Characteristic Matrix Method for the Study of Polymer Dissolution by Laser Interferometry

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A new method to analyze experimental results based on laser interferometry is reported. The method was applied to study the dissolution of thin poly(methyl methacrylate) [PMMA] films. Two fundamental parameters of the solvent-swollen gel layer at the solvent–polymer interface were taken into account: its thickness and its refractive index profile. This method is more complete than earlier models.

The dissolution of glassy polymers often involves the formation of a solvent-swollen gel layer at the polymer–solvent interface. Even when this layer is too thin to be observed by optical microscopy, its presence can be inferred through optical interferometry studies. During the past decade, much effort has been made in describing, fundamentally and experimentally, the mechanism of polymer dissolution,[1] with particular emphasis on the transition layer.[2,3] The ultimate objective is to be able to determine the thickness of the gel layer and its solvent concentration profile. The Rodriguez group,[2] at Cornell, has made extensive use of interferometry experiments to study aspects of thin polymer film dissolution.

In our laboratory, we augmented the laser interferometry (LI) technique with simultaneous fluorescence quenching (FQ) measurements.[3] The LIFQ methodology employs polymer films labeled with a trace of fluorescence dye (phenanthrene) and takes advantage of the ability of the ketone solvents to quench its fluorescence. In this way one gets an independent measurement of the solvent penetration rate into the film.

In our previous publications, we compared the gel layer thickness (Δ_g) inferred from the LIFQ results with those obtained exclusively by LI using an expression reported without derivation and without reference by Krasicky and Rodriguez (KR). This equation (see eq 11) was accompanied by the comment that "optical theory gives (this expression) as a good approximation" for a linear refractive index profile across the gel layer. In our early experiments, both methods gave similar values, within experimental error, for Δ_g. Recently, as our skills and equipment have improved, particularly in the stability in the new diode laser used for the LI measurements, we have noticed systematic deviations in the results when the LIFQ method was compared to the KR method. This prompted us to examine the optical theory from which Δ_g values are calculated. We developed a more complete theory and find that the approximation reported by KR leads to values of Δ_g which are too large by typically 30–40%.

Our theoretical approach is based on the description of the optical properties of a stratified medium by a characteristic matrix. We will start by presenting some elements of the theory, as developed by Abelès[4] and then show how this method can be applied to the description of a thin poly(methyl methacrylate) [PMMA] film undergoing dissolution. Abelès[4] showed that the optical properties of a stratified medium can be fully described by a 2 × 2 matrix, called the characteristic matrix of the medium. This matrix expresses the relationship between the electric and magnetic fields propagating through the medium. If one obtains

$$\mathbf{M} = \begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix} \tag{1}$$

the reflection coefficient of the system is related to the elements of the matrix by

$$r = \frac{(m_{11} + n_s m_{12})n_1 - (m_{21} + n_s m_{22})}{(m_{11} + n_s m_{12})n_1 + (m_{21} + n_s m_{22})} \tag{2}$$

where n_1 is the refractive index of the first layer and n_s that of the final layer: r can be a complex number, and the reflectivity of the system is given by

$$R = rr^* = |r|^2 \tag{3}$$

In the case of a stratified medium composed of n homogeneous layers, each of them characterized by a matrix, $\mathbf{M}_i$, one can show that the characteristic matrix, $\mathbf{M}$, of the complete system is obtained by multiplication of the different matrices (i.e., $\mathbf{M} = \mathbf{M}_1\mathbf{M}_2...\mathbf{M}_n$).[4,5]

Application to a thin PMMA film undergoing dissolution: The system of interest to us is shown in Figure 1. It is composed of a polymer film and two semiinfinite media, solvent and substrate, characterized by two fixed refractive indices (n_1 and n_3). The polymer film is divided

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(1) See for example: (a) Thomas, N. L.; Windle, A. H. *Polymer* **1982**, *23*, 529. (b) Mills, P. J.; Palmstrøm, C. J.; Kramer, E. J. *J. Mater. Sci.* **1986**, *21*, 1479. (c) Ouano, A. C.; Carothers, J. A. *Polym. Eng. Sci.* **1980**, *20*, 160. (d) Lee, P. I.; Peppas, N. A. *J. Controlled Release* **1987**, *6*, 207. (e) Saenger, K. L.; Tong, H. M. *Polym. Eng. Sci.* **1991**, *31*, 432. (f) Crank, J. *The Mathematics of Diffusion*; Clarendon: Oxford, 1975, and references therein.

