

THEORY

In the previous study,⁸ a simplified formula has been presented correlating the variation in bending curvature of a given bilayered structure caused by solvent diffusion-induced swelling in its polymer overcoat to diffusion time under case II diffusion. To obtain the formula, it has been assumed that the thickness of the polymer overcoat is much smaller than that of the substrate. In other words, the for-

mula may not be suitable for structures comprising a thick polymer layer. Since most of the derivations are similar for both cases, a brief review of the theoretical background of the "thin-film model" is given.

As known, case II diffusion of a given solvent in a polymer film can be characterized as follows: (1) upon sorption, the weight gain with respect to time is linear; (2) a sharp swelling interface separates the inner unswollen region from the outer swollen region, and there is a uniform concentration of penetrant across the swollen layer; and (3) the sharp swelling interface advances at a constant velocity. If the polymer is cast as a film on a layered substrate, swelling in the polymer film upon intaking solvent will cause the substrate to bend. By measuring the variation of the bending curvature in the polymer-coated bilayered structure, one would be able to monitor the diffusion process and calculate the corresponding diffusion front velocity, if the bending curvature variation of the structure is correlated to diffusion time.

According to the three basic balance equations presented in the thin-film model,⁸ one can express the bending curvature of a given polymer or solvent-swallowable layer-containing bilayer structure at any given diffusion time, $1/R(t)$, as follows:

$$\frac{1}{R(t)} = \frac{6E_1^*d_1E_2^*d_2(t)[d_1 + d_2(t)]\epsilon_I + 6E_1^*d_1E_3^*d_3(t)[d_1 + 2d_2(t) + d_3(t)](\epsilon_I + \epsilon_H) + 6E_2^*d_2(t)E_3^*d_3(t)[d_2(t) + d_3(t)]\epsilon_H}{[E_1^*d_1 + E_2^*d_2(t) + E_3^*d_3(t)][E_1^*d_1^3 + E_2^*d_2^3(0) + E_3^*d_3^3(t)] + 3\{E_1^*d_1E_2^*d_2(0)[d_1 + d_2(t)]^2 + E_1^*d_1E_3^*d_3(t)[d_1 + 2d_2(t) + d_3(t)]^2 + E_2^*d_2(t)E_3^*d_3(t)[d_2(t) + d_3(t)]^2\}} \quad (1)$$

where E^* denotes the biaxial modulus and d thickness. Subscript 1 corresponds to the solvent non-swallowable layer or substrate, and subscripts 2 and 3 correspond, respectively, to the unswollen and swollen regions of the polymer or solvent swallowable layer. ϵ_I and ϵ_H are the intrinsic and hygroscopic strains of the solvent-swallowable layer, respectively.

$$\epsilon_H = SC_0$$

where C_0 is the concentration of penetrant or solvent in the swollen layer and S is the linear swelling parameter of polymer in the film plane direction.

If $d_2 \ll d_1$, and E_2 is not too much greater than E_1 , the above $1/R(t)$ expression can be simplified as that presented in the thin-film model and shown below:

$$\frac{1}{R(t)} = \frac{6[E_2^*d_2(t) + E_3^*d_3(t)]\epsilon_I + 6E_3^*d_3(t)\epsilon_H}{E_1^*d_1^2} \quad (2)$$

According to the three balance equations or Eq. (1) or (2) herein, the initial bending curvature, $1/R(0)$, can be expressed as

$$\frac{1}{R(0)} = \frac{6E_1^*d_1E_2^*d_2(0)[d_1 + d_2(0)]\epsilon_I}{[E_1^*d_1 + E_2^*d_2(0)][E_1^*d_1^3 + E_2^*d_2^3(0)] + 3E_1^*d_1E_2^*d_2(0)[d_1 + d_2(0)]^2} \quad (3)$$

Or

$$\frac{1}{R(0)} = \frac{6E_2^*d_2(0)\epsilon_I}{E_1^*d_1^2} \quad (4)$$

in case of thin polymer film, where $d_2(0)$ is the initial polymer layer thickness.

At equilibrium, $1/R(\infty)$ can be expressed as

$$\frac{1}{R(\infty)} = \frac{6E_1^*d_1E_3^*d_3(\infty)[d_1 + d_3(\infty)](\epsilon_I + \epsilon_H)}{[E_1^*d_1 + E_3^*d_3(\infty)][E_1^*d_1^3 + E_3^*d_3^3(\infty)] + 3E_1^*d_1E_3^*d_3(\infty)[d_1 + d_3(\infty)]^2} \quad (5)$$

Or

$$\frac{1}{R(\infty)} = \frac{6E_3^*d_3(\infty)(\epsilon_I + \epsilon_H)}{E_1^*d_1^2} \quad (6)$$

in case of thin polymer film, where $d_3(\infty)$ is the thickness of the swollen polymer layer at equilibrium.

Correlation between the above bending curvature and the diffusion front velocity, v , can be established according to the above-mentioned case II diffusion characteristics; i.e., the diffusion front will advance at a constant velocity. Hence,

$$d_2(t) = d_2(0) - vt \quad (7)$$

This means that the thickness of the unswollen region of the polymer layer will decrease at a rate constantly proportional to the diffusion front velocity, v , prior to equilibrate. The thickness of the solvent-induced swollen region will, on the contrary, increase at the same rate and

$$d_3(t) = S_T vt \quad (8)$$

where S_T is the linear swelling parameter of the polymer layer in the thickness direction and is defined as

$$S_T = d_3(\infty)/d_2(0) \quad (9)$$

One can therefore reexpress $d_3(t)$ of Eq. (8) in terms of experimentally measureable variables as follows:

$$d_3(t) = vtd_3(\infty)/d_2(0) \quad (10)$$

Furthermore, to examine how the polymer layer is plasticized upon intaking solvent in the diffusion

process, an arbitrarily defined plasticization factor, P , is used.

$$P = E_2^*d_2(0)/E_3^*d_3(\infty) \quad (11)$$

$P = 1$ if plasticization does not occur, and $P > 1$ if does.

