Application Note: 51718

Confocal Raman Microscopy Analysis of Multilayer Polymer Films

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Key Words

- **Nicolet Almega XR**
- **DXR Raman Microscope**
- **Confocal Raman Microscopy**
- **Dispersive Raman Microscopy**
- **Laminates**
- **Multi-layer Films**
- **Polymers**

Abstract

Polymer multi-layer films are used in a variety of industries and are made by co-extrusion and lamination techniques. Strictly controlling the quality and composition of these films is important both to the manufacturers of polymer film and to the industries using them. Raman microscopy provides an excellent means by which to accomplish this. The technique is highly sensitive to small changes in molecular backbone and branching configurations and is thus ideal for polymer identification. Raman requires almost no sample preparation. Confocal analysis generates rapid depth profiles with a 2 µm spatial resolution, while cross-sectional analysis of multi-layered films provides 1 µm resolution or better. Spectral differences can be exploited to estimate thickness of the constituent layers, while searching spectral libraries identify their composition. While not shown in this application note, the confocal analysis and high spatial resolution of Raman microscopy also makes this technique ideal for identifying the source and identity of defects and inclusions in polymer films. The results in this application note were generated using the Thermo Scientific Nicolet Almega XR. The Thermo Scientific DXR Raman microscope is also ideal for these applications.

Introduction

Polymer multi-layer films are used in variety of industries. In food packaging, for example, polymer laminates are used not only to protect the food, but also to retain aroma and flavors, and to extend shelf life. Multi-layer films are produced using co-extrusion and lamination techniques. Some of the problems that can occur during film manufacture include the introduction of defect particles and separation of the layers. Current analytical methods examine the materials during and after production include NMR and DSC. Vibrational spectroscopy is a valuable addition to these techniques as it provides definitive molecular information. Raman spectroscopy is complementary to FT-IR spectroscopy and offers advantages that include higher spatial resolution and easier sample preparation.

Dispersive Raman spectroscopy uses visible (400–785 nm) lasers for sample excitation. In comparison with FT-Raman, the use of visible lasers permits higher spatial resolution (better than one micron) and, since Raman emission is proportional to $1/\lambda^4$, much greater sensitivity. Raman spectroscopy is sensitive to both chemical and physical properties and its unique selection rules generate a molecular fingerprint that is well-suited to material identification. The technique is particularly sensitive to molecular backbone and branching structures. This makes it ideal for polymer identification and defect analysis.

Experimental

In this study the Nicolet™ Almega™ XR, shown in Figure 1, was used to analyze the layers of a polymer multi-layer film. The DXR Raman microscope can also be used for this application and will give similar results. The Thermo Scientific OMNIC software suite provided the analytical tools used to estimate film thickness and composition. OMNIC™ is also invaluable for defect analysis and studies in layer cohesion.

Figure 1: Nicolet Almega XR Dispersive Raman spectrometer

Confocal Analysis

The confocal design of the Almega XR makes it possible to target individual layers in a multi-layered sample. The pinhole aperture at the entrance to the spectrograph allows only the Raman scatter from the focal point of the objective to reach the detector (Figure 2). By changing the

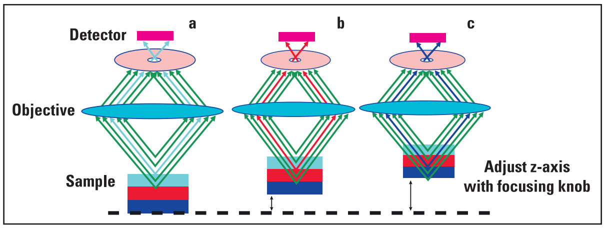

Figure 2: Confocal analysis. The pinhole aperture at the focal plane of the microscope permits only the Raman scatter originating from the focal point of the objective to fall on the detector. (a) the detector collects Raman scatter from the top sample layer; (b) after raising the sampling stage, the detector now collects Raman scatter from the middle sample layer; (c) the detector collects Raman scatter from the bottom layer.

position of the microscope stage in the vertical direction, confocal analysis can be used for depth profiling and can permit the analysis of individual layers of a sample while requiring little or no sample preparation. This technique is very effective for rapid identification of sample layers. Spatial resolution in the vertical direction for both the Almega XR and the DXR Raman microscope is < 2 µm.

