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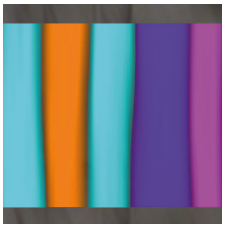
Raman Spectroscopy

Resolving micron-sized layers in multilayer films with Raman microscopy by cross-section analysis and confocal depth profiling



Application Note

Polymers RA89

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Abstract: Multilayer polymer films, composed of different materials, are used in a variety of industrial applications. The analysis of these multilayers is important to support production, identify defects and perform failure analysis, understand delamination problems due to adhesion issue (lack or non-uniform distribution of the adhesive) and for reverse engineering investigation. Here, we use Raman microscopy for cross-section analysis and confocal depth profiling to investigate the chemical composition of two multilayer films. It is also shown how Layers, the new LabSpec6 software app from HORIBA for cross-section and confocal analysis, can efficiently provide such information, allowing a detailed identification of the chemical composition and spatial distribution of each component within a multilayer structure.

Keywords: Raman microscopy, Cross-section analysis, Confocal depth profiling, Polymer multilayers, Layers.

Introduction

Multilayer polymer films, produced using co-extrusion and lamination processes, exhibit characteristics and properties not achievable by their individual constituent monolayers. These composite materials are widely used in several industrial applications, including consumer product and food packaging, as they are strong and flexible thus able to preserve their contents. Each layer of the complex structure provides a specific functionality to the full film, acting as oxygen, moisture, dust, microbes, or light barrier. Typically, conventional polymers like ethylene vinyl alcohol (EVOH), ethylene vinyl acetate (EVA), polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET) and polyamide (PA) are employed to produce multilayer structures.

Since the design of such structures has become more complex and the manufacturing specifications have become tighter, there is an increasing need of new hardware and software solutions that can easily and straightforwardly characterize these multilayer films. In this respect, the solution should provide both chemical and thickness information and moreover it should consider that nowadays the new multilayer structure has an overall thickness that is decreasing (few tens of microns) and that the number of layers is increasing (10 to 15 layers) with respect to the past.

Confocal Raman microscopy is the perfect technique to probe multilayer polymer film and the combination of Raman microscopy together with our customized polymer vice (Figure 1) and the “Layers” software app of LabSpec6 is the perfect solution. Raman microscopy combines the advantages of Raman spectroscopy allowing chemical identification of the constituents with those of optical imaging (i.e., optical microscopy) showing a high spatial resolution image of the films and of the different layers. By using Raman microscopy, the layer identification (chemical nature and thickness) of multilayer polymer film can be made by cross-section analysis or by confocal depth profiling. The advantage of confocal measurement is that it requires no or minimal sample preparation for samples that cannot be cross-sectioned and allows defect analysis without the need to bring the defect to the surface by sectioning the sample, which can lead to loss of defects. Cross-section Raman mapping, on the other hand, offers the best lateral resolution ensuring the analysis of layers down to sub-micron thickness.

In this application note, two different samples, namely a multilayer polymer film and a screen protection film, are analyzed using the cross-section and confocal modes, respectively. It is also shown how Layers, the new LabSpec6

software application for Raman cross-section and confocal depth analyses, allows an automatic identification of the chemistry and thickness of each constituent layer within the multilayer film.

Instrument and methods

Two distinct samples were selected for the analysis: a multilayer polymer film and a screen protection film. The multilayer polymer film was analyzed in cross-section mode using the easy-to-use kit developed by HORIBA. This includes a "polymer vice" to hold the multilayer films in cross-section or to allow an easy cut of them, a stage mount to securely hold the vice on the manual and/or automatic stage of the HORIBA Raman microscopes, single-use sharp blades to cut the multilayer films, and a screwdriver to lock the polymer vice into the stage holder for reliable and accurate Raman measurements (see Figure 1).

Due to its hardness, the screen protection film was not cross-sectioned; it was analyzed in confocal depth profiling mode after immobilization on a glass slide. For both samples, the micro-Raman measurements were performed using the confocal HORIBA LabRAM Soleil™ (Figure 2), offering full automation. A 532 nm laser excitation was focused down to a micrometric spot on both sample surfaces through a 100x objective (NA = 0.9; WD = 1 mm). The selected spectrometer grating allowed collection of a full spectral window from 30 cm^{-1} to 3600 cm^{-1} in one shot. The laser power was set to 4.8 mW and 6.2 mW at the surface of the multilayer film and screen protection film, respectively. The LabRAM Soleil™ instrument was directly controlled via the LabSpec6 software.

