ANASYS INSTRUMENTS
The nanoscale spectroscopy company

The world leader in nanoscale IR spectroscopy

Submicron spatial resolution IR characterization of polymer based food packaging materials

- **Mirage demonstrates submicron spatial resolution IR imaging and spectroscopy on thin multilayer food packaging materials**
- **New reflection mode imaging significantly simplifies sample preparation and improves data turnaround time**

mIRage™
Sub-µm IR spectroscopy

The Mirage IR microscope changes the field of IR spectroscopy with a novel approach to achieving submicron resolution IR

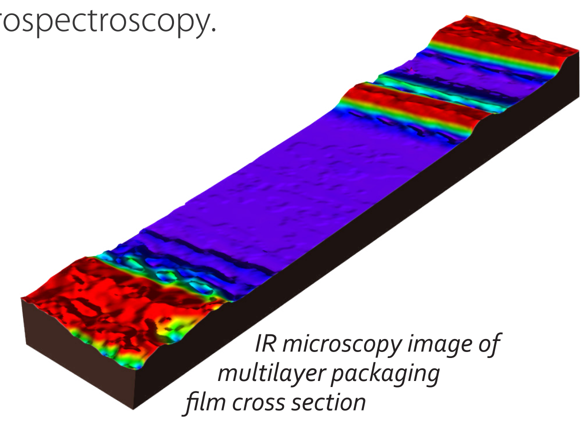
Food packaging characterization

Since it was introduced in the 19th century, food packaging has made great advances focused on improving food protection and quality, health and safety, providing longer shelf life and adhering to more demanding environmental and international standards.

To address these requirements, a wide range of new materials and improved processing techniques have been developed to generate sophisticated, thin, multilayer food packaging.

Multilayer food packaging has routinely been characterized using FT-IR spectroscopy, however, the need to chemically characterize the larger number of increasingly thin layers in the multilayer packaging films being developed and manufactured today often exceeds the spatial resolution limits of convention al FT-IR microspectroscopy.

The Mirage IR microscope using photothermal IR spectroscopy (PTIR), provides a new level of capability to provide submicron IR characterization of thin multilayer film while eliminating or significantly reducing sample preparation and improving data turnaround times.



IR microscopy image of multilayer packaging film cross section

Key words

Submicron IR spectroscopy | Multilayer films | Food packaging

Mirage IR microscope

The Mirage™ IR microscope is an innovative new system, uniquely providing submicron IR spectroscopy and imaging across a wide variety of applications. Using a proprietary Anasys technique based upon photothermal IR spectroscopy, Mirage breaks the diffraction limit and bridges the gap between conventional IR microspectroscopy and nanoscale IR spectroscopy. The Mirage solves two of the biggest problems facing the field of IR microscopy:

- Achieving submicron IR spatial resolution (an improvement of over 10X) without the need for contact-based ATR accessories.
- Measurement of thick samples in reflection mode, providing transmission quality IR spectra that correlate to industry standard IR databases.

Additionally, Mirage allows for these new unique capabilities with fast, easy measurement of samples using a new optical, non-contact based technique which utilizes established IR technology.

Photothermal infrared (IR) spectroscopy

The photothermal infrared spectroscopy (PTIR) methodology used on the Mirage IR microscope is a result of over a decade of expertise in photothermal physics that Anasys Instruments and it collaborators have built up since starting research on the AFM-based nanoscale IR spectroscopy platform.

Submicron spatial resolution IR microscopy

PTIR overcomes the IR diffraction limit by combining a mid-IR pulsed, tunable laser that heats the sample. When the IR laser is at a wavelength that excites a molecular vibration in the sample, absorption occurs, thereby creating photothermal effects. A visible probe laser, focused to 0.5 µm spot size, measures the photothermal response via the scattered light, as shown in figure 1.

The IR pump laser can be tuned through the entire fingerprint region in one second or less, to obtain an IR spectrum.

