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Infrared Refractive Index and Extinction Coefficient of Polyimide Films [1]

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ABSTRACT

We have measured the transmittance of several polyimide ($C_{22}H_{10}N_2O_4$) films at frequencies from 6000 - 500 cm^{-1} (wavelengths from 1.67 - 20 μm) using a Fourier transform infrared (FT-IR) spectrometer. The free-standing polyimide films are made by spin coating and thermal curing processes. The thickness of the films ranges from 0.1 - 4 μm. In the nonabsorbing region from 6000 - 4000 cm^{-1}, the minimum transmittance caused by interference is used to obtain the refractive index for film thickness greater than 1 μm. The film thicknesses are determined by fitting the spectral transmittance using the refractive index. Molecular absorption strongly reduces the transmittance at frequencies from 2000 - 500 cm^{-1}. The optical constants, i.e., the refractive index and the extinction coefficient, are determined from the measured transmittance for several films of different thickness using a least-squares method. A Lorentzian oscillator model is also developed, which in general agrees well with the measured transmittance. This study will facilitate the application of polyimide films in the fabrication of infrared filters and other optoelectronic applications. The methods presented in this paper can be used to determine the optical constants of other types of thin-film materials.

KEY WORDS: Fourier transform infrared spectrometer (FT-IR); infrared filters; optical constants; polyimide films; radiative properties; refractive index; transmittance.

1. INTRODUCTION

Polyimide films have received much attention due to their mechanical strength, low thermal expansion coefficient, and low dielectric constant.[1,2] The applications of polyimide range from optoelectronics to X-ray astronomy.[1-10] The standard fabrication method includes a spin coating from solution followed by a thermal curing to induce imidization.[3,4] Molecular beam deposition and ionized beam deposition have also been used to produce polyimide films.[5,6]

Frenkel and Zhang[11] reported the development of neutral-density infrared filters using metallic coatings on polycarbonate thin films (≈100 nm thick) to eliminate transmittance variation caused by interference effects in the conventional dielectric substrates of thickness on the order of 1 mm. Because polyimide possesses larger tensile strength and can withstand higher temperature than polycarbonate, it may be a better candidate for fabrication of neutral-density infrared filters.[4] Knowledge of the optical constants (i.e., refractive index and extinction coefficient) is essential for the design of infrared filters. Fourier-transform infrared (FT-IR) spectrometers have been widely used to study the infrared absorption of polyimides. Most studies, however, dealt with the locations of the absorption peaks rather than the magnitudes of the refractive index and the extinction coefficient.[5-7] Saito et al.[8] obtained the optical constants of several polymer coatings from the measured transmittance, with a limited wavelength range from 2 - 12 μm.

This paper present the infrared transmittance measurement of five polyimide films using an FT-IR spectrometer. Different methods are used to determine the optical constants and thickness of these films for infrared applications.

2. MEASUREMENTS

The polyimide ($C_{22}H_{10}N_2O_4$) films were made from a solution by spin coating and were cured with optimized time and temperature parameters to provide the best

combination of strength and ductility.[4] The polyimide film was peeled from the substrate and mounted on a ring with an opening of 15 mm in diameter, which defines the clear aperture for optical applications. The film thickness was measured with a surface profilometer. Table I lists the thicknesses of the five specimens used in the present study. The method of determining the film thickness from the transmittance spectrum is discussed in the following section.

A Bomem MB100 Fourier-transform infrared (FT-IR) spectrometer was employed to measure the transmittance from 6000 - 500 cm^{-1}. The spectrometer is equipped with an external SiC infrared source, a KBr-on-Ge beamsplitter, and a DTGS pyroelectric detector. The interferometer is sealed and ZnSe windows are used for beam in and out. No purge gases are used in the sample, detector, and source chambers. Therefore, H_2O and CO_2 absorption lines become visible in the response spectra. The effect is not significant for the transmittance (i.e., the ratio of the sample spectrum to the reference spectrum) since the specimens are thin and the time span between the sample and reference measurements is no more than a few minutes. Calibrations were made to eliminate the effects of detector nonlinearity and nonequivalent responsivity on the measurements accuracy.[12,13] A sample holder with a 6-mm-diameter hole was used to limit the beam spot on the sample. The specimen was placed normal to the beam axis. The maximum beam divergence is ≈9.6° (f/3 optics). Calibration using a single-crystal optical-quality Si wafer showed that the absolute uncertainty in transmittance is 0.01 (a coverage factor of 2, i.e., 95% confidence, is used in this paper). A spectral resolution of 2 cm^{-1} was used, and it took approximately one minute to collect 10 scans.

