

FT-IR Imaging

Author

Jerry Sellors, Ph.D.

PerkinElmer, Inc.
Shelton, CT 06484 USA

ATR Imaging of Laminates

Introduction

The use of polymer laminates is widespread in many industries, and their structure and composition vary greatly. Individual layer thicknesses can range from less than 4 microns to many tens of microns or more. Transmission infrared microscopy is an excellent tool for the study of these materials and widely employed, along with other micro-spectroscopy techniques such as Raman.¹

ATR imaging is a relatively new technique offering additional advantages compared with other FT-IR imaging methods, and is poised to become highly useful for laminates studies. For successful FT-IR microscopy, it is necessary to avoid too strong FT-IR infrared absorption by cutting the samples into thin sections (~10 micron thickness). Presenting samples in this manner is quite challenging from a practical viewpoint, and maintaining integrity of the sample can be difficult. In addition, the presence of the sample of finite thickness in a highly converging FT-IR beam can lead to issues that can limit the spatial resolution achievable² regardless of microscope used.

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to avoid too strong FT-IR infrared absorption by cutting the samples into thin sections (~10 micron thickness). Presenting samples in this manner is quite challenging from a practical viewpoint, and maintaining integrity of the sample

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resolution achievable² regardless of microscope used.

ATR imaging can overcome some of these limitations and resolve detail which is difficult, if not impossible, to observe using conventional FT-IR microscopes. First, as a reflectance

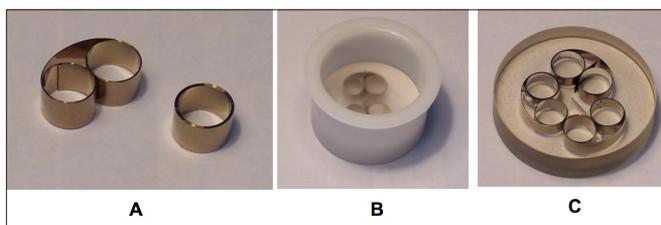


Figure 1. Fixing and embedding laminate samples.

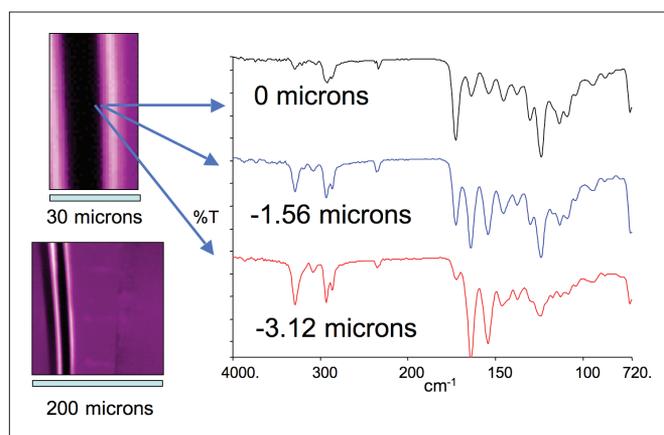


Figure 2. Spectra across layer boundary.

technique, the samples need not be cut into such thin cross sections, making it easier to conserve the integrity of the samples. Typically, samples are mounted in an embedding resin or between blocks and polished to a flat surface. Second, the amount of sample interrogated by the FT-IR beam is relatively low – of the order 1-2 microns using germanium ATR crystals. Images tend to be sharper and spectra show fewer artifact problems since they do not suffer the same beam divergence issues as in transmission through the samples in air.² Another potential problem with transmission work is when samples are presented as thin films. Multiple reflections within the sample can lead to interference fringe artifacts or ‘channel spectra’ superimposed on the measured spectra. This problem is not evident with ATR work. Another major advantage with ATR imaging is the ability to measure with higher spatial resolution than transmission imaging.³ The description and measurement of spatial resolution is described in another technical note⁴ where it is shown that a resolution of less than 4 microns is achievable with ATR, whereas the physical diffraction limit for transmission work is typically 3-4 times this figure in the mid-infrared fingerprint region – and that is assuming the sample limitations described above can be overcome.

An ATR imaging accessory has been developed for the PerkinElmer® Spotlight™ FT-IR imaging system which can deliver these advantages.³ The device uses a germanium cone which is pressed against the cross section of the laminate. One important feature of this accessory is the relatively large tip area. The standard tip diameter of ca. 500 microns means that many more samples can be scanned over the entire laminate structure using a single contact with the sample. In addition, a larger diameter of ca 1200 microns diameter is available. With other devices using much smaller active areas, multiple impressions into the sample would be needed to cover the entire thickness of the sample.

