Infra-red spectra and optical constants of polytetrafluoroethylene films

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Transmission and reflection infra-red spectroscopy were used to determine refractive indices in thin films of poly(tetrafluoroethylene) and poly(tetrafluoroethylene–hexafluoropropylene) over the range 2200 to 800 cm^{-1}. The results showed the expected pattern over the strong absorption region but they also showed that film anisotropy exhibits a significant effect on the measurements. In addition, a calculation of the real and imaginary dielectric constants was performed on one of the thin films of poly(tetrafluoroethylene) to validate the refractive index measurements. The real dielectric constant curve showed an unexpected dip below zero on the high frequency sides of the two strong absorption bands. This suggests that surface excited waves may be observed under restricted conditions for films of poly(tetrafluoroethylene) and its copolymers.

(Keywords: infra-red spectroscopy; refractive index; polytetrafluoroethylene; dielectric constant; film; reflection spectra)

INTRODUCTION

Optical constants of polymer films are often difficult to obtain because of the care and precision required to determine them. In an article by Jones[1], who has been one of the chief proponents in understanding the nature of the measurement of optical constants, he described a method for measuring them in polymer films by comparing computer simulations with 'measurements on real films'. In an earlier publication Jones[2] reviewed four different methods that can be used for the measurement on liquids, but in the recent article he describes only the use of transmission method for their measurement.

Optical constants have been reported on many polymer materials[3,4] in the infra-red, but most of them have been obtained in the far infra-red. Carlon[5], however, reported the value of 1.56 for the refractive index (n) at 10.0 μm (1000 cm^{-1}) for Teflon fluoropolymer resin. Robinson and Price[6] described the results they obtained on polytetrafluoroethylene (PTFE) in the 8.5 μm (1180 cm^{-1}) region of the infra-red. They determined both refractive indices and absorption indices over the range of about 1100 to 1400 cm^{-1}. For the bands centered at 1154 and 1213 cm^{-1} they found the absorption index to peak at about 1.0. The refractive indices, on the other hand, are seen to vary from a maximum of 2.4 to a minimum of 0.8.

Our effort was directed at obtaining optical constant data on both PTFE and its hexafluoropropylene (HFP) modified material in the mid infra-red region of the spectrum. We used the method first described by Kagarise[7,8] for the measurement of interference fringes and applied it to the region of low absorbance. In contrast to this, for the region of high absorbance, dispersion analysis of the reflection spectra was used.

The high i.r. transparency of PTFE films over a wide spectral region (excluding a few strongly absorbing bands) and the good thermal and mechanical properties of PTFE make it a very useful construction material for many applications (filters, polarizers, etc.). Modification of the film properties by, for example, stretching or doping actually expands the use of the material in its applications. Orientation of macromolecules due to uniaxial stretching gives transparent anisotropic films that are very useful in optical construction. To use such materials in these various applications, it is necessary to know their optical constants.

EXPERIMENTAL

Instrumental

In our work we used the Bruker (model IFS-113V) *FT*i.r. spectrometer. It was operated as a single-beam instrument over the range 4000 to 400 cm^{-1} of the infra-red but only the mid range from about 2400 to 400 cm^{-1} was used in our calculations to compare with data obtained previously on other instruments. A resolution of 2 cm^{-1} was used in making the examinations and data used in the calculations were taken at about 2–3 cm^{-1} intervals.

Materials

Films of two different polymers of several thicknesses were used in the examinations. The polymers were polytetrafluoroethylene (PTFE) and poly(tetrafluoroethylene–hexafluoropropylene) (poly(TFE/HFP)) with the HFP content being about 10 wt%. Each was a commercially prepared sample. As a result of the film fabrication process, they were found to be generally anisotropic. Only one of the PTFE films (22 μm thick) was found to be essentially isotropic.

Measurement

We used both transmission and reflection spectra in our analyses. In the region of high absorbance the dispersion analysis method taken from the reflection spectra was used, and in the high transparency region the interferometric method was used. In calculating the reflection spectra the dielectric function[9] used was in the

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form of

$$E(\nu)=E_{\infty}\prod_{i=1}^{2}\frac{\nu_{\mathrm{L}i}^{2}-\nu^{2}-i\gamma_{i}\nu}{\nu_{\mathrm{T}i}^{2}-\nu^{2}-i\gamma_{i}\nu} \qquad (1)$$

where $\nu_{\mathrm{L}i}$ is the longitudinal frequency of the ith vibration (in the region of main interest there are two vibrations), $\nu_{\mathrm{T}i}$ is the transverse frequency of the ith vibration, γ_i is the damping of the ith vibration and E_{∞} is the high-frequency dielectric constant.

Our procedure, then, was to use some initial values for all the parameters and to calculate the reflection spectrum from them. Based on the degree of fit between the calculated and experimental spectra, the different parameters could be changed to minimize the deviation between both spectra. The best fit yielded the parameters used.

