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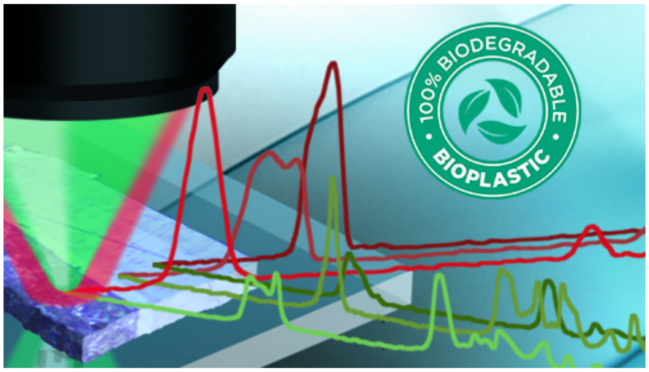
Comprehensive multilayer laminate film analysis using submicron simultaneous IR+Raman spectroscopy

Packaging materials have been routinely characterized using FTIR spectroscopy. However, the increasingly thin layers in packaging materials currently being developed often exceeds the spatial resolution limits of conventional FTIR techniques. (O-PTIR) Optical Photothermal IR spectroscopy enables submicron IR characterization of thin multilayer films in a non-contact reflection mode and simplifies sample preparation. The IR probe laser generates Raman scattering resulting in simultaneous acquisition of IR and Raman spectra.



From these results and we can understand the entire composition of these films

Introduction

In this Application Note, we will focus on the analysis of a variety of multilayered film samples using the mIRage+R microscope, which simultaneously captures IR and Raman spectra from the same spot on a sample, with the same submicron resolution. Packaging materials have previously been routinely characterized using FTIR spectroscopy for decades. However, the increasingly thin layers in packaging materials currently being developed often exceeds the spatial resolution limits of conventional FTIR techniques. The principal behind the mIRage, Optical Photothermal IR (O-PTIR) spectroscopy enables, for the first time, submicron IR characterization of thin multilayer films via a non-contact reflection mode IR technique, while also significantly simplifying sample preparation and improving time-to-data. Furthermore, the IR probe laser generates Raman scattering, which when collected, allows for the simultaneous acquisition of both IR and Raman spectra.

(O-PTIR) Optical Photothermal IR spectroscopy

O-PTIR overcomes the IR diffraction limit by combining a mid-IR pulsed tunable laser with a visible probe beam. When the IR laser is tuned to a wavelength that excites a molecular vibration in the sample, absorption occurs, thereby creating photothermal effects. The visible probe laser, focused to ~ 0.5 µm spot size, measures the