Transmission FT-IR quality in reflection mode

Due to its unique operating principle, PTIR can be used in both transmission and reflection mode. However, its primary method of operation is in reflection mode, which eliminates several longstanding limitations for IR microscopy. This provides substantial benefits for the IR community, including minimizing sample preparation and enabling submicron spectroscopy. PTIR has consistently shown transmission quality spectra in reflection mode across a wide range of sample types. The submicron resolution is

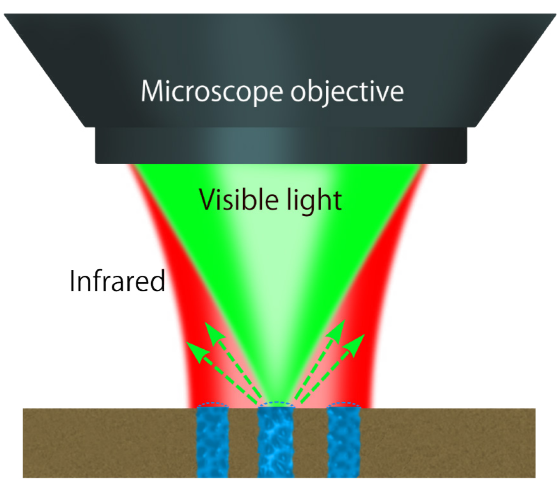


Figure 1: A pulsed tunable, IR source is focused on sample. Absorbed IR light causes sample to heat up, creating a photothermal response in the sample. A visible laser probe measures the photothermal response due to IR absorption

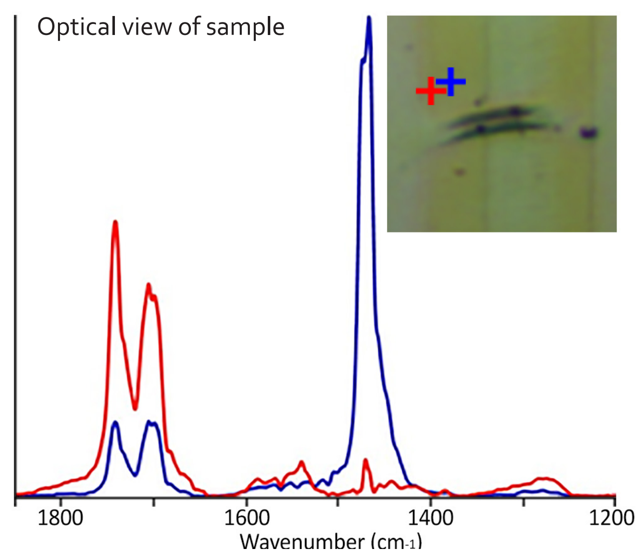


Figure 2: Spectra 0.5µm spacing showing different polymer materials in a multilayer film

demonstrated in figure 2, showing reflection mode spectra on a multilayer packaging film measured 0.5 µm apart with highly differentiated chemical fingerprints indicating different materials.

Correlates to bulk FT-IR databases

PTIR measurements of common polymeric materials have shown excellent correlation with bulk FT-IR spectra. Figure 3 shows excellent correlation for polystyrene (PS), polyethylene terephthalate (PET) and polymethyl methacrylate (PMMA) with high correlation to spectra from the KnowItAll® database.

PTIR measurements shown in figure 3 were made on samples of over 20 µm thickness in reflection mode, yet the strongest bands show no evidence of saturation. This is due to the reflected signal sampling only the top couple microns of the sample, making the depth of penetration comparable to what is achieved using ATR accessories, but without the optical band-shape distortions present in many ATR spectra.