All the reflection spectra were recorded with a Bruker reflection unit. The angle of incidence was 11°. The incident radiation was polarized perpendicular to the plane of incidence (S-polarization). For these polarized measurements we used a grid-wire polarizer on polyethylene film. To determine the anisotropy of each film, we examined them twice by measuring them first in a parallel orientation with respect to the film direction and then by turning the film through a 90° interval to record the spectra for the two principal axes of the film dielectric tensor. Even though the third principal axis is directed perpendicular to the film surface, it is not important for near-normal incidence of the optical properties. The reference spectrum used throughout was a polished silicon monocrystal hemicylinder. Since the flat silicon surface reflectivity is 31%, the relative reflectivity spectra obtained experimentally must be multiplied by this correction value to obtain the absolute value of reflectivity. This procedure is, however, valid only for smooth surfaces. For unsmoothed surfaces as in our case with polymer films we used a simple but not a completely exact correction procedure. We measured the reflectivity of the metallized surface of a film in the holder and compared it with a smooth metallized surface. We found for real films the correction factor to be from 0.35 to 0.5 instead of 0.31. From the reflection spectra we used two methods to determine the film optical constants: (1) classical dispersion oscillator analysis[9], and (2) interferometric analysis.

Note that film and bulk Teflon optical properties were studied[10,11] extensively for the C–F stretching bands in the region of 1250 to 1100 cm^{-1} using ATR (absorbance, transmittance ratio). From these studies the surface transition layer of about 2000 Å thickness was found to yield optical constants that were different from the bulk because as expected the fabrication process preferentially orients molecules near the surface.

Our films were stretched on a holder to obtain the flat surface required for the specular reflection measurements. For polymer films, thickness variations are possible due to deformations in the holder during stretching. To determine these variations, we obtained transmission spectra on stretched and free-standing films. For PTFE thicknesses larger than 20 μm the spectra were essentially identical, but for thicknesses less than this they were not. The interference pattern is unaffected by stretching. For thin films there is a reduction of thickness but it is relatively small. The change is comparable to the error from the mechanical measurement of thickness.

Transmission spectra alone are not sufficient to characterize PTFE films because of strong band intensities. In the region of total absorption, reflection spectra must be used to obtain the optical constants. In the region of transparency, interference extrema can be used. Thus, we needed to obtain both reflection spectra and transmission spectra to determine the constants. In the high transparency region the positions of the minima and maxima of the interference pattern were used for determining the refractive indices.

It follows from the spectral patterns that the condition for an inerference extrema is

$$2nd=N\Lambda \qquad (2)$$

where n is the refractive index, d is the thickness, N is the order of the interference extrema and Λ is the wavelength. Each interference extrema gives one point in the refractive index frequency dependence pattern. The values for N are chosen on the basis of the following two expressions for the minima and maxima in the interference pattern,

$$N=\frac{2m}{2} \qquad \text{(minima)} \qquad (3)$$

$$N=\frac{2m+1}{2} \qquad \text{(maxima)} \qquad (4)$$

where m is a whole integer. The choice of N is not unambiguous, but it has to be made consistent with the minima and maxima patterns observed. We obtained several sets of n values but a physically reasonable choice is possible using the known high-frequency refractive index value and the static dielectric constant. Both values are not well defined but approximate values can be used in the determination of n.

Thickness measurements are critical to the determination of the refractive indices of polymer films. This was especially noted by Jones[1] but was mentioned by other workers as well. In our work we used a mechanical contact device that yielded an accuracy of ~ 0.5 μm and a precision of $\sim \pm 0.25$ μm. This method of measurement is possible only for relatively hard or thick film samples. For PTFE films the measured thickness values can be 1–2 μm less than the true thickness due to elastic deformation under test. To eliminate it we used the reflection spectrum, which we will discuss later. The final accuracy is 0.5 μm for 5–10 μm thick films and about 1 μm for >20 μm thick films. From these thickness measurements, the values of d can be established to evaluate the refractive indices for a polymer film at a given wavelength through the use of equation (2).

RESULTS AND DISCUSSION

Transmission infra-red spectra of two of the four different thickness films of PTFE that we examined and one film of poly(TFE/HFP) are shown in *Figures 1a* and *2*. Reflection spectra of these same films are shown in *Figures 1b* and *3*.