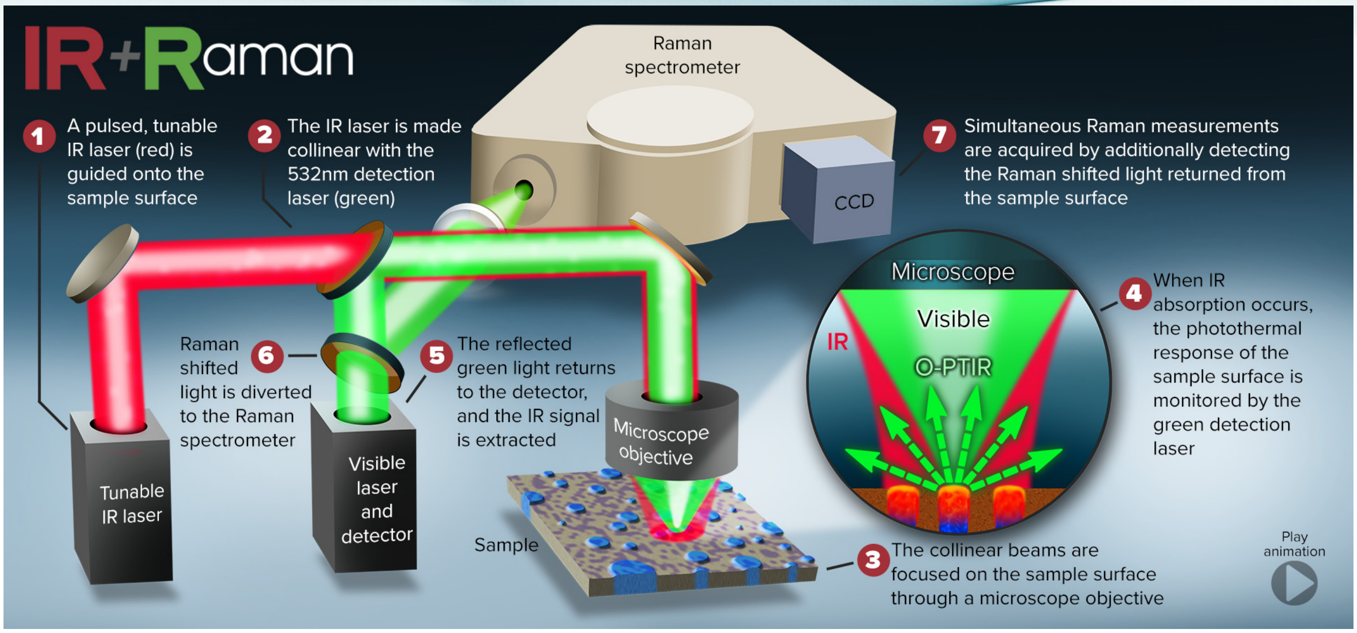


Figure 1: Schematic representation of the beam paths for the generation of simultaneous IR and Raman spectra.

photothermal response via the scattered light, as shown in figure 1. The IR laser can be swept through the entire fingerprint region in one second or less to obtain an IR spectrum.

Minimizing sample preparation

Since it is a non-contact technique, O-PTIR provides IR measurements on thick samples and eliminates the need for thin samples for many sample types. This leads to dramatically easier sample preparation, improved ease of use and faster turnaround times. Conventional transmission mid-IR spectroscopy typically cannot be used to measure thick samples, because the light can be totally absorbed or scattered before it has finished transmitting through the sample, resulting in little photon energy reaching the detector. However, these materials are now able to be analyzed with O-PTIR. In this study all films have been analyzed by making a bulk cross section of the sample embedded in epoxy. Thin sections are not required.

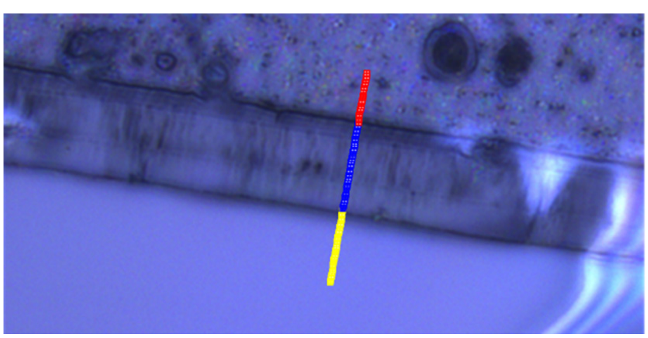


Figure 2: 40x Optical image of cross sectioned film 1. Markers indicate position for simultaneous IR and Raman spectra.

Simultaneous IR and Raman line array measurements

In this first example we can see the power of the simultaneously acquired IR and Raman analysis, with each technique being used to uniquely identify various components.

