A new approach to sample preparation free micro ATR FTIR chemical imaging of polymer laminates

Application Note

Materials Testing & Research

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Abstract

Micro ATR chemical imaging of polymers and in particular polymer laminates typically requires significant application of pressure to ensure good contact between the ATR crystal and the sample. To ensure that such thin samples can withstand the pressure without buckling, elaborate sample preparation procedures are often required to support cross-sectioned materials: embedding of sample in resin, cutting the resin and polishing the contact surface. Such procedures are tedious, require overnight resin curing and carry the added risk of cross-contamination. Presented here is a novel method of ultralow pressure micro ATR FTIR chemical imaging that removes the need for any structural support. This allows samples to be measured "as-is" using direct contact with the ATR crystal. This unique capability is made possible through the use of Agilent's "Live ATR imaging" technique which provides enhanced chemical contrast, and enables the exact moment of contact between the sample and ATR crystal to be determined and provides a visual measure of the quality of contact. Adhesive layers as thin as a few microns can be clearly observed in 50-micron thick polymer laminates without sample preparation.

Introduction

What are polymer laminates and what are they used for?

Polymer laminates are film structures consisting of two or more layers adhered together to make a structure. The polymeric materials forming these laminates have varying thickness—from a few microns to tens of microns. This can influence a variety of properties, such as chemical, mechanical and barrier (e.g., impervious to oxygen and/or moisture) properties.

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To construct these materials, adhesive (tie) layers are often required between two adjacent but chemical incompatible layers. Typically these incompatibilities are between materials with differing polarities, such as nylon and polyethylene.

The adhesives typically have intermediate polarity or contain functional groups with an affinity to both polar and non-polar layers and hence act as good binding material. Such adhesive layers in laminates can be very thin, e.g., between 2 to 10 microns.

Polymer laminates can range in complexity and thickness from those containing only two layers to more than 10 layers (not including adhesive layers). With total cross-sectional thicknesses ranging from <50 microns to >200 microns, polymer laminates are used in a variety of packaging applications, which are employed in industries such as food and pharmaceuticals.

What are the analytical challenges/requirements for polymer laminates?

With ever increasing manufacturing sophistication enabling more complex and thinner laminate structures to be produced, the analytical challenges to ensure good product quality control, troubleshooting or the reverse engineering of competitive products are also increasing in complexity.

The analytical tools available to analyze such laminates are wide and varied and include a range of optical microscopy techniques, thermal techniques (such as differential scanning calorimetry) and various spectroscopic techniques.

In particular, Fourier Transform Infrared (FTIR) microscopy has proven most useful for the analysis of polymer laminates. This has resulted from the core application of FTIR spectroscopy in the identification and characterization of polymers, combined with the ability to obtain this information from small areas.

When applied to polymer laminate analysis, FTIR microscopy is typically performed in transmission mode and requires that the total sampled thickness be within a certain limit. For polymeric materials, this is typically 10–20 microns. Preparing thinly sliced polymer and polymer laminate materials at a thickness of 10–20 microns presents some challenges. Typically, dedicated (and often expensive) specialized cutting devices such as microtomes are required. Even then, the cut samples are often difficult to handle due to curling or difficulties with static stick. To minimize these effects, samples can be embedded in resin before cutting and microtomed together within the resin support (Figure1). This unfortunately adds another material with a complex IR spectrum to the sample. Once cut, if the sample is flat, it can be placed in a sandwich between infrared transparent windows and sampled in transmission mode. However, because of internal reflections between the front and back surfaces of the sample, “fringing effects” can commonly be observed. This results in a sinusoidal baseline during such measurements.

With these issues and sampling preparation steps aside, transmission FTIR microscopy is a relatively simple technique to obtain spectra from small areas. It does however suffer from one major limitation: spatial resolution is relatively poor, especially when compared to optical microscopy techniques. Typical spatial resolution limits for transmission mode FTIR microscopy are about 10–15 microns.

