Application Note: 50832

Confocal Raman Microscopy Applications in the Polymer Industry

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Key Words

- Nicolet Almega
- Atlμs
- Confocal
- Polymer
- Raman

Overview

In any Raman application, the analytical signal is strongest from the point where the laser reaches a tight focus. This fact allows Raman spectra to be obtained from materials in bags, vials, or cuvettes by simply focusing the laser and collection optics at a point inside the sample container. Unlike absorption spectroscopy, the signal is not integrated over the whole optical path. The resulting spectrum only weakly shows features from outside of the in-focus region of the sample.

Different optical designs allow the size of the in-focus region to vary according to the application. For example, an optical system with a large depth of focus might be used to make the sample spectrum more representative of the total sample. On the other hand, if the goal were to characterize the nature of small domains within a sample, a small laser-spot size, and shallow depth of focus would be an advantage.

To provide the best ability to spatially resolve features within a sample, the Thermo Scientific Nicolet™ Almega™ XR and the Thermo Scientific DXR Raman microscope spectrometer systems include integrated confocal microscopes. A confocal microscope is an optical arrangement that inserts a limiting aperture in an image plane. The aperture allows the spectrograph to view a very specific region of the sample, producing a Raman spectrum characteristic of that region alone. Figure 1 illustrates how a confocal aperture improves spatial resolution.

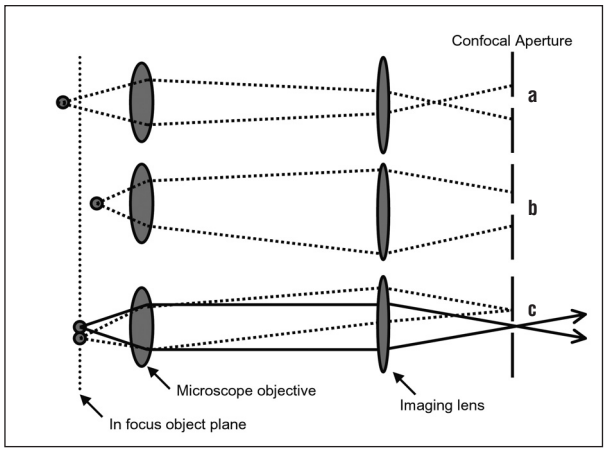

Figure 1: Dotted lines show ray traces demonstrating why the Raman signal, originating from points (a) deeper, (b) shallower, and (c) off axis from the in-focus and on-axis regions of the sample, was rejected by the confocal aperture. Only in-focus and on-axis portions of the sample, represented by the solid line, were passed onto the spectrograph.

Applications

As a first example, a dispersed release agent applied to the surface of a cellulose film product was examined under high magnification. The agent was observed as small crystals ranging from less than one micron to a few microns in size. The data in Figure 2 was obtained by first focusing the microscope on the film and then on a single crystallite. These results demonstrate how the confocal aperture allows analysis of a specific point while suppressing the contribution from the surrounding media. An almost pure spectrum of the surface particle, calcium carbonate, was obtained.

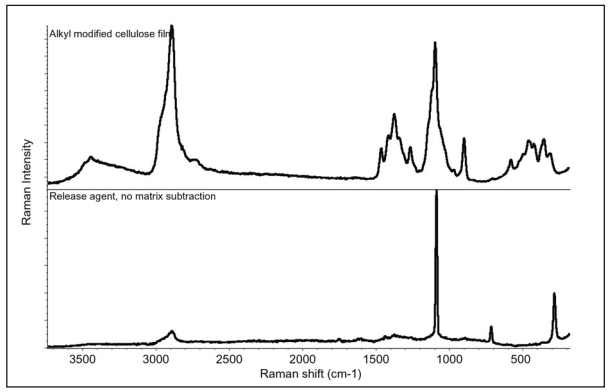

Figure 2: Components of the polymer film sample. The top spectrum represents the film that shows the characteristic feature of an alkyl cellulose product. The lower spectrum is from a small crystallite and was identified as calcium carbonate. Conditions: 633 nm Laser, 100X objective.

A small cluster of crystals was selected and mapped using Thermo Scientific Atlμs™ mapping software. Figure 3 shows the video image and the associated Raman map based on a response to the 1088 cm^{-1} band of calcium carbonate. Note the close correspondence of the particle shapes between the images. The quality of the image was maintained by a combination of high-spatial resolution and precision microscope stage control.

Using confocal Raman to explore the interior of the specimens nondestructively is one of the more powerful applications of the technique. Complex laminated polymer films can be examined quite easily by simply focusing into progressively deeper layers of the film. Figure 4 is a study of such a case. This polymer film was chemically modified and the nature of the modification was examined as a function of depth. The band at 1605 cm^{-1} is directly related to the modification.

