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**INFRARED INTERFEROMETRIC THICKNESS MEASUREMENT OF
POLYMERIC THIN FILMS AND COATINGS**

N. R. Smyrl

June 1979

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INFRARED INTERFEROMETRIC THICKNESS MEASUREMENT OF POLYMERIC THIN FILMS AND COATINGS

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ABSTRACT

Thickness measurements of thin polymeric films and coatings, utilizing state-of-the-art rapid-scan interferometric technology, have been demonstrated for possible future application.

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SUMMARY

Infrared interference thickness measurements of polymeric films and coatings have been performed on transparent and reflective substrates. A white-light interference method, utilizing a rapid-scan Michelson interferometer, has been used and compared with the interference-fringe technique. Although both methods yield satisfactory results, the white-light technique is much faster and more accurate. Future application of these methods to a wide variety of coatings and substrates is indicated.

INTRODUCTION

Recent interest at the Oak Ridge Y-12 Plant^(a) in the use of organic polymer coatings for the protection of metal surfaces from various oxidative and corrosive reactions has prompted the need for a reliable and nondestructive technique for monitoring the thickness of such coatings. It has been known for a long time that optical interferometric techniques can be applied to the thickness measurement of optically transparent thin films. With the recent technological advancements associated with the development of rapid-scan interferometers, a new dimension in terms of speed and accuracy has been added to this method of thickness measurement. Commercial instrumentation, based on these developments, is currently available and is widely used in the semiconductor industry. The Y-12 Plant Laboratory has recently acquired a Digilab Model FTS-15B Fourier transform infrared spectrometer, and this report describes the preliminary experiments which have been performed in an effort to establish its applicability to the thickness measurement and characterization of polymeric films and coatings.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the Department of Energy.

THICKNESS MEASUREMENT OF THIN FILMS AND COATINGS

BRIEF THEORY OF FOURIER TRANSFORM INFRARED SPECTROSCOPY

The rapid-scan Michelson interferometer is the principal component of the Fourier transform infrared spectrometer which was utilized for the present film-thickness measurements. The interferometer consists of a beam splitter (semimirror), a fixed mirror, and a constant-velocity, movable mirror, as illustrated in Figure 1. The incident beam is split into two components at the beam splitter, with approximately half of the beam reflected to the fixed mirror and the other half transmitted to the moving mirror. These two beams, on reflection, are recombined at the beam splitter; and, depending on the position of the moving mirror, the two beams will interfere either constructively or destructively to produce an interference pattern or interferogram (light intensity as a function of the optical-path separation of the moving and fixed mirrors). The interferogram of a broad-band source (Globar) produced by one stroke of the moving mirror is seen in Curve a of Figure 2, while Curve b emphasizes the effect of placing a thin sample, such as polystyrene, in the beam. The center burst of the interferogram occurs where the two mirrors are equidistant from the beam splitter. All frequencies of the two light beams are in phase at that point and interfere constructively. These interferogram data are typically converted to normal infrared spectra (light intensity as a function of frequency) which are useful for characterizing and identifying molecular species. This conversion is carried out by a mathematical process referred to as a Fourier transformation which involves an integration similar to the following expression:¹

$$B(\bar{\nu}) = \int_{-\infty}^{+\infty} I(\delta) \cos 2\pi \bar{\nu} \delta \cdot d\delta, \quad (1)$$

where $B(\bar{\nu})$ represents the intensity of the source at frequency $\bar{\nu}$, in cm^{-1} , as modified by instrumental characteristics and $I(\delta)$ represents the intensity

Figure 1. PRINCIPAL COMPONENTS OF THE MICHELSON INTERFEROMETER.

Figure 2. TWO TYPES OF INTERFEROGRAMS.

as a function of mirror separation, δ . In practice it is necessary to place finite limits on the integral with a truncation or apodizing function. The two curves (a and b) of Figure 3

Figure 3. INFRARED SPECTRA. [Curve a - Broad-Band Source (Globar); Curve b - Thin Sheet of Polystyrene]

represent the results of the Fourier transformation of the corresponding interferograms in Figure 2. The transmittance spectrum is obtained by the ratio, Curve b/Curve a. Computation of the Fourier transform integral requires manipulation of large numbers of data points and is extremely impractical without the aid of a high-speed computer. Most commercial instrumentation, therefore, is designed around a small, dedicated minicomputer. For the present study, the interferogram data prior to the Fourier transformation will be of primary interest.