In comparison to transmission mode, the use of micro attenuated total reflectance (ATR) as the mode of analysis removes the requirement for samples to be a certain thickness, so samples no longer need to be thinly cut. However, as ATR requires intimate contact with the samples, there are still some important sample preparation requirements. Primarily, the sample must be flat and smooth to ensure that there is full and complete contact across the ATR measurement’s field of view. Additionally, and of paramount importance to the detection of ultrathin layers, micro ATR FTIR

microscopy provides for a factor of four spatial resolution enhancement over transmission mode.

To ensure complete and intimate contact, a significant amount of pressure must be applied between the sample and ATR crystal. Many micro ATR imaging systems rely on indirect methods of ensuring good contact, by using coarse pressure sensors, often with preset pressure levels.

The inability to directly monitor the exact moment and quality of contact in most micro ATR imaging systems is also another factor that requires the use of higher pressures to ensure good contact. For naturally hard materials, the pressures needed to ensure a good contact between the ATR and surface is typically not an issue. However, given samples may have cross-sectional thicknesses of only 50–200 microns, even very slight pressures will cause an unsupported polymer laminate to buckle or deform in a way that prevents good contact.

Therefore, to avoid buckling or other structural distortions of delicate and thin samples under applied ATR pressure, it is mandatory to provide some degree of support. This is most commonly achieved by resin embedding of the sample, followed by cutting and polishing of the surface (Figure 1).

The process of resin embedding is tedious and time consuming (>12 hours), typically consisting of the following steps:

1. Cut a small piece of sample and place it vertically in a holding clamp.
2. Place sample and clamp into a mold and pour in resin to fully cover sample.
3. Allow resin to cure, typically overnight, and then remove the resin-embedded sample from mold.
4. Cut the top surface of resin, so as to expose a cross section of the sample.
5. Polish the cut surface with successively finer and finer lapping paper (from 30 microns to 1 micron).

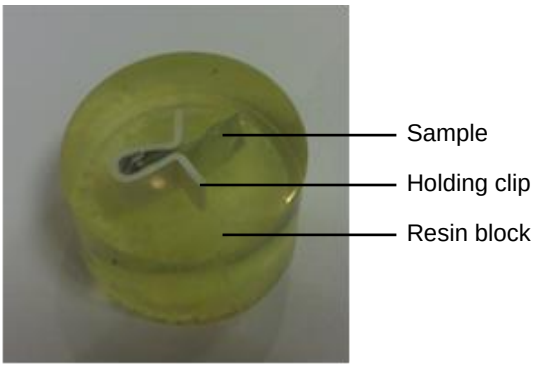


Figure 1. An example of a polymer film, held by a clip and embedded in a resin block

Cutting and polishing also introduces the risk that resin and polishing material may contaminate the sample or complicate the image and spectral interpretation.

Once prepared, resin-embedded samples are brought into contact with the micro ATR and pressure is applied. Often, the levels of pressure applied—even at lower settings—are enough to produce indentations at the surface of the samples, potentially preventing the subsequent analysis of the sample with other analytical techniques. This technique is then potentially destructive.

A new approach to *"pressure free"* micro ATR imaging

Agilent Technologies has developed a radically new approach that removes the need for resin embedding or any other sample preparation. This enables delicate and thin samples to be measured "as-is". The new approach hinges upon the fact that the infrared detector in an Agilent FTIR imaging system is a focal plane array (FPA*) and so affords simultaneous two-dimensional (2-D) data collection. And, most importantly and uniquely, it utilizes the "Live ATR imaging" feature with enhanced chemical contrast to ensure that the minimum pressure necessary for good contact is applied. This results in a non-destructive measurement—a remarkable capability.

Unlike linear array IR detectors, which must be scanned across an area to generate a 2-D image, FPAs provide instantaneous "real-time" imaging of the sample's surface, as it is in contact with the ATR. Such real-time imaging permits a visual assessment of the quality of sample contact before any data collection.

