Complementary Use of Raman and FT-IR Imaging for the Analysis of Multi-Layer Polymer Composites

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Overview

Purpose: To compare and contrast the benefits of FT-IR and Raman microscopy mapping and imaging for the analysis of layered polymer composites.

Methods: FT-IR and dispersive Raman microscopes were used to analyze multi-layered polymer composite materials.

Results: An important advantage of FT-IR micro-spectroscopy is that the spectra highlight polar functional groups which are particularly important when characterizing different types of polymers. A large number of FT-IR spectral data bases are available for identification of polymeric materials.

Raman micro-spectroscopy offers excellent spatial resolution as well as convenient sampling options. Raman spectroscopy tends to highlight molecular backbone structure and is sensitive to molecular structure. Raman spectroscopy typically provides access to a greater spectral range that is useful for analyzing a wider range of different types of materials such as pigments.

These techniques work very well together and provide complementary information, so rather than considering these as an either or proposition, a concerted approach using both FT-IR and Raman imaging would be an excellent solution for the analysis of layered polymer composites.

Introduction

A variety of different industries utilize multi-layered polymer composites specifically engineered for particular performance characteristics. Confirming the composition and integrity of these materials is important both for the industries that manufacture these products as well as for industries that utilize these materials in their own products. The diversity of the materials used and the microscopic construction of these materials requires analytical techniques with unique capabilities.

Raman and FT-IR micro-spectroscopy are both uniquely suited for the analysis of polymer composites. They both can be used to readily identify unknown materials as well as providing information on molecular structure and chemical environment. Microscopic applications are available for both of these techniques even though there are some difference in the expected spatial resolutions. FT-IR and Raman mapping and imaging provide a convenient way to visualize the distribution of components or differences in molecular structure in polymer composites. Each of these analytical methods has its own advantages and challenges associated with it. Raman and FT-IR spectroscopy should not be viewed as mutually exclusive; rather than choosing between the two, a better approach would be to view them as complementary and to use both to get a much better overall understanding of the samples.

Methods

Vibrational Spectroscopy

A Thermo Scientific™ DXR™xi Raman imaging microscope was used to collect the Raman imaging data. The transmission FT-IR mapping data was obtained using a Thermo Scientific™ Nicolet™ iN™10 FT-IR microscope. The attenuated total reflectance (ATR) imaging data was obtained using a Thermo Scientific™ Nicolet™ iN™10 MX FT-IR microscope and imaging ATR accessory for microscopy.

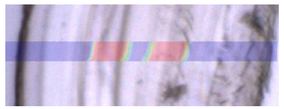
Sample Preparation

The cross-sectioned samples for Raman analysis were prepared using the Thermo Scientific™ Polymer Slicing Tool for DXR Raman microscopes. For confocal depth profiling experiments the polymer films were mounted flat across a small hole in a microscope slide. For FT-IR transmission analysis the samples were cross-sectioned by hand using razor blades and mounted in a Thermo Scientific micro-compression cell with diamond windows. Cross-sectioned slices of the layered composites were used for the ATR analyses.

Results

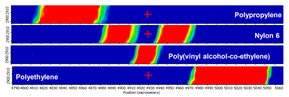
Figure 1 shows the results of a FT-IR transmission mapping analysis of a layered polymer film. Five distinct layers were identified with two of the layers being the same material (polyamide). While it was relatively easy to identify the layers from the FT-IR spectra, it is clear that the sample preparation has resulted in layer deformation. It may be possible to prepare these types of samples using a microtome to get the samples thin enough for transmission analysis samples thinner without having to use as much as compression but that type of sample preparation requires more extensive experience and specialized equipment. The FT-IR spectra show diagnostic peaks for functional groups such as the amide peaks and the hydroxyl peak. The chemical images of the layers were generated based on correlation profiles.

