Leveraging the lateral spatial resolution of a confocal Raman microscope to resolve micron to sub-micron layers in polymer laminates

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Keywords

laminates, polymer, confocal Raman microscope, spatial resolution

Application benefits

With a properly configured Thermo Scientific™ DXR™2 Raman microscope, it was possible to resolve a thin polymer layer with a thickness (≈0.4 µm) that's very close to the theoretical spatial resolution limit.

Thermo Fisher Scientific solutions

- DXR2 Raman microscope

- Thermo Scientific™ OMNIC™ for Dispersive Raman software suite

Introduction

Polymer laminates are used in a wide range of industries from food to pharmaceuticals. By adhering together multiple polymeric layers of different chemistry, physical properties, and thickness, desired chemical, mechanical and barrier properties can be achieved to suit different packaging applications. As the technological advancement and manufacturing sophistication continue to drive the production of more complex and thinner laminate structures, there is an ever-increasing demand on laminate analysis for product quality control, failure analysis, and competitive reverse engineering.

The analytical tools for laminate analysis include optical microscopy, differential scanning calorimetry (DSC), Fourier Transform infrared spectroscopy (FT-IR), and Raman spectroscopy. Confocal Raman microscopy, in particular, offers many advantages. Raman spectroscopy is sensitive to both chemical and physical properties. Its unique selection rules generate a molecular fingerprint that is well suited to material identification. Confocal Raman microscopy often utilizes short-wavelength visible and NIR (400 – 785 nm) lasers for sample excitation, which renders increased sensitivity because Raman signal intensity is inversely proportional to the 4th power of the laser wavelength. Furthermore, the spatial resolution is also inversely proportional to the laser wavelength. The shorter the wavelength, the higher the resolution.[1,2]

In this application note, two cases of polymer laminate analysis using a Thermo Scientific DXR2 Raman Microscope are presented. The implications of instrument configurations, including laser wavelength, magnification objective, and pinhole size, on lateral spatial resolution are discussed in details.

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Materials and methods

Two polymer laminate samples, A and B, were microtomed and cut into films. The microfilms were placed onto glass slides and pentane was added to flatten the microfilms. The glass slide was then placed on the microscope stage insert for Raman mapping. A Thermo Scientific DXR2 Raman Microscope was used for all analyses. A 532 nm laser was used and the laser power was set at 5 mW. A 100× objective and a 25 µm confocal pinhole were used. The Raman line map (27.4 µm) was collected with a 0.2-µm step size and contains 138 spectra. The Raman area map (3 µm [X] x 20 µm [Y]) was collected with 1 µm (X) and 0.2 µm (Y) step sizes and contains 584 spectra. Data acquisition and processing were done by Thermo Scientific OMNIC for Dispersive Raman software suite.

Results and discussion

Identification of the layers of polymer laminates using Raman microscopy can be done by confocal depth profiling and cross-section analysis. While depth profiling is advantageous in that it requires little to no sample preparation, cross-section analysis via line/area mapping offers superior spatial resolution, which lends itself to the identification of micron to sub-micron layers in polymer laminates.