For convenience, a dimensionless bending curvature variation ratio, Ω , is used and defined as follows:

$$\Omega = [1/R(t) - 1/R(0)]/[1/R(\infty) - 1/R(0)] \quad (12)$$

Based on the relationships given in Eqs. (10) and (11), the dimensionless bending curvature variation ratio, Ω , can be correlated to v . It is not only a function of the mechanical and geometrical parameters of the solvent-swallowable layer and solvent nonswallowable layer or substrate but also a function of the intrinsic strain, hygroscopic strain, and plasticization factor.

For thin polymer films, i.e., $d_2 \ll d_1$, Eq. (12) can be simplified as follows:

$$\Omega = vt/d_2(0) \quad (13)$$

Ω becomes independent of the intrinsic strain, hygroscopic strain, and plasticization factor.

EXPERIMENTS

Materials

The starting materials used in this study were dianhydride: pyromellitic dianhydride (PMDA), and diamine: *p*-phenylene-diamine (PDA). The solvent used was *N*-methyl pyrrolidinone (NMP). These materials were used as received.

Polycondensation of the Polyamic Acid

The polycondensation procedure of PMDA-PDA polyamic acid was conducted as follows: In a four-neck round-bottom flask, diamine (PDA) was dis-

Table I Material Constants Used in Theoretical Calculation

| Material | E^* (N/m ²) | d (μ m) | S_T | P | ϵ_I | ϵ_H | v (cm/s) |
|-----------|---------------------------|----------------|------------------|----------------|---------------------|--------------------|--------------------|
| Polyimide | 1.63×10^{10} | 19.5 | 1.3 ^a | 1 ^a | -0.001 ^a | 0.001 ^a | 1×10^{-8} |
| Silicon | 1.82×10^{11} | 390 | — | — | 0 | 0 | |

^a Defaulted value unless otherwise specified.

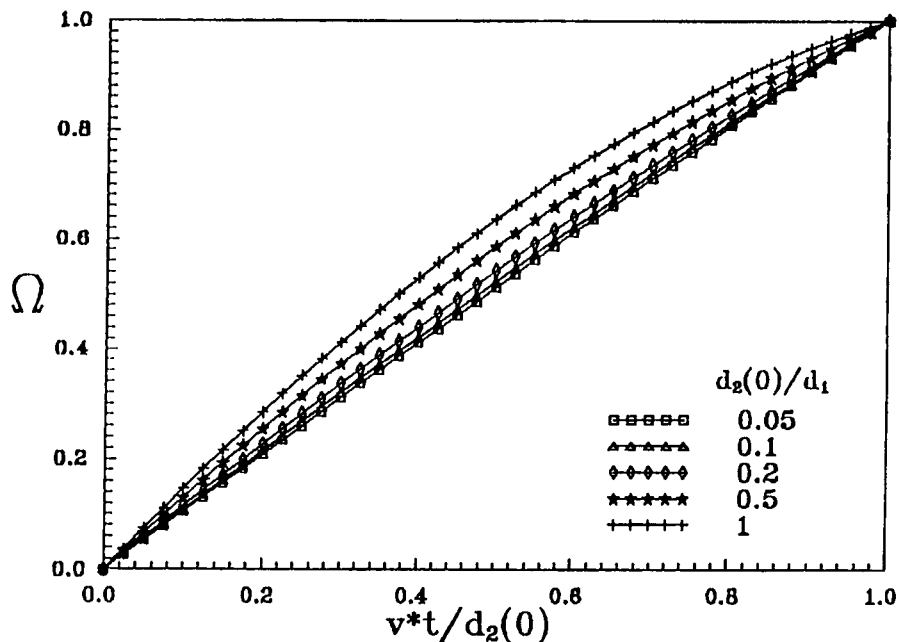


Figure 1 Calculated bending curvature variation ratio, Ω , vs. diffusion time for different $d_2(0)/d_1$ ratios for the diffusion of solvent in thin solvent-swellable film on thick substrate.

solved in NMP solvent. Equal molar dianhydride (PMDA) was then gradually added after complete dissolution of diamine. The reaction proceeded for

5 h by continuous stirring under nitrogen atmosphere at 40°C. The resulting solution had a solid content of 15 wt %.