The wavenumber accuracy was calibrated using a polystyrene film, certified by the National Institute of Standards and Technology.[14] The agreement of the peak wavenumbers for the four absorption bands that are less sensitive to the peak-finding method is within 1 cm^{-1} by observing the wavenumbers near the transmittance minima

(absorption peaks). Figure 1 shows a typical transmittance spectrum for a 2.45-μm-thick polyimide film. At wavenumbers greater than 2000 cm^{-1}, the interference between the multiple reflected waves results in a periodic variation in the transmittance. The maximum transmittance is 1 between 6000 cm^{-1} and 4000 cm^{-1}, indicating little absorption in this region. Both the interference effects and absorption caused by molecular vibrations influence the transmittance at wavenumbers less than 2000 cm^{-1}.

3. ANALYSIS

Consider a thin film of thickness d with optically smooth, parallel surfaces. The complex refractive index is $\bar{n} = n + i\kappa$, where the real part n is called the refractive index and the imaginary part κ is called the extinction coefficient. The optical constants, n and κ, are frequency dependent. If the film thickness is much less than the coherence length of the incident radiation, the spectral transmittance is [15,16]

$$T = \left| \frac{(1-r)(1+r)e^{i\delta}}{1-r^2 e^{i2\delta}} \right|^2 \qquad (1)$$

where r is the complex Fresnel's reflection coefficient at the air-film interface and δ is the complex phase change inside the film. At normal incidence, $r = (1-\bar{n})/(1+\bar{n})$ and $\delta = 2\pi\bar{n}\nu d$, where ν is the wavenumber (frequency) of the incident radiation.

In the nonabsorbing region, $\kappa = 0$. Let $\rho = r^2 = [(1-n)/(1+n)]^2$, then

$$T = \frac{(1-\rho)^2}{1+\rho^2 - 2\rho\cos(4\pi n\nu d)} \qquad (2)$$

For a given material and film thickness, the transmittance oscillates as the wavenumber changes because of interference effects, as shown in Fig. 2. The wavenumbers corresponding to the maximum transmittance and the minimum transmittance are $\nu_{\max,m} = m/(2nd)$ and $\nu_{\min,m} = (m+\frac{1}{2})/(2nd)$, where the integer m = 0, 1, 2, ...[16] The free spectral range is the wavenumber separation between two interference maxima, i.e.,

$\Delta\nu = (2nd)^{-1}$. Notice that $T_{\max} = 1$ and $T_{\min} = [2n/(1+n^2)]^2$. The measured $T_{\min}$ can be used to determine the refractive index n and the measured $\Delta\nu$ can then be used to determine the film thickness d. The refractive index changes little for 6000 cm^{-1} < ν < 4000 cm^{-1}. A curve fit for the transmittance in this spectral region determines both n and d. The curve-fitting method takes advantage of the numerous data points in the transmittance spectrum and, therefore, reduces the uncertainty caused by the measurement. The free spectral range increases as the film thickness decreases. For film thickness equal to or less than ≈0.2 μm, the wavenumber corresponding to the first transmittance minimum is greater than 6000 cm^{-1}. For the three thicker specimens, the resulting refractive index is 1.75±0.01 at wavenumbers between 6000 cm^{-1} and 4000 cm^{-1}, within the uncertainty of the measured transmittance. Notice that a change of 0.01 in n results in a change of ≈0.005 in $T_{\min}$ for $n \approx 2$. The thickness of the two thinner specimens are determined by fitting the transmittance spectra using the average refractive index obtained from the thicker specimens. The thicknesses of the five specimens obtained from the transmittance are listed in Table I, which agree with the data measured with a surface profilometer within the overall uncertainties of the two methods. For films thicker than 1 μm, the spectroscopic method is more accurate than the direct measurement with the surface profilometer.