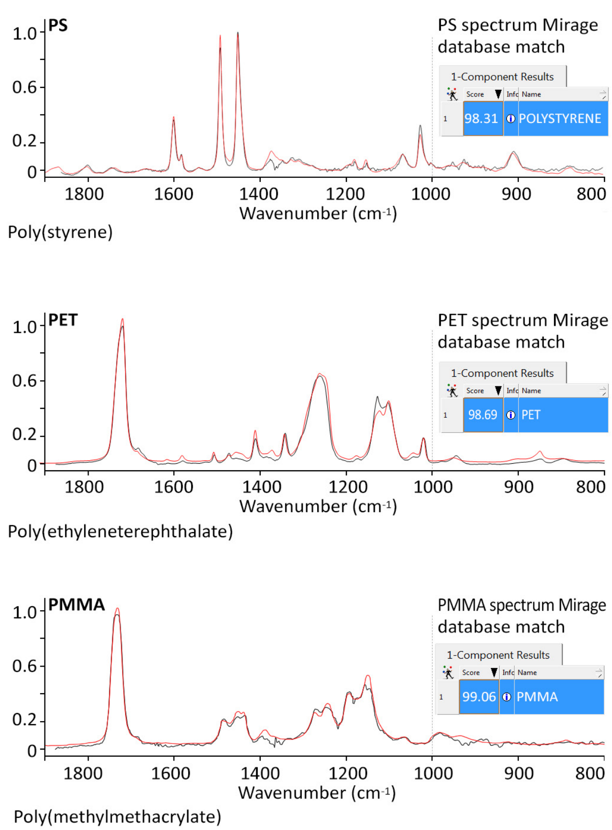


Figure 3: Three different spectra from Mirage searched against the database with high matches for PS (Top) PET (middle) and PMMA (bottom)

Ease of use and minimizing sample preparation

PTIR is an optical, non-contact based approach, making it fast and easy to use, while maintaining transmission quality spectra. In addition its high quality spectra in reflection mode enables IR measurement on thick samples and eliminates the need for thin samples in many sample types. This leads to dramatically easier sample preparation, improved ease of use and faster turnaround times.

Next generation infrared spectroscopy

PTIR eliminates several longstanding limitations for IR microscopy enabling submicron IR spectroscopy and minimizing sample preparation. PTIR is a unique technique that provides a huge step forward for the IR spectroscopy community.

Submicron resolution of multilayer packaging film with Mirage

There is a wide variety of food packing materials in use in the food industry. This application report provides a specific example of characterization for a thin, multilayer packaging using the Mirage IR microscope to demonstrate the novel capabilities of the system. Conventional transmission mid-IR spectroscopy typically cannot be used to measure thick samples because the light is totally absorbed or scattered before it has finished transmitting through the sample. Thus, there is little photon energy reaching the detector. The film layers are shown in figure 4.

Various measurements were performed with Mirage on both thin cross sections and block face samples. All measurements were taken in reflection mode, using a variety of techniques, including point spectroscopy, hyperspectral imaging and single wavelength imaging.

Material	Layer Thickness (µm)
Ethylene vinyl acetate blend	16
Polyethylene	10
Polyamide	12
Ethylene vinyl alcohol	12
Polyamide	9
Ethylene vinyl acetate	38
Polyamide	20

