Application of a New Quantitative Optical Depth Profiling Technique for the Diffusion of Polymers

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The concentration profiles of amorphous polystyrene in a polystyrene/polyvinyl methyl ether laminated film after heat treatments have been investigated by a new depth profiling technique using multiple-angle attenuated total reflection Fourier transform infrared (ATR/FT-IR) spectroscopy. An estimated profile or information about the wave form of the profile is not required in order to perform the depth profiling calculation. All angle-dependent spectra are obtained with a nonpolarized incident beam of known degree of polarization. The accuracy of the calculated profiles has been confirmed by comparisons between spectral intensities from experiment and those from exact optical theory at frequencies other than the profiling frequency. The quantitative nature of this technique has been shown via consistent areas under the volume fraction profiles of polystyrene in the laminated film after consecutive heat treatments.

Index Headings: Attenuated total reflection Fourier transform infrared spectroscopy; Depth profiling; Interdiffusion; Laminated film.

INTRODUCTION

Attenuated total reflection Fourier transform infrared (ATR/FT-IR) spectroscopy is capable of performing depth profiling, as can photoacoustic Fourier transform infrared spectroscopy, neutron scattering, and forward recoil spectrometry. ATR/FT-IR spectroscopy has advantages over other techniques because of its simplicity, availability, ease of specimen preparation, nondestructive measurement, well-established spectral characterization, and straightforward calculation. In the past, depth profiling by multiple-angle ATR/FT-IR spectroscopy has been limited by the fact that an estimated complex refractive index profile is required in order to perform the calculations.¹⁻³ Recently, we have developed a new depth profiling method based on exact optical theory.^{4,5} It is comprised of three steps of calculations: estimation of the complex refractive index profile, linear least-squares fitting of absorptance, and nonlinear fitting of reflectance. By solving linear equations of absorptance at a probing frequency, one obtains the estimated complex reflective index profile. The profile is used as a trial profile for linear least-squares fitting of absorptance. The converged profile from the linear fitting is then used as a trial profile for nonlinear fitting of reflectance. The converged profile from nonlinear fitting is defined as *the complex refractive* index profile of the film. The major advantage of this method is that neither the wave form nor prior knowledge of the profile is required. It can also be applied to angledependent spectra taken with an incident beam of known degree of polarization including nonpolarized incident beams.5

Since the new method has been successfully applied to simulated spectra with high accuracy in terms of the calculated complex refractive index profiles, this paper is designed to illustrate the applicability of this method to actual experiments. This approach will permit evaluation of the experimental limitations of this technique.

THEORY

A film of thickness h with anisotropic properties in the depth direction (z-direction) can be represented by a stratified system comprised of n layers. Each stratified layer is assumed to be homogeneous in the x-y direction, isotropic, and parallel plane-bound with neighboring layers. The interaction between an incident beam and the film can be represented by that of the beam with the stratified medium. Spectral intensities of the film medium (i.e., reflectance, transmittance, and absorptance) are the same as those of the stratified medium.^{4,5}

In ATR/FT-IR spectroscopy, absorptance of the film can be expressed as the summation of absorptances of each stratified layer as^{4-7}

$$A(\theta) = \frac{4\pi v}{n_0 \cos\theta} \sum_{j=1}^n \left\{ \int_{z_j}^{z_{j+1}} n_j(\mathbf{v}) k_j(\mathbf{v}) \langle E_z^2(\theta) \rangle \ dz \right\}$$
(1)

where v is the frequency of the incident beam, n_j (v) is the refractive index and k_j (v) the extinction coefficient at the *j*th layer of the stratified medium, and $\langle E_z^2(\theta) \rangle$ is the mean-square electric field at depth *z*. The number of the stratified layer is given by *n*, and the *n*th layer corresponds to the depth where the mean-square electric field is negligibly small. The electric field decays exponentially with respect to depth from the reflecting surface. The decay characteristic of the electric field of an absorbing film is slightly different from that of the evanescent field of a nonabsorbing film.⁴

