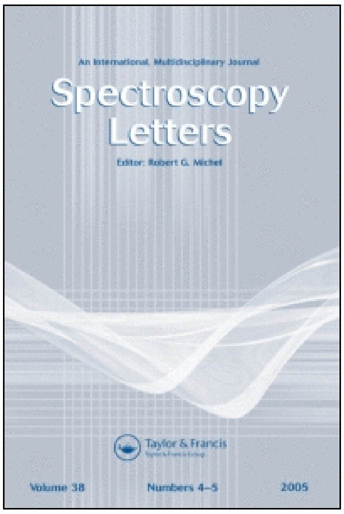

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Measuring Properties of Industrial Polymer Films Using Interference Fringes in the Infrared Region

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To cite this Article Larena, A. and Pinto, G.(1992) 'Measuring Properties of Industrial Polymer Films Using Interference Fringes in the Infrared Region', Spectroscopy Letters, 25: 4, 447 — 461
To link to this Article: DOI: 10.1080/00387019208021520
URL: http://dx.doi.org/10.1080/00387019208021520

SPECTROSCOPY LETTERS, 25(4), 447-461 (1992)

MEASURING PROPERTIES OF INDUSTRIAL POLYMER FILMS USING INTERFERENCE FRINGES IN THE INFRARED REGION

Key Words: IR Spectroscopy, Optical interferences,
Polymer properties, Industrial films.

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ABSTRACT

A study about the interference fringes caused in the infrared region by polymer films and their applications to the evaluation of some properties is reported. Interference fringes, a sinusoidal waveform superimposed on the baseline, arise from reinforcement and destructive interference of various wavelengths of radiation reflected from the internal surfaces of the film when the IR spectrum is carried out.

An optical interference method is proposed for measuring the thickness and the refractive index, both within an accuracy better than 1%, and for evaluating the surface texture of polymer films. Each one of these procedures is explained by its application for polypropylene, polystyrene and polyethylene films, respectively, three commercially available industrial films widely used for packing and membranes.

These methods can easily be extended to any fair thin film of transparent or weakly absorbing solid materials.

INTRODUCTION

Synthetic polymers have a wide range of applications and the demand for plastic components is on the increase. There are many types of polymers with different physical and chemical properties [1]. Polymer films find use in a broad variety of applications, such as protective layers, adhesives, or membranes for separation, purification and enrichment [2]. Methods are developed to cope with the role of laboratory quality control to ascertain the conformity of these products at every stage of production.

This work is a continuation of our earlier investigation of optical characterization for polymer films [3,4]. In the present paper we describe an experimental study of the evaluation of some film properties (thickness, refractive index and surface texture) by the analysis of interference fringes in infrared spectroscopy. Other interference methods related to these properties but with the use of a laser light have been reported recently [5,6].

The materials selected for this study were polypropylene, polystyrene and polyethylene films, commercially available industrial films widely used for packing due to their resistence, transparency and shiny aspect.

If a sample for infrared spectroscopy is thin, smooth and their sides are parallel, the spectrum shows in zones of low absorbance regularly spaced peaks with sinusoidal waveforms, known as interference fringes or channel spectra. This is due to the constructive and destructive interferences of internally reflected various wavelengths of light inside the sample itself [7-10].

This effect can be observed, for example, in the IR spectrum of the polystyrene film usually provided as standard of IR spectrometry, and it usually represents a problem in the study of thin samples such as polymer films because it confuses the spectral pattern. The fringes may be avoided mainly by ATR techniques or tilting the sample so the radiation beam strikes it at Brewster´s angle [11].

As it is well known, the distance between windows in a cell for IR spectrometry is widely calculated accurately (in the range 0.03-0.6 mm) by the method of interference fringes [7], and it is one of the most important applications of this effect.

INTERPRETATION OF INTERFERENCE FRINGES

As referred to above, interference fringes in an IR spectrum of a film arise from reinforcement and destructive interference of radiation reflected from the surfaces inside the sample.

When a radiation impinges on an interface a fraction of this radiation is reflected. For normal incidence, the ratio of the reflected intensity to the incident intensity, known as reflectance, R, is given by Fresnel´s formula:

$$R = \left((n_1-n_2)/(n_1+n_2)\right)^2 , \qquad (1)$$

where n_1 and n_2 are the refractive indices of the two media. In our case, an air-polymer interface, n_2 is equal to 1 and n_1 is the refractive index of polymer.