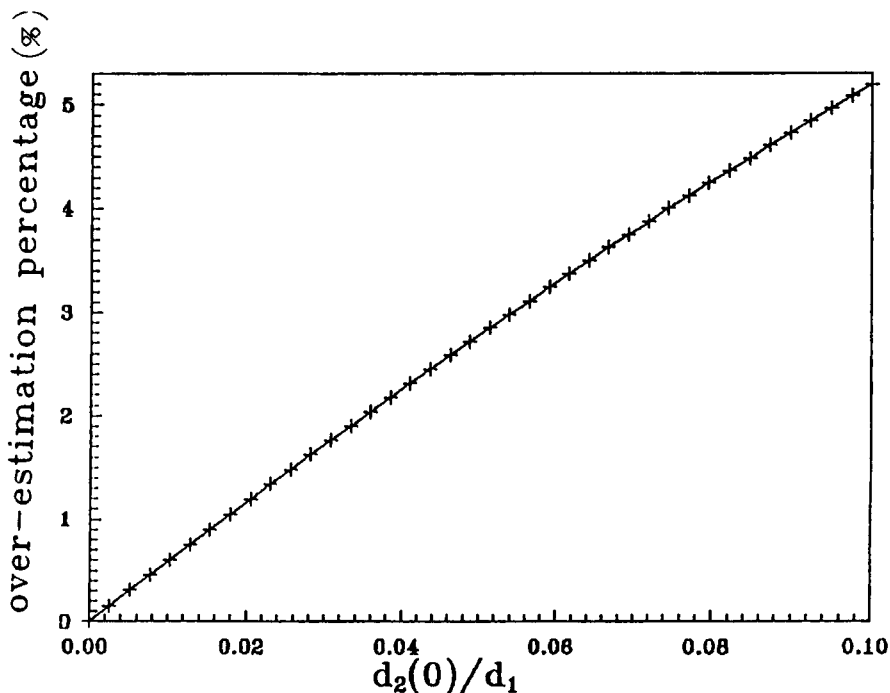


Figure 2 Overestimation of the diffusion front velocity resulting from using the thin film model.

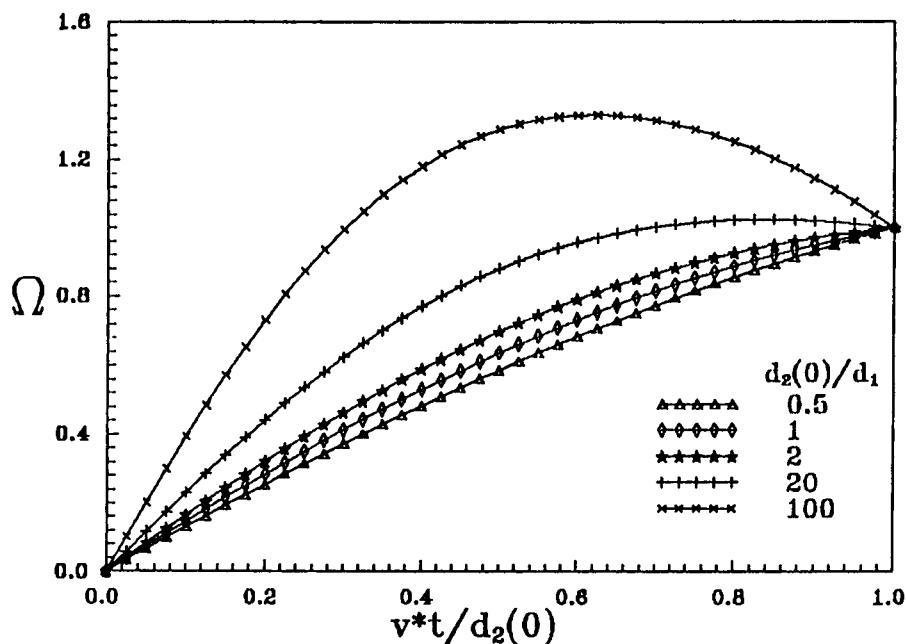


Figure 3 Calculated bending curvature variation ratio, Ω , vs. diffusion time for different $d_2(0)/d_1$ ratios for the diffusion of solvent in thick solvent-swellaible film on thin substrate.

Bending Beam Specimen Preparation

The substrates used in this experiment were thin silicon strips of 2.5 cm in length, 0.4 cm in width, and 75 μm in thickness. The polyamic acid was spin-casted on the substrates and then cured to 300°C with a ramp rate of 2°C/min.

Bending Curvature Variation Measurement

The schematic diagram of the bending beam apparatus designed for the diffusion experiments can be referred to in Ref. 8. The specimen was mounted on a clamp and then immersed in a sample cell containing NMP solvent to continuously measure its

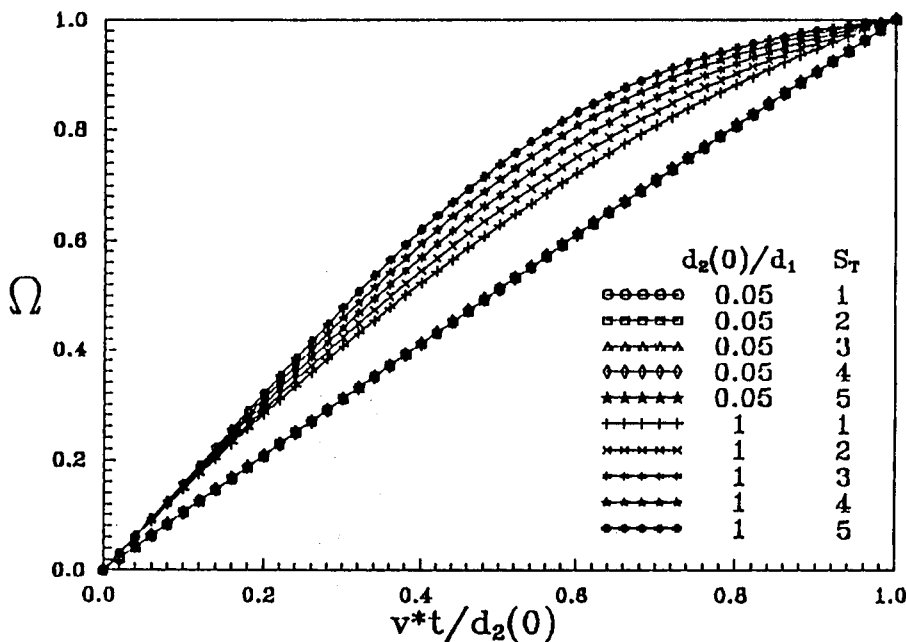


Figure 4 Effect of swelling parameter in the thickness direction, S_T , on the bending curvature variation ratio, Ω , for structures with $d_2(0)/d_1$ of 0.05 and 1.