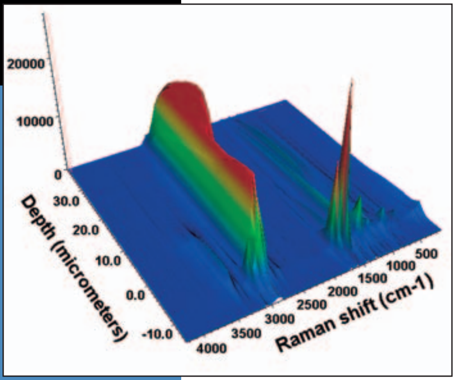

Figure 3: Waterfall display of the depth profile of a multi-layer polymer laminate sample

Depth profiles are commonly shown as a waterfall display and reveal spectral changes as the focal point passes through the sample. In the example shown in Figure 3, the sample appears to contain at least four distinct regions. The components can be identified by library searching and the thickness of the four layers monitored by following spectral changes.

Visible Microscopy

The Thermo Scientific Raman microscopes incorporate powerful research microscopes with advanced viewing capabilities that include brightfield and darkfield illumination, visual polarization and differential interference contrast (DIC). DIC is useful for observing multilayer films as it improves the contrast between different layers and helps to define the layer boundaries. By rotating a Nomarski prism in the DIC optics, the changes in the light interference result in pseudo three-dimensional images, giving rise to differing regions of color in the sample. In a polymer multi-layer material, this allows the user to selectively analyze different layers in a cross-section of the sample (Figure 4).

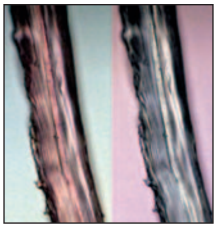

Figure 4: Differential Interference Contrast (DIC) video images of a multi-layer polymer laminate sample. DIC helps to improve visual contrast between the constituent layers. The sample was mounted edge-up on a reflective glass slide.

Sample Preparation

Cross-sectional Analysis

Most multi-layer samples are prepared for microscopic analysis by immobilizing the film in epoxy followed by carefully microtoming into micrometer-thin slices. This is necessary for an absorption technique such as infrared spectroscopy in order to prevent over-saturation of the bands. However since Raman is an emission technique, sample thickness is not a critical concern. The microtome slices can be much thicker, since only the cross-sectioned end will be analyzed. Samples can also be simply cross-sectioned, placed cut side up on a glass slide, and immobilized using a small piece of double-sided adhesive tape or putty. For this application note the microscope was focused on the sample edge and a line map constructed.

Depth Profile Analysis

The depth profile line maps were the easiest to collect. The film was simply immobilized on a slide and the depth profile map collected using a precision motorized stage with a Z-axis controller. The stage was moved in 1 µm steps and resolution of better than 2 µm was observed.

Results

Initial depth profile observations of the sample revealed the presence of six layers. Some of the layers were tens of microns thick, while others were much thinner. At the interfaces between the thinnest layers (1 – 3 microns) it was difficult to resolve the spectra of the individual layers. A line map was also constructed across a cross-section of the sample. Figure 5 shows a comparison of spectra extracted from the line map and from the depth profile, showing excellent agreement between the two ways of profiling the sample.

Analysis of Layer Composition and Thickness

Layer composition and thickness can be estimated from both the cross-section map and from the confocal depth profile of the sample.

The cross-sectional map takes advantage of the excellent spatial resolution that is achieved by both the Almega XR and the DXR Raman microscope. When samples are mapped using sufficiently small steps, layers of the order of 500 nm can be detected. The sample was placed cut end up on a reflective glass slide and analyzed using a line map across the sample. The resulting map is shown in Figure 6. A video image of the sample is in the upper right, a waterfall display of the spectra is shown in the upper left and the spectrum at the crosshairs of the video image is shown in the lower half of the figure.