The two patterns shown in each of the transmission spectra result from the difference in thickness caused by clamping the sample in the film holder and by allowing it to be essentially free-standing. As expected, the thinner PTFE films showed a larger change due to this effect in the

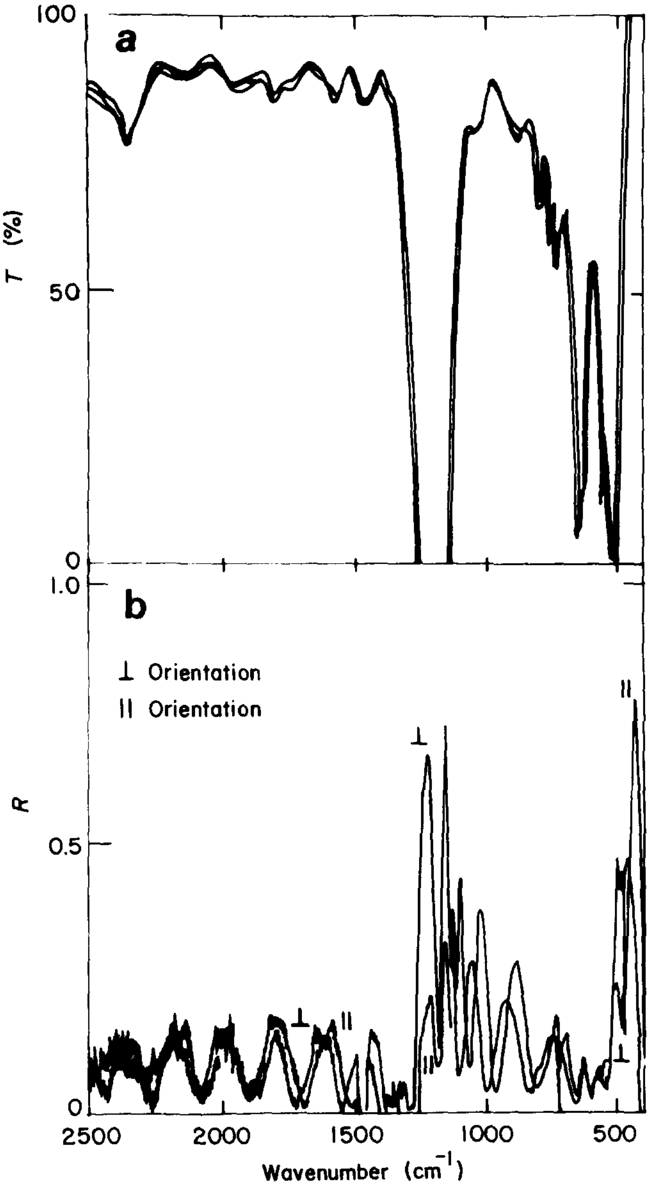

Figure 1 (a) Transmission and (b) reflection spectra of PTFE film that is 18 μm thick: (a) shows two different thicknesses and (b) shows two different orientations

transmission spectrum than did the thicker PTFE films. The reflection spectra show the effect of the film orientation with respect to the direction of the polarizer. For the reflection spectra shown there is a difference in the perpendicular and parallel orientation, with the perpendicular being more intense. This is the result of the fact that the molecular axes are oriented mainly in the parallel direction while the C–F groups are oriented primarily in the perpendicular direction. Because of the C–F orientation, the absorption of energy will be stronger in the perpendicular direction for the C–F stretching vibration[12].

Among the different thickness films of PTFE examined in this work, only the 22 μm thick film shows essentially no anisotropy. The other films show significant anisotropy. The amount of anisotropy found is seen in the refractive index plots of *Figures 4*, *5* and *6*. The larger the difference in refractive index between the perpendicular and parallel orientation, the larger is the anisotropy seen. From this measurement the degree of anisotropy can be determined. Among the refractive index plots shown here, the two thinnest PTFE films (6.5 and 9.5 μm) are seen to show the largest anisotropy.

Experimental values of refractive index were obtained with the use of equation (2). In addition to the film thickness measurement, which we described previously, we used refractive index values that are known from the visible spectrum to be of the order of 1.35 (ref. 10) for obtaining the order values in the high-frequency portion of the spectrum. That represents one reference point. The other reference point used was the interference minimum nearest the absorption band. It is the point of equality between the refractive index of 1 and an absorption index of $k \ll 1$. Thus, the frequency of this minimum is $n = 1$. For the next minimum it is $n > 1$. This continues to provide a smooth curve for $n(\nu)$. The low-frequency branch of the