(2) (a) Krasicky, P. D.; Groele, R. J.; Rodriguez, F. *Chem. Eng. Commun.* **1987**, *54*, 279. (b) Krasicky, P. D.; Groele, R. J.; Jubinsky, J. A.; Rodriguez, F.; Namaste, Y. M. N.; Obendorf, S. K. *Polym. Eng. Sci.* **1987**, *27*, 282.

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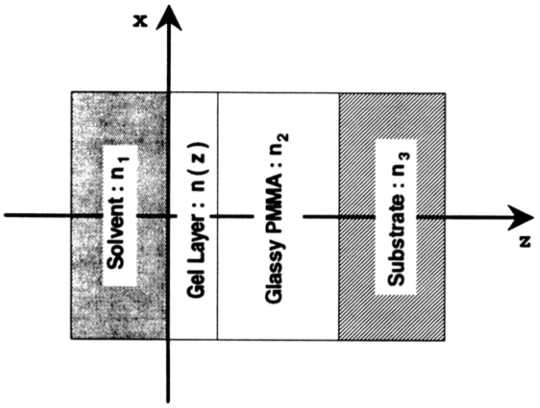

Figure 1. Schematic representation of a PMMA film undergoing dissolution. The polymer has been divided into two regions: the glassy part, characterized by the fixed refractive index of the polymer, n_2 and the solvent-swollen gel layer, characterized by a distance dependent refractive index $n(z)$.

into two regions. One is the glassy part, characterized by the uniform refractive index of the polymer (n_2). The other is the solvent-swollen gel layer (at the polymer–solvent interface) and is characterized by a refractive index which is a function of z ($n(z)$). This system is a stratified medium along the z axis and can be described in terms of the different characteristic matrices constituting this medium. We will consider only the case of normal incidence which is the arrangement in our experiment. A glassy PMMA layer, of thickness h, can be associated with the following matrix:[4,5]

$$\mathbf{M}_1 = \begin{bmatrix} \cos(a) & -i/n_2 \sin(a) \\ -in_2 \sin(a) & \cos(a) \end{bmatrix} \tag{4}$$

where $a = k_0 h n_2$, k_0 being the wave vector (i.e., $k_0 = 2\pi/\lambda$, where λ is the laser wavelength).

We can decompose the solvent-swollen gel layer into an infinite number of slices of thickness h_i in which it is possible to regard n within each slice as being constant. Associated with such a system, neglecting second order terms in h_i, is the matrix[4,5]

$$\mathbf{M}_\infty = \begin{bmatrix} 1 & -ik_0 B \\ -ik_0 A & 1 \end{bmatrix} \tag{5}$$

with $A = \int n^2(z)\, dz$ and $B = \int \mu\, dz = \Delta_g$ (nonmagnetic materials), where Δ_g represents the total thickness of the solvent-swollen gel layer and $n(z)$ its refractive index profile.

The complete system is described by the product $\mathbf{M}_\infty \mathbf{M}_1$:

$$\mathbf{M} = \mathbf{M}_\infty \mathbf{M}_1 =$$

$$\begin{bmatrix} \cos(a) - k_0 n_2 \Delta_g \sin(a) & -i[k_0 \Delta_g \cos(a) + (1/n_2) \sin(a)] \\ -i[k_0 A \cos(a) + n_2 \sin(a)] & \cos(a) - (k_0 A/n_2) \sin(a) \end{bmatrix} \tag{6}$$

Substituting the coefficients of matrix **M** into eq 2, one obtains, after some simplifications

$$r = e^{i\Psi}\left(\frac{fr_{12} + r_{23}e^{i\phi}}{1 + fr_{12}r_{23}e^{i\phi}}\right) \tag{7}$$

where r_{12} and r_{23} are the classical Fresnel coefficients (i.e., at normal incidence, $r_{ij} = (n_i - n_j)/(n_i + n_j)$). The terms Ψ, ϕ, and f are dependent on A and Δ_g and are defined in eqs 12–14. Equation 7 leads directly to