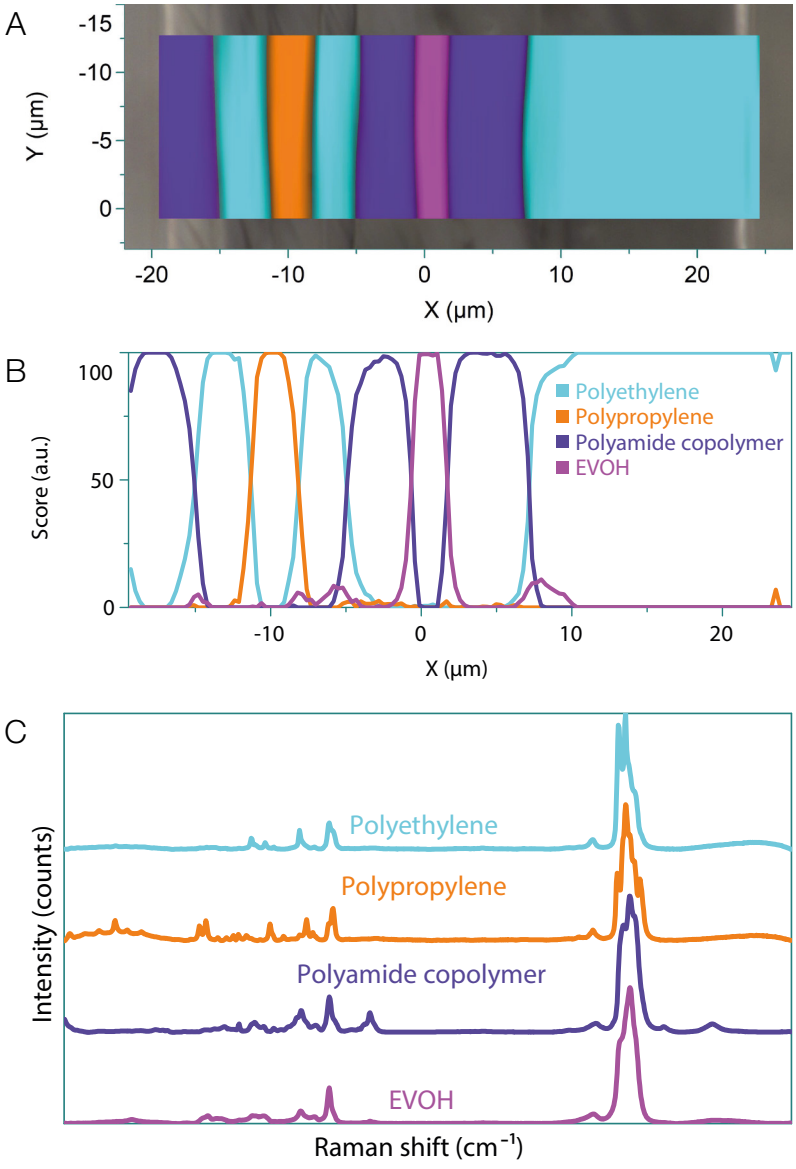
The Layers app, integrated as part of the LabSpec6 software, was used to analyse the Raman maps of the two samples and to determine the chemical structure, by means of a customised HORIBA polymer library, and thickness of each of the layers. Layers app is also exploiting other modules to display and analysis the data such as the Multivariate Analysis Plus (MVA Plus™) application which is embedded in it.

Figure 2: LabRAM Soleil Raman microscope.

Figure 1: Multilayer kit made of a multilayer sample holder, sharp single-use blades, and a screwdriver.

Results

The chemical identification of the different components was carried out using the HORIBA polymer library integrated in the KnowItAll® software, after applying minimal preprocessing step (i.e., baseline correction) to the raw spectral data. Figure 3a shows the optical image of the multilayer polymer film on which the Raman map is superimposed (each color identifies a different polymer). Four compounds were found by means of the Multivariate Analysis Plus (MVA Plus™) module: linear low density polyethylene (cyan), polypropylene (orange), polyamide copolymer (blue), and poly(ethylene vinyl alcohol) (EVOH; purple); see their representative Raman spectra in Figure 3c. Note that the presence and thickness of EVOH is of great importance in food packaging as it acts as an oxygen barrier; its barrier properties change according to the thickness. In Figure 3a, we present the distribution of these compounds across the mapped region. From this distribution it is possible to automatically determine the thickness of each component, which is then displayed in a table, Figure 3d. Some comments can also be added to the table (see Figure 3d), which can be very useful to describe the layer functionality for non-expert users and/or to detail any features and characteristics of the specific layer. Here, the thickness of the thinnest layer (EVOH layer) is 2.40 µm, directly determined from Figure 3d. Layers app hence combines both chemical and morphological information to provide a complete picture of each individual layer in a multilayered sample.