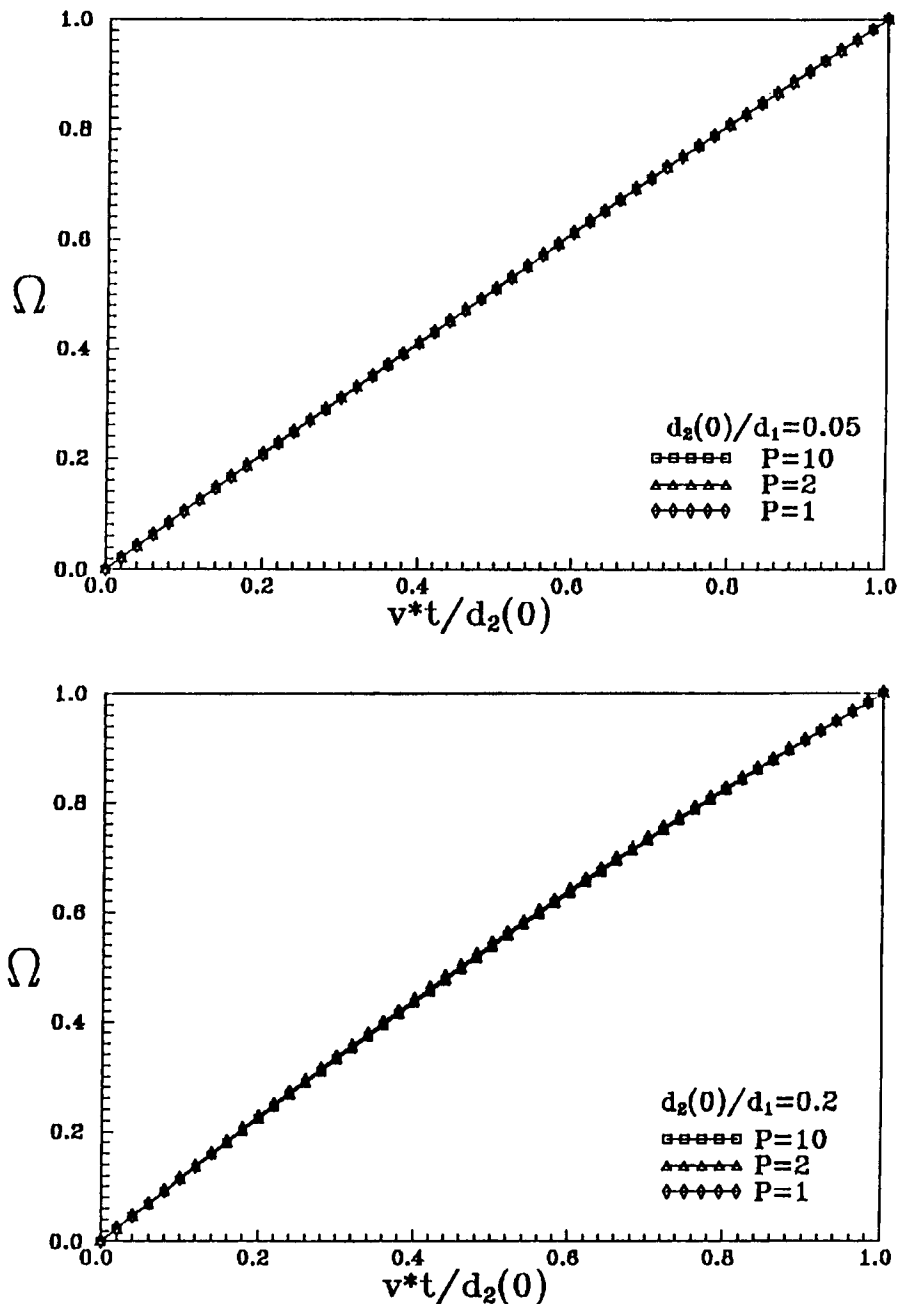


Figure 5 Effect of plasticization factor, P , on the bending curvature variation ratio, Ω , for structures with $d_2(0)/d_1$ of (a) 0.05, (b) 0.2, (c) 1, and (d) 10.

bending curvature variation upon diffusion. The diffusion processes were performed at room temperature.

RESULTS AND DISCUSSION

To delineate the characteristics of the current model and to compare with the thin-film model, a commonly encountered polyimide-silicon (PI-Si) bilayer

structure was assumed for the calculation of Ω with respect to t under case II diffusion. The material constants used in the calculation are listed in Table I.

Effect of Film to Substrate Thickness Ratio

Figure 1 shows the effect of thickness ratio of polyimide film to substrate on the bending curvature variation curve vs. diffusion time under case II dif-