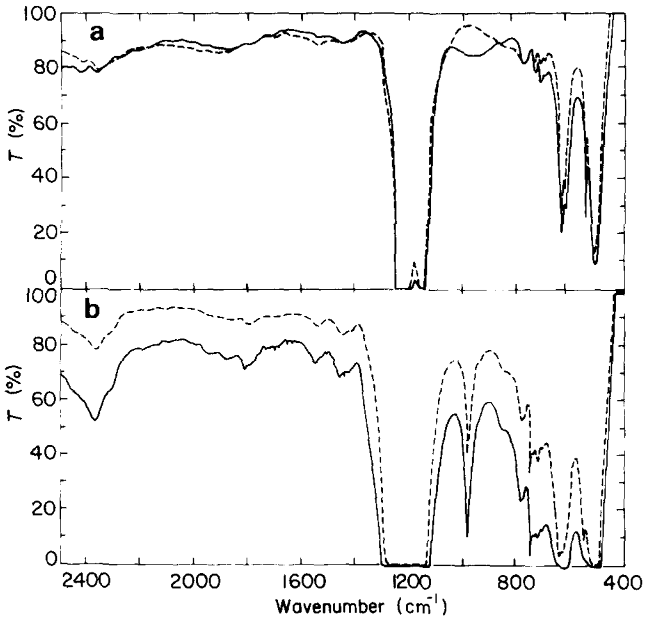

Figure 2 Transmission spectra of (a) a PTFE film that is 8.5 μm thick and (b) a poly(TFE/HFP) film that is 26 μm thick. Broken curves are for the holder stretched film and full curves are for the free-standing film

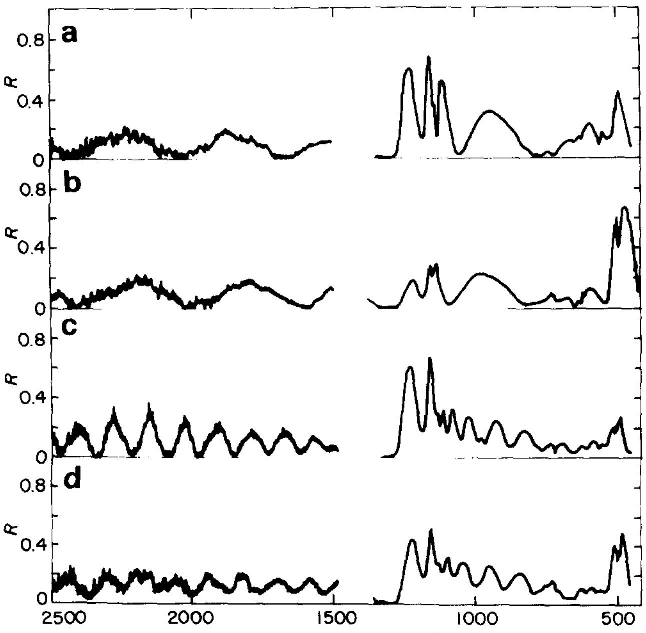

Figure 3 Reflection spectra of (a, b) a PTFE film that is 8.5 μm thick and (c, d) a poly(TFE/HFP) film that is 26 μm thick. Perpendicular spectra are (a) and (c) while parallel spectra are (b) and (d)

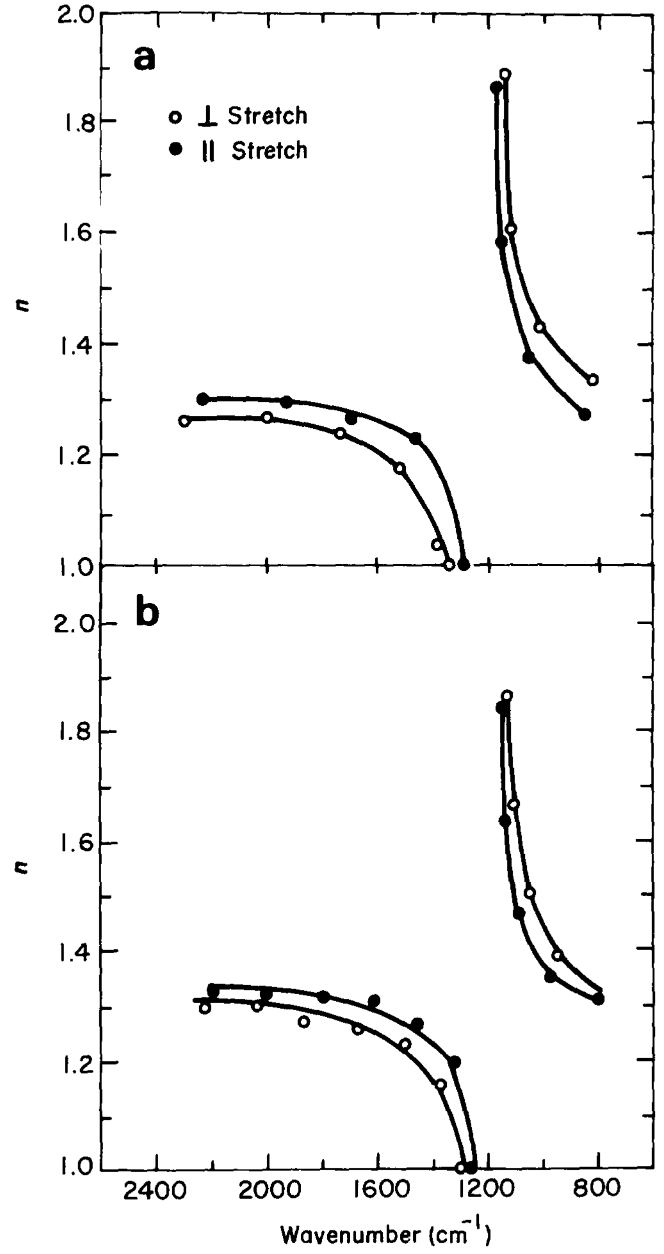

Figure 4 Refractive index curves of (a) a PTFE film that is 6.5 μm thick and (b) a PTFE film that is 8.5 μm thick