In the absorbing region (ν < 2000 cm^{-1}), the frequency-dependent n and κ can be determined from Eq. (1) using the spectral transmittance of two films (of different thicknesses). Due to the experimental uncertainty, the solution does not always exist, especially in the strongly absorbing bands. Therefore, a multiple-parameter least-squares fitting program is employed.[17] It determines the best fitting parameters by minimizing the quantity Chi-Square defined as

$$\chi^2(\nu) \equiv \sum_{j=1}^{M} \left[\frac{T_m(\nu, d_j) - T_c(\nu, d_j; n, \kappa)}{\sigma_m} \right]^2 \qquad (3)$$

where T_m and σ_m are the measured transmittance and its standard deviation, M is the total number of specimens (5 in the present study), and T_c is the transmittance calculated from Eq. (1). The computer program determines the n and κ values that minimize χ^2 for each wavenumber from an initial guess. The standard deviation between the fitted and the measured transmittance is

$$\sigma_{st} = \sigma_m [\chi^2 / (M-1)]^{1/2} \tag{4}$$

For M = 5 and σ_m = 0.01, σ_{st} = 0.005 for χ^2 = 1 and $\sigma_{st} \approx 0.03$ for χ^2 = 30. The fitted transmittance agrees extremely well with the measured for 4000 cm^{-1} < ν < 500 cm^{-1}, with an average χ^2 of 1.2 and a maximum χ^2 of 30. When the least-squares method is applied to wavenumbers greater than 4000 cm^{-1}, it is found that n decreases for about 0.01 from 6000 cm^{-1} to 4000 cm^{-1} and κ < 0.001 in this region. Because the thickest film is ≈4 μm, these films can be considered as nonabsorbing at ν > 4000 cm^{-1}.

The dielectric function is modeled by a superposition of many Lorentzian oscillators, viz.[18]

$$\varepsilon(\nu) = [n(\nu) + i\kappa(\nu)]^2 = \varepsilon_\infty + \sum_{j=1}^{N} \frac{S_j \omega_j^2}{\omega_j^2 - \omega^2 - i\gamma_j \omega} \tag{5}$$

where ε_∞ is a high-frequency constant, N is the number of oscillators, and S_j, ω_j, and γ_j are the strength, center frequency, and width (damping coefficient) of the jth oscillator, respectively. By comparing the calculated transmittance from the Lorentz model and the measured transmittance for all specimens, the best fitting parameters (i.e., ε_∞, S_j's, ω_j's, and γ_j's) can be obtained. The initial guesses of the ε_∞, S_j's, ω_j's, and γ_j's are determined using the n and κ values obtained from the least-squares method, as discussed by Zhang et al.[19] A few absorption bands are not symmetric that cannot be fitted well by the simple Lorentzian oscillator model. The large number of the Lorentzian oscillators makes a least-squares fit impractical. Hence, the fit-by-eyes method is used, which requires a large

amount of time and fine adjustments to obtain the best fitting parameters. The results are discussed in the following section.

4. RESULTS AND DISCUSSION

The measured transmittance and that calculated from the Lorentz model with 31 oscillators are shown in Fig. 3 (for 6000 $cm^{-1} < \nu < 2000$ cm^{-1}) and Fig. 4 (for 2000 $cm^{-1} < \nu < 500$ cm^{-1}). The fitted parameters for the Lorentz model are listed in Table II. The transmittance calculated using the optical constants obtained from the least-squares method is almost the same as the measured transmittance, which is not shown.

As seen from Fig. 3, absorption by CO_2 (near 2350 cm^{-1}) and by H_2O (in the region 3900 $cm^{-1} < \nu < 3600$ cm^{-1}) is discernible. A nitrogen gas or a CO_2-free dry air may be used to reduce the H_2O and CO_2 structures in the future. The data become noisier towards 6000 cm^{-1} because of the rapid decrease in the signal towards the cut-off frequency. The disagreement between the measured and the calculated transmittance for the 0.98-μm-thick film near 4400 cm^{-1} is slightly greater than 0.01. This is because the same Lorentzian parameters are used for all films. The refractive index calculated from the Lorentz model is 1.75 at 6000 cm^{-1} and reduces to 1.73 at 2500 cm^{-1}. The extinction coefficient is less than 0.001 for most wavenumbers except near the center frequencies as listed in Table II. The extinction coefficients at the center frequencies are $\kappa(\nu_{28}) = 0.004$, $\kappa(\nu_{29}) = 0.006$, $\kappa(\nu_{30}) = 0.005$, and $\kappa(\nu_{31}) = 0.003$. The refractive index obtained by Saito et al.[8] is 1.59 for a polyimide coating of 2.12 μm thick. The large difference (10%) could be associated with the different sample preparation methods. Goeschel et al.[10] measured the refractive index of several polyimide samples at 0.633 μm using a He-Ne laser, and observed a large anisotropy between the in-plane and the out-of-plane refractive indices. The average refractive index is 1.76, which compares well with the present study. The radiation in the