Figure 1A shows the video image of microfilm A and the location where the Raman line mapping was performed (red line). The corresponding Raman line map is shown in Figure 1B. The Raman line map is displayed in a 2-D contour plot and reveals the compositional changes across different layers (y-direction). The rainbow color scheme of the contour plot reflects the intensity of the Raman peaks, with red indicating the highest intensity and blue the lowest. Based on the Raman spectral changes in the vertical direction, seven distinct layers were identified by library search: the layers 1, 3, 5 and 7 are polyethylene (PE), the layers 2 and 6 are polypropylene (PP), and the layer 4 is polyvinyl alcohol (PVA). The representative Raman spectra for those layers are shown in Figure 1C. No cross-contamination between the adjacent layers was observed, demonstrating an adequate spatial resolution to distinguish adjacent layers. The thickness of the thinnest layer (Layer 4) was estimated to be 1.2 µm based on the full width at half maximum (FWHM) method (Figure 1D).[3]
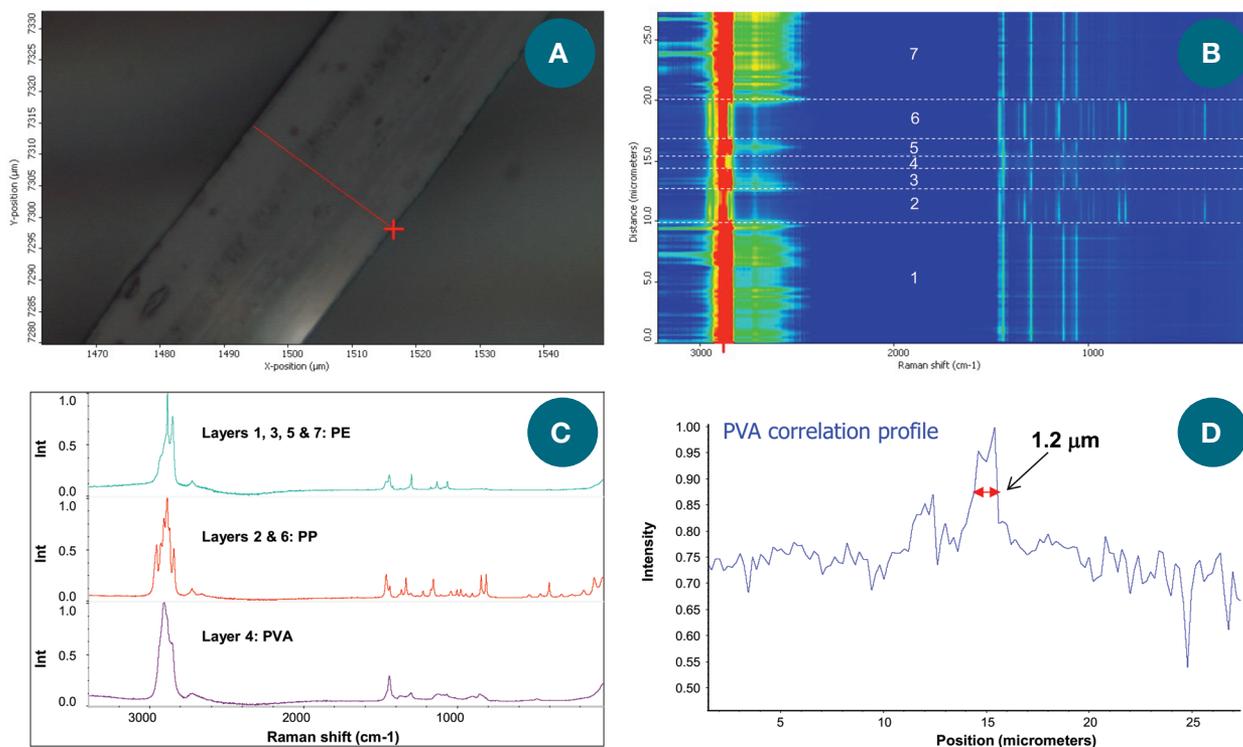

Figure 1. (A) Video image of microfilm A showing the region where Raman line mapping was performed (red line); (B) Raman line map of microfilm A; (C) representative Raman spectra of each layer. PE = polyethylene, PP = polypropylene, PVA = poly vinyl alcohol; and (D) Raman correlation profile obtained using a PVA reference spectrum.

Figure 2A-2C shows the 3-D Raman area images of microfilm B. PE, PP and PVA spectra were carefully selected from the map as the references to construct the Raman area images with correlation profiling. The red color indicates a high correlation with the reference material and the blue color indicates low correlation. Similar to microfilm A, seven layers are clearly identified: the layers 1, 3, 5 and 7 are PE, the layers 2 and 6 are PP, and the layer 4 at the center is PVA. In order to estimate the layer 4 thickness, a line map was first extracted from the area map, delineated by the white, dashed line in Figure 2C. The extracted line was then subject to