asymptotic curve is larger than it is for the high-frequency one. This is defined by the static dielectric constant, which for PTFE is of the order of 1.8 to 2.3. Then, with the use of these limits, refractive indices were calculated from the interference equation. Plots of refractive indices for the different film thicknesses of PTFE and poly(TFE/HFP) are seen in *Figures 4* to *6*. Some of the data in these plots are included in *Table 1* for comparison with data obtained by other workers. Upon examining them we find that they show very good agreement. We should say here that only for the 22 μm thick film of PTFE is the refractive index essentially the same for the two different orientations. The thinner films showed the refractive index to be not only different but generally lower for the two orientations. This is seen clearly in the refractive index plots of *Figures 4* and *5b*. The refractive index data for the poly(TFE/HFP) is different by 0.05 for the two orientations at 10 μm (1000 cm^{-1}) even though this film (which was 26 μm thick) was the thickest film used in our work. But because it is a copolymer instead of a homopolymer its properties showed it to be more flexible for a given film thickness than is the case for the homopolymer. Nevertheless, the refractive index results shown in *Table 1* for the copolymer are comparable with the homopolymer.

In order to determine the refractive index values over the high absorption spectral region, we calculated spectral patterns from initially suggested refractive index values for calculating the experimental reflection spectra. In the calculation we assumed that the absorption bands are Lorentzian and that the weaker bands at low frequencies were not important. Then, using equation (1) we first calculated the reflectivity for a smooth film and followed this with corrections of the refractive indices to make the calculated fit as good as possible. The dielectric function values and the oscillator parameters for our films are actually effective ones. *Figures 7* and *8* show the results of two trials in comparing calculated spectra with experimental reflection spectra for the 8.5 μm film of PTFE. The data shown in *Table 2* include this thickness film of PTFE. The other data in *Table 2* were obtained in a similar fashion from the different spectra. Upon comparing these data on the three different PTFE films

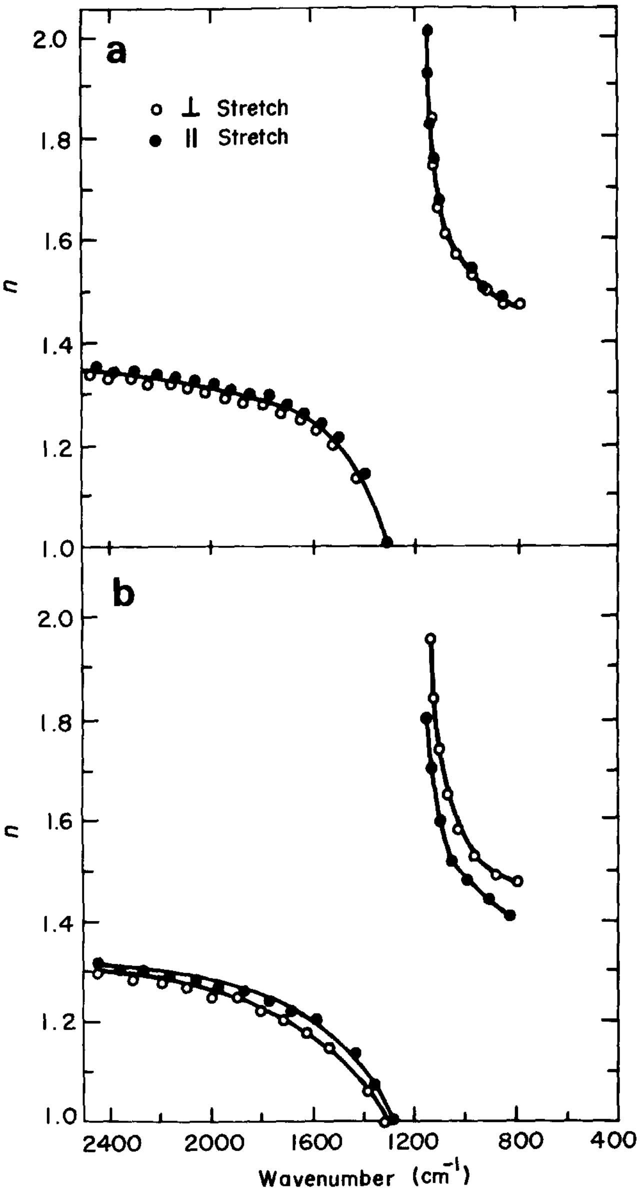

Figure 5 Refractive index curves of (a) a PTFE film that is 22 μm thick and (b) a PTFE film that is 18 μm thick

examined, we see that there is generally good agreement among them. From the reasonably good fit obtained between the calculated patterns and the experimental spectra, we can say that the dispersion analysis provides optical constant values that are in good agreement with the actual values.