FT-IR spectrometer is assumed to be randomly polarized.[20] The issue of polarization dependence of the optical constants merits further investigation.

In Fig. 4, the transmittance spectra are stacked. The transmittance scales are from 0.5 - 1 for the two upper panels and 0 - 1 for the lower panels. The agreement between the model and the data is quite good, except for several asymmetric absorption bands near 1700 cm^{-1} and 1100 cm^{-1}. The model overpredicts the transmittance for the 3.93-μm-thick film near 500 cm^{-1}, indicating that additional oscillators exist below 500 cm^{-1}. The center frequencies of the Lorentzian oscillators correspond to the absorption peaks due to molecular vibration. The identification and assignment of the vibration modes are beyond the scope of the present study. A detailed discussion can be found in the work of Ishida and Huang.[7] Many of the absorption peaks reported by Ishida and Huang[7] agree with the present study. The differences could be caused by the different methods of preparation of the polyimide specimens.

Figure 5 compares n and κ obtained from the least-squares method and the Lorentz model for 2000 $cm^{-1} < \nu < 500$ cm^{-1}. The extinction coefficients obtained from the two methods agree very well, whereas there appears to be a larger discrepancy in the refractive index near 1515 cm^{-1} and 1356 cm^{-1}. The transmittance predicted by the Lorentz model agrees fairly well with the experiments, suggesting that the transmittance is much more sensitive to κ than to n. The dielectric function given by Eq. (5) and Table 2 can be easily programmed for infrared design applications.

5. CONCLUDING REMARKS

The optical constants of polyimide films are determined based on the transmittance measured by an FT-IR spectrometer at frequencies from 6000 - 500 cm^{-1}. Several methods are used to infer the frequency-dependent refractive index and extinction coefficient. The interference effects are used to determine the refractive index and film thickness in the

weakly absorbing region. A least-squares method is used to determine n and κ in the absorbing region. A Lorentzian oscillator model is developed by fitting the transmittance. The results show that the refractive index and extinction coefficient are thickness independent for specimen thicknesses from 0.11 μm to 4 μm. The optical constants obtained from this study can be applied to design infrared filters and other optoelectronics devices. The methods presented in this paper can be used to determine the optical constants of other types of thin-film materials.

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Table I. Thickness of the polyimide films used in the present study.

Specimen Number	1	2	3	4	5
Measured by a profilometer (μm)	0.105±0.01	0.198±0.02	0.97±0.10	2.34±0.23	3.77±0.38
Determined from transmittance (μm)	0.11±0.01	0.20±0.01	0.98±0.01	2.45±0.02	3.93±0.03

Table II. Fitted parameters for the Lorentzian oscillator model (ε_∞ = 3.075±0.03), where the estimated uncertainty is 1 cm^{-1} for ν_j and 10% for S_j and γ_j.

j	ν_j (cm^{-1})	γ_j (cm^{-1})	S_j
1	529.5	8	0.004
2	551	10	0.0065
3	568	10	0.002
4	590	14	0.0035
5	636.5	10.5	0.001
6	673	5.5	0.0018
7	698.5	12.5	0.01
8	736.5	6.5	0.0106
9	752	3	0.00035
10	763.5	8	0.0008
11	795.5	5	0.0007
12	832	17	0.02
13	865.5	18	0.0016
14	890	8.5	0.0035
15	1023	9	0.001
15	1082.5	35	0.016
17	1123	14	0.004
18	1177.5	10	0.00065
19	1224	19	0.0068
20	1267	17	0.0025
21	1356	25	0.06
22	1421	11	0.0032
23	1472	15	0.0004
24	1515	10	0.011
25	1620	19	0.002
26	1717	20	0.026
27	1773	10.5	0.0054
28	2718	40	0.00018
29	3070	80	0.00055
30	3476	40	0.00017
31	3630	80	0.00025

FIGURE CAPTIONS

Fig. 1. Transmittance spectrum of a 2.45-μm-thick polyimide film.