In the case of interdiffusion between media C and D, the product of the refractive index and the extinction coefficient at frequency v of the *j*th layer is given by⁴

$$n_j(v)k_j(v) = \phi_j n_{\rm C}(v)k_{\rm C}(v) + (1 - \phi_j(n_{\rm D}(v)k_{\rm D}(v)$$
(2)

where is ϕ_j is the volume fraction of medium C in the *j*th layer; $n_C(v)$ is the refractive index and $k_C(v)$ the extinction coefficient of medium C, while $n_D(v)$ and $k_D(v)$ are those of medium D. The method for calculating the refractive index and the extinction coefficient from their product is given elsewhere.⁴ By substitution of Eq. 2 into Eq. 1, absorptance of the stratified medium is then given by

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FIG. 1. The composition-dependent characteristics of complex refractive index profiles as a result of interdiffusion between an absorbing medium and nonabsorbing medium of the same refractive indices. (A) Volume fraction profile of the absorbing medium as a function of depth. (B–D) Complex refractive index profiles of the interdiffused medium with various extinction coefficients for the absorbing medium calculated from composition-dependent (solid lines) and constant (dotted line, n = 1.5) refractive indices. Note: at $k 2_{\rm C} = 0.1$, the reflectance with composition-dependent and constant refractive indices cannot be differentiated by the graphical illustration. The optical parameters are $n_0 = 2.41$, $\hbar_{\rm C} = 1.5 + ik$, $n_{\rm D} = 1.5$, and v = 1500 cm⁻¹.

$$A(\theta) = \frac{4\pi v}{n_0 \cos \theta}$$

$$\cdot \sum_{j=1}^{n} \left[\int_{z_j}^{z_{j+1}} \{ \phi_j n_C(\mathbf{v}) k_C(\mathbf{v}) + (1 - \phi_j) n_D(\mathbf{v}) k_D(\mathbf{v}) \} \right]$$

$$\cdot \langle E_z^2(\theta) \rangle \, dz \right]. \tag{3}$$

In a simple case where medium D is nonabsorbing [i.e., $k_D(v) = 0$], Eq. 3 is then simplified to

$$A(\theta) = \frac{4\pi v n_C(v) k_C(v)}{n_0 \cos \theta} \sum_{j=1}^n \left[\int_{z_j}^{z_{j+1}} \phi_j \langle E_z^2(\theta) \rangle \, dz \right].$$
(4)

Since the complex refractive index is a composition-dependent parameter, the complex refractive index profile of the stratified medium is used to calculate the mean-square electric field. There are small variations of the refractive index of the stratified medium, although the refractive indices of the interdiffused media are the same. Under certain conditions [i.e., $n_{\rm C}(v) \cong n_{\rm D}(v)$, and $k_{\rm C}(v)$ is small], refractive indices of the stratified medium can be assumed to be unchanged and equal to that of the absorbing medium. Figures 1B–1D show variations of the complex refractive index profile as a function of com-



FIG. 2. The composition-dependent characteristics of complex refractive index profiles as a result of interdiffusion between an absorbing medium and nonabsorbing medium of different refractive indices. The volume fraction profile of the absorbing medium is the same as that of Fig. 1A. (A–C) Complex refractive index profiles of the interdiffused medium with various extinction coefficients for the absorbing medium. (**D**) A comparison between reflectances of the interdiffused medium calculated from composition-dependent (solid lines) and constant (dotted line, n = 1.52) refractive indices. The optical parameters are $n_0 =$ 2.41, $\hat{n}_c = 1.52 + ik$, $n_D = 1.5$, and v = 1500 cm⁻¹.

position when medium C is adsorbing while medium D is nonabsorbing. The volume fraction profile of medium C is shown in Fig. 1A. Although refractive indices of media C and D are the same, the refractive index of the stratified medium varies as a function of composition. Figure 1E shows the comparison between reflectances calculated from constant refractive index and those from composition-dependent refractive index. The constant refractive index assumption is valid only when the extinction coefficient of the absorbing medium is small. Analogous to Fig. 1, with the same volume fraction profile of the absorbing medium, Fig. 2 shows profiles in the case where the refractive indices of media C and D are different. The deviations of the calculated reflectance from the constant refractive index assumption are greater than those in Fig. 1.