In order to use a line map to calculate the thicknesses of the constituent layers of a multi-layer sample, it is convenient to select a spectral feature that is unique to a specific layer and calculate a profile of this feature across the line map. An example is shown in Figure 7. This profile was constructed using the corrected peak area of a Raman band centered at 1727 cm^{-1} in a spectrum of polyester. The profile shows that this band occurs only in the sixth layer of the sample. The thickness of the layer can be estimated by measuring the full width at half maximum of the profile of this band and was calculated to be 5 µm. Figure 8 shows similar results were obtained after performing a depth profile analysis of the sample and calculating the thickness of the polyester layer using the same peak at 1727 cm^{-1}. A similar approach was used to calculate the thickness of the other five layers in the sample.

The composition of the six layers was identified by using spectral search to compare the spectra from the layers with those in the Thermo Scientific High Resolution Raman Polymer Library. The calculated results are shown in Table 1 and are compared with data showing the actual thickness and composition of the sample.

Layer	Experimental Results Thickness	 Composition	Reported Results Thickness	 Composition
1	1.5 mil (40 µm)	Polyethylene	1.61 mil (40.9 µm)	LLDPE, linear low density polyethylene
2	0.1 mil (3 µm)	Polyethylene/vinyl acetate copolymer	0.08 mil (2.03 µm)	Polyethylene 1
3	0.2 mil (7 µm)	Vinyl OH	0.27 mil (6.86 µm)	Ethylene vinyl alcohol with ~48 mole % ethylene
4	0.7 mil (20 µm)	Nylon	0.79 mil (20.1 µm)	Nylon 6 with a small amount of nylon 6,6
5	0.1 mil (3 µm)	Polyethylene	0.09 mil (2.29 µm)	Ethylene alpha-olefin copolymer
6	0.2 mil (5 µm)	Polyester	0.14 mil (3.56 µm)	Polyester

Table 1: Multi-Layer Polymer Sample: Thickness and Composition of the Layers; Experimental and Reported Results

The calculated values match very well with the reported values and the results were comparable with those obtained using differential scanning calorimetry (DSC), and took less time to obtain because Raman microscopy is a single technique analysis. The spectral matches could have been enhanced by building a specific library against which to search the data, using spectra collected from the specific polymer formulations in use.

Conclusion

Dispersive Raman microscopy is an excellent technique for the analysis of multi-thin-layer polymer materials. The spatial resolution of the Almega XR enables the analysis and detection of layers less than one micron in thickness. The confocal optical design allows for quick identification of the layers, and the excellent spatial resolution in the x, y dimensions permits a more rigorous examination of the material by cross-sectioning.

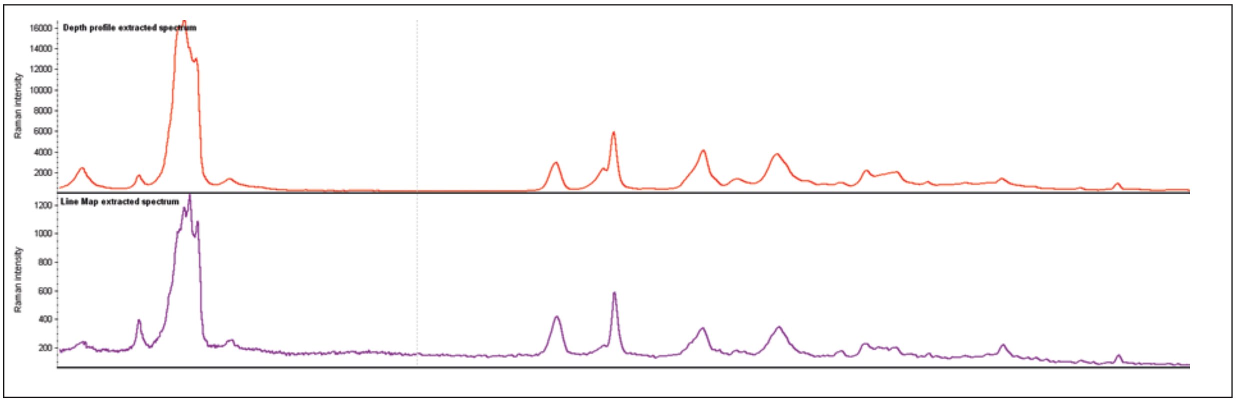

Figure 5: Comparison of spectra extracted from a line map and a depth profile of the multi-layer sample