Fig. 2. Predicted transmittance for a 1-μm-thick film with $n = 1.75$ and $\kappa = 0$.

Fig. 3. Measured and calculated transmittance for 2000 $cm^{-1} < \nu < 6000$ cm^{-1}. Note that the markers are used for identification and the data intervals are ≈1 cm^{-1}.

Fig. 4. Transmittance of all five samples for 500 $cm^{-1} < \nu < 2000$ cm^{-1}. Solid lines are measured and dotted lines are calculated from the Lorentz model. Note that the vertical scales are from 0.5 - 1 for the two upper panels and 0 - 1 for the others.

Fig. 5. Optical constants obtained from the least-squares method and from the Lorentz model: a) refractive index n. b) extinction coefficient κ.

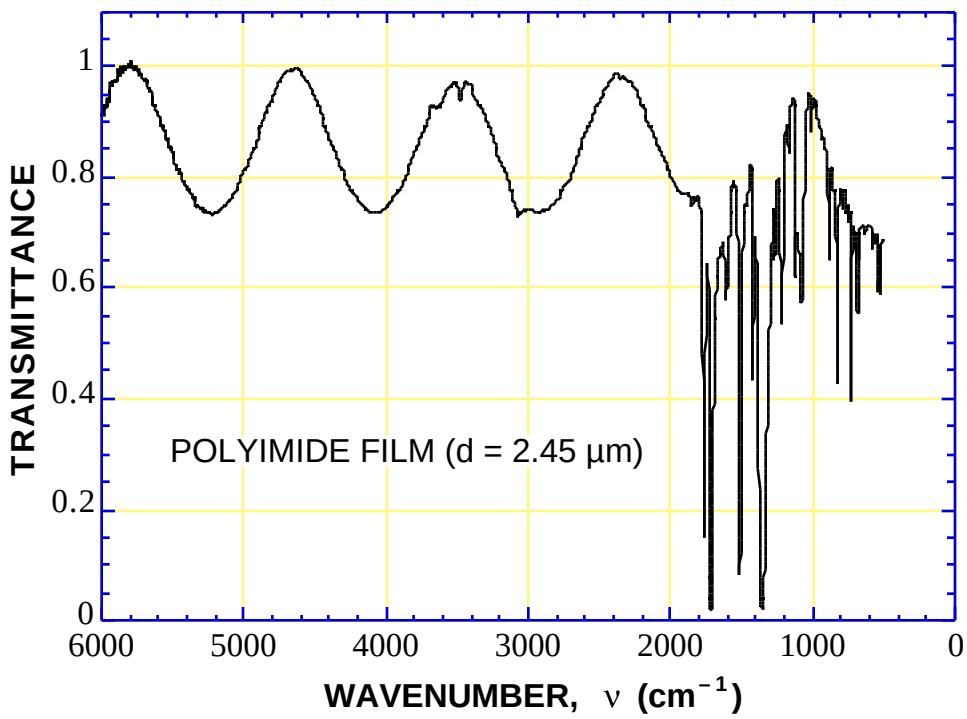
TRANSMITTANCE
1
0.8
0.6
0.4
0.2
0
6000
5000
4000
3000
2000
1000
0
WAVENUMBER, ν (cm⁻¹)
POLYIMIDE FILM (d = 2.45 µm)