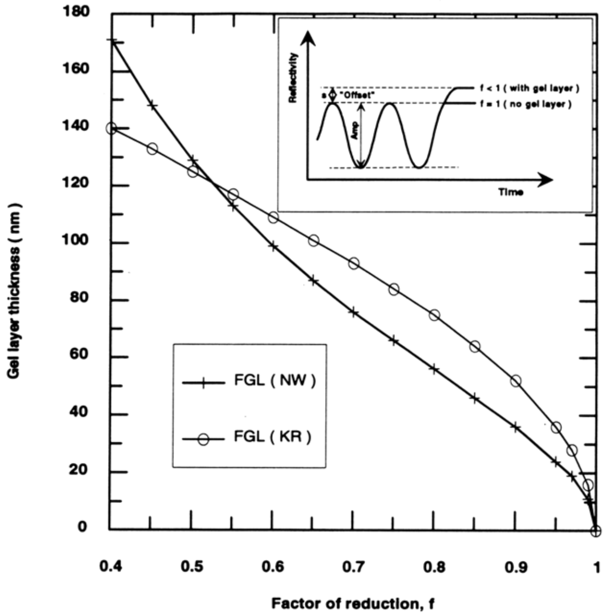

Figure 2. Gel layer thickness as a function of the factor of reduction, f. Two different methods of calculation are compared: the Krasicky–Rodriguez method (KR, eq 11) and the method (NW, eq 15) developed here. In both cases a linear refractive index profile across the gel layer is assumed. The insert depicts an idealized reflectivity versus time plot for a dissolution process with ($f = 1$) and without ($f < 1$) gel layer, and defines terms used in the text: Amp represents the amplitude of oscillations, and s is the "offset".

$$R = \frac{f^2{r_2}^2 + 2fr_{12}r_{23}\cos\phi + {r_{23}}^2}{1 + f^2{r_{12}}^2{r_{23}}^2 + 2fr_{12}r_{23}\cos\phi} \tag{8}$$

In the case of PMMA undergoing dissolution in typical organic solvents such as 2-pentanone, $r_{12} \approx 0.04$ and $r_{23} \approx 0.09$.[6,8] Thus, to a good approximation

$$R \approx f^2{r_{12}}^2 + 2fr_{12}r_{23}\cos\phi + {r_{23}}^2 \tag{9}$$

From equation 9, one can see that the reflectivity is a sinusoidal function of the film thickness (which is commonly observed during a film dissolution experiment) and that the amplitude of the oscillations depends on the value of f. As shown by Krasicky and Rodriguez,[2] if no gel layer is present, $f = 1$, and at the end of the experiment the intensity reaches the same value as that reached by the maxima during the dissolution. If a gel layer is present, $f < 1$, and the amplitude of the oscillations is reduced. Hence, f is called the "factor of reduction". Since the gel layer is intermediate in refractive index between the solvent and the polymer, it acts as an antireflection coating for the polymer–solvent interface. A characteristic feature of dissolution involving gel layers is that, at the end of the process, the reflectivity reaches a plateau (bare substrate) higher in intensity than the maxima of the sinusoidal trace. The difference in intensity between the plateau and the maxima is called the "offset", s. These two cases can be depicted as shown in the insert of Figure 2. In the case

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(6) Nivaggioli, T.; Dimnik, G.; Wang, F.; Winnik, M. A.; Smith, B. A. *Appl. Opt.* **1992**, *31*, 5956.

(7) Nivaggioli, T.; Wang, F.; Winnik, M. A. *J. Phys. Chem.* **1992**, *96*, 7462.

(8) Nivaggioli, T. In Situ Studies of Thin Polymer Film Dissolution by Simultaneous Laser Interferometry and Fluorescence Quenching Measurements. Ph.D. Thesis, University of Toronto, 1993.

where a gel layer is present, the experimental value of f can be calculated as

$$f_{\text{exp}} = \frac{\text{Amp}}{\text{Amp} + 2s} \tag{10}$$

where Amp represents the amplitude of the oscillations and s the magnitude of the "offset".

To evaluate f in eq 9, Krasicky and Rodriguez used the expression given in eq 11, which they say is based upon

$$f_{\text{KR}} = (\sin \alpha/2)/(\alpha/2) \tag{11}$$

an optical approximation in conjunction with an assumed linear refractive index profile. Here $\alpha = \Delta_g/\zeta$ and $\zeta = \lambda_0/4n_t$, at normal incidence, and n_t represents the average refractive index between the solvent and the polymer.