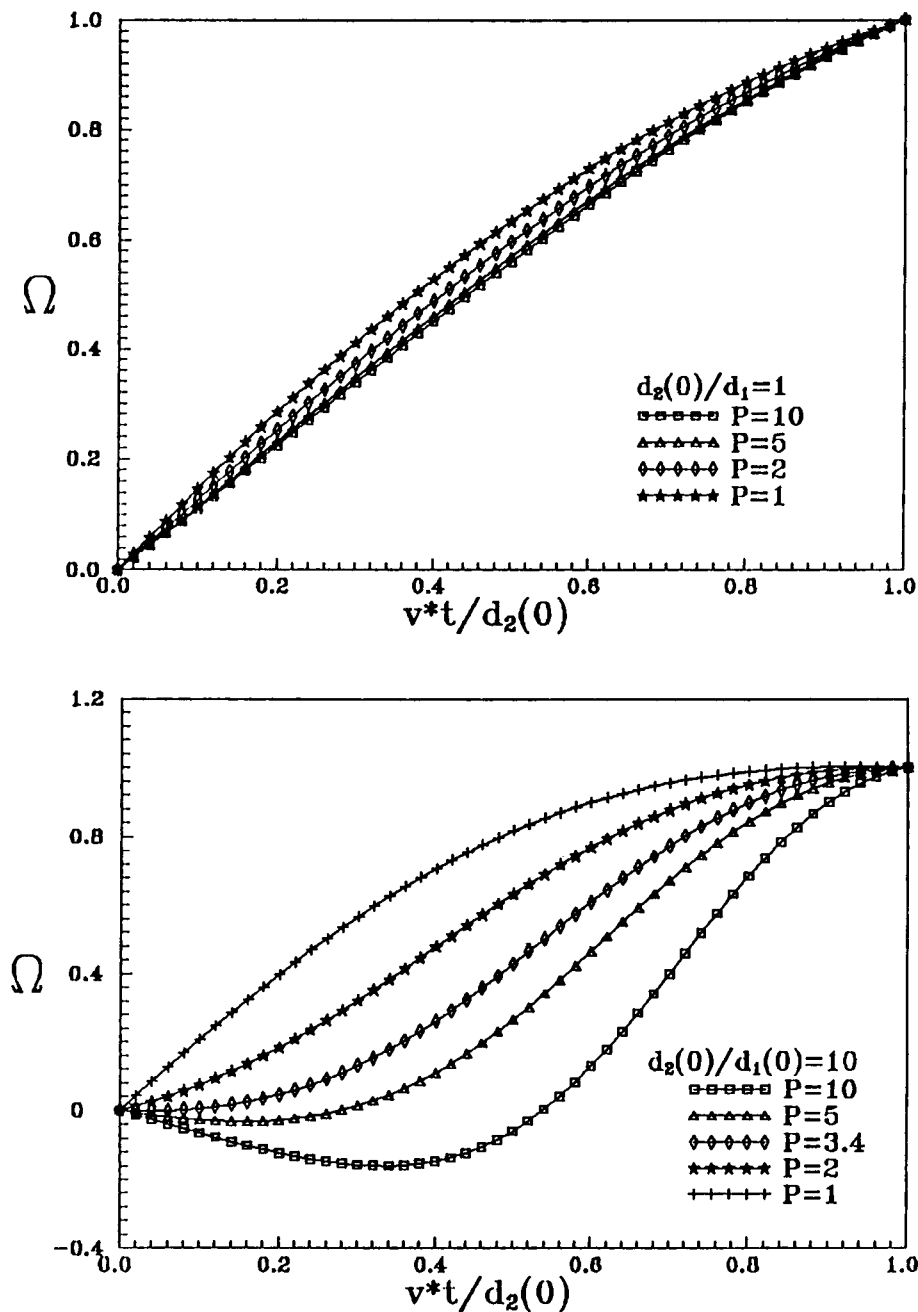


Figure 5 (Continued from the previous page)

fusion. These curves are generated according to the exact formula of Eq. (12). As seen, the dimensionless bending curvature variation ratio vs. diffusion time is linear over the entire diffusion process when the polymer film is relatively thin compared with the substrate. This result can be used to back-verify the appropriateness of the thin-film model.⁸ With the increase of the film-substrate thickness ratio, the curve markedly deviates from linearity. For a thick polymer coating, using the thin-film model will result

to a serious error in the determination of the diffusion front velocity.

Figure 2 shows the percentages of overestimation of the diffusion front velocity that resulted from using the thin-film model for thick films. With the film-substrate thickness ratio less than 0.05, the overestimation is less than 5% and the thin-film model seems to be relatively accurate and very useful for its simplicity in calculation.