Figure 1

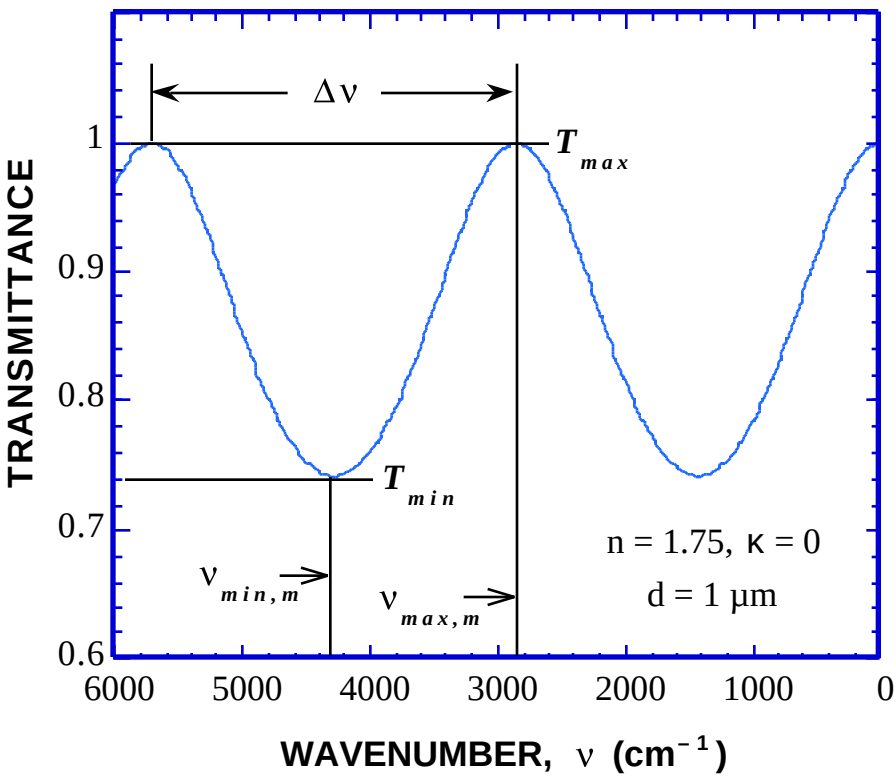
Δν
1
0.9
0.8
0.7
0.6
T max
T min
ν min, m
ν max, m
n = 1.75, κ = 0
d = 1 μm
TRANSMITTANCE
6000
5000
4000
3000
2000
1000
0
WAVENUMBER, ν (cm⁻¹)

Figure 2

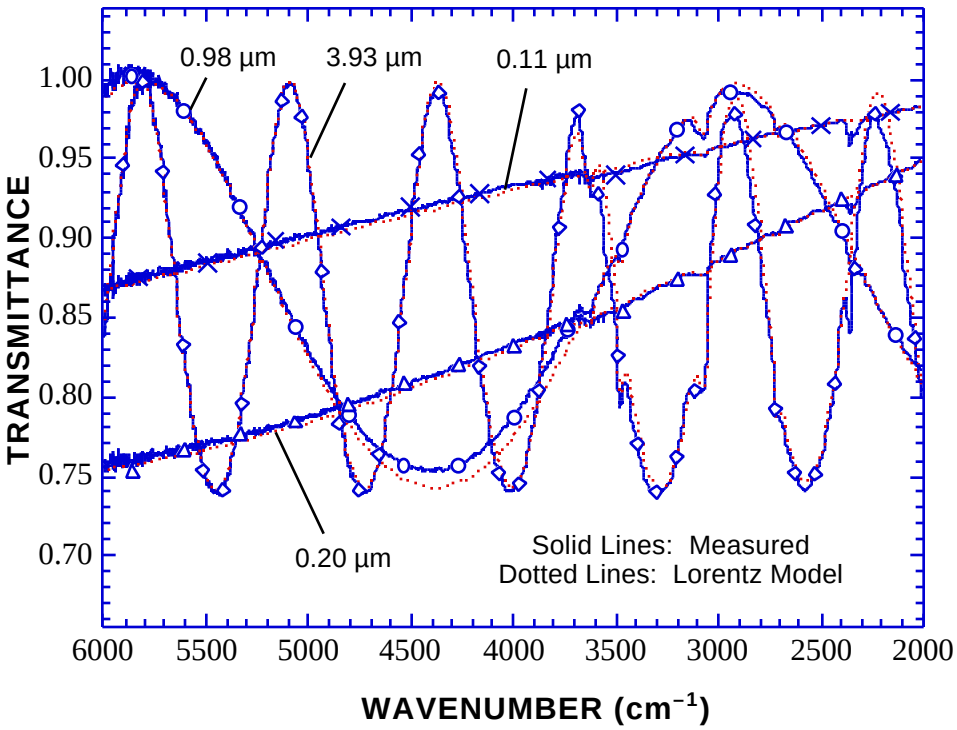
0.98 µm
3.93 µm
0.11 µm
0.20 µm
Solid Lines: Measured
Dotted Lines: Lorentz Model
TRANSMITTANCE
1.00
0.95
0.90
0.85
0.80
0.75
0.70
6000
5500
5000
4500
4000
3500
3000
2500
2000
WAVENUMBER (cm⁻¹)