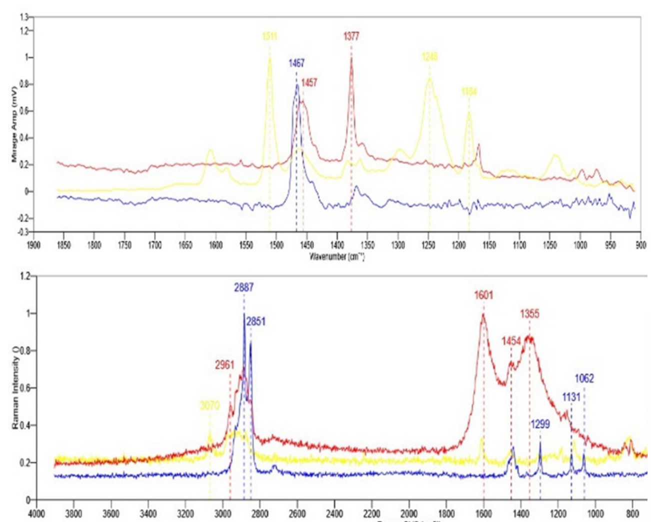


Figure 3: Top- IR spectra collected from film 1. Bottom- Simultaneously collected Raman spectra.

Representative IR and Raman spectra from each color-coded point, as seen in figure 2 are shown in figure 3. The data spacing between points in the line array was 500 nm.

Due to the fact the O-PTIR spectra correlate excellently with traditional FTIR spectra, they can be easily searched using existing spectral databases. In this case, each of the spectra was searched against the KnowItAll spectral database from BioRad. The searches for the IR spectra clearly identify two main polymer layers, polyethylene and polypropylene, along with the embedding epoxy (not shown).

Interestingly, one of the main components of the film is not observed or identified using the IR analysis. However, the Raman spectra are used to complete the full picture. The simultaneously acquired Raman spectra are searched against the KnowItAll Raman database for identification, as seen below in Figure 4.

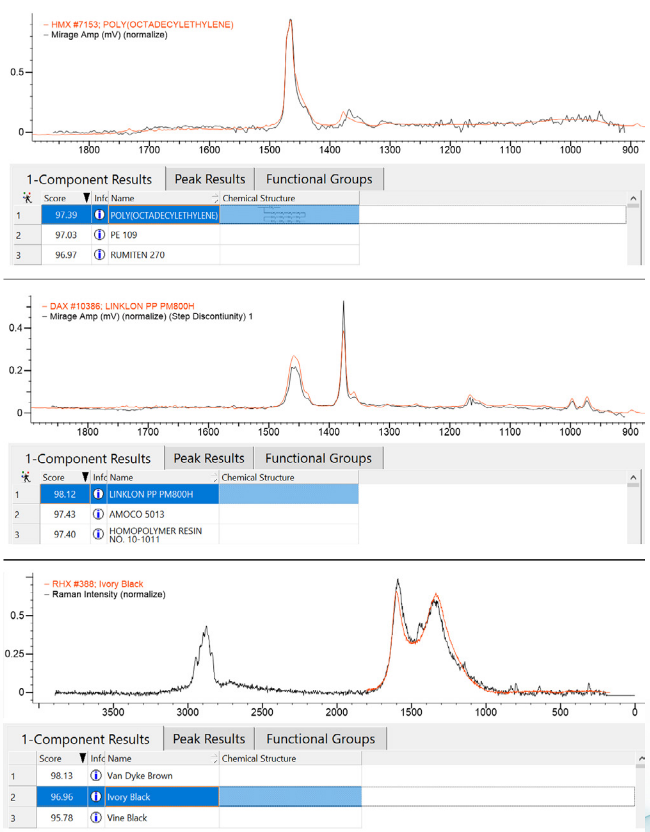


Figure 4: KnowItAll spectra database results for the main polymer layers in film 1. Top-Blue spectra identified as PE, Middle-Red spectra identified as PP, Bottom-KnowItAll spectral database identifies the red spectrum as carbon black.

From the combinational analysis of both IR and Raman we can tell that the layer represented by the red spectrum is composed of polypropylene loaded with carbon black.

Single wavelength imaging for visualizing chemical distribution

When producing layered films, chemical distribution within the products is an essential part of product integrity. mIRage uniquely enables high resolution single wavelength imaging to highlight the chemical distribution of specific components in any sample. Once the O-PTIR spectra are collected on the film, images can be acquired at unique absorption bands to each layer, highlighting the layer boundaries and interfaces. Figure 5 shows an optical image of another cross sectioned multilayer film from a second sample.