For structures with a thick polymer film coated

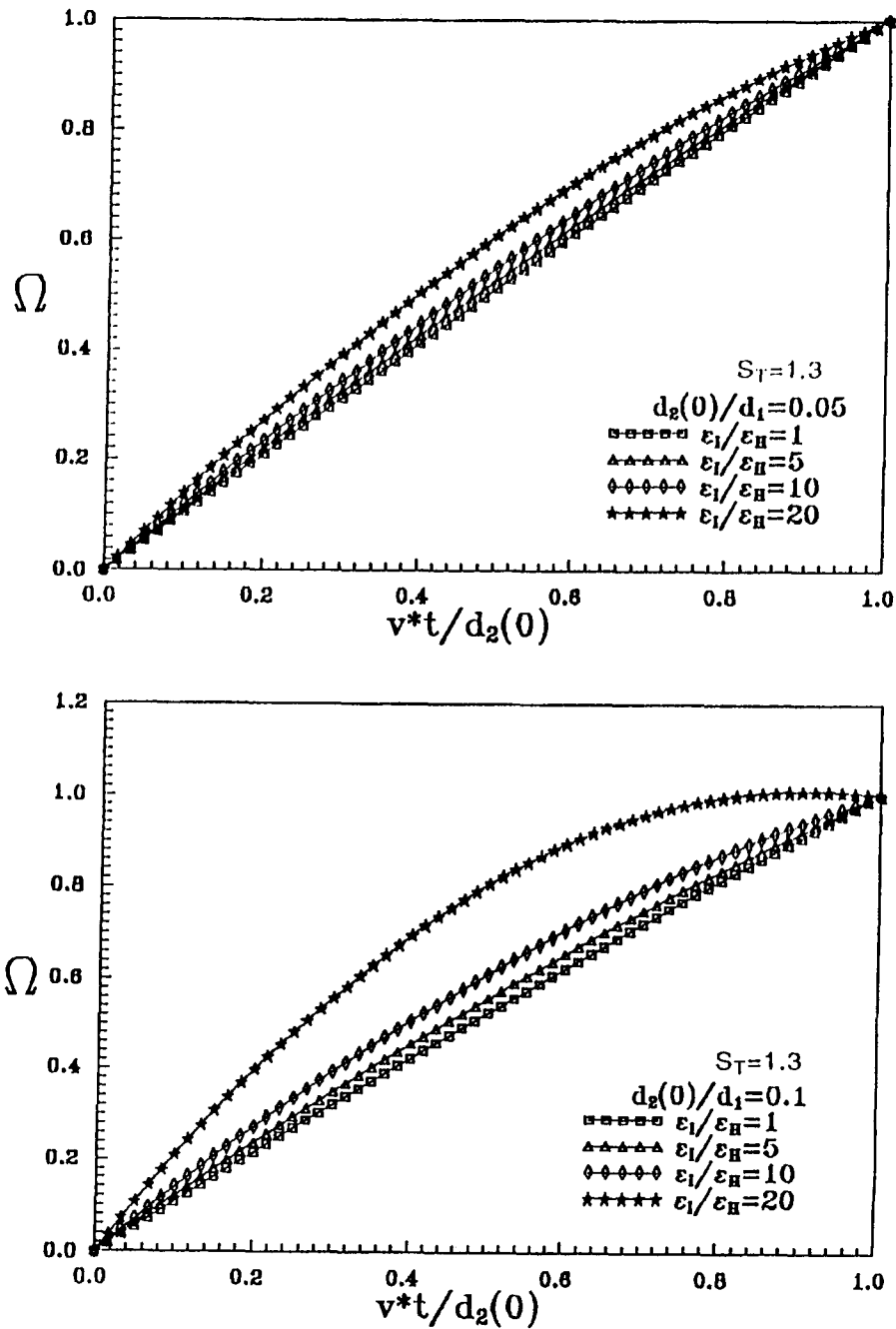


Figure 6 Effect of the ratio of intrinsic strain to hygroscopic strain, ϵ_I/ϵ_{II} , on the bending curvature variation ratio, Ω , for structures with (a) $d_2(0)/d_1 = 0.05$ and $S_T = 1.3$, (b) $d_2(0)/d_1 = 0.1$ and $S_T = 1.3$, and (c) $d_2(0)/d_1 = 0.05$ and $S_T = 1$.

on a thin substrate or a solvent nonswellable film deposited on a thick polymer substrate, the bending curvature or its variation behavior in the event of case II diffusion can also be predicted. Figure 3 shows the calculated bending curvature variation ratio with respect to time for bilayer structures with various thick polyimide films on silicon substrates. The Ω

curve apparently becomes curvelike as the thickness ratio of PI to Si increases.

Effect of Swelling in the Thickness Direction

The swelling parameter of PI films in the thickness direction in NMP may, at least, range from 1.1 to

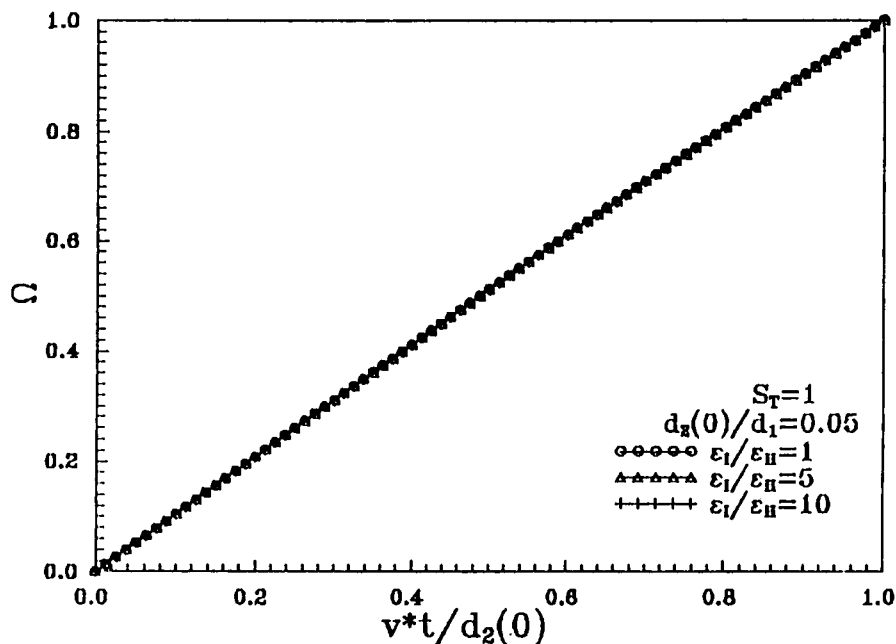


Figure 6 (Continued from the previous page)

2.0, which varies with different imide structures and coating thicknesses.⁹ For a rubberlike film, the degree of swelling may be even higher. The effect of swelling on the curve of Ω vs. t has been examined and is shown in Figure 4. Here, the swelling parameter, S_T , has been set to vary from 1 to 5. However, no marked effect can be observed for thin PI films with $d_2(0)/d_1 = 0.05$. For a relatively thick PI film, such as $d_2(0)/d_1 = 1$, the diffusion curve of Ω vs. t markedly varies with S_T varying from 1 to 5.