Due to the existence of two air-polymer interfaces in a film, there is also a fraction of radiation that is twice reflected and transmitted, as it is illustrated in figure 1.

For various wavelengths the two beams transmitted showed in figure 1 will have constructive interferences.

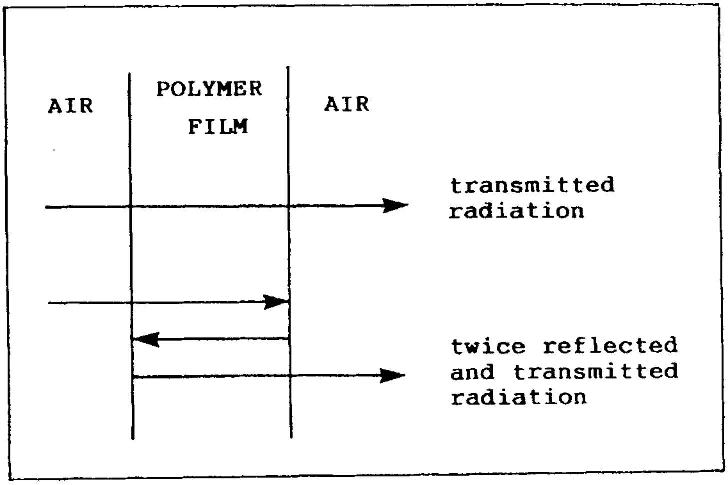

FIG. 1. Schematic representation of transmitted radiation and twice reflected and transmitted radiation when the radiation strikes the sample perpendicularly to the plane of incidence.

This arises if the wavelength carries out the relationship:

$$a \cdot \lambda_1 = 2 \cdot t \cdot n \qquad (2)$$

where a is an integer number, λ_1 is the wavelength of incident radiation, t is the film thickness and n is the refractive index of sample. At the λ_1 wavelength more radiation reaches the detector than at the near wavelengths, due to the reinforcement of radiation and so the apparent absorbance presents a minimum, because the transmission is reinforced.

At wavelengths greater than λ_1, constructive interferences will appear when the following relationships are carried out:

$$(a-1)\cdot\lambda_{1+1} = 2\cdot t\cdot n \qquad (3)$$

$$(a-2)\cdot\lambda_{1+2} = 2\cdot t\cdot n \qquad (4)$$

$$\vdots$$

$$(a-m)\cdot\lambda_{1+m} = 2\cdot t\cdot n \quad , \qquad (5)$$

where m is an integer number equal to the number of peak maxima existing between the corresponding minima to λ_1 and λ_{1+m}.

If we substitute $2\cdot t\cdot n/\lambda_1$ for a, as it can be deduced from expression (2), in the equation (5), we obtain:

$$(2\cdot t\cdot n/\lambda_1)\cdot\lambda_{1+m} - m\cdot\lambda_{1+m} = 2\cdot t\cdot n \qquad (6)$$

And by grouping terms, we arrive to:

$$(2\cdot t\cdot n/\lambda_1) - (2\cdot t\cdot n/\lambda_{1+m}) = m \qquad (7)$$

Assuming that in IR spectrometry the wavenumber, $\tilde{v}$, is usually more utilized than the wavelength, the film thickness will be done by:

$$t = m / [2\cdot n\cdot(\tilde{v}_1 - \tilde{v}_2)] \quad , \qquad (8)$$

where $\tilde{v}_1$ and $\tilde{v}_2$ are the wavenumbers corresponding to the two extreme minima in an ensemble of m interference fringes.

Obviously the argument is similar by considering two maxima in the interference fringes and the number of minima between they.

EXPERIMENTAL PROCEDURE

Samples of extruded polypropylene, polystyrene and polyethylene, commonly used industrial packaging polymers, were cut to size, mounted into 20 mm slide sample holders for analysis and their infrared spectra were recorded on a Mattson Galaxy model 3020 FTIR Spectrophotometer, over the range of 4000-400 cm^{-1}, operated at 2 cm^{-1} resolution and set to 25 scans.

