Combined FTIR and Raman microspectroscopy analysis of laminates

Multilayer polymer laminate packaging materials are carefully engineered composite materials in which different polymer layers are selected to provide specific physical and chemical characteristics. This way, it is possible to customize properties such as mechanical strength and flexibility and to add barriers to environmental factors such as gases, moisture, and light. There is considerable variation in the thickness of the different polymer layers, ranging from a micron or less to more than 100 microns thick.

Confirming the identity of the various layers, as well as the thickness, is important for quality assurance and failure analysis, as well as for the reverse engineering of unknown multilayer polymer materials. Both Fourier transform infrared (FTIR) and Raman spectroscopy can be used to identify and distinguish among a wide range of different polymeric materials. When these techniques are coupled with a microscope, they are uniquely suited for the analysis of the individual layers in such multilayer materials.

FTIR and Raman microspectroscopy are often regarded as complementary techniques. Both are vibrational spectroscopy techniques that provide information about chemical identity and molecular structure, but there are some distinct differences. FTIR selectivity is based on dipole moments, so it tends to be better at emphasizing the different functional groups found in polymers, such as carbonyls, esters, amides, and hydroxyl constituents. There also tends to be a greater number of FTIR libraries available, which is an advantage in the identification of unknown materials. Raman selectivity is based on polarizability and tends to emphasize polymer backbones as well as delocalized bonding such as aromatic structures. Raman spectroscopy provides easier access to lower wavenumber parts of the vibrational spectrum, making it is easier to observe molecules with heavier atoms, such as inorganic pigments. Because visible Raman spectroscopy utilizes visible lasers, it can achieve better spatial resolution than FTIR microspectroscopy. While both techniques have advantages and disadvantages, they are both very effective for the analysis of individual layers in multilayered polymer packaging materials.

This technical note will compare the results of the analysis of a cross-section of a multilayer polymer laminate using both FTIR and Raman microspectroscopy. It was necessary to obtain a thin cross-section for FTIR transmission analysis. While this was not necessary for the Raman analysis, the same cross-section was used for both analyses to avoid any potential variations that might arise from different sample preparation methods.

Experimental

The cross-section of the multilayer laminate was prepared by sandwiching the polymer film between two rigid layers of polytetrafluoroethylene (PTFE). This assembly was clamped in a holder, and thin cross-sections were obtained using a Thermo Scientific™ Shandon Finesse™ E+ Microtome. Cross-sections of the multilayer polymer film were easily separated from the PTFE and were positioned flat on a barium fluoride window for analysis. The FTIR microscopy analysis was carried out in transmission mode using a Thermo Scientific™ Nicolet™ RaptIR™ FTIR Microscope, and the Raman analysis was done using a Thermo Scientific™ DXR3xi Raman Imaging Microscope.

DXR3xi Raman Imaging Microscope and Nicolet RaptIR FTIR Microscope.

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FTIR analysis results

The Nicolet RaptIR FTIR Microscope makes finding the sample on the window simple by first quickly collecting a high-quality visual mosaic of the entire window using a 4X visual objective and then automatically switching to the 15X infrared objective. The initial mosaic provides a visual guide to allow the user to find samples and areas of interest, and the 15X objective allows for more detailed visual mosaics, as well as infrared analysis. Figure 1 illustrates this workflow, showing both the large 4X visual mosaic as well as the higher magnification visual mosaic. The defined area shown in Figure 1 is the portion of the cross-section that was analyzed. The aperture was 5 microns in the direction perpendicular to the polymer layers, and spectra were collected across the cross-section using 2-micron steps.

Figure 2 shows an FTIR image based on a multivariate curve resolution (MCR) analysis. This analysis compares each spectrum to all the other spectra in the image and groups similar spectra together as components. The various components are assigned a color to generate the image. In this case, there are five different components (blue, green, light blue, yellow, and red) and six different layers. The advantage of the MCR analysis is that no prior knowledge of specific spectral features is required for the analysis.

These results can be used as a starting point for utilization of some of the other profile choices that might better define the various layers. The FTIR images in Figure 3 are based on correlation profiles using the spectra shown as the reference spectra. Searching the spectra against libraries can help to identify the various layers. Layer 5 was identified as poly(propylene-ethylene) by comparison of the spectrum to spectra from layers 1 and 6. The thicknesses of the various layers were measured using the ruler tool provided in the software. In this way, it was possible to not only identify the various layers in this multi-layer polymer film but also to determine the thickness of each layer.