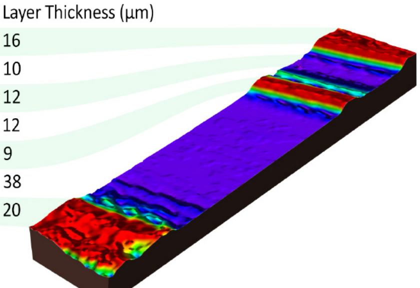


Figure 4: Multilayer packaging film

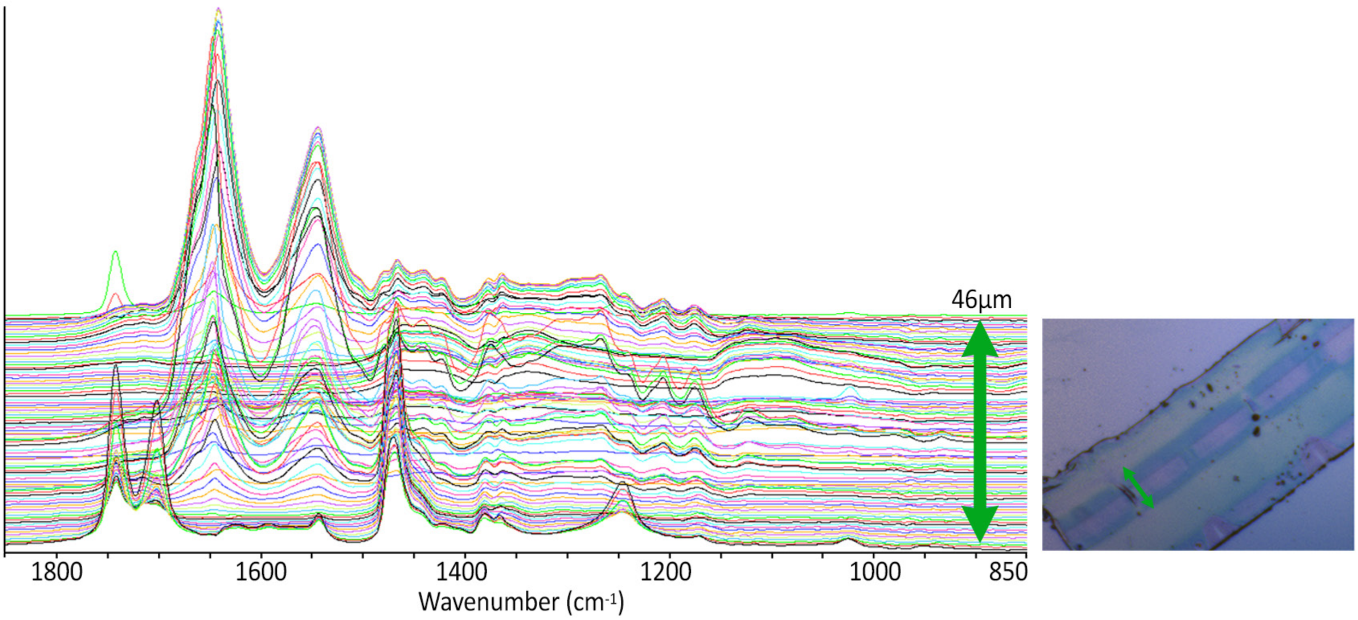


Figure 5: Multilayer packaging film – thin section. reflection mode spectroscopy – 93 spectra, 10 sec/spectrum 10 co-averages/spectra. 0.5 µm spacing, 46 µm line array. *Data courtesy of G. Meyers, M. Rickard Dow Chemical Company*

Line array measurements of multilayer films

The data in figure 5 shows a line array of 93 spectra (46 µm length) across the entire cross section of a multilayer polymer film (optical image inset is shown). The data is spaced by 0.5µm and each spectrum displayed took ten seconds to collect. This data can then be used to easily identify each layer within the film, by comparing to a third party spectral database or internal company IR database. Mirage also allows for the detection of defects within the film by looking for differences between various spectra within a single layer. Submicron defects are easily detected and chemically identified within these multilayer films or within polymer blend sample.

Hyperspectral imaging of multilayer packaging film

Mirage provides hyperspectral capability to quickly identify the spectra and chemical composition over a wide region. Figure 6 highlights an example of hyperspectral imaging with Mirage. The left image shows a Hyperspectral IR image at 1730 cm^{-1} of a multilayer film cross section. Within the software the wavelength distribution visualized in the hyperspectral image can be changed by selecting different wavenumber points (denoted by the blue lines) in the spectra. The middle image shows the hyperspectral image at 1545 cm^{-1}, showing the polyamide layers within the multilayer film. This image is displayed by simply selecting this peak with the blue line in software. The top center hyperspectral image highlights the IR absorbance at 1470 cm^{-1}, showing the layers within the multilayer film that contain polyethylene chains.

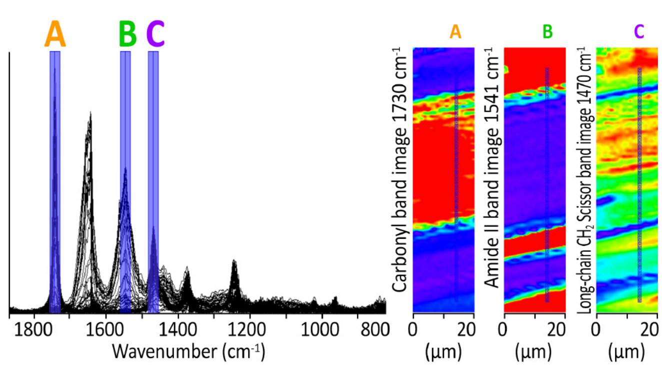


Figure 6: Packaging sample - block face - multilayer sample – seven layers. Reflection mode - hyperspectral imaging - 1 sec/spectra. 1 scan/spectra. 20 x 85 µm size. 1 µm spacing. Image shows carbonyl band and amide II bands and CH bending bands