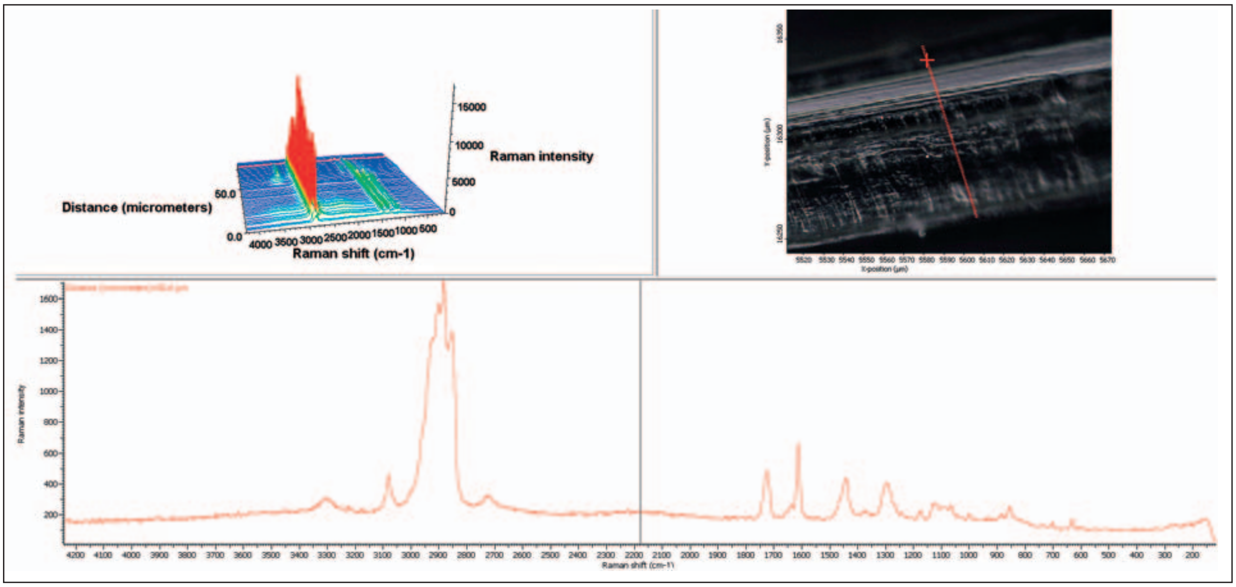

Figure 6: OMNIC Atlµs™ software display of raw data from a line map of a cross-section of the polymer multi-layer film. Top left: waterfall display of data. Top right: video image of multi-layer film. Red line shows the position of the line map. Lower section: spectrum collected at the point marked by the cross hairs in the video image.