By performing depth profiling on a set of angle-dependent reflectance, one can obtain the volume fraction of each component with respect to depth from the reflecting surface if the complex refractive indices of both media at the profiling frequency are known. The new depth profiling method consists of three steps: estimation of complex refractive index profile, linear least-squares fitting of absorptance, and nonlinear fitting of reflectance.⁴ Unlike the first step, which can be applied only to frequencies with small extinction coefficients (i.e., k < 0.2), the second and third step can be applied to frequencies with large extinction coefficients since they utilize exact optical theory for their calculations. In order to perform depth profiling at frequencies with large extinction coefficients, the estimated complex refractive index profile at those frequencies can be calculated from the estimated



FIG. 3. Schematic illustration of PS/PVME laminated film on a ZnSe internal reflection element.

volume fraction profile at the frequencies with small extinction coefficients. The new depth profiling method has advantages over the others since an estimated complex refractive index profile or the wave form of the profile is not required. Furthermore, our approach is not restricted to spectra with *s*- or *p*-polarized incident beams, since spectra of an incident beam with a known degree of polarization can be utilized. This condition means that socalled nonpolarized light can be used, as long as the minor degree of polarization caused by the imperfection of the spectrometer is determined. The details of the depth profiling calculations are given elsewhere.^{4, 5}

EXPERIMENTAL

The presented spectra were obtained from a Bio-Rad FTS-60A Fourier transform infrared spectrometer with a liquid nitrogen-cooled, narrow-bandpass, linearized mercury-cadmium-telluride (MCT) detector. All ATR/FT-IR spectra were taken with the Seagull attachment (Harrick Scientific Corporation). The internal reflection element (IRE) was a ZnSe hemisphere with a radius of 12.5 mm. The spectra were taken at incident angles ranging from 46° to 74° with a nonpolarized incident beam. Angles of incidence were continuously changed without realignment of the attachment. The incident beam from the light source was found to be partially polarized. The degrees of polarization are 0.018, 0.024, and 0.036 at 3060, 3026, and 1492 cm⁻¹, respectively. The degree of polarization of the incident beam is not affected by the reflection in the attachment and the changes in the angles of incidence.⁸ Typically, 1024 scans were coadded with a resolution of 4 cm⁻¹. In order to obtain a narrow beam divergence, a small aperture was utilized.

Polystyrene (PS; Polyscience, Inc.), was used as received. The PS has a weight average molecular weight of 273,200 and polydispersity of 5.00 as measured by using gel permeation chromatography (GPC) based on a PS standard.⁹ The polyvinyl methyl ether (PVME), 50% solids in toluene (Scientific Polymer Product, Inc.), was also used as received without further purification. Mixtures of PS and PVME have been found to produce clear films with a single glass transition temperature, T_g , when cast from toluene.¹⁰

A laminated film of PS on the IRE was prepared. In order to obtain optical contact between the IRE and the laminated film, the PS thin film was spin-coated on the IRE surface from a dilute solution of PS in carbon tetrachloride. The spin-coating was performed by depositing 0.5 mL of 0.05 g/mL PS solution on the IRE surface.



FIG. 4. Comparisons of reflectance from the experiment (open symbols) and those from the theoretical calculation with the thickness of the PS equal to 0.475 μ m (filled symbols) at 3026 cm⁻¹ (**A**) and 1492 cm⁻¹ (**B**). The optical parameters are $n_0 = 2.41$, $\hat{n}_{\text{PS}, 3026 \text{ cm}^{-1}} = 1.52 + 0.034i$, $\hat{n}_{\text{PS}, 1492 \text{ cm}^{-1}} = 1.52 + 0.098i$, $n_{\text{PVME}} = 1.5$, and $n_{\text{AIR}} = 1.0$.

The IRE was then spun at 2000 rpm for 5 min. The film was left at room temperature to allow the solvent to evaporate, then dried at 100 °C under vacuum for 1 h. In an effort to ensure that there was no chloroform left in the film, an ATR spectrum of the film was taken, and no bands at 670 and 759 cm⁻¹ were observed. A thick PVME film, about 0.5 mm, was prepared separately. The film was spin-coated from a 25% solid PVME in toluene on a micro glass slide cover. The film was left at room temperature for 2 h and then dried at 100 °C under vacuum for 3 h. In an effort to ensure that there was no toluene left in the film, an ATR spectrum of the film was taken, and the band at 728 cm⁻¹ was not observed. The thick PVME film was then pressed on the PS-coated IRE. The system was then allowed to remain at 60 °C for 1 h. A schematic illustration of the laminated film is shown in Fig. 3. Subsequent diffusion between PS and PVME was achieved by heating the laminated film at 140 °C



FIG. 5. An enhancement of absorptance of polystyrene thin film by the presence of the PVME substrate. The optical parameters are $n_0 = 2.41$ and $\theta = 50^\circ$.