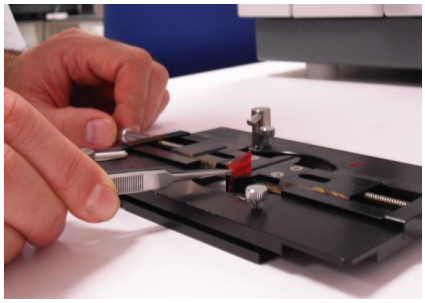
However, having a 2-D FPA alone does not provide for enough contrast to determine the moment of sample contact with the ATR. To overcome these issues Agilent Technologies has recently developed a unique "Live ATR imaging" mode, which significantly enhances the chemical contrast of the real-time FPA image, so the exact moment of sample contact can be visualized and contact monitored as the pressure is increased.

This mode provides for direct and real-time monitoring of the quality of contact (i.e., has the sample made complete contact across the entire field of view), which allows for extremely low levels of pressure to be applied. And it is this extremely low level of pressure that now allows for delicate and thin samples to be mounted, cross-sectioned end on, without any need for sample support using resin.

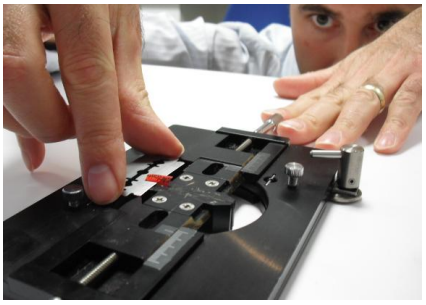
Sample measurement with "Live ATR imaging"

In five simple steps which only take only a few minutes (Figure 2), a sample of polymer laminate (i.e., a sausage wrapper) can be prepared for measurement using "Live ATR imaging"—removing the need to spend hours embedding, cutting, and polishing!

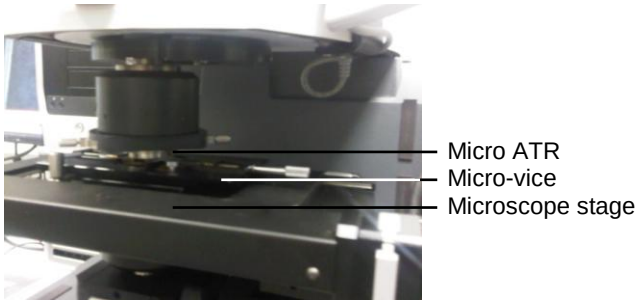
Step 1. Cut a small piece of sample.



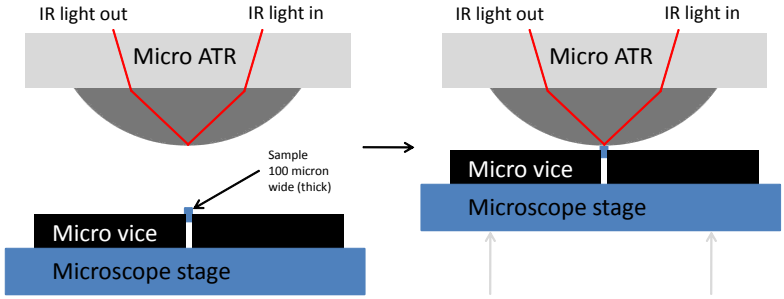
Step 2. Place sample into micro-vice.



Step 3. Cross-section sample with razor.



Step 4. Place micro-vice onto microscope stage.



Step 5. Raise stage to make contact and then collect data.

Figure 2. Easy five-step process—from raw sample to data collection—allows sample measurement of polymer laminates to be achieved in minutes using "Live ATR imaging" with enhanced chemical contrast. Note: Micro ATR and sample are drawn to scale