Interference fringes are clearly visible in figure 2, although not all films gave such definite peaks.

RESULTS AND DISCUSSION

Evaluation of film thickness

Equation (8) allows the calculation of film thickness from interference fringes. A most accurate value of thickness can be obtained by calculating the linear function between number of consecutive maxima and respective wavenumber of these maxima. The slope of this relationship will be $-2 \cdot t \cdot n$, where the thickness $\underline{t}$ will be expressed in cm.

As example, we have selected nine samples of polypropylene films. Figure 2 shows the IR spectrum for

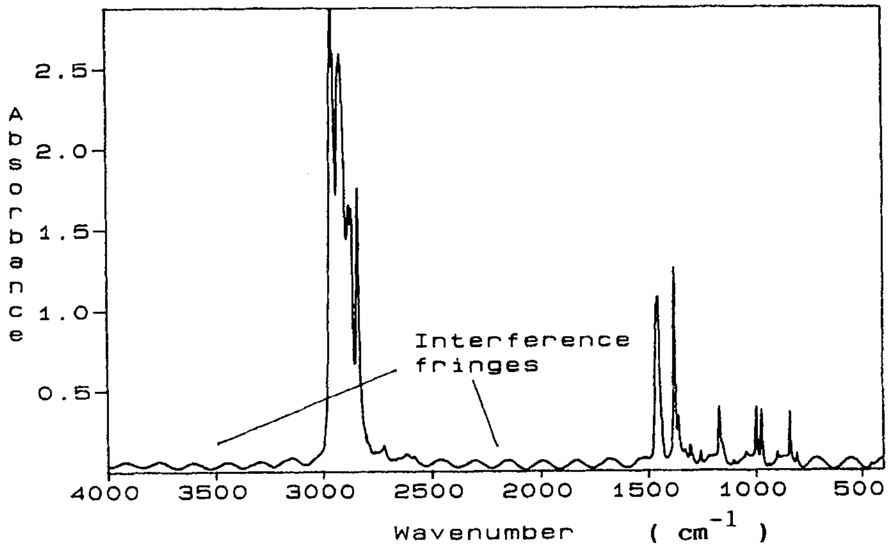

FIG. 2. The infrared spectrum of a polypropylene film. Note the regularly spaced interference fringes.

a sample, where the interference fringes are clearly distinguished. For these samples we have selected the interference fringes over the wavenumber range 2500--1850 cm^{-1}, where they are most sharp.

The correlation coefficients for the relations between number of consecutive maxima and respective wavenumbers varied between -0.9990 and -0.9999, indicating as expected, a high degree of linearity.

As refractive index, we have considered the value of 1.49, obtained from standard tables for polypropylene. We have neglected the variation of refractive

TABLE 1

Calculated film thickness and measured infrared absorbance values of polypropylene film at 841 cm^{-1}.

thickness (μm)	IR absorbance value at 841 cm^{-1}
21.0	0.342
21.0	0.344
21.1	0.344
21.2	0.347
21.4	0.345
21.4	0.348
21.6	0.352
21.8	0.351
22.2	0.365

index with wavelength, but in practise there is only a slight variation if there is not an absorption band.

The absorption peak at 841 cm^{-1} was selected for examination of film thickness values. This band was chosen because it gaves an absorbance between 0.2 and 0.8 for all the different thicknesses and hence should obey Beer-Lambert's law for calibrating purposes.

Table 1 lists the thicknesses calculated as above mentioned and the infrared absorbance values at 841 cm^{-1} (after baseline correction) for all the samples. A simple linear regression was carried out to examine