Figures 9 and *10* show the real and imaginary dielectric curves, respectively, that we obtained over the high absorption range of the spectrum from the calculation for the PTFE film whose reflection spectra are shown in *Figures 3a,b*, *7* and *8*. Some difference as expected is seen

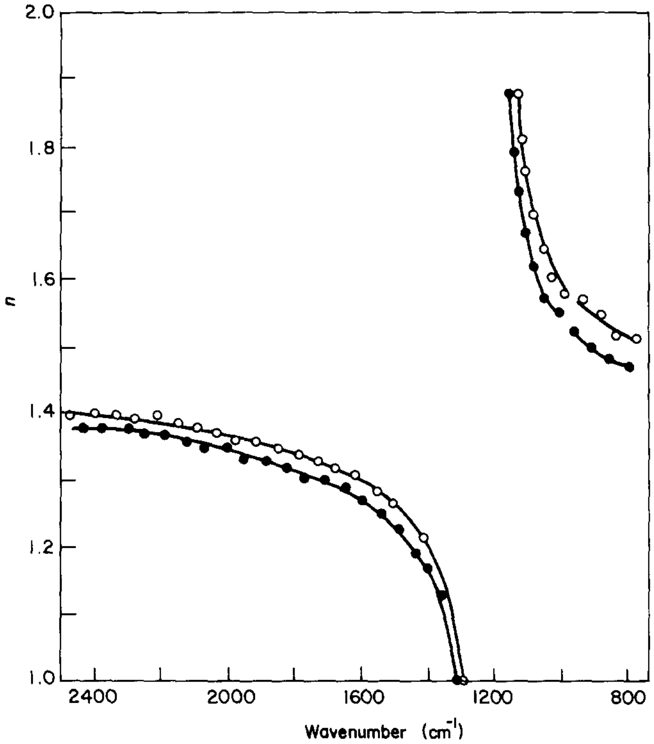

Figure 6 Refractive index curve of a poly(TFE/HFP) film that is 26 μm thick. The open circles are for the perpendicular orientation and the closed circles are for the parallel orientation

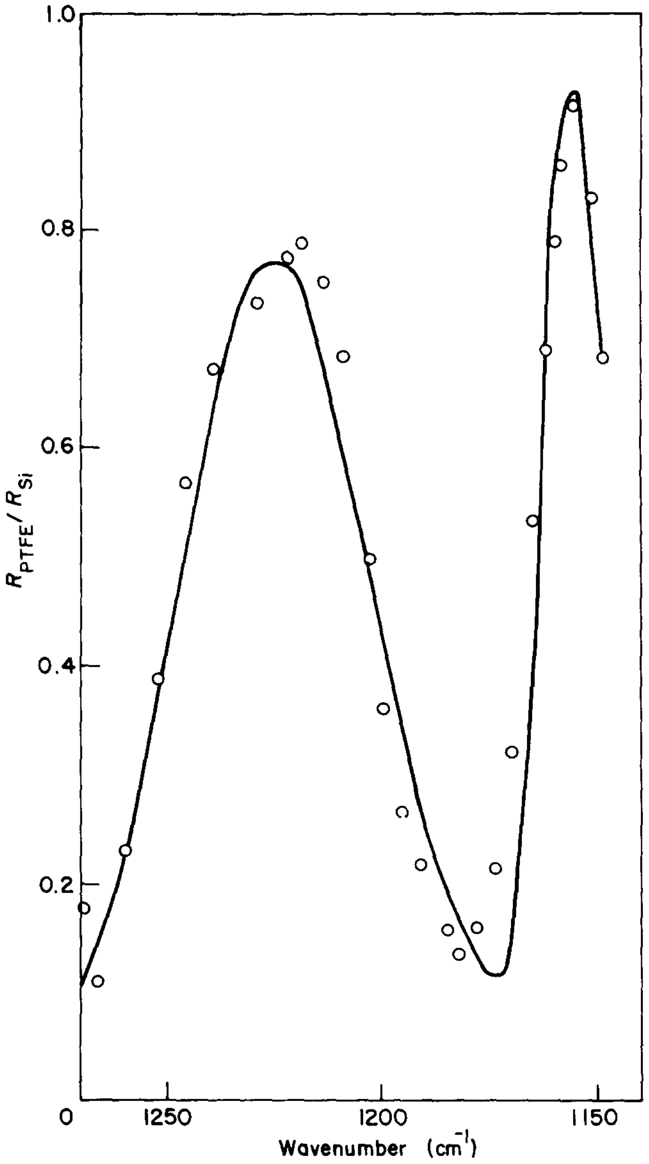

Figure 7 Reflection spectra comparing calculated with experimental points (perpendicular orientation) for the PTFE film that is 8.5 μm thick