This note describes use of the ATR imaging accessory to measure polymer laminate samples, to show the level of detail that can be revealed routinely, and to provide some practical considerations for laminate measurements using the ATR technique.

Experimental

Sample Presentation: To obtain good ATR images, the sample must be brought into close, uniform contact with the ATR crystal across the entire area to be imaged. This requirement is particularly important and becomes increasingly so for measurements at shorter FT-IR wavelengths (e.g., the C-H stretching fundamental region at ca. 3 microns). This is because the evanescent wave at the crystal/sample interface decays more rapidly at higher frequencies.³ To achieve this,

the laminate needs to have a flat surface at the point of contact, and be adequately supported to avoid distortion as the sample is pressed against the crystal.

A number of techniques have been explored and, presently, the preferred techniques involve (a) embedding the sample in an appropriate resin and polishing the surface and (b) clamping the sample between two blocks and polishing. We have found in general that method (a) provides slightly superior consistency of sample quality and is ultimately easier from a practical perspective despite initial impressions to the contrary. The sample is clamped vertically in a spring clip (Figure 1A), placed in a mold (Figure 1B), and set in an epoxy or other resin to a depth of ca. 1-2 mm above the clip and below the edge of the sample. After curing, the top surface is cut and polished to a flat surface. Polishing typically involves use of lapping paper with distilled water at grit sizes of ca. 30 microns down to ca. 1 micron to produce a smooth, highly polished surface (Figure 1C). The thickness of the polished block is ca. 5-8 mm. This is placed directly on an anvil on the ATR accessory and the anvil is raised to bring the sample into firm contact with the crystal. Using the embedding technique, there is of course some risk of spectral interference from the resin in the images, but in practice (provided the materials are chemically distinct) this does not create a problem in the subsequent data analysis. Samples of this nature usually have a clearly defined edge and the data analysis software 'Hyperview' incorporates a feature to readily mask out pixels due to the embedding material from the image analysis.

The Spotlight system typically runs with scan conditions between 1-16 scans per pixel with a spectral resolution of 4-16 cm^{-1} for these samples. The data collection software allows rectangular image areas of various aspect ratios to be defined – a useful advantage of using small linear detector arrays. This is very useful for laminates where a long, thin image shape is often more efficient for scanning across a laminate sample. Image collection times are usually of the

order of minutes to tens of minutes depending on the conditions selected.

Results

Example 1: High Image Contrast

It is possible to obtain an idea of the contrast achievable by examining the spectral mixing between component spectra as one scans across a sharp boundary between two layers in the sample. Part of the instrument factory test for spatial resolution involves imaging across a special polymer material with a 'rooftop' cross section to provide a very distinct edge. The steepness of change of the FT-IR signal across the boundary is used to estimate spatial resolution.⁴ Laminate samples often provide sharp boundaries between materials. Figure 2 shows spectra of a polyamide layer at such a boundary, measured in steps of 1.56 microns across the boundary. One can see that at a distance of 3.12 microns, the degree of spectral mixing between the polyamide and neighboring layer is sufficiently low to allow excellent discrimination at these distances. In the FT-IR fingerprint region, materials a distance of ca. 3 microns apart can be clearly distinguished provided their spectra are sufficiently different.

Example 2: Packaging Material

Figure 3A shows the visible image of a packaging material section embedded in epoxy resin. In this example, the quality of finish due to polishing was relatively poor as seen by the surface scratches in the image. Despite this relatively poor surface finish, it was possible to generate good ATR images because (a) the sample was slightly compliant, allowing the crystal tip to be pushed into the sample, and (b) by appropriate data analysis to minimize the effects of the slightly varying contact across the image. Figure 3B shows the FT-IR-reconstructed image where the scratches are no longer apparent.

To obtain the reconstructed image, and with no prior knowledge of the sample composition, the image spectra

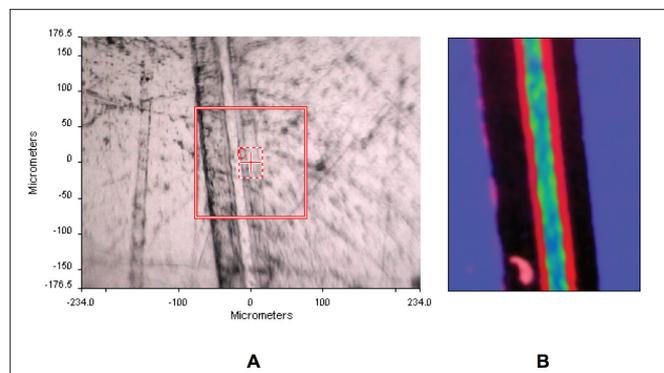


Figure 3. Visible and IR-reconstructed images from embedded laminate.