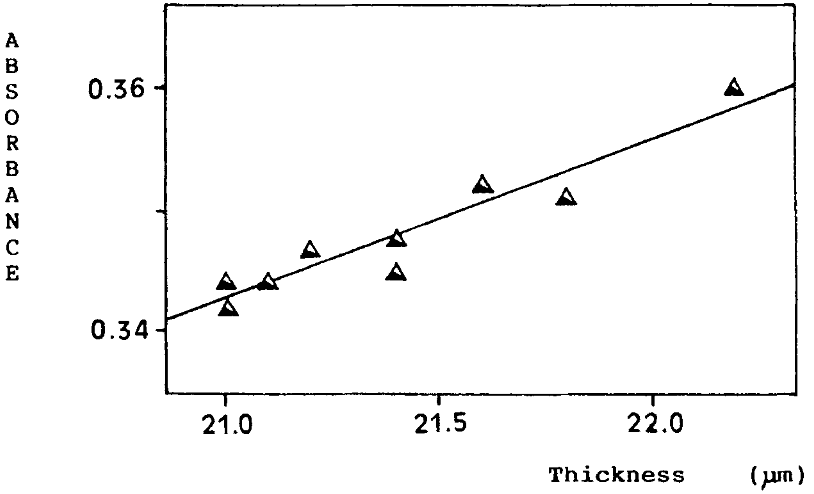

FIG. 3. Calibration plot of calculated film thickness versus infrared absorbance at 841 cm^{-1}.

the correlation of the data to a linear fit, as represented in figure 3. The correlation coefficient is 0.947, i.e. 90% of the variation of absorbance values overlaps with the variation in film thickness.

Thus, this optical-interference method allows the accurate measuring of film thickness inclusive in a narrow range of thicknesses as in the example showed.

Evaluation of refractive index

From interference fringes in the infrared region it is possible to evaluate the refractive index of a transparent film if the sample thickness is known, by a proceeding similar to the method described previously.

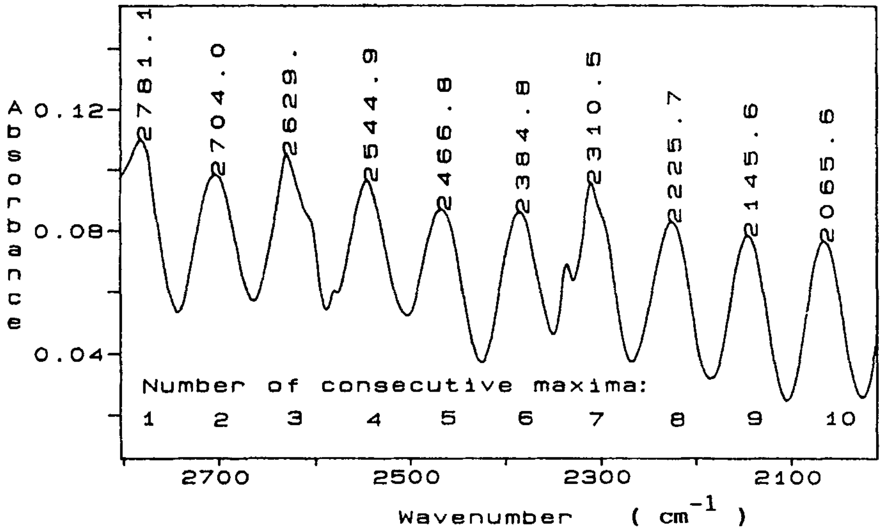

FIG. 4. Interference fringes in the spectrum of a selected polystyrene film and counting of consecutive maxima over the range of 2800-2050 cm^{-1}.

For this purpose we have chosen a polystyrene film whose thickness was 40.8 µm (measured by means of a micometer).

We have selected the interference fringes over the ranges of 4000-3200 cm^{-1} and 2800-2050 cm^{-1}. For each of these zones the number of consecutive maxima (counted as shown in figure 4) is a linear function of the wavenumber corresponding to these maxima, as shown in figure 5. In both ranges the correlation coefficient was -0.99994. From the slopes of these relationships, assuming that, as above-mentioned, they represent $-2 \cdot t \cdot n$, we have obtained for this film the refractive