Table 1 Refractive index data

Sample	Wavelength (μm)	Method	Refractive index	Reference
PTFE	336.7	Reflection	1.391	McCubbin and Sinton[13]
PTFE	49.5	Reflection	1.389	Chamberlain and Gebbie[4]
PTFE	10.0	Transmission	1.56	Carlon[5]
PTFE (22 μm)	10.0	Reflection	1.55	This work
Poly(TFE/HFP)	10.0	Reflection	1.60 (⊥) 1.55 (∥)	This work

Table 2 Dispersion analysis data

d (μm)	Orientation	ε_∞	ν_{T1}	γ_1	ν_{L1}	ν_{T2}	γ_2	ν_{L2}
8.5	⊥	1.8	1154.0	12	1166.5	1210.0	33	1253.5
	∥	1.9	1152.0	15	1160.0	1219.5	35	1238.0
18	⊥	1.8	1152.0	16	1168.5	1209.0	27	1252.0
	∥	1.8	1153.5	20	1163.0	1216.0	45	1242.5
22	⊥	1.8	1155.0	18	1165.5	1214.5	38	1253.0
	∥	1.8	1157.5	17	1166.0	1217.5	35	1253.0

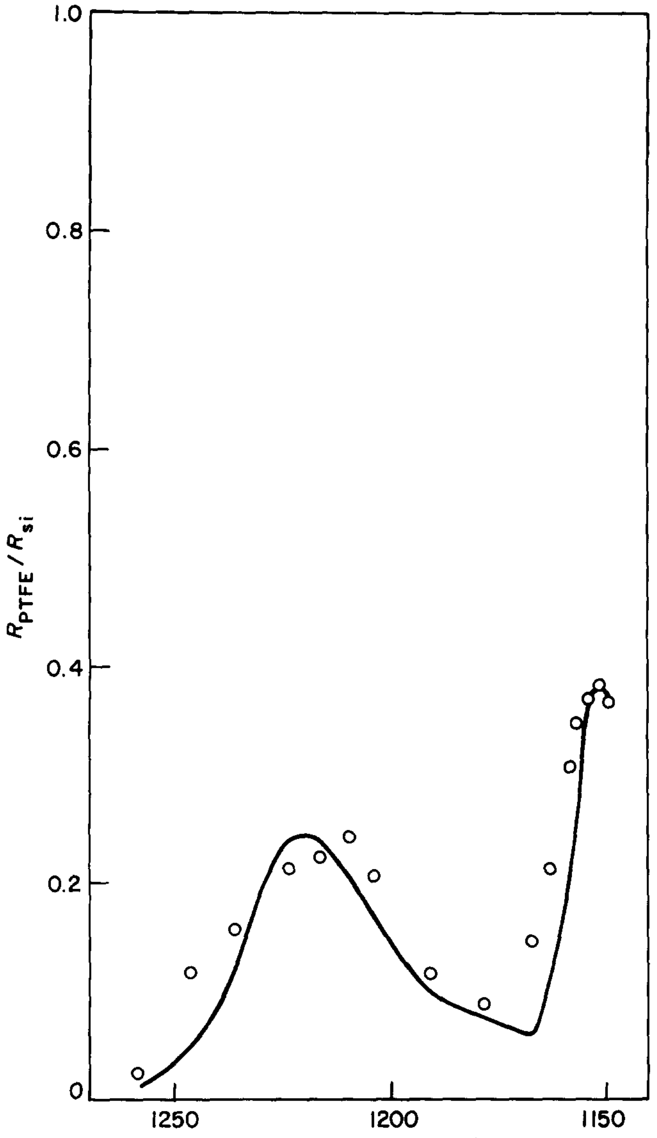

Figure 8 Reflection spectra comparing calculated with experimental points (parallel orientation) for the same sample as shown in *Figure 7*