Raman analysis results

The same laminate sample was analyzed using a DXR3xi Raman Imaging Microscope. Figure 4 shows the visual mosaic image obtained using a 50X objective on the Raman microscope. The defined area indicates the portion of the cross-section that was analyzed. The MCR image generated from the Raman spectra is very similar to what was seen in the FTIR analysis, in that there are five components and six layers.

Figure 3: Representative FTIR spectra from each of the polymer layers along with associated correlation FTIR images that show the locations of the different types of polymeric materials. The materials were identified by spectral searching against commercial libraries, and the thicknesses of the layers were determined using the ruler option in the software.
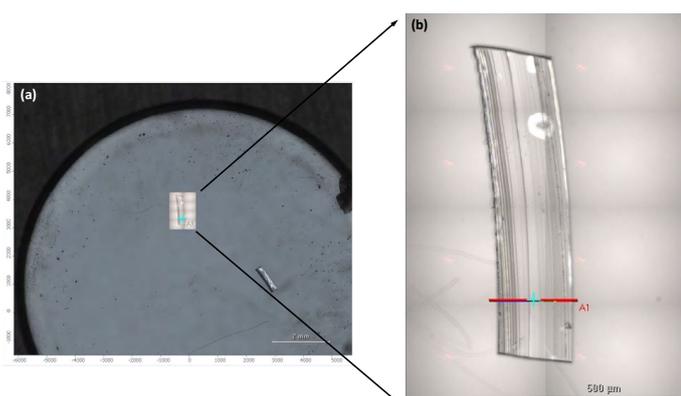

Figure 1: (a) Initial visual mosaic image collected with a 4X visual objective showing essentially the entire barium fluoride window. This view is used to locate the cross-section on the window. (b) Second visual mosaic of the cross-section collected with the 15X infrared objective. Area A1 indicates the portion of the cross-section that was analyzed.
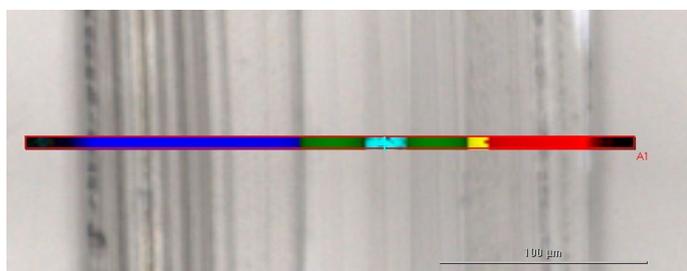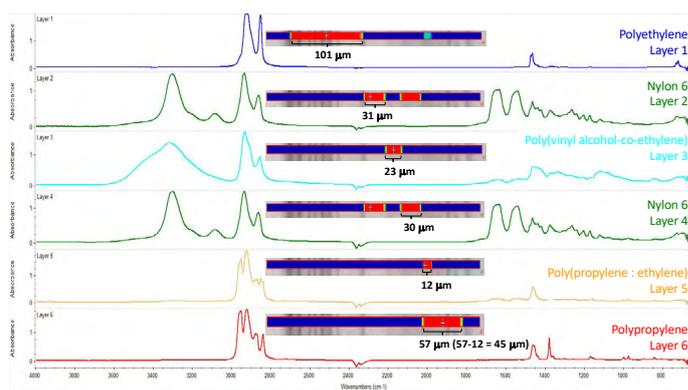

Figure 2: MCR FTIR image of the cross-section of the multilayer polymer film. Each color represents a different polymer material; there are five different polymer materials and six layers.
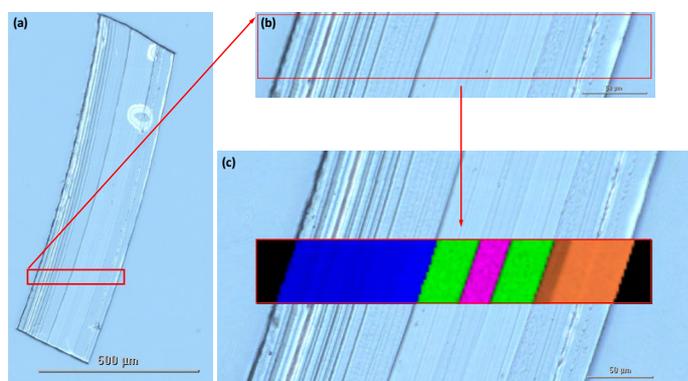

Figure 4: (a) Visible mosaic of the cross-section collected using a 50X objective on the Raman microscope. (b) Area on the cross-section selected for Raman analysis. (c) MCR Raman image showing five different polymer materials and six layers.