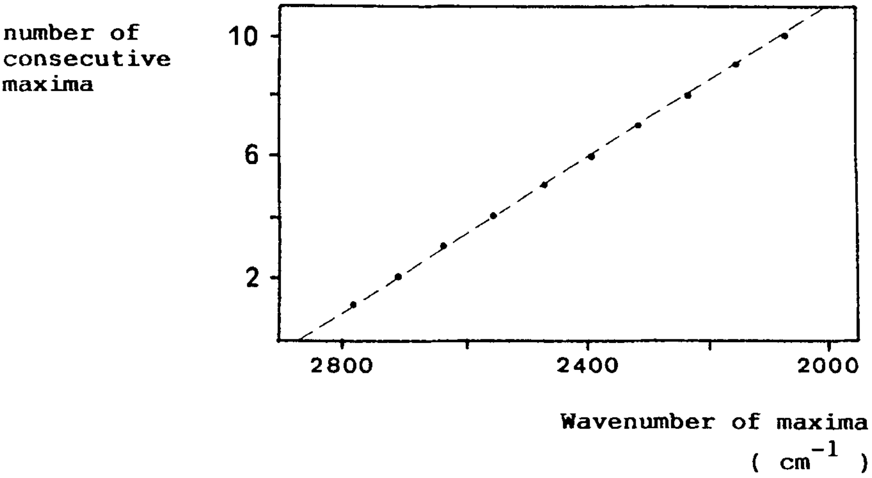

FIG. 5. Number of consecutive maxima versus the wavenumber corresponding to these maxima of the selected polystyrene film over the range of 2800-2050 cm^{-1}.

index values of 1.525 and 1.537 respectively. The difference between these two values is lesser than 0.8%, but the method does not allow the evaluation of the variation of refractive index with wavelength because of the slight variation of this magnitude. The refractive index is then determinated within an accuracy better than 1%.

Evaluation of surface texture

Another polymer film property to be evaluated from interference fringes in the infrared region is the sur-

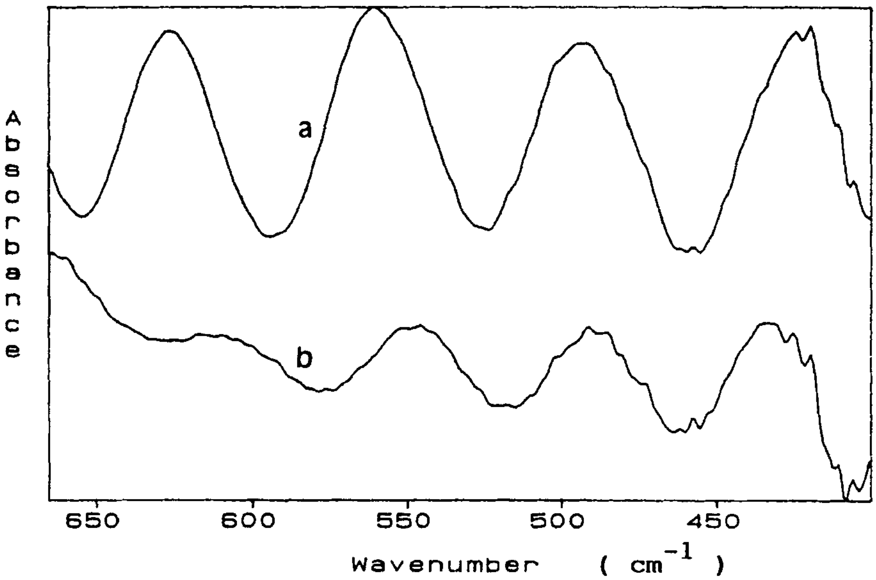

FIG. 6. Interference fringes in the spectrum of two polyethylene films (thickness of 50 µm). The average roughnesses are 0.21 µm (a) and 1.17 µm (b).

face texture. This is due to the fact that if the film surface are rugous there is an ensemble of wavelengths that obeys expression (2) and the interference fringes are distorted.

With the aim of illustrate this subject, we have selected two polyethylene film samples. Both of them have a thickness of around 50 µm, but their average roughness varies, and it is 1.17 µm and 0.21 µm (obtained as referred in a previous work ^{3}) for each one. Figure 6 shows the less definite interference fringes, in the same scale of absorbances, for the most rugous film.

In this way, it is possible to evaluate the surface texture of a given polymer film and a given thickness by confronting the interference fringes of a sample with several standards of known roughness.

CONCLUDING REMARKS

In conclusion, the analysis of interference fringes in the infrared region is a good way of assessing properties as thickness, refractive index and surface texture of transparent or weakly absorbing films such as polymer films.

ACKNOWLEDGEMENT

The studies described have been supported in part by the "Oficina Madrileña de Fomento a la Investigación de la Consejería de Educación de la Comunidad de Madrid", under Project No. C112/91. The authors gratefully acknowledge this assistance.

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Date Received: 09/13/91
Date Accepted: 12/13/91