As we can see from the line array data, there is a region with a width of roughly 2 µm that shows a significantly different spectrum from surrounding regions. Red spectra, as seen in figure 6, show significantly increased C-H stretching with an additional peak at 1462 cm^{-1}.

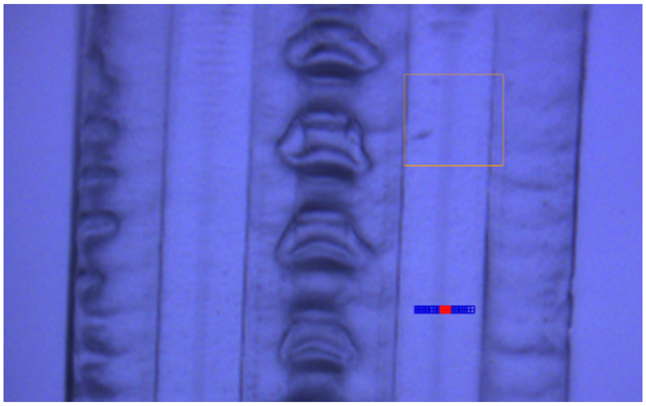


Figure 5: 40 x optical image of film two embedded in epoxy. Markers represent an 11 µm line array with 250 nm spacing.

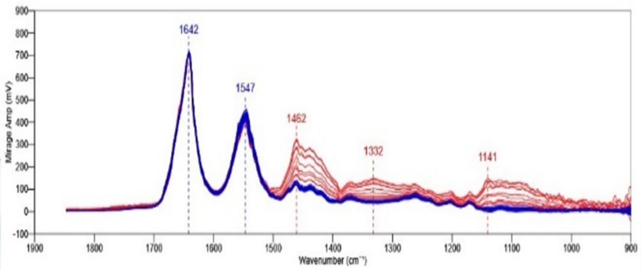


Figure 6: mIRage line array spectra collected from locations shown in figure 5. Data has been normalized to 1642 cm^{-1}.

Single wavelength imaging allows us to visualize the clear thickness and distributions of various layers as shown in figure 7.

As we can see from the images, the mIRage IR microscope can provide single wavelength images with unparalleled spatial resolution while operating in a reflective non-contact regime.

Summary

The mIRage+R microscope has been used to analyze various multilayer films by collecting both IR and Raman spectra simultaneously. The spectra that are collected show excellent correlation to traditional FTIR spectra and are searchable in existing databases. From these results and searches we can understand the entire composition of these films, when one technique alone may not be enough to obtain a complete understanding. Additionally, single wavelength imaging with O-PTIR allows for the complete visualization of the components within the sample with submicron resolution. Overall,

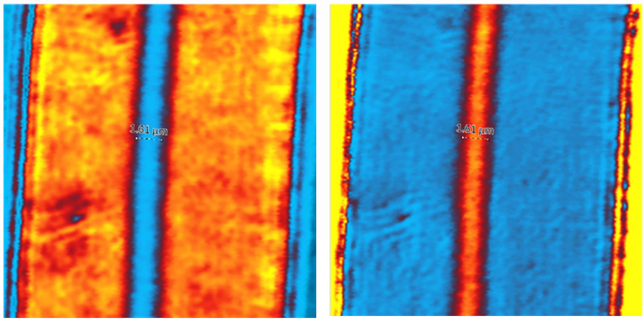


Figure 7: Top- IR spectra collected from film 1. Bottom- Simultaneously collected Raman spectra.

O-PTIR provides reliable and reproducible sub-micron IR spectroscopy for the first time, making it a promising technique to solve many analytical and production challenges.

Acknowledgments

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Watch the realted webinar: Bioplastic laminate characterization IR+Raman spectroscopy

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