D

Layer #	From (µm)	To (µm)	Thickness(µm)	ID	Color	Loading	Spectrum	Comment
1	-19.30	-14.96	4.34	Polyamide copolymer				
2	-14.96	-11.37	3.59	Polyethylene				
3	-11.37	-8.07	3.30	Polypropylene				
4	-8.07	-5.08	3.00	Polyethylene				
5	-5.08	-0.58	4.49	Polyamide copolymer				
6	-0.58	1.81	2.40	EVOH				Oxygen barrier
7	1.81	7.21	5.39	Polyamide copolymer				
8	7.21	24.43	17.22	Polyethylene				

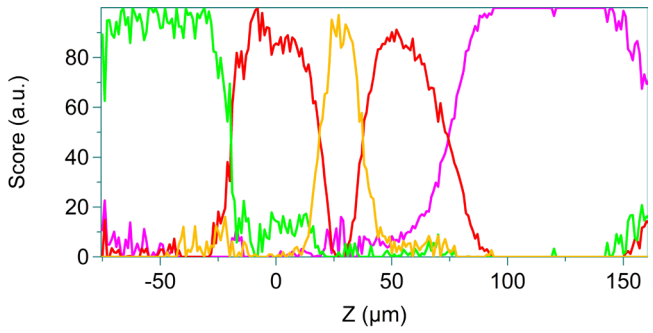
Figure 3: A) Raman map of the multilayer polymer film superimposed on the optical image. Cyan, orange, blue and purple colours correspond to linear low density polyethylene, polypropylene, polyamide copolymer, and poly(ethylene vinyl alcohol) (EVOH), respectively. B) Score profile showing the distribution of the different components. C) Raman reference spectra of the different components. D) Table generated by the Layers application, displaying the thickness, chemical ID, loading (calculated spectra from the multivariate analysis) and average spectrum for each layer.

As mentioned, the screen protection film was analyzed in confocal depth profiling mode without any sample preparation; for this type of analysis the size of the pinhole is an important parameter in the instrument configuration, as it spatially filters the volume to be analysed allowing perfect control of the confocal resolution. The highly flexible HORIBA LabRAM Soleil™ Raman microscope allows the pinhole size to be tuned from 500 µm to 1 µm directly through the LabSpec6 software, ensuring a fine adjustment of the confocal resolution; here, the confocal resolution was set to ≈1 µm. Figure 4a shows the depth profile of the protection film consisting of multiple layers of bis(2-ethylhexyl) adipate (purple), polyethylene terephthalate (PET; red), silicone oil and PET (orange), and a coating layer (green). The corresponding Raman spectra of these pure and mixed chemical compounds within the protection film are presented in Figure 4b. Figure 4c shows the table obtained from the Layers application, displaying the thickness of each individual layer. As shown in Figure 4, a detailed information on the structure of the protection multi-layered film was obtained using the depth profiling capabilities of LabRAM Soleil™.

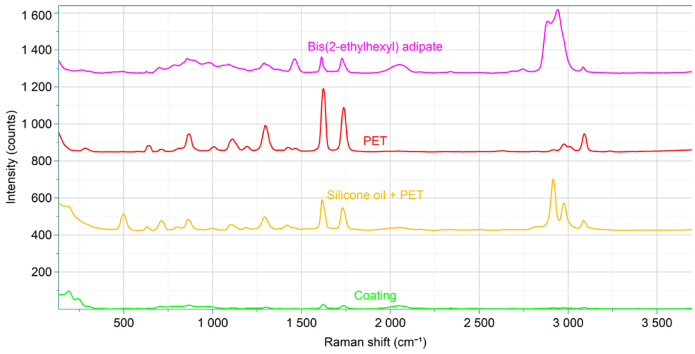
Conclusion

To conclude, we have analyzed two samples using Raman microscopy in cross-section and confocal depth profiling mode. Raman microscopy was not only able to probe the chemical composition of the constituent layers, but also to determine the distribution and thickness of each component. It was also shown that the HORIBA polymer kit in combination with the Layers application and the high sensitivity and spatial resolution capabilities of the LabRAM Soleil™ can provide a full solution for analysing any multilayer structure.

A



B



C

Layer #	From (µm)	To (µm)	Thickness(µm)	ID	Color	Loading	Spectrum	Comment
1	-75.00	-19.50	55.50	Coating				
2	-19.50	18.50	38.00	PET				
3	18.50	37.50	19.00	Silicone oil + PET				
4	37.50	74.50	37.00	PET				
5	74.50	160.00	85.50	Bis(2-ethylhexyl) a...				

Figure 4: A) Depth profile acquired from the protection film, showing the thickness of the constitutive layers. B) Raman reference spectra of the layers, identified as bis(2-ethylhexyl) adipate (purple), polyethylene terephthalate (PET; red), silicone oil and PET (orange), and a coating layer (green). C) Table obtained from Layers, revealing the thickness, chemical ID, loading (calculated spectra from the multivariate analysis) and average spectrum of each individual layer.

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