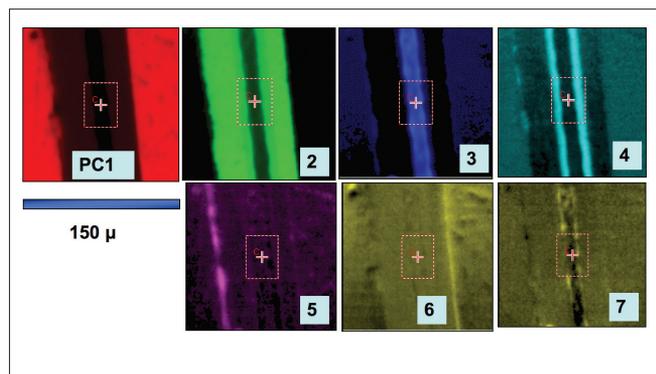


Figure 4. Principal component score images.

were derivatized, offset-corrected, and subject to principal components analysis (PCA). This technique effectively sorts the image spectra into an independent set of sub-spectra (principal components, or factors) from which the image spectra can be reconstructed. Ideally, if there are, for example, five layers present in an image of, say, 1000 spectra, then five sub-spectra would be sufficient to describe all the 1000 image spectra. In practice, more than five spectra are usually required due to the presence of impurities and other spectral contribution, such as baseline variations, and other artifacts, such as variable amounts of atmospheric absorption. This technique does filter out much of the random noise in spectra very effectively without broadening the spectral features due to the sheer numbers of spectra contained in the image; hence, it is a very useful tool for assisting exploratory studies where survey images are required in the shortest time possible. The amounts of the principal components in the original image spectra, or scores, are calculated at each pixel, and the resulting score images are extremely useful in enhancing the FT-IR image contrast. For this sample, the first seven PC score images are shown in Figure 4. Here, the major layers are all accentuated using PCA, along with some minor, more subtle features which will be described. The first score

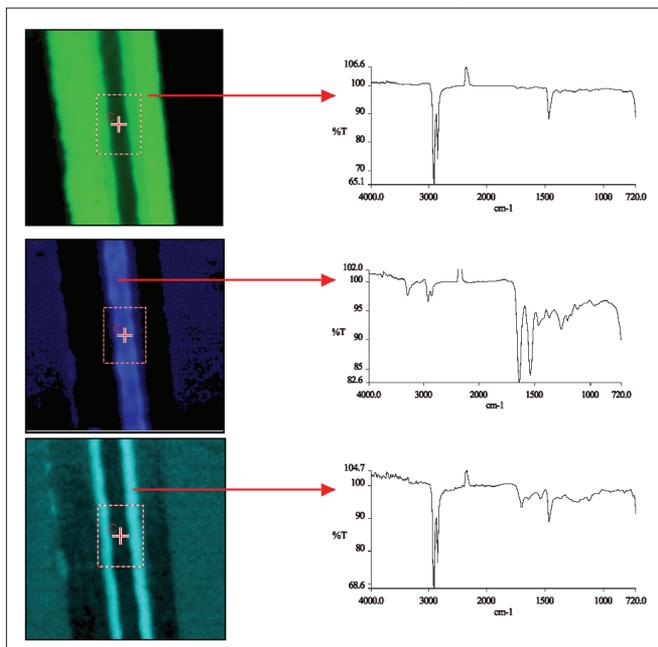


Figure 5. Score images for PCs 2, 3, and 4.

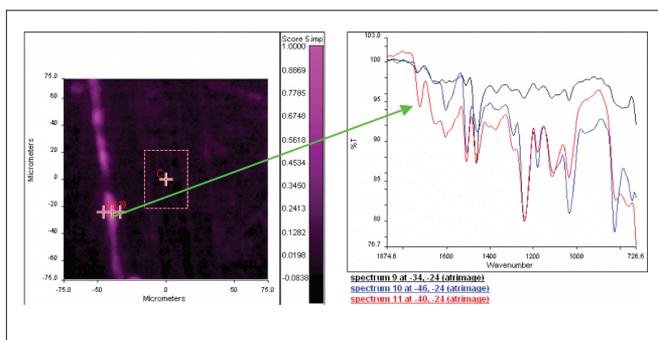


Figure 6. Score image for PC5.

