

focus on

Spectroscopy

Transmission Measurements of Polymer Thin Films

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NIR thin film interference allows you to do the unlikely – use light you can't see to measure the thickness of a polymer film that is too thin and flexible to submit accurately to a micrometer. With a variety of configurations available, the NIRQuest512 (see *Figure 1*) near infrared spectrometer has the versatility and power to tackle a wide range of polymer films.



Figure 1. NIRQuest512.

Polymer film and sheeting are everywhere, used in applications ranging from lamination of glass, plastic and labels for mechanical or UV light protection to medical devices, packaging and printing. Polymer films came into their own in the post-World War II years, when transparent packaging lured consumers to pour money back into the economy by making products visible on the store shelf. Those original acetate films based on cellulose have been joined by a variety of synthetic films, including Mylar®, PVC (vinyl), polyethylene, polypropylene, PET, nylon, polyester and even magnetically coated films used in recording devices like cassettes and hard disks. These materials are created by blown film, extrusion, casting and other processes. The medical industry uses polymer films to make X-ray film and test strips, and polymer films are even finding their way into sensor applications.

Typically, plastic films are less than 250µm thick and can be challenging to measure accurately due to their pliable nature. Thin film interference offers a novel measurement solution, as this technique can use transmission measurements to study a material's index of refraction or its thickness non-destructively and with minimal sample preparation. Interference is the same effect that gives soap bubbles their iridescence when illuminated (see *Figure 2*). If the light source is monochromatic and the thickness varies across the sample, dark and light bands are seen. If the light source is broadband and the thickness varies across the sample, the bands appear coloured (as with soap bubbles). When the light source is broadband and the thickness of the sample is uniform, the transmitted light alternates between constructive and destructive interference, depending on the wavelength, and appears as a sinusoidal pattern when measured with a spectrometer.

The interference pattern seen depends on both the material and thickness of the sample, making it very important to select the correct wavelength range of light for the application. An example of thin polymer sheets analysed using a NIRQuest512 spectrometer shows why near infrared light is ideal for polymer film thickness measurement.

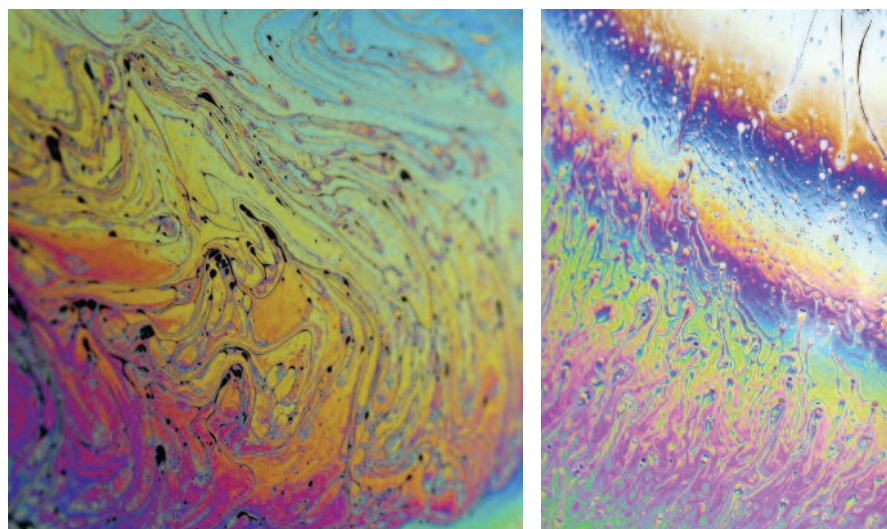


Figure 2. Soap bubble interference.

Introduction

When light moves from one material to another it begins a 'dance', a portion of it being reflected immediately, and the remainder being transmitted. The ratio is governed by the Fresnel equations, dependent on the materials' indices of refraction and the angle of incidence of the light. If the material is a thin film, the second interface splits the dancers once again and the two reflected beams have an opportunity to interact.

If they are in step with one another (for example, in phase), they will interfere constructively and, if completely out of phase, they will negate each other. The same happens with the first transmitted beam and the second, as seen in *Figure 3*.