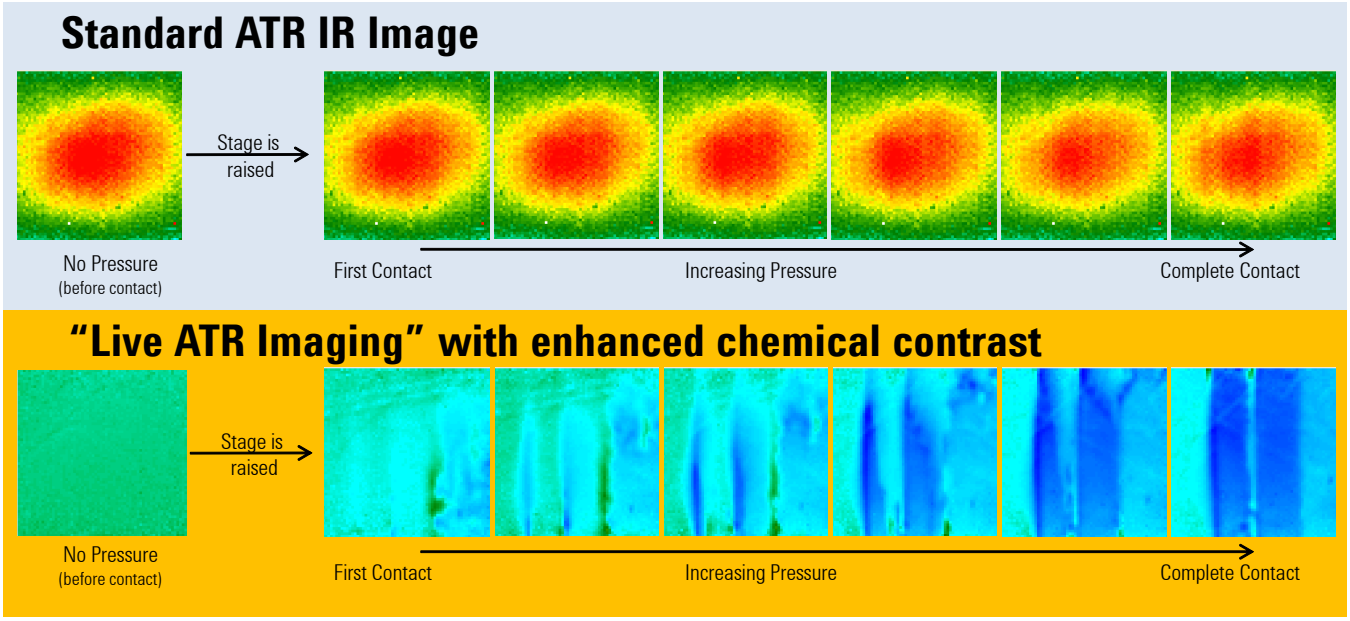


Figure 3. Comparison of a standard ATR IR image and Agilent's "Live ATR imaging" with enhanced chemical contrast—clearly showing the latter can detect first contact of the ATR crystal with the sample and that contact quality can be monitored real-time as the pressure is increased and before any data collection

Figure 3 shows a side-by-side comparison of Agilent's unique "Live ATR imaging" with enhanced chemical contrast and a standard ATR IR image.

Reviewing the upper series of images, the similarity of all the standard ATR IR images makes it impossible to determine when the ATR crystal makes contact with the sample's surface or make any reasonable assessment of the quality of the contact as the pressure being applied increases.

Whereas, as seen in the lower series of images, Agilent's unique "Live ATR imaging" with enhanced chemical contrast enables real-time monitoring of the sample contact as the sample is being raised and pushed up against the germanium crystal of the Micro ATR. The real-time monitoring allows for a near "pressure free" contact to be made between the sample's surface and the Micro ATR, this means unsupported cross-sections of ultrathin polymer laminates can be measured directly—even very thin samples of less than 50 microns—without the need for being embedded in resin!

Results

To further demonstrate the capabilities of "Live ATR imaging", a polymer laminate sample was obtained from the plastic wrapper of a sausage (~55 microns total thickness).