INSTRUMENTATION

The present polymeric-film-thickness measurements were made by using a Digilab Model FTS-15B Fourier transform infrared spectrometer. A block diagram of the spectrometer and data system is given in Figure 4. The system is configured around a Data General Nova 2 computer with 32K of core memory and operates with the real-time disk operating system (RDOS) software of Data General. A diagram of the interferometer, which has a maximum mirror stroke of 4 cm (corresponding to 0.25 cm^{-1} spectral resolution), and the other optical components of the FTS-15B are illustrated in Figure 5. The modulated infrared radiation exiting from the Michelson interferometer is directed first to a sampling area and then to the triglycine sulfate (TGS) room-temperature pyroelectric detector. The analog

Figure 4. PRINCIPAL COMPONENTS OF THE DIGILAB MODEL FTS-15B INFRARED SPECTROMETER AND DATA SYSTEM.

Figure 5. DIGILAB MODEL FTS-15B INFRARED SPECTROMETER. (Schematic courtesy of Digilab, Inc., Cambridge, MA)

signal from the detector is digitized and transmitted to the computer for computation of the Fourier transform and subsequent data manipulation.

EXPERIMENTAL WORK

Typical film-thickness measurements were obtained from interferograms resulting from the coaddition of 10 double-precision (32-bit-word-length) scans with a mirror stroke of 0.5 cm (2 cm^{-1} spectral resolution, file size—8192 data points). Total data collection time for each sample was slightly less than 20 seconds. Selected interferogram data were transformed in order to observe the infrared "fingerprint" spectrum of the polymer coating and to compare with the interference-fringe-thickness measurement technique.

Samples consisting of a variety of substrate materials coated with thin polymeric films were submitted to the Y-12 laboratory for film-thickness measurement.^(b) The thin polymeric films were produced by the passage of gaseous perfluoro-2-butene (PFB-2) monomer through a radio-frequency electric discharge. The initial measurements were made with infrared transparent substrates, including sodium chloride and silver chloride, and then extended to include coated uranium pieces.

Reflectance from the various samples was measured with the aid of a Perkin-Elmer combination beam condenser and specular reflectance accessory which is diagrammed in Figure 6. The samples are mounted at Position M3 in the diagram with an angle of incidence of 6.5 degrees. In the thickness calculations, the angles of incidence and refraction are assumed to be zero, which introduces no significant error to the measurements.

THEORY OF REFLECTION FROM A PLANE-PARALLEL FILM

The interference phenomenon of two light waves reflected from a plane-parallel film can best be understood by referring to Figure 7. A light beam of intensity I_0 impinges on the surface of a film of refractive index n_2 and of thickness d at an angle of incidence, θ . At the first surface of the film, a small fraction of the incident light is reflected and the remainder is refracted at an angle, ϕ , in the film. A portion of the refracted light is reflected at the second surface of the film and then refracted again at the first surface. The optical-path difference, L , generated between the two reflected beams, I_1 and I_2 , is given by the relationship:²

$$L = 2 n_2 d \cos \phi. \quad (2)$$

(b) Film-thickness work was performed for C. C. Edwards; Chemical and Plastics Department, Development Division.

Figure 6. PERKIN-ELMER COMBINATION BEAM CONDENSER (Schematic courtesy of Perkin-Elmer Corp, Norwalk, CT) AND SPECULAR REFLECTANCE ACCESSORY.

The phase shift between the two beams due to the optical-path difference produces an interference of the two rays. Since I_1 undergoes a phase change of 180 degrees due to reflection at the surface, and I_2 does not because it is internally reflected, the condition for destructive interference can be described by the equation:²

$$2n_2d \cos \phi = m\lambda. \quad (3)$$

The terms n_2 , d , and ϕ are defined in Equation 2, m (an integer) represents the order of interference, and λ represents the wavelength of the light.

Figure 7. REFLECTION OF LIGHT FROM A PLANE-PARALLEL FILM.