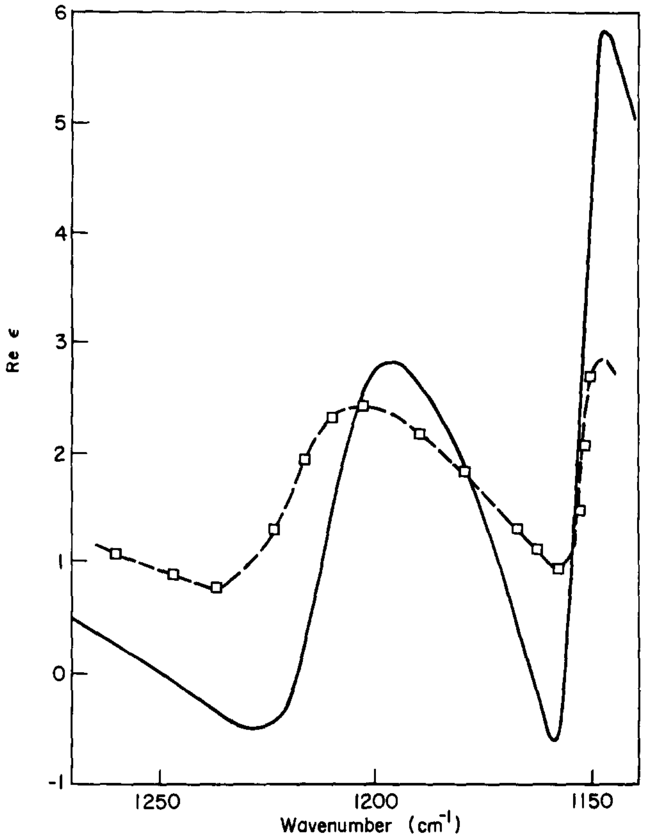

Figure 9 Plot of the real dielectric function (Re ε) *versus* frequency (wavenumber) for the 8.5 μm thick film of PTFE. The full curve shows the perpendicular orientation and the broken curve shows the parallel orientation

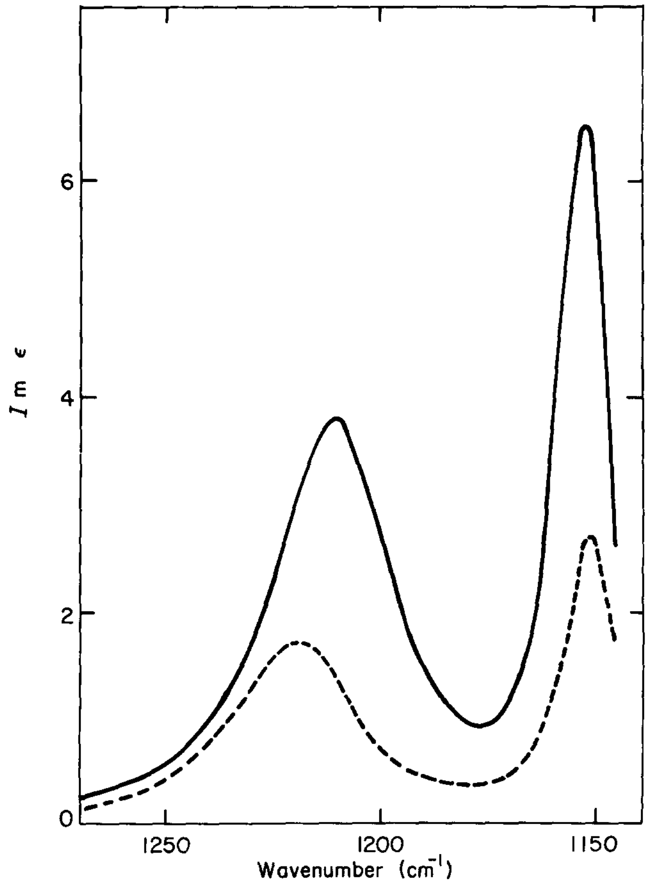

Figure 10 Plot of the imaginary dielectric function of (Im ε) *versus* frequency (wavenumber) for the 8.5 μm thick film of PTFE. The full curve shows the perpendicular orientation and the broken curve shows the parallel orientation

between the two dielectric spectra, but otherwise they follow the same general pattern obtained experimentally but without the interference pattern superimposed in the expanded frequency range shown. There is reasonable agreement between the square of refractive index taken from the interference data and the real part of ε obtained from dispersion analysis. However, we could not obtain the best possible fit with the dispersion data for two reasons: (1) the film is not perfectly clear and therefore causes scattering; and (2) the Lorentzian shape is not the best approximation of the lineshape because inhomogeneous broadening leads to Gaussian shapes. Nevertheless, the relationships shown here can be useful. They indicate that even without achieving the best possible fit, reasonably good data can be obtained.

CONCLUSION

We obtained the infra-red spectra and determined optical constants on a set of PTFE films and a poly(TFE/HLP) film in the region of the C–F stretch vibration. The value of the refractive index difference was found to be no more than about 0.10 for the different thickness films of PTFE examined. The refractive index of the thickest film (22 μm) used agreed with results obtained from other works and also showed essentially no anisotropy.

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