The results below were collected using the following conditions:

FTIR Spectrometer	Agilent Cary 670 FTIR
FTIR Microscope	Agilent Cary 620 FTIR
Focal Plane Array*	64 × 64 MCT
Spectral Resolution	4 cm^{-1}
Number of Scans	64 (2 mins)
Spatial Resolution	1.1 microns (pixel size)
Collection mode	Micro ATR (Ge)
Sample Type:	Sausage wrapper

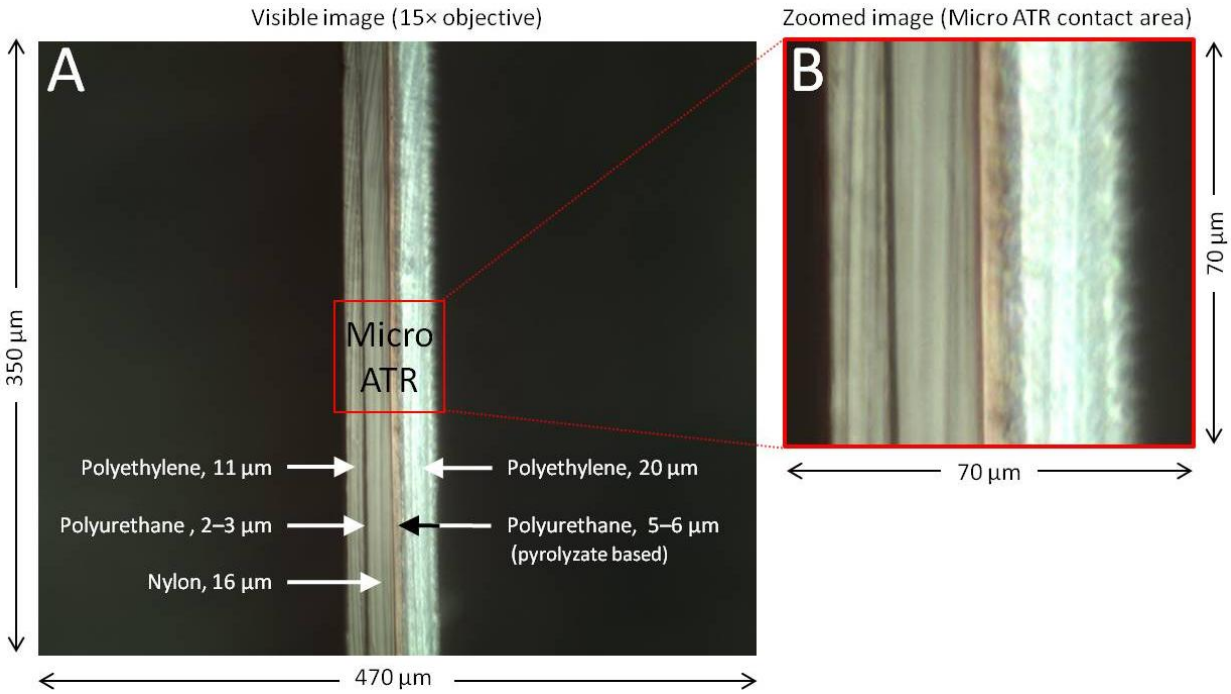


Figure 4. Optical images: A—the full field of view visible through microscope, annotated with the chemical composition and approximate thickness of the various layers in the sample; and B—zoomed image corresponding to the contact area of the Micro ATR