correlation profiling using a PVA spectrum from the map as the reference, and the result is shown in Figure 2D. The sharp peak at ~ 14.5 µm corresponds to the layer 4, with an estimated thickness of ~ 0.4 µm based on the FWHM of the profile peak.[3] It's important to note that the methodology described above relies heavily on the quality of the spectra as well as the spectral differences between adjacent layers. The layer thickness derived from the correlation profile should therefore be considered an estimate. Precise measurement of layer thickness requires such technique as scanning electron microscopy (SEM).
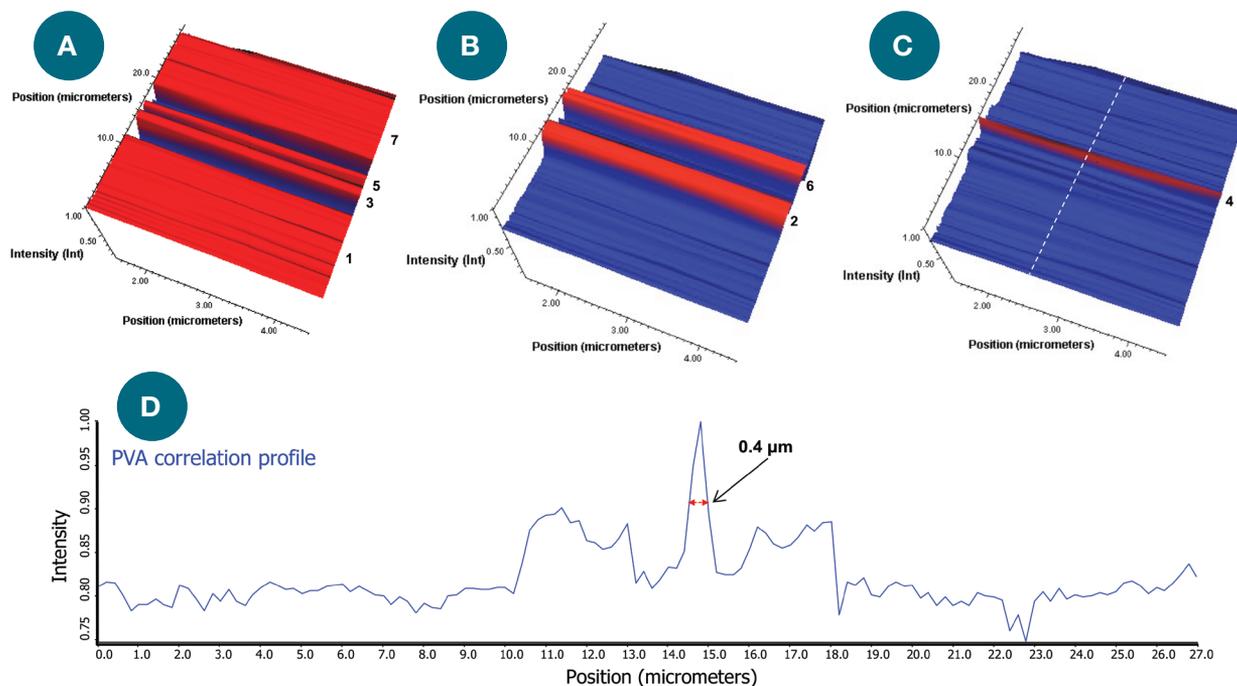

Figure 2. 3-D Raman correlation images for microfilm B. (A)-(C): Raman correlation images for PE, PP, and PVA, respectively. (D) Raman correlation profile obtained using a PVA reference spectrum on a line extracted from the area map (white dashed line on C).

Diffraction-limited resolution in optical microscopy is often empirically assessed by the Rayleigh criterion shown below, where d denotes the Rayleigh criterion, λ is the laser wavelength, η is the refractive index of the immersion/mounting media, and $N.A.$ is the microscope objective numerical aperture.

Rayleigh Criterion

x, y plane (lateral): $\qquad d = 0.61 \dfrac{\lambda}{N.A.}$

z-axis (axial): $\qquad d = \dfrac{2\lambda\eta}{(N.A.)^2}$

As indicated in the equations, both lateral and axial Rayleigh criteria are directly proportional to the wavelength, but inversely proportional to the objective numerical aperture. In addition, the axial Rayleigh criterion is proportional to the refractive index of the material under investigation. For any

sample that is optically denser than air, the axial resolution is usually 4-6 times lower the lateral one. For a 532 nm laser and a 100× objective ($N.A.$ = 0.90), assuming the refraction index 1.5 for the laminates, the theoretical lateral spatial resolution and axial resolution are approximately 0.4 µm and 2 µm, respectively. However, many factors such as scattering of the laser/Raman photons and interaction with interfaces in the sample can reduce this resolution. Another important consideration in instrument configuration is the pinhole size. The confocal pinhole acts as a spatial filter, by allowing the Raman spectrometer to look into a smaller spatial domain than with a conventional configuration without the pinhole, attenuating the out-of-focus regions of the sample.[2] In the current study, the combination of a 532 nm laser, a 100× objective with an N.A. of 0.9, and a 25 µm confocal pinhole enabled the resolution of a 0.4 µm-thick PVA layer, approaching the theoretical limit of the lateral spatial resolution.

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Conclusions

In this communication, we have demonstrated the analysis of polymer laminates using Raman line and area mapping. In both cases, seven layers were identified. With a properly configured Raman microscope, it was possible to resolve a thin polymer layer with a thickness (≈0.4 µm) that's very close to the theoretical spatial resolution limit.

References

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