Effect of Plasticization

The biaxial modulus of the swollen film will significantly decrease, if the solvent used can plasticize the polymer film studied. This will result to a P much larger than unity. The effect of plasticization on the case II diffusion curve with Ω vs. t can be seen in Figure 5(a). Nearly no effect can be observed for thin PI films with $d_2(0)/d_1 = 0.05$ even if the P value has increased by one order; i.e., the biaxial modulus of the film upon swelling has decreased by, at least, one order. For $d_2(0)/d_1 = 0.2$, there still exhibits no significant effect on the diffusion curve from plasticization, as shown in Figure 5(b). However, for thick PI films, like $d_2(0)/d_1 = 1$, plasticization does affect the diffusion curve markedly. The effect of plasticization becomes more pronounced for $d_2(0)/d_1 \gg 1$, as illustrated in Figures 5(c) and (d).

Effect of Intrinsic Strain to Hygroscopic Strain Ratio

It is learned from these calculations that the diffusion curves of Ω vs. t are the same for different PI films with different intrinsic or hygroscopic strains if the intrinsic strain to hygroscopic strain ratio is kept constant. In other words, the diffusion curve is a function of ϵ_I/ϵ_H .

If diffusion is performed under an intrinsic strain-free condition, i.e., $\epsilon_I = 0$, the same diffusion curve will result regardless of the magnitude of the hygroscopic strain, providing all the other parameters are kept the same. For thin PI films, i.e., $d_2(0)/d_1 = 0.05$, the diffusion curves are nearly the same for ϵ_I/ϵ_H ranging from 0 to 1. Within the range, a maximum of 5% overestimation can result in the calculation of v if using the thin-film model. For ϵ_I/ϵ_H greater than unity, the resulting curve of Ω vs. t apparently becomes curvelike [Fig. 6(a)] and the usage of the thin-film model is not recommended. In such a circumstance, the exact formula should be used and the magnitude of ϵ_I/ϵ_H should be known beforehand. The deviation from linearity is more pronounced for thicker films, such as $d_2(0)/d_1 = 0.1$, as demonstrated in Figure 6(b).

In the above calculations, the transverse swelling parameter S_T is assumed to be 1.3. For $S_T = 1$ and $d_2(0)/d_1 = 0.05$, all the diffusion curves with different ϵ_I/ϵ_H values almost fall on one another [Fig. 6(c)].

The greater than unity S_T value accounts for why some of the above diffusion curves bend in an opposite direction when ϵ_I/ϵ_H are greater than some certain values. Therefore, S_T should also be known prior to determining the value of v if the intrinsic strain of a given film to be investigated is much greater than its hygroscopic strain, i.e., $\epsilon_I/\epsilon_H \gg 1$.

Comparison of the Theoretical and Experimental Curves

The diffusion of NMP in a rodlike polyimide film coated on a thin silicon substrate is shown in Figure 7. The film is $18 \mu\text{m}$ thick and the substrate $75 \mu\text{m}$. The theory gives a slightly bending diffusion curve, which fits reasonably well to the experimental data for Ω ranging from 0.2 to 0.7. The diffusion front velocity, v , as calculated is $1.84 \times 10^{-7} \text{ cm/s}$. In the calculation, ϵ_I/ϵ_H and S_T are set to be equal to $0.002392/-0.002387$ and 1.3 . These values are determined according to some separate studies. The obtained v value will not change much if the above parameters are set differently within the experimentally observable uncertainty range.

As also shown in the figure, there exist discrepancies between the theoretical and experimental curves in the initial and near-equilibrium stages. For Ω less than 0.2, the discrepancy may be attributed to an induction behavior occurring in the initial dif-

fusion stage.⁶ Such an induction phenomenon is frequently observed in solvent diffusions in polymers regardless of diffusion mechanism.^{6,9} After the induction period, the diffusion follows a curve that matches well the theoretical diffusion curve of case II till Ω is greater than 0.7.

The experimental curve obviously deviates from the theoretical curve of dashed line for Ω greater than 0.7. This discrepancy may mainly be attributed to the nonuniformity in thickness of the studied polyimide film. The film prepared exhibits bumps at the edges, as illustrated in Figure 8. The average thickness of the film is $18 \mu\text{m}$. The thickness is $29 \mu\text{m}$ for the bumps and $12 \mu\text{m}$ for the thinnest part of the film. In the bending beam-diffusion experiment, the two ends of the film were removed by 1 cm in the length direction for mounting on a clamp and reflecting the laser beam to a sensor. The bumps at the edges of the length direction were then removed concurrently. Hence, only the bumps at the edges of the width direction are seen and they span throughout the whole length.

For $\Omega < 0.7$, the diffusion front should have not yet, presumably, reached the film-substrate interface. The film is then thought to consistently have the same full surface area available for the solvent to diffuse forward. Therefore, the diffusion front advances at a constant, ultimate rate toward the film-substrate interface. Since the film is not uniform,