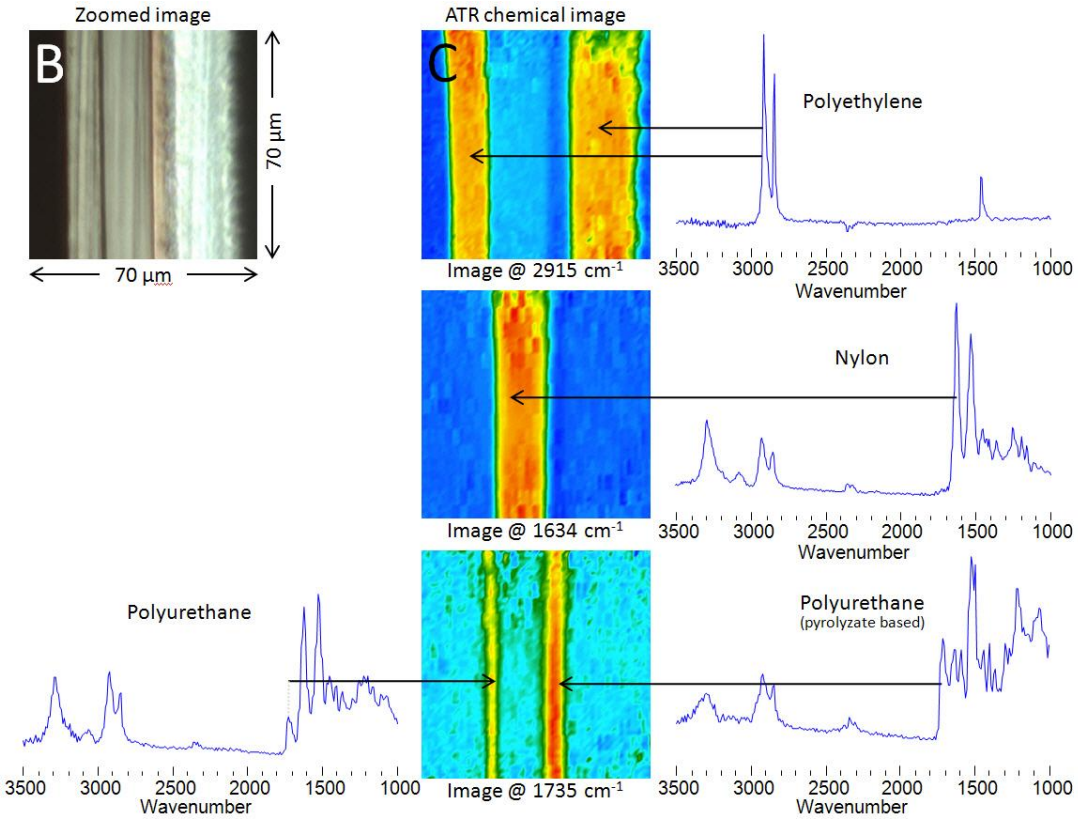


Figure 5. Identifying layers: B—as per Figure 4, above; and C–three chemical images created with different wavenumbers to highlight the main layers and tie layers with corresponding representative spectra as indicated by the arrows. Note: All spectra are shown in absorbance units, with axes omitted for clarity

A visual inspection of the sample using the standard binocular or internal visible camera revealed the sample to be a polymer film containing three main layers with two adhesive layers (Figure 4).

A summary of the results is presented in Figure 5. This shows how the three main layers are clearly identified: a 16-micron thick layer of nylon sandwiched between two layers of polyethylene, 11 and 20 microns in thickness.

However, as demonstrated, the power of Micro ATR chemical imaging with an Agilent FPA detector is in its ability to measure layers as thin as a few microns. Two tie layers were clearly identified and easily determined as being composed of subtly different polyurethane adhesives. The thinner of the two polyurethane layers was only 2–3 microns across and the pyrolyzate-based layer was thicker at 5–6 microns. The measurement of both these layers would be impossible with any other technique other than micro ATR chemical imaging on the Agilent Cary 620 FTIR chemical imaging system.

Summary

There are two clear benefits to analyzing polymeric laminates using Agilent's Cary 620 FTIR chemical imaging system:

1. Analyze ultra-thin samples without resin embedding

Through the use of Agilent's unique "Live ATR imaging", ultra-thin films of 50 microns or less can be measured as-is with Micro ATR chemical imaging.This avoids the need for any of the traditional and complicated resin embedding requirements. As such, instead of waiting hours for resin to cure and then spending time cutting and then polishing the surface, multiple samples or multiple locations on one sample can be measured in a few minutes.

2. Unrivalled spatial resolution

In combination with the use of a FPA detector*, Agilent's unique Micro ATR design provides for a pixel size of 1.1 microns that allows ultra-thin adhesive layers as narrow as two microns to be identified. This level of spatial resolution provides unrivalled levels of detail and chemical information to assist in the most complicated and difficult sample measurements.

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