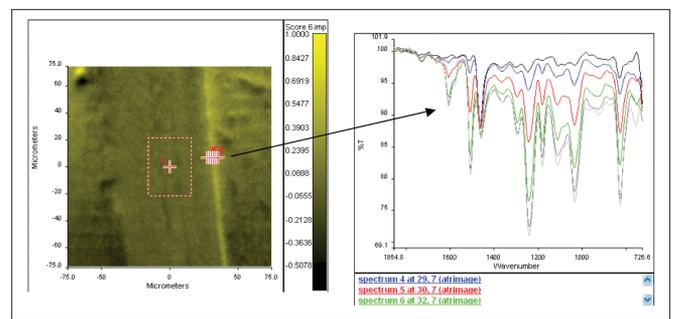


Figure 7. Score image for PC6.

image, PC1, is due to the embedding medium.

The second and third PC score images in Figure 5 show the major laminate layers, a polyethylene and polyamide with intermediate layers ca. 6 microns in thickness, sandwiched by the PE and PA, as revealed in the PC4 image. Here, the layers are readily identified by examination of the underlying raw image pixel spectra. In addition, the features due to the minor variance are shown in the PC5 and PC6 score images in Figure 6. The PC5 image shows a feature of 3-4 microns thick, close to the outer edge of the sample. Using the Spotlight Overlay Manager software, it is possible to view the raw spectra underlying these features, tracking through the feature at steps of 1.56 microns. In the layer itself, there are unique carbonyl features in the spectra which are not present on either side of the layer, thus confirming the distinct chemical composition of the layer. This can be compared with the situation in Figure 7. Here, the PC score image also reveals a 'layer'; however, no distinct chemical

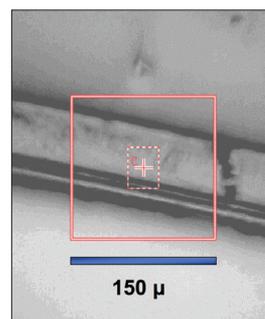


Figure 8. Visible image of laminate with thin adhesive layer.

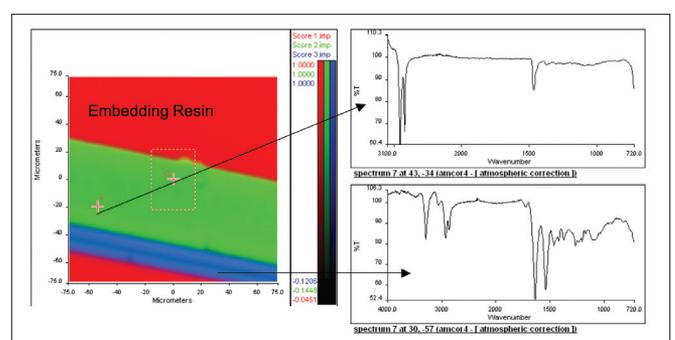


Figure 9. 1st three principal component score images overlaid.

feature appears on examination of the spectra throughout the layer, rather a relatively smooth gradation in spectral intensity from one material to the next. The inference here is the presence of a physical boundary such as a ridge in the sample itself rather than a distinct chemical constituent.

Example 3: Revealing Fine Detail

This example shows a laminated film with common components but with intermediate layers of less than 5 microns in thickness. As with the previous samples, the material was embedded in resin and polished. The ATR image was collected over a 150x150 micron area using a spectral resolution of 8 cm⁻¹. Figure 8 shows the visible image of the sample with the ATR image area highlighted by the red boundary. The image was analyzed using principal components analysis in the 'Show Structure' function in Spotlight and peak height/ratio methods. The overlaid PC score image (Figure 9) shows the embedding material readily differentiated and the major layer (polyethylene) shown in green. Of interest in this example was the layer structure immediately below the thick PE layer. Here, there are more than three chemical constituents present in the image. With three or less components, using a simple red/green/blue (RGB) representation to view the combined image works well with the human eye. But attempting to show more than three components/colors in such an overlaid image can lead to problems when there

is overlap between constituents. The overlapped pixels could be represented as the average of the contributing pixels: white, black, or other ways. This invariably confuses image interpretation. The Overlay Manager function in Spotlight has the ability to change the rules for displaying pixels where overlap occurs, for example, giving priority to the highest intensity color and thereby changing the image contrast. Used in conjunction with examination of the underlying spectra, this feature can be very useful in enhancing contrast. Figure 10 shows the resulting score composite image where, first, the image is shown with colors averaged in regions of overlap and, second, where the pixel colors are set by the most intense component in overlap regions. The improvement is quite striking, and overlaying the color-enhanced image with the raw data confirms that real chemical differences are observed within the different colored regions (Figure 11). Once one is satisfied that all the layers are revealed, it can be helpful to overlay the individual images and adjust the brightness and contrast of the individual layers to generate the most appropriate display for reporting purposes. Figure 12 shows such a composite created from the individual PC score images after exporting to the ImageJ public domain software package.⁵

Discussion

These examples demonstrate the measurement capability of the ATR imaging accessory with polymer laminate materials.