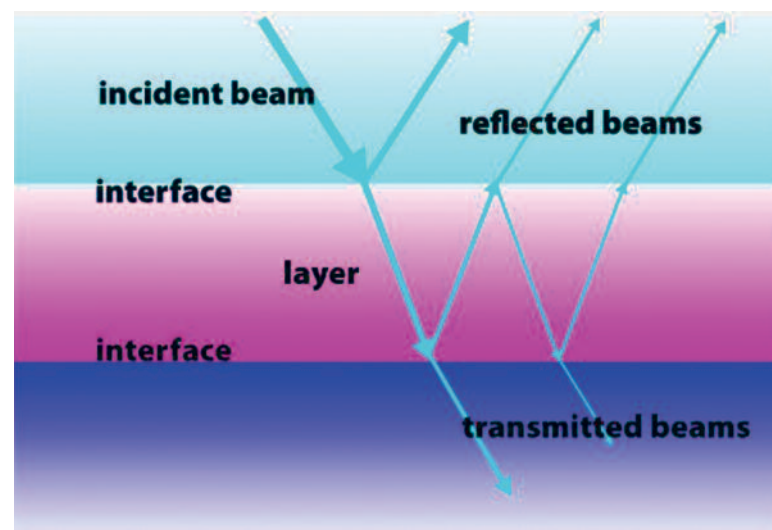


Figure 3. Light transmission theory.

For a given sample of uniform thickness, the resulting transmission spectrum will display a sinusoidal pattern of interference called 'fringes' superimposed on the material's native transmission spectrum as the dancers at each wavelength either reinforce or negate one another.

When light is incident at 90° (as in transmission), maxima will appear at fractions of the optical path length difference:

$$2nd = (m - \frac{1}{2}) \lambda$$

where n is the index of refraction of the material, d is its thickness, m is the fringe number and λ is the wavelength of light at which the maximum occurs.

When the maxima's wavelengths are plotted versus fringe number starting at x (... $x+1$, $x+2$, etc.), a straight line emerges with a slope equal to $1/(2nd)$. The thickness can then easily be calculated if the index of refraction is known, or vice versa.

For best results, a wavelength of light should be chosen that yields at least 5-10 fringes in the transmission spectrum across the spectrometer's wavelength range. Each fringe should have enough data points to allow the maximum to be easily identified or interpolated by drawing a smooth line through the data. Maxima will be more widely spaced at longer wavelengths, so if too few fringes are seen, the wavelength range may need to be shifted to the blue. The minima can also be plotted as a separate line to verify results, as it should yield the same slope.

Experimental Conditions

Three translucent polymer film samples were examined in transmission over the range 0.9-1.7µm using a NIRQuest512 spectrometer configured with a 25µm slit, yielding an optical resolution of ~3.1nm (FWHM). An HL-2000-HP high power tungsten halogen lamp was chosen as the light source, with two 600µm VIS/NIR fibre assemblies routing light to and from a 74-ACH adjustable collimating lens holder.

A high power lamp is warranted when using an NIR spectrometer to keep data acquisition time short, as the InGaAs detector at the core of the NIR512 is not as sensitive as the silicon detectors used in visible spectrometers. Larger core fibres help to maximise light throughput as well.

The polymer films were affixed directly to an arm of the 74-ACH, ensuring that the films remained flat against the arm. Transmission spectra were acquired in SpectraSuite spectroscopy software using a 50ms integration time, averaging 10 scans, with boxcar (smoothing) set to 0. In this case, averaging is preferred over boxcar smoothing to preserve the resolution of the spectrometer.