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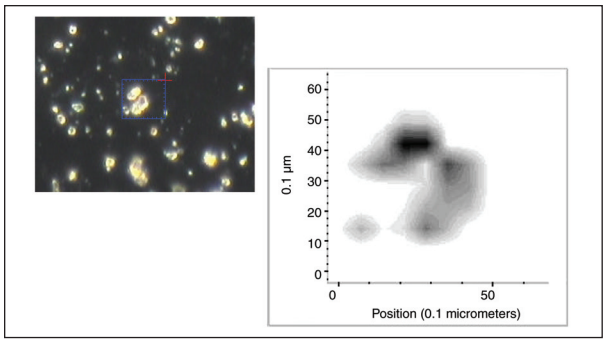

Figure 3: Video image and Raman response map of calcium carbonate crystals on cellulose film. The mapped portion of the specimen corresponds to the box at the center of the video image. Conditions: 633 nm Laser, 100X objective.

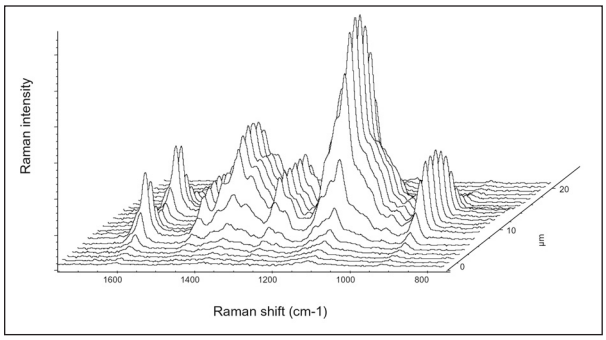

Figure 4: Series of confocal Raman spectra collected at progressive depths through a chemically modified cellulose based film. Conditions: 633 nm laser, 100X objective.

A profile based on the intensity of the 1605 cm^{-1} band is shown in Figure 5. The total film thickness was approximately 12 microns and the thickness of the surface modifications, estimated in this case from the zero crossings of the second derivative plot, was approximately 1.8 microns. The advantage of confocal Raman in this application was the ability to obtain spectra of the surface layers, in order to study the modification chemistry, and approximate the thickness of each layer. The analysis was completed without sectioning or damaging the sample.

The confocal technique does not require the buried structures to be distinct layers or domains. Figure 6 shows the results of probing the composition of a gel defect in a polyethylene film. These defects are sometimes referred to as "fish-eyes." The data shows a gradient rather than a distinct outer and inner composition. The ratio of the 2850/2885 cm^{-1} peaks decreases continuously as deeper regions of the defect are probed. The sample was moved a total of 45 microns in the progression. The distribution of C-H substitution represented by the ratio clearly is related to the formation of the gel. The normal polyethylene surrounding the defect has a structure similar to an intermediate case in the series.

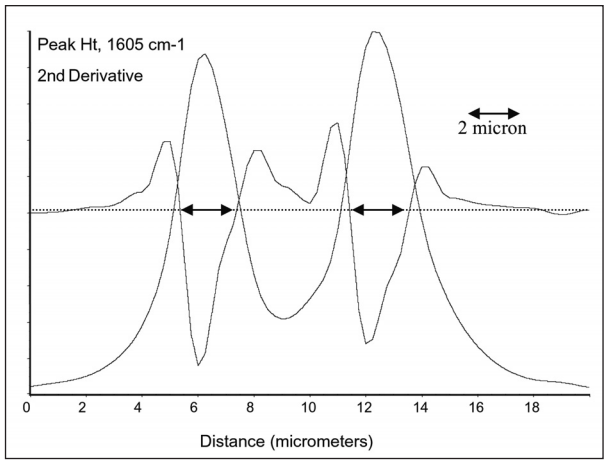

Figure 5: Raman response from the 1605 cm^{-1} band associated with film surface modification with the 2nd derivative of the profile. The plot can be used to estimate the order of the layers and approximate thickness.

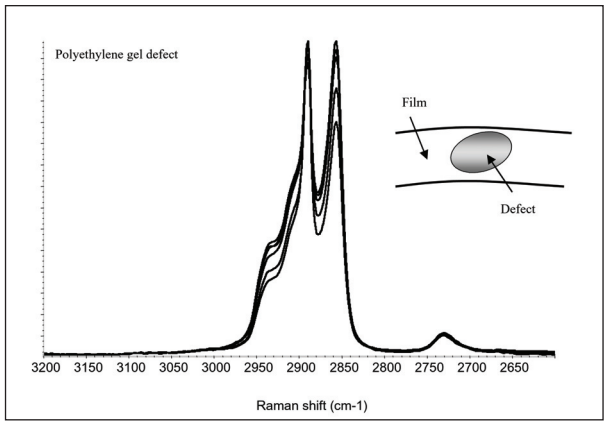

Figure 6: Series of spectra collected at progressively deeper points within a gel defect using Almega confocal Raman microscope. Conditions: 532 nm laser, 50X objective.

Conclusion

Raman spectroscopy, in general, is well suited for polymer studies. The sample may be in any form, including beads, films, or molded parts, and analyzed nondestructively with little or no preparation. Raman is sensitive to polymer microstructure along the backbone, crystallinity and conformation. Reliable quantitative methods are available to measure parameters such as copolymer ratios. As the popularity of confocal Raman microscopy grows, many other applications related to defect analysis, product characterization, and studies of competitive products will emerge.

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