A more complete approach to evaluating f is available through the elements of the matrix **M** that are used in deriving eq 7.[8] The terms Ψ, ϕ, and f are described by the three expressions

$$fe^{i\mu} = \frac{\left(1 + k_0{}^2\frac{\alpha\beta}{\gamma\epsilon}\right) + ik_0\left(\frac{\beta}{\epsilon} - \frac{\alpha}{\gamma}\right)}{\left(1 + k_0{}^2\frac{\alpha^2}{\gamma^2}\right)} \tag{12}$$

$$\phi = 2a - \mu \tag{13}$$

$$\tan\left(\frac{\Psi - \mu}{2}\right) = k_0\frac{\alpha}{\gamma} \tag{14}$$

where $\alpha = A + n_1n_2\Delta_g$, $\beta = A - n_1n_2\Delta_g$, $\gamma = n_1 + n_2$ and $\epsilon = n_1 - n_2$.

From eq 12 one can derive the expression

$$f = \sqrt{\left(1 + \frac{k_0{}^2}{\epsilon^2}\beta^2\right)\Big/\left(1 + \frac{k_0{}^2}{\gamma^2}\alpha^2\right)} \tag{15}$$

Equation 15 makes it clear that the value of f depends on both the thickness of the gel layer and its refractive index profile.

There are two ways of using expression 15. The first is to assume a refractive index profile throughout the gel layer and calculate Δ_g from the experimental value of f. This method allows us to compare values of Δ_g with the ones obtained using the Krasicky–Rodriguez method, assuming a linear refractive index profile. A more satisfying approach would be to obtain both f and Δ_g experimentally and then to determine the "best" refractive index profile to fit the data. The LIFQ[3,6] provides an independent measure of Δ_g. Here we are interested only in the proper interpretation of the interferometry experiment.

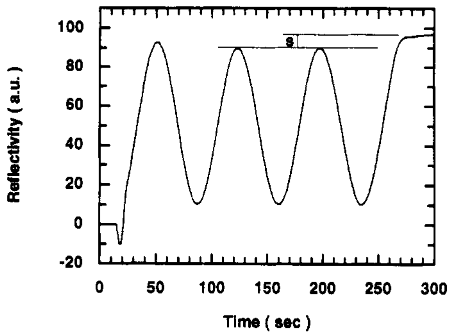

Figure 3. Experimental laser interferometry result of a 0.79-μm-thick PMMA film (annealed at 140 °C/1 h) undergoing dissolution at 22 °C showing the offset, s. The solvent is a 2:1 mixture of methyl ethyl ketone and isopropyl alcohol.

The LI part of our setup consists of a flow cell connected to a 1-mW diode laser (673.0 nm) via a three-branch randomized fiber-optic cable oriented at normal incidence. A classical interferogram is presented in Figure 3. From these data one can calculate the initial thickness of the film, t_0, and its dissolution rate, DR.[6] The increase in intensity at the end of the interferogram reveals the presence of the solvent-swollen gel layer as predicted by eq 9 and described subsequently. The experimental factor of reduction, f_{exp}, can be calculated using eq 10, in this case $f_{\text{exp}} = 0.86 \pm 0.03$. Using $\lambda_0 = 673.0$ nm, $n_1 = 1.38$ (solvent), $n_2 = 1.49$ (PMMA) and solving for Δ_g in eq 15 (assuming a linear profile) leads to $\Delta_g = 44 \pm 6$ nm; the value obtained using the Krasicky–Rodriguez method (eq 11) leads to $\Delta_g = 62 \pm 6$ nm. The value obtained by the Krasicky–Rodriguez method is larger.

Figure 2 compares values of Δ_g calculated from eqs 11 and 15. In the practical range (i.e., when f varies from 0.6 to 0.9) the KR method gives results 20–40% higher than the method derived here. Thus, whatever assumptions were made in deriving eq 11, they lead to significant errors in calculating Δ_g values from experimental data.

We have presented a new method, based on laser interferometry experiments, to analyze the transition layer of thin PMMA films undergoing dissolution. This method takes into account two fundamental parameters of the gel layer: its thickness and its refractive index profile. It is more rigorous than that developped earlier and can be easily adapted to the study of similar systems. It also opens the possibility that in conjunction with other methods to measure Δ_g independently, one can obtain deeper insights into the evolution of the gel layer thickness and its refractive index profile.[7]