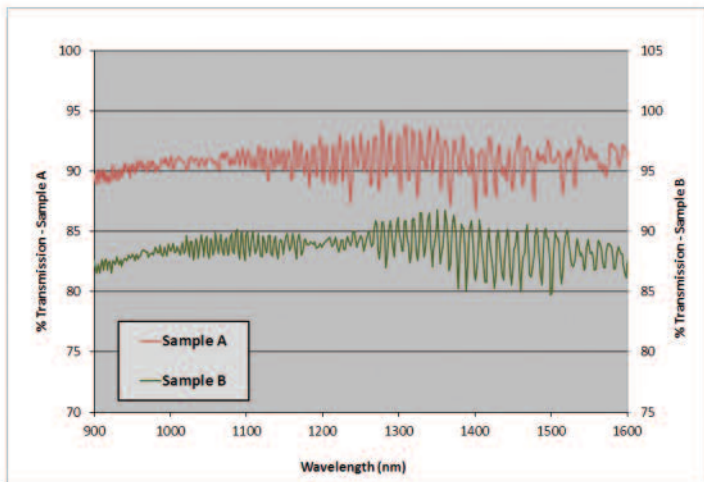


Figure 4. Transmission spectra with good fringe patterns.

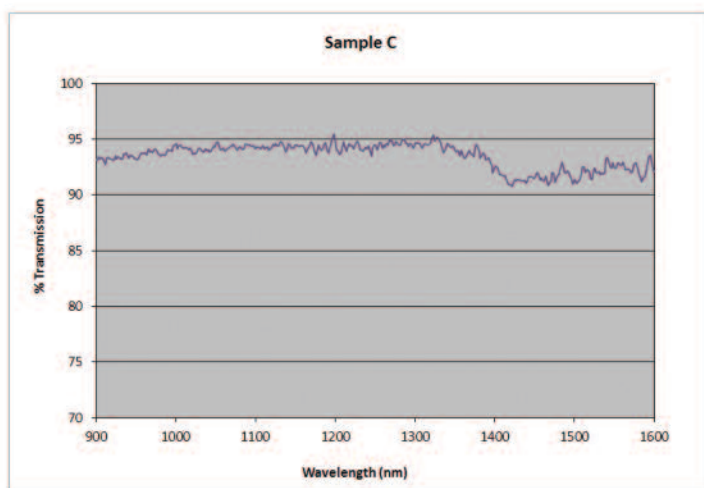


Figure 5. Transmission spectra with no clear patterns.

Results

The transmission spectra obtained for the three samples are shown in *Figures 4-5*. Samples A and B (*Figure 4*) showed clear, regular interference fringes spaced roughly every 10nm in the central portion of the wavelength range, with 5-6 data points between maxima. Ideally, there would be 10 or more points per fringe for optimum interpolation of the maxima.

Sample C (*Figure 5*) did not show a clear, regular interference spectrum, which could be due to its thickness or index of refraction being too high to show fringes within the resolution limits of the system. Or, it may not be smooth or uniform enough in thickness to yield clear interference fringes, in which case moving to another location on the film could potentially improve the spectrum.

With Samples A and B, the user of a smaller spectrometer entrance slit would offer no improvement, as it would increase only the optical resolution of the system, not yield more data points (the number of pixels and wavelength range of the spectrometer are fixed). Fortunately there were enough maxima to make a reasonable estimation of each one and yield a good quality fit to each line, with R^2 values of 1 (see *Figure 6*).

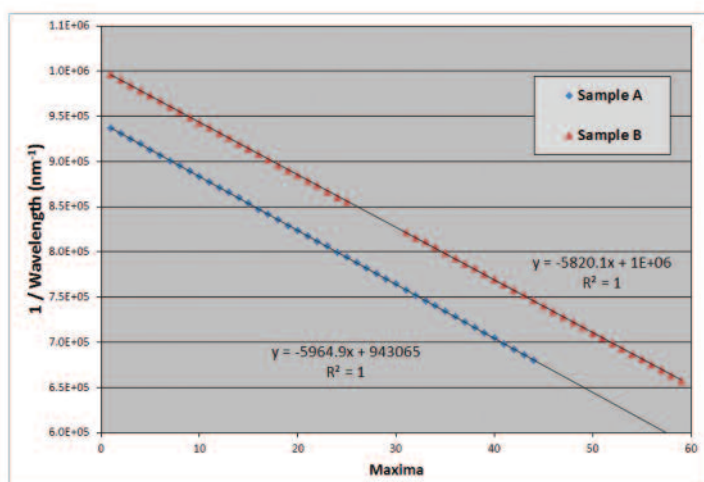


Figure 6. Analysis of sample interference patterns.