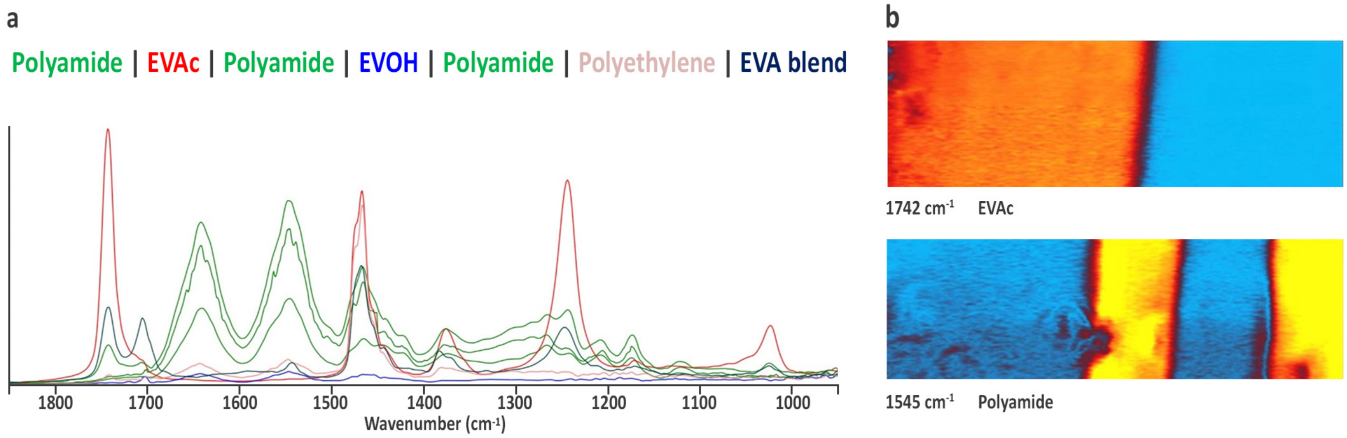


Figure 7: Multilayer packaging film, thin section sample showing (a) Fingerprint section spectra measured using reflection mode spectroscopy – 10 spectra, 100 coaverages. 140 sec total time per spectrum. (b) High resolution, single wavelength chemical images with a resolution of 0.5µm showing Polyamide layers at 1545cm^{-1} and EVAc layer at 1742cm^{-1}. Scan size is 60µm x 20 µm. Imaging time is about 1min 40sec

High speed point spectroscopy of block face multilayer film

The data in figure 7 shows reflection mode based, line array point spectra across the thin section sample of the multilayer polymer film. The data is spaced manually by the user to identify specific layers. Mirage also uniquely enables high resolution single wavelength imaging to highlight the chemical distribution of specific components in the sample. Here polyamide and EVAc layers are provided in high resolution.

Layer seven is a unique blend of EVAc and a proprietary material. The spectra in the high wavenumber range (not shown) confirm that the 1710 cm^{-1} band in layer seven is due to a carboxylic acid. Upon closer examination there is an extremely broad weak band underlying the entire CH-stretching region in the spectrum of layer seven. This is expected to be an OH-stretching band from a carboxylic acid and confirms the tentative assignment 1710 cm^{-1} as due to a carboxylic acid.

Polymer defect identification

This application shows the characterization of a defect in a multilayer polymer film. The sample is a 240 µm thick two layer film with defects only visible in the top layer. The sample was mounted to a sample holder and was examined without further preparation in a standard top-down reflection mode operation. The defect represents a typical "gel" particle observed in polymers which could be foreign material stuck in the exterior of the polymer matrix or the matrix material itself with different physical properties, such as, loss of crystallinity due to degradation.