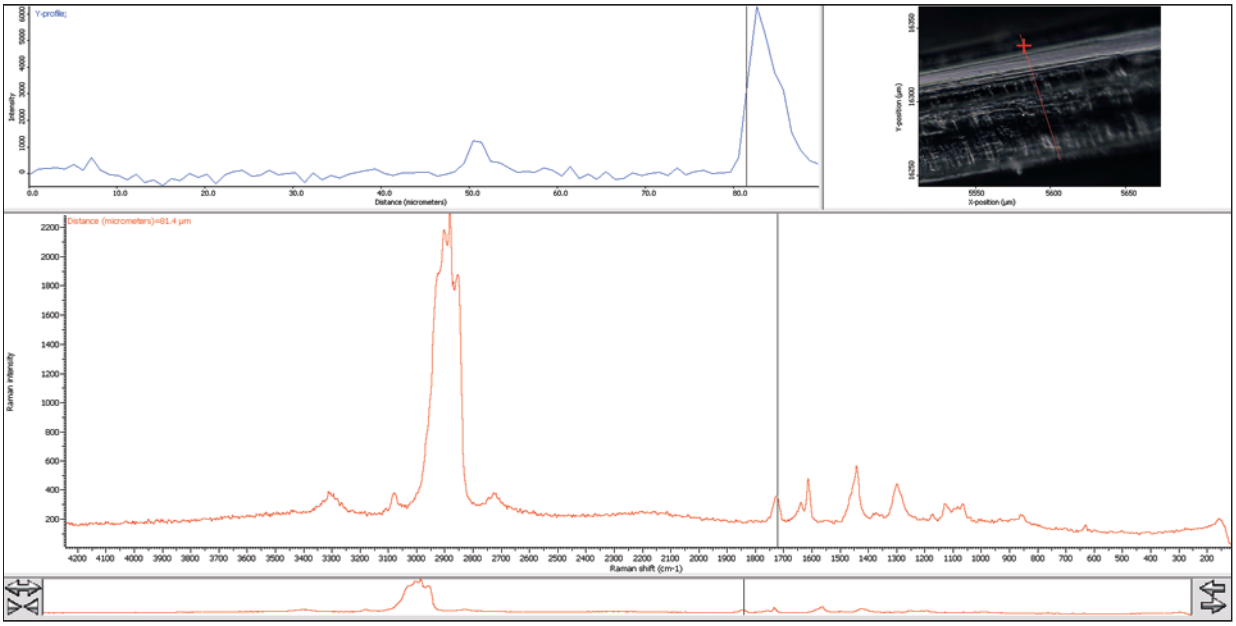

Figure 7: Data from the line map of the multi-layer sample shows the profile calculated using area of the peak centered at 1727 cm^{-1}. The width of the 6th layer of the multi-layer film can be estimated from the full width half maximum (FWHM) of the profile peak. Below: spectrum collected at the point marked by the cross hairs in the video image.

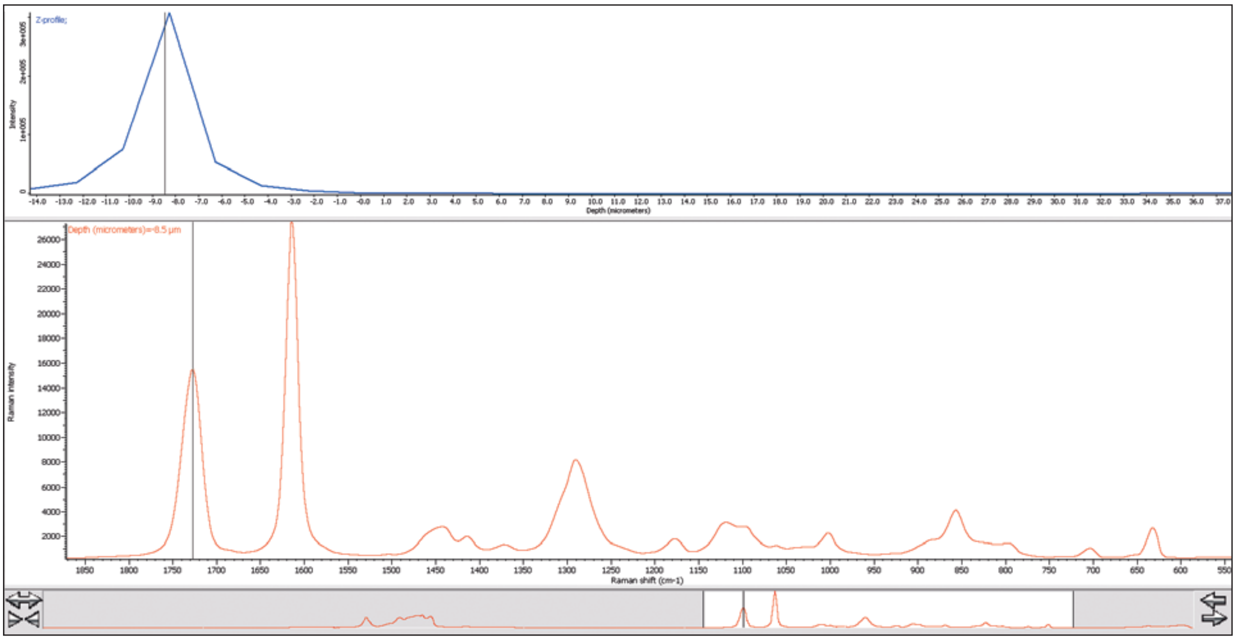

Figure 8: Data from the confocal analysis of the multi-layer sample shows the profile calculated using area of the peak centered at 1727 cm^{-1}. The width of the 6th layer calculated from the FWHM of the profile gives the same result as that obtained in Figure 7 from the cross section line map of this sample.

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