FIG. 6. The changes of reflectance of the laminated film at 1492 cm⁻¹ (A) and 1452 cm⁻¹ (B) indicate interdiffusion between PS and PVME as a result of heat treatments. The optical parameter is $n_0 = 2.41$.

under an argon purge for 1 h for the first heating and an additional 2 h for the second heating.

The extinction coefficient and volume fraction profiles of PS in the laminated film were calculated from angledependent spectra under the assumption that there is no volume change upon mixing.

RESULTS AND DISCUSSION

One of the limitations of depth profiling by ATR/FT-IR spectroscopy is that it can probe spectral changes only up to the working depth. Any molecular characteristics beyond the working depth make a very small contribution to the spectral intensity. The working depth is defined as the depth where the evanescent field decays to 0.25% of that of the surface,^{4,5,11} which is approximately three times the penetration depth. As shown in Fig. 3, the thickness of the PS thin film, approximately $0.475 \mu m$, is calculated from angle-dependent spectral intensities of the film via three-layer models (i.e., ZnSe/PS/air and ZnSe/PS/PVME). Figure 4 shows comparisons between reflectances from experiment and those from the exact optical



FIG. 7. The extinction coefficient and volume fraction profiles of PS in the laminated film calculated from angle-dependent reflectances shown in Fig. 6A. A constant refractive index of the interdiffused medium (n = 1.52) is used for depth profiling calculations. The optical parameters are $n_0 = 2.41$, $n_{\text{PVME}} = 1.5$, v = 1492 cm⁻¹, and $\hat{n}_{\text{PS}, 1492}$ cm⁻¹ = 1.52 + 0.098*i*; the number of stratified layer is 200.

TABLE I. Integration of the extinction coefficient profiles obtained from the depth profiling at 1492 cm⁻¹ after subsequent heat treatments.

Thin PS filma 4.66×10^{-2} Untreated laminate filmb 4.44×10^{-2} 1st heat treatmentb 4.57×10^{-2} 2nd heat treatmentb 4.78×10^{-2}	

^a $\hat{n}_{PS, 1492 \text{ cm}^{-1}} = 1.52 + 0.098 i$, and film thickness is 0.475 µm. ^b Extinction coefficient profiles shown in Fig. 7.

theory at 3026 and 1492 cm⁻¹. At 3026 and 1492 cm⁻¹, PVME is infrared-transparent and a refractive index of 1.5 is assumed.^{9,12}

The major problem in ATR/FT-IR spectroscopy is the air gap between the IRE and the film. According to visual and spectroscopic observations, there is no air gap in the system. Figure 5 shows reflectance spectra of the PS thin film and PS/PVME laminated films at a 50° angle of incidence. Absorptance of the bands associated with the PS in the laminate is enhanced because of the presence of PVME substrate, which is expected from the theoretical point of view. Reflectances in the regions 3100–3000 and 1510–1480 cm⁻¹ are enhanced by the optical effect, while those of 3000–2750 and 1480–1400 cm⁻¹ are a combination of the optical effect and absorption of the substrate. As a result of the above observation (i.e., Figs. 4 and 5), optical contacts between the IRE and PS film and between the PS film and PVME substrate are assumed.

Figure 6 shows angular-dependent reflectances of the laminated film at 1492 and 1452 cm⁻¹ at various heat treatments. The reflectance changes after consecutive heat treatments indicate interdiffusion between the PS thin film and PVME substrate. Since PVME is infrared-transparent at 1492 cm⁻¹, reflectance increases after heat treatment as a result of interdiffusion. Unlike those at 1492 cm⁻¹, PS and PVME are infrared-absorbing at 1452 cm⁻¹. Reflectance decreases after heat treatment, since the extinction coefficient of PVME is greater than that of PS. Reflectances at 1492 cm⁻¹ are used for depth profiling



FIG. 8. Comparisons between reflectance from the experiment (open symbols) and those from the theoretical calculation (filled symbols) at 1492 cm⁻¹. The extinction coefficient profiles of PS shown in Fig. 7 are used for the calculation. The refractive index of the interdiffused medium is assumed to be constant and equal to that of PS. The optical parameters are $n_0 = 2.41$, $n_{\text{PS}} = 1.52$, $n_{\text{PVME}} = 1.5$, and v = 1492 cm⁻¹.