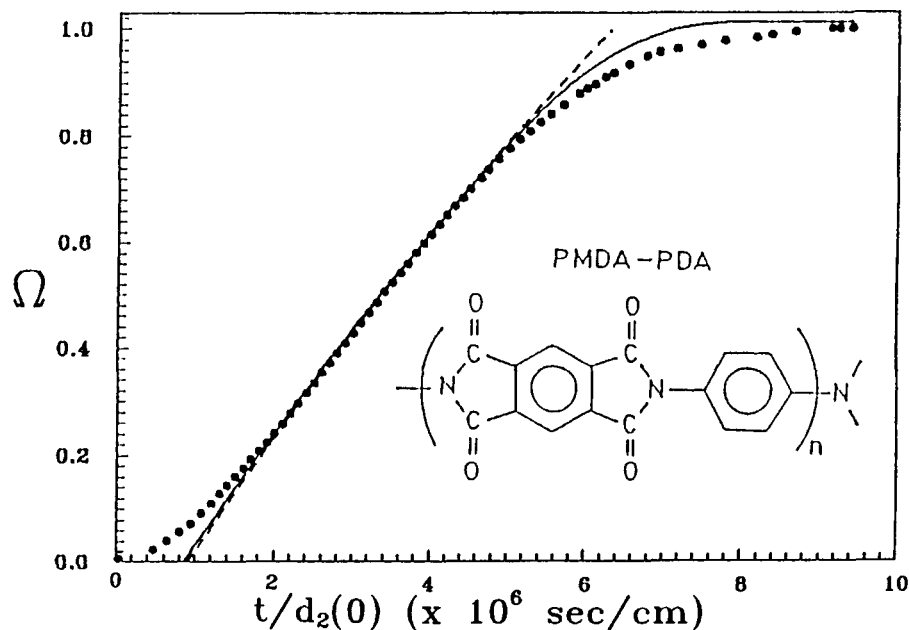


Figure 7 Comparison of the experimental data with the theoretical curves for the diffusion of NMP in a PMDA-PDA film. The theoretical curve of dashed line is obtained by assuming the polyimide film is uniform in thickness, while that of solid line is obtained by taking the real, nonuniform film structure into calculation.

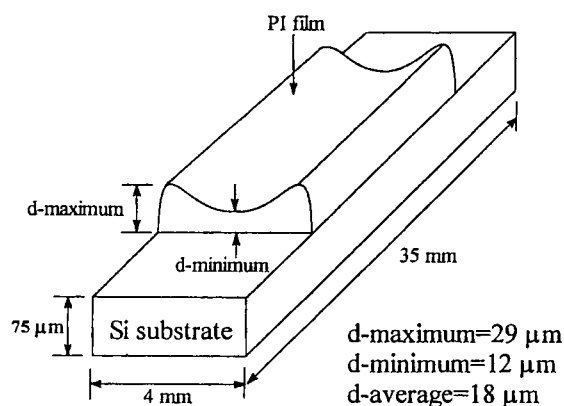


Figure 8 Schematic illustration of the film structure of a typical spin-cast polyimide film cured on a silicon strip.

the film-substrate interface at the thinnest part of the film would be first reached by the diffusion front and no further diffusion would proceed afterward in this equilibrated part. For $\Omega > 0.7$, some of the thinner parts of the film may be equilibrated, and less surface area is then available for the diffusion to further proceed. The entire diffusion would therefore likely proceed at a lower rate. The diffusion rate would become even lower with time since a greater part of the film would be equilibrated and less surface area would be left available for diffusion. This explains why the experimental diffusion curve deviates away from the theoretical one and exhibits a smaller and smaller slope with time on at the end of diffusion.

The theoretical curve has been recalculated using the same theoretical formulas, coupled with the use of a numerical approach to take into account the effect of the nonuniform film thickness on the variation of the surface area available for diffusion at various stages. The new diffusion curve (Fig. 7, solid line) is shown to be significantly different from the original one (Fig. 7, dashed line) at the stages near equilibrium. It fits fairly well with the experimental data for Ω ranging from 0.2 to 1. This can be used to confirm the above discussion regarding the effect of the nonuniform film structure on the resultant diffusion curve at the near-equilibrium stage.

CONCLUSION

An exact formula is presented to correlate the bending curvature variation of a polymer-containing bi-

layered structure, caused by solvent-induced swelling, with diffusion time under case II diffusion. Unlike the previously developed thin-film model, the current formula can be applied for layered structures comprising either a thick polymer film on a thin substrate or a thin film on a thick polymer substrate. According to the calculation results, there is little effect on the diffusion curve from plasticization or swelling in the film thickness direction if the polymer layer is relatively thin and the intrinsic to hydroscopic strain ratio is small. For a thick polymer coating on a thin substrate, it is required to know the values of the intrinsic strain, plasticization factor, and swelling factors in the directions parallel and perpendicular to the film so that the diffusion front velocity can be accurately determined. By using the current model, the diffusion of NMP in a 18- μm rodlike polyimide film coated on a 75- μm silicon substrate is found to be case II with a diffusion front velocity of 1.84×10^{-7} cm/s.

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REFERENCES

1. H. M. Tong and K. I. Saenger, *J. Polym. Sci. Polym. Phys. Ed.*, **27**, 689 (1989).
2. R. M. Yang and H. M. Tong, *J. Polym. Sci. Polym. Lett. Ed.*, **23**, 583 (1985).
3. D. D. Denton, D. R. Day, D. F. Priore, S. D. Senturia, E. S. Anolick, and D. Scheider, *J. Electron. Mat.*, **14**, 119 (1985).
4. R. C. Lasky, E. J. Kramer, and C. Y. Hui, *Polymer*, **29**, 673 (1988).
5. B. S. Berry and W. C. Pritchett, *IBM J. Res. Dev.*, **28**, 662 (1984).
6. J. H. Jou, R. Huang, P. T. Huang, and W. P. Shen, *J. Appl. Polym. Sci.*, **43**, 857 (1991).
7. J. H. Jou, L. Hsu, P. T. Huang, W. P. Shen, and R. Huang, *Polym. J.*, **23**, 1123 (1991).
8. J. H. Jou and L. Hsu, *J. Appl. Polym. Sci.*, **44**, 191 (1992).
9. J. H. Jou, Y. L. Chang, and C. H. Liu, *Macromolecules*, **25**(20), 5186 (1992).

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