Figure 3

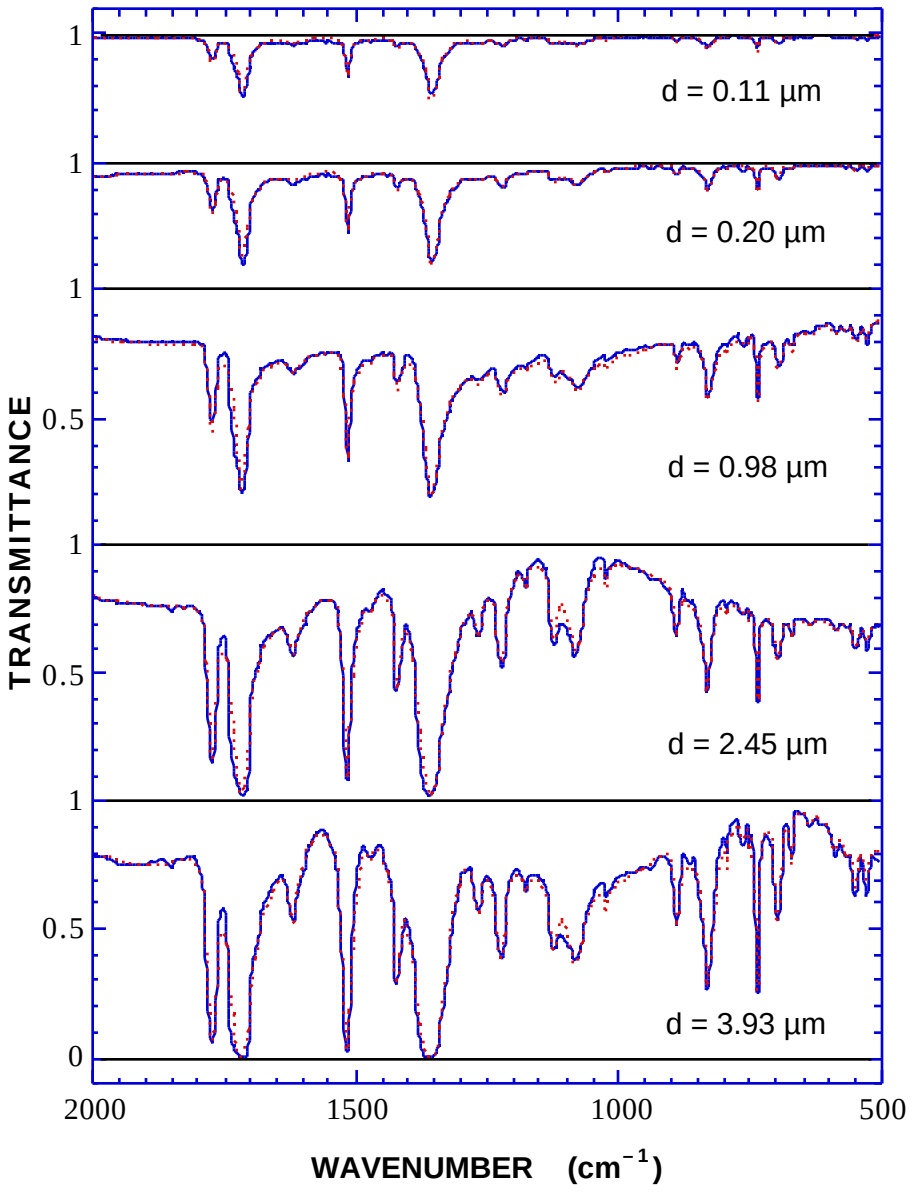
TRANSMITTANCE
WAVENUMBER (cm⁻¹)
d = 0.11 µm
d = 0.20 µm
d = 0.98 µm
d = 2.45 µm
d = 3.93 µm
1
0.5
0
2000
1500
1000
500