FIG. 9. Comparisons between reflectances from the experimental (open symbols) and those from the theoretical calculation (filled symbols) at 3060 cm⁻¹. The volume fraction profiles of PS shown in Fig. 7 are used for the calculation. The refractive index of the interdiffused medium is assumed to be constant and equal to that of PS. The optical parameters are $n_0 = 2.41$, $\hat{n}_{\text{PS}, 3060 \text{ cm}^{-1}} = 1.52 + 0.022i$, and $n_{\text{PVME}} = 1.5$.

calculation, since PVME is transparent in this region and there is no spectral distortion upon heat treatment. As a result, spectral changes in this region are assumed to be associated solely with interdiffusion between PS and PVME. The penetration depth at 1492 cm⁻¹ with a 46° angle of incidence is 1.28 μ m; therefore the working depth is about 3.84 μ m. This observation implies that the molecular characteristics at a depth beyond 3.84 μ m in the laminated film cannot be recognized by the incident beam and will make a negligible contribution to the spectral intensity at 1492 cm⁻¹.

The extinction coefficient and volume fraction profiles of PS in the laminated film at various heat treatments are shown in Fig. 7. The extinction coefficient profiles are calculated from angular-dependent reflectances shown in Fig. 6A by using the new depth profiling method. The volume fraction profiles are calculated from the calculated extinction coefficient profiles by using $\hat{n}_{PS, 1492 \text{ cm}^{-1}} = 1.52$ + 0.098i.⁹ Figure 7 also shows quantitative properties of the profiles, since areas under the profiles, which are proportional to the amount of PS in the laminated film, are consistent with a standard deviation (SD) of 0.14×10^{-2} . The integrations of the calculated extinction coefficient profiles at various heat treatments are shown in Table I. The accuracy of the calculated profiles are shown in Fig. 8 where reflectances from the experiment are compared to those from theoretical calculation with the use of the profile shown in Fig. 7. The agreements between experimental results and those from theoretical calculations are well within the experimental error. The accuracy of the calculated extinction coefficient profiles is also confirmed by the comparisons between reflectances from the experiment and those from theoretical calculations at 3060 and 3026 cm⁻¹, as shown in Figs. 9 and 10, respectively. The complex refractive index profiles are calculated from the volume fraction profiles shown in Fig. 7 by using



FIG. 10. Comparisons between reflectances from the experiment (open symbols) and those from the theoretical calculation (filled symbols) at 3026 cm⁻¹. The volume fraction profiles of PS shown in Fig. 7 are used for the calculation. The refractive index of the interdiffused medium is assumed to be constant and equal to that of PS. The optical parameters are $n_0 = 2.41$, $\hat{n}_{\text{PS}, 3026}$ cm⁻¹ = 1.52 + 0.043*i*, and $n_{\text{PVME}} = 1.5$.

 $\hat{n}_{\rm PS, 3060 \ \rm cm^{-1}} = 1.52 + 0.022i$ and $\hat{n}_{\rm PS, 3026 \ \rm cm^{-1}} = 1.52 + 0.043i$.⁹ The complex refractive index profiles are then used to calculate angle-dependent reflectances by exact optical theory. The reflectances from the experimental results and those from theoretical calculations agree well within the experimental error.

CONCLUSION

The complex refractive index and volume fraction profiles of the PS in the PS/PVME laminated film have been successfully determined by the new depth profiling method using multiple-angle ATR/FT-IR spectroscopy. Neither the wave form nor prior knowledge about the profile is required in order to perform the calculation. The quantitative nature of this technique has been shown through the consistent values of the integration of extinction coefficient profiles after consecutive heat treatments. The accuracy of the calculated profiles is shown via the good agreement between reflectances from the experiment and those from theoretical calculation. It has also been confirmed by experimental results at frequencies other than the profiling frequency.

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