As shown in Figure 8, the optical image in the inset (top left) shows the defect in the polymer sample. Colored markers on the optical image indicate the measurement locations and correspond to the spectra in the main graphic. Mirage IR spectrum on the polymer (red trace) shows characteristic IR absorption features of isotactic polypropylene (PP), in particular, the sharp

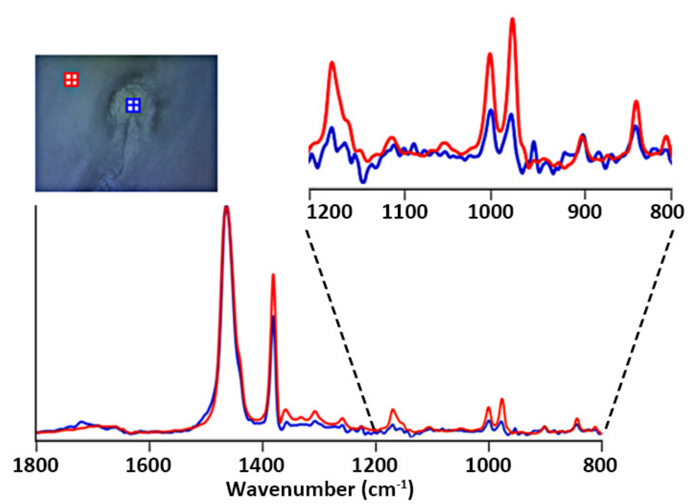


Figure 8: Mirage IR spectra collected on the polymer (red) and the defect (blue) region

band around 998 cm^{-1} highlights the crystallinity of the PP matrix. The spectrum collected on the defect (blue trace) looks similar to that of the polymer matrix, however, with subtle variation, e.g., reduction of overall intensity of the PP specific IR bands (800-1400 cm^{-1}, inset top right). This indicates loss of crystallinity as well as local degradation of polypropylene in the defect sites.

IR spectroscopy from macroscale to microscale and down to nanoscale

The combination of Mirage with the nano**IR** nanoscale IR spectroscopy systems allows for the complete chemical characterization of various materials covering a wide range of spatial resolutions.

Figure 9 shows the characterization of multilayer films with nanoIR™ spectroscopy. The interphase region between a polyamide and polyethylene layer were sampled using nanoIR. These two materials commonly used in multilayer films often require the need for a tie layer between them, as they do not bind well together. These tie layers can be only nanometers in thickness, and thus not detectable using other techniques. The unique nanoscale chemical characterization capabilities of AFM-IR allow the chemical visualization of the tie layer within the film.

The photothermal AFM-IR spectra were collected in the high wavenumber region across the interface between polyamide and polyethylene layers. This data is spaced by 100 nm and there is a region in the purple spectra where the C-H stretching peak narrows. This indicates a change in the crystallinity of the PE in this region, a common feature in tie layers.

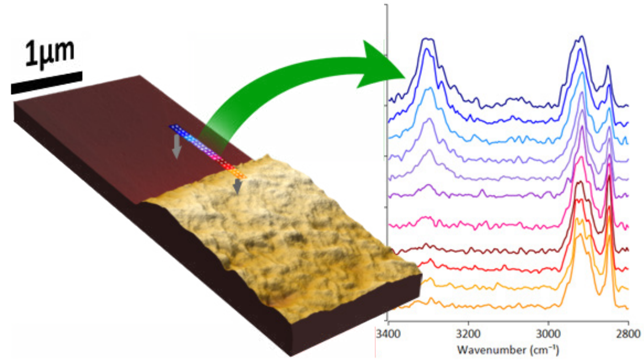


Figure 9: nanoIR spectra of the boundary between two polymers showing evidence of a TIE layer, 100nm pixel spacing between spectra using nanoIR photothermal technique. AFM image (5µm x 5 µm)

Summary

The Mirage IR Microscope has been shown to provide a number of effective food packaging analysis methods, including spectral arrays, hyperspectral imaging, and individual sub-micron IR spectra of films and contaminants in commonly used packaging materials. PTIR provides reliable and reproducible sub-micron IR spectroscopy for the first time, making it a promising technique to solve many production challenges.

Acknowledgments

Anasys Instruments acknowledges Dr. Greg Meyers and Dr. Mark Rickard of Dow Corporation for permission to show the packaging film data.

ANASYS INSTRUMENTS
The nanoscale spectroscopy company

info@anasysinstruments.com Tel: +1 (805) 730 3310
http://www.anasysinstruments.com/products/Mirage/