FILM-THICKNESS MEASUREMENT BY THE INTERFERENCE-FRINGE TECHNIQUE

One of the primary methods that was utilized for measuring film thicknesses prior to the application of rapid-scan interferometers was the interference-fringe technique, using a standard dispersion-type infrared spectrometer. The infrared transmission spectrum of a thin film of polystyrene, with the superimposed interference pattern presented in Figure 8, will serve as an illustration of this technique. Utilizing these data, the thickness of the polystyrene film can be calculated by an equation. [This equation can be derived from Equation 3 and Snell's Law (with Medium 1 being air)] :

$$d = \frac{N}{2(\bar{\nu}_1 - \bar{\nu}_2) (n_2^2 - \sin^2\theta)^{1/2}}, \quad (4)$$

where d and n_2 are defined as in Equation 3; $\bar{\nu}_1$ and $\bar{\nu}_2$ represent, respectively, the maximum and minimum frequencies in cm^{-1} utilized for the fringe measurement; N represents the number of fringes between $\bar{\nu}_1$ and $\bar{\nu}_2$, and θ represents the incident angle.

There are a number of distinct disadvantages associated with the fringe method of thickness measurement, namely: (1) a limited thickness range, (2) considerable time required for measurement and calculation, and (3) errors associated with locating the fringe maxima.

WHITE-LIGHT INTERFEROMETRIC THICKNESS MEASUREMENT

The thickness measurement of thin films and coatings, utilizing a scanning Michelson interferometer and a white-light source, was first developed and patented by Fluornoy.³

Figure 8. INFRARED TRANSMISSION SPECTRUM OF A THIN FILM OF POLYSTYRENE.

These developments, which were later documented in the literature,⁵ were the basis for commercial interferometric thickness gages marketed by Block Engineering^(c) and DuPont.^(d) This technique also relies on the interference phenomenon of infrared radiation reflected by two parallel surfaces, described in a previous section, producing secondary interferograms or side bursts in the primary interferogram. An example of this effect is illustrated in the reflection interferogram of an unsupported film of polystyrene (appearing in Figure 9). In addition to the normal interferogram maximum observed at zero retardation of the moving mirror, smaller side bursts are produced at a distance, L , from the center burst. The film thickness, d , is related to L by Equation 2. The Digilab scanning interferometers utilize a He/Ne laser reference interferogram for accurate measurement of mirror displacement. For the present measurements, an equation can be utilized for the determination of L in cm from the hard-copy interferogram, namely:

$$L = (LIN) \times (NPTS/XSL) \times (UDR) \times (LWN/ZCR), \quad (5)$$

where LIN represents the distance in inches from the center burst to the side burst measured from the hard-copy plot; $NPTS$ the number of collected data points (8192 for 2 cm^{-1}

(c) Block Engineering, Inc, Cambridge, Massachusetts.

(d) E. I. duPont de Nemours Company, Wilmington, Delaware.

Figure 9. REFLECTION INTERFEROGRAM OF A THIN, UNSUPPORTED FILM OF POLYSTYRENE.

resolution); XSL the total length of the hard-copy plot in inches (maximum value - XSL = 160); UDR the undersampling factor representing the number of zero crossings of the laser interferogram per data point (normal value - UDR = 2), LWN the He/Ne laser wavelength in cm (LWN = 0.6328×10^{-4} cm), and ZCR the number of zero crossings for each wavelength (ZCR = 2).

The interferogram displayed in Figure 9 represents only one of three general cases that may arise in reflectivity measurements of thin-film coatings.⁶ In this particular case, the sample is configured in such a way that only the radiation reflected from the first surface and interface surface of the coating ($\sim 10\%$ of the incident radiation) is measured, while the remaining radiation is dissipated and lost by transmission through the transparent substrate (air). The interferogram side bursts, for this case, are strong and well pronounced relative to the center burst.

A second case involving a transparent substrate results when the sample is configured so that the radiation transmitted through the sample ($\sim 90\%$ of the incident radiation) is measured as well as the internally reflected radiation from the coating ($\sim 0.2\%$). An example of this case is illustrated in Figure 2, Interferogram b. The third case involves coatings on reflective substrates, such as various metals. For this case, the radiation reflected at the first surface and the interface of the coating ($\sim 10\%$ of the incident radiation) is measured as well as the

radiation reflected from the metallic substrate ($\sim 80\%$ - double pass through the coating). The latter two cases produce very weak side bursts which may often be buried in the wings of the interferogram and, thus, require subtractive techniques to accurately locate their position.^{5,6} The case involving reflective substrates has important implications to the present film-thickness measurements and will be dealt with in greater detail in the next section:

The white-light interferometric technique can be utilized to measure transparent coatings with thicknesses ranging from < 2.5 to $500\ \mu\text{m}$, with $\sim 1\%$ accuracy.⁵ Multiple coatings can be detected, provided there is a finite change in the refractive index (± 0.05) at the interface between the coating and the substrate. A simultaneous measurement of both film thickness and refractive index is also possible by utilizing two different angles of incidence. This method is also applicable to the determination of the two refractive-index components of a birefringent film by measuring the interferogram with both parallel and perpendicularly polarized light. The two primary advantages of the white-light interferometric technique are the added speed and accuracy which can be attained.

ANALYSIS AND DISCUSSION

The Digilab Model FTS-15B Fourier transform infrared spectrometer was obtained by Y-12 as a general-purpose analytical instrument to be utilized primarily for the analysis and characterization of organic and inorganic molecular species. As previously mentioned, however, the interferogram data prior to transformation may often contain thickness information for polymeric thin films and coatings, and it is the purpose of the present study to explore the methods for extracting this secondary information. Initial efforts to establish the applicability of the present instrumentation to the measurement of film thickness consisted of experiments involving thin sheets of unsupported polymers as well as PFB-2 polymer coated onto infrared transparent substrate materials. Table 1 lists the results from a thickness measurement of a thin, unsupported polystyrene film by the two interference methods discussed here and by an actual physical measurement with a micrometer. A comparison of these results indicates good agreement for the measured film thickness by the three methods, which would be considered consistent with the accuracy limitations for the respective techniques.

Table 1
THICKNESS MEASUREMENT OF THE SAME
POLYSTYRENE FILM BY
THREE METHODS

Method	Thickness (μm)
White-Light Interference	50.3
Interference Fringe	51.2
Micrometer	53.3

As mentioned in the Introduction, there is considerable interest in the use of polymer coatings for the protection of metal surfaces and, therefore, a need to monitor the thickness of such coatings. The next logical extension of this work involved attempts to measure the thickness of a PFB-2 polymer coating on a machined uranium substrate. The respective reflection interferograms for the blank, uncoated uranium surface and the PFB-2 polymeric-coated surface are illustrated in Curves a and b of Figure 10. It is observed from

Figure 10. REFLECTION INTERFEROGRAMS.

Curve b that the side bursts observed for this case are quite weak relative to the center burst. If this film was much thinner than the calculated $18.3 \mu\text{m}$, it would be extremely difficult to locate its position accurately. A method which can be utilized successfully to resolve such a situation would be to measure the interferogram of a very thick coating with side bursts beyond the normal measurement range. This interferogram could then be subtracted from the interferograms of thinner coatings, which have the side bursts buried in the wings, effectively canceling the common features of both interferograms and revealing the side-burst information for the thinner coating.⁵ Another way to obtain the same result is to arrange the optics of the instrumentation so that the subtraction is performed optically, with two different beams that traverse identical pathlengths which are subsequently recombined at the detector.⁶ The opportunity did not present itself in the present study to implement either of these techniques.

Alternately, the fringe technique can be relied on if the interferogram data fail to yield a satisfactory result. The transmission spectrum of the same PFB-2 coating from Figure 10 was obtained by the transformation of Curves a and b and is displayed in Figure 11. The

Figure 11. SINGLE-REFLECTION INFRARED SPECTRUM OF URANIUM THAT WAS COATED WITH PFB-2 POLYMER.

thickness determined by the fringe technique is observed to be in excellent agreement with the white-light method. The spectrum appearing in Figure 11 can also be utilized to characterize the PFB-2 polymeric coating, although this particular sample is considerably thicker than is usually required. The region below 1300 cm^{-1} contains common features due to three carbon fluoride (CF_3 , CF_2 , and CF) groups which are features analogous to fluorinated polymers such as TFE and FEP.⁸ The features observed at 1725 and 1790 cm^{-1} can apparently be attributed to oxidation during formation of the polymer resulting from residual oxygen present as an impurity either in the monomer or the discharge chamber. Since oxidative by-products and other types of impurities may adversely affect the physical integrity and properties of the coating, it is important to be able to monitor the polymer for various impurity species, and infrared methods have been of considerable value in this regard.

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