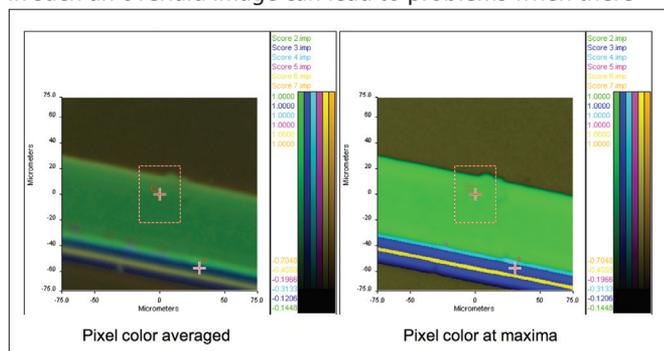


Figure 10. Use of color overlay options to enhance detail.

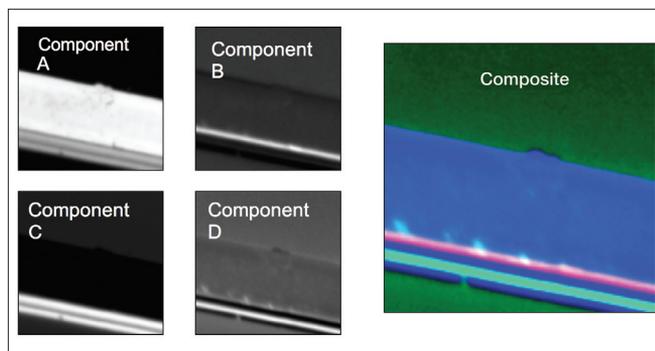


Figure 12. Composite image.

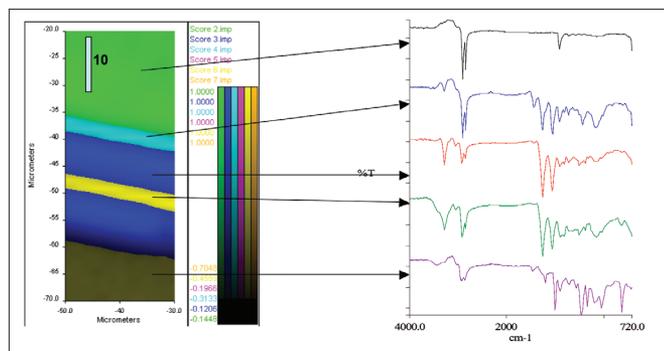


Figure 11. Spectra from individual layers.

With these examples, the sample embedding technique works well with little or no sample degradation. When information on the film constituents is not available, principal components analysis can be useful (compared with peak height/ratio methods) for analyzing survey images and helps reveal fine structure. It is, however, advisable to view the derived score images in conjunction with the raw data to verify the basis for the calculated image structure, as the PCA can effectively 'find' physical and morphological structure in the sample, which can be confused with chemical differences. For presentation of calculated images, it is worthwhile to consider alternative mechanisms for displaying pixels in overlap regions, provided again that the results are checked with the raw data to confirm the contrast revealed.

The data quality obtained with this system is generally good enough to be used directly with commercial spectral search libraries to assist interpretation, which has been performed successfully with a number of samples not reported here. When using standard libraries containing spectra scanned in transmission, search results can potentially be improved by applying ATR correction software to correct for the wavelength dependence of ATR absorption prior to spectral searching.

Conclusion

Using the Spotlight imaging system, the ATR imaging technique adds a number of benefits compared with the tried and tested method of transmission FT-IR imaging for polymer laminate samples. In addition to somewhat simpler sample presentation and lower risk of spectral artifacts, such as interference fringes, ATR imaging can provide improved spatial resolution. Individual layers of 4 microns or less can be identified. This is particularly important for a number of laminate materials where adhesives and other components may have thicknesses less than 5 microns. As such, use of the technique is likely to grow significantly in laminate studies in the coming years.

References

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PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com



For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

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