Figure 4

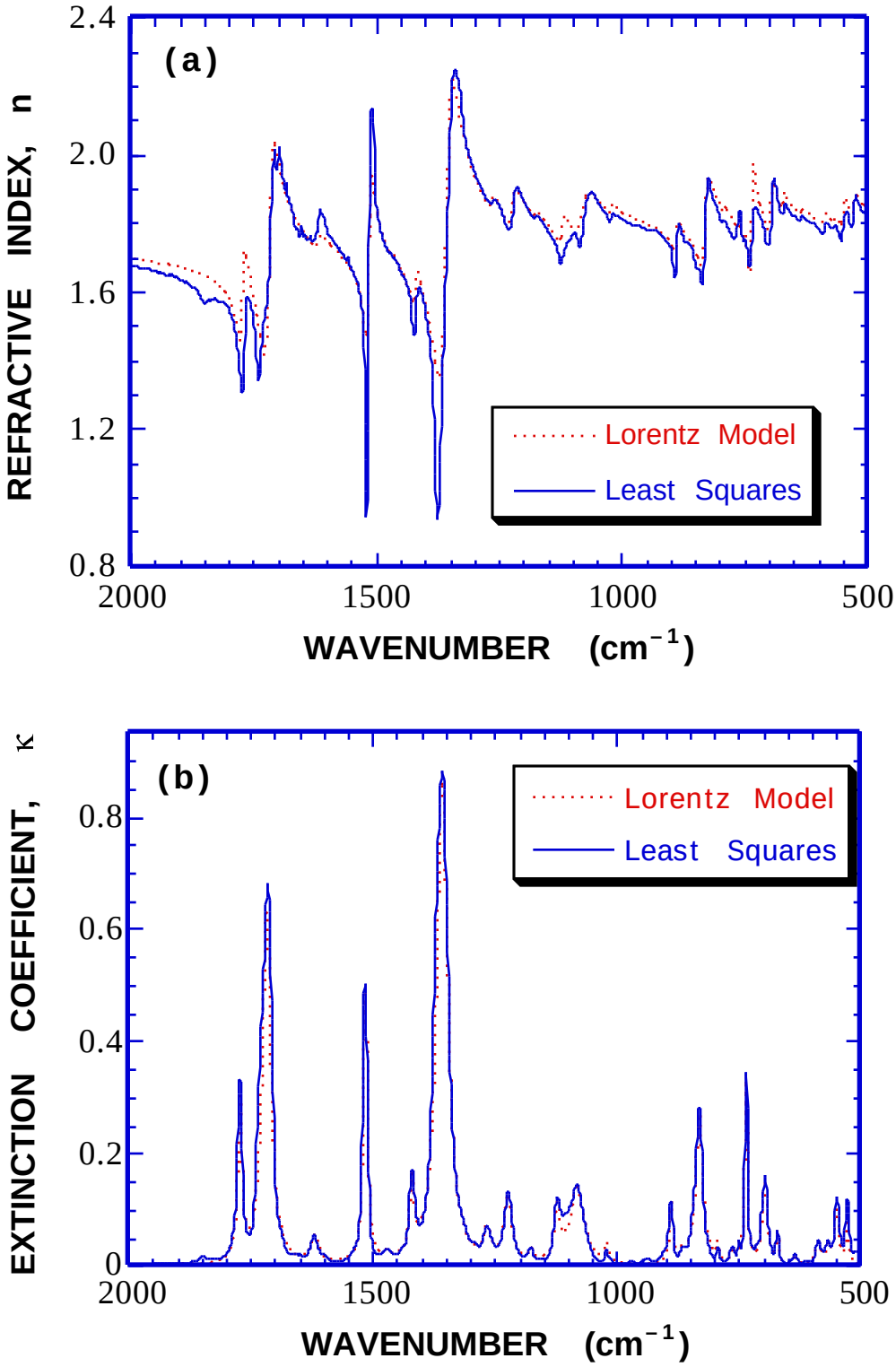
(a)
REFRACTIVE INDEX, n
2.4
2.0
1.6
1.2
0.8
2000
1500
1000
500
WAVENUMBER (cm⁻¹)
Lorentz Model
Least Squares
(b)
EXTINCTION COEFFICIENT, κ
0.8
0.6
0.4
0.2
0
2000
1500
1000
500
WAVENUMBER (cm⁻¹)
Lorentz Model
Least Squares

Figure 5