Each layer of the sample was defined using correlation profiles, and the results of those profiles are shown in Figure 5. It was possible to identify the various layers in the laminate by searching against Raman spectral libraries, but the Raman spectra lack the strong spectral features associated with the polar functional groups that were so readily apparent with the FTIR spectra. The N-H peaks in the nylon spectra are visible, but their appearance is much weaker in the Raman spectra compared to the FTIR spectra. Identification is even more difficult with the poly(vinyl alcohol-ethylene) layer because the O-H peak is not apparent in the Raman spectra.

It was still possible to get a library match for this spectrum, but the match was not nearly as definitive as it was with the FTIR spectrum. Conversely, the identification of the polyethylene in the poly(propylene-ethylene) layer was more readily apparent from the Raman spectra because of the presence of the 1295 cm^{-1} peak that is associated with polyethylene and that does not overlap with any polypropylene peaks. The polyethylene and polypropylene peaks in the FTIR spectra overlap quite a bit, so the differences are more subtle in these spectra.

The thicknesses of the layers were measured using the ruler tool in the software of the Raman microscope, and the thicknesses of the layers were very consistent with the values determined in the FTIR analysis. While the Raman analysis provided higher resolution, that did not really affect the determination of the layer thicknesses.
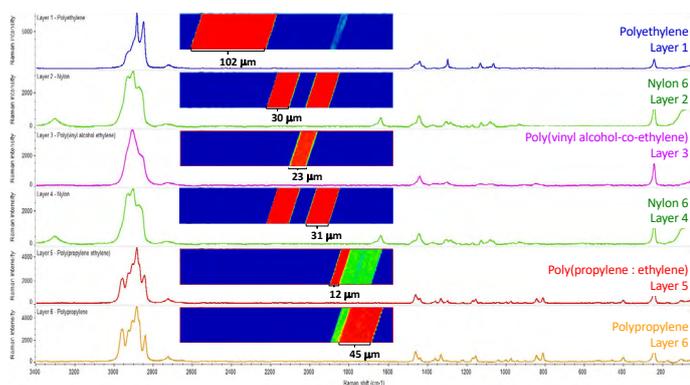

Figure 5: Representative Raman spectra from each of the six layers and the corresponding Raman correlation images showing the location of each type of polymer material. The polymer layers were identified by spectral searching against commercial libraries, and the thicknesses of the layers were determined using the ruler tool in the software.

Conclusions

FTIR and Raman microspectroscopy provided comparable results for the analysis of a multilayer polymer film. The collection times for the two data sets were similar. The step size for the FTIR mapping and the image pixel size for the Raman imaging were both 2 microns, and, clearly, any spatial resolution differences were not a factor in the analysis of this sample.

While the FTIR spectra had a slightly better signal-to-noise ratio, both the FTIR and Raman spectra were good quality and allowed for layer identification as well as layer thickness determinations. The differences in the selection rules for FTIR and Raman means that there are variations in peak intensities associated with molecular functionalities. This means that each technique highlights distinct aspects of the various polymers in the laminate. For instance, the poly(vinyl alcohol-ethylene) layer was more readily identified with the FTIR data, but the presence of the small amount of polyethylene in the poly(propylene-ethylene) layer was more apparent in the Raman data. The same cross-section was used for each of these analyses, but the Raman analysis is not a transmission technique, so it is not necessary to prepare a thin cross-section for use with the Raman microscope. This means that sample preparation for Raman analysis can be simpler and save time and effort.

There are other considerations such as fluorescence, resolution of ultra-thin layers, and the analysis of pigments that might drive the choice in one direction or another Clearly, both the Nicolet RaptIR FTIR Microscope and the DXR3xi Raman Imaging Microscope are excellent choices for the analysis of multilayer laminates.

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