Even when the index of refraction of the samples is unknown, this method can still be used for process control, where limits can be set on the slope value based on a group of known acceptable samples. In this discussion, an assumption about the index of refraction will be made for illustration purposes. Water has an index of refraction of 1.33, typical crown glass is 1.5 and diamond is 2.42. Most plastics are in the range 1.3-1.7, but some high refractive index polymers can be up to 1.76. (These polymers find their way into AR coatings, LEDs and image sensors due to their high optical dispersion.) A material's index of refraction varies with wavelength, and though it can be considerably higher in the infrared, the NIRQuest512 still operates close enough to the visible to minimise the impact of this effect.

If the samples are assumed to have an index of refraction of 1.5, then samples A and B would be 55.9 μ m and 57.3 μ m thick, respectively. Varying the index of refraction within the 1.3-1.7 range expected for a polymer would alter these thickness values by <15%, demonstrating that the range and resolution of the preconfigured NIRQuest512 is well-suited to measurement of polymer films in the ~50 μ m thickness range. Thicker films, however, would result in more closely spaced maxima. Modeling the expected spacing between maxima (Δ) at the wavelength extremes of the NIRQuest512 (900nm and 1700nm, a function of grating and detector response) for a material of refractive index 1.5 shows how the spacing decreases with increasing thickness (see table below). Looking at how fringe spacing varies with wavelength, it is obvious that fringe measurement in the visible portion of the spectrum would require a very high-resolution spectrometer.

d (μ m)	Δ @900 nm	Δ @1700 nm
50	5.3	19.1
100	2.7	9.6
150	1.8	6.4
200	1.4	4.8
250	1.1	3.8

The model indicates that even at 100 μ m, a NIRQuest512 in standard configuration begins to lack the resolution and data point spacing to allow thickness measurement of many typical polymer films. Looking at 250 μ m as the thickest polymer film that could be expected, the ideal spectrometer would be configured to allow measurement of maxima spaced as close as ~2.0nm (with 5-6 data points between maxima). This would require a grating with 4x higher groove density than the NIR3 grating used in the standard NIRQuest512 (such gratings are available within the NIRQuest line of spectrometers). These gratings would allow measurement over a wavelength range of 150-200nm, with a resolution of 0.6-0.8nm (more than adequate to resolve the fringe maxima).

Though this wavelength range may seem small, it is important to remember that it is not the specific wavelength of fringes that is important in thin film interference, but that a sufficient number of fringes is seen clearly. A spectrometer configured for a 150-200nm wavelength range would show >60 fringes for any 250 μ m polymer film and >15 fringes for any 50 μ m film, sufficient for a good quality regression analysis. Integration time with the standard NIRQuest512 spectrometer was relatively low when using a 150 line/mm grating, and the samples were stationary, so even with a 600 line/mm grating, the integration time would only increase to ~200ms. This would keep the total scan time to a very reasonable 2 s with 10 averages.

Conclusions

The success of a thin film interference measurement depends heavily on the spectrometer being well matched to the samples under study. In the case of thin polymer films, an index of refraction range of 1.3-1.7 and typical thicknesses of <250 μ m calls for measurement in the near infrared. The NIRQuest512 spectrometer can be configured to tackle almost any sample within this range, leaving the user with only one challenge – making the polymer film in the first place.

Going Beyond

For those who need more from an interference measurement, reflectometry may be the solution. A system such as the NanoCalc Thin Film Reflectometry System takes the next step and fits the spectrum to a well-understood model, provided that thickness or index of refraction of the layers is known. This method is very accurate and allows analysis of several layers of differing composition, not just a single film.

When index of refraction is unknown, ellipsometry may be the solution. The SpecIE Ellipsometer System uses polarised light at a known angle to determine the phase change upon reflection, extracting thickness, index of refraction and absorbance of a sample quickly and easily using user-friendly software.