FIGURE 1. FT-IR transmission analysis. Mapping parameters: Nicolet iN10 - transmission mode; Cross-sectioned sample; Mounted on a diamond window; Area: 280 x 20 µm; Aperture: 5 x 20 µm; Step Size: X: 2.0 µm, Y: 5.0µm; 750 spectra

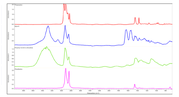


Video Image of the cross-section; FT-IR image superimposed showing Nylon 6 layers

FT-IR profile images showing components distributions



Component spectra



One advantage of FT-IR analysis is the different modes of data collection available. ATR has the advantage of requiring less sample preparation and the potential to achieve higher spatial resolution due to the higher index of refraction of the ATR crystal. An example of ATR imaging is shown in Figure 2. These results show that even the very thin polyurethane adhesive layers could be distinguished. These layers were expected to be three µm thick instead of five. This is probably due to sample deformation by ATR crystal.

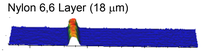
FIGURE 2. ATR imaging of a layered polymer composite. Imaging parameters: Nicolet iN10 MX with linear array detector; imaging ATR accessory for microscopy; effective area 412 x 43 µm; 7685 spectra

Imaging ATR accessory for microscopy

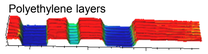
Video image before contact

Sample deformation & delamination

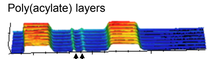
Nylon 6,6 Layer (18 µm)



Polyethylene layers



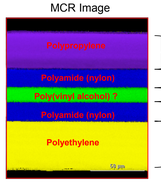
Poly(acylate) layers



Polyurethane adhesive layers approximately 5 µm thick

FIGURE 3. Raman imaging of a layered polymer film. Collection parameters: DXRxi Raman imaging microscope, 532 nm laser (10 mW), 132 x 150 µm area, 0.5 µm image pixel size, 79200 spectra, 0.020 s exposure time, 3 scans

MCR Image



Component spectra

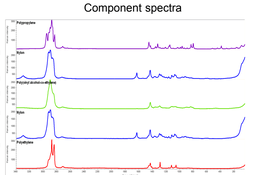
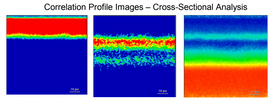


Figure 3 show the results of Raman imaging a new portion of the film that was used in Figure 1. The Raman imaging analysis required much less sample preparation (sample thickness is not an issue) and the spatial resolution is significantly better. There was no evidence of sample deformation and analysis does not require any sample contact. However, the Raman spectra do not have the strong peaks for the polar functionalities that are present in the FT-IR spectra, making identification of the polymer materials more challenging in some cases (for instance with the poly(ethylene vinyl alcohol) layer). It is also possible to do confocal depth analysis of polymers using Raman imaging without the need to cross-section the sample (see Figure 4). However, while this is more expedient the results are often better using cross-sections.

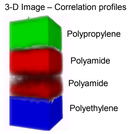
FIGURE 4. Confocal depth imaging of a layered polymer composite

Correlation Profile Images – Cross-Sectional Analysis



Polypropylene | Polyamide (nylon) | Polyethylene

3-D Image – Correlation profiles



Combining Both FT-IR mapping & Raman Imaging

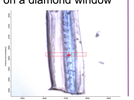
The complementary nature of these two forms of vibrational spectroscopy can be illustrated from the analysis of the blue polymer film shown in Figures 5 and 6. The FT-IR transmission analysis involved cross-sectioning the sample by hand and compressing the cross-section between two diamond windows. This was done to flatten the sample and to slightly compress the film to make the whole cross-section thinner. The sample area shown in Figure 5 was mapped using transmission analysis with an aperture that was 5 x 20 µm and using step sizes of 2 µm in the X direction and 5 µm in the Y direction. The image was formed from 576 individual spectra. The chemical images shown are the result of either correlation or peak height profiles. Four distinct layers were identified using these profiles. The first was a layer of predominately polyethylene with a smaller amount of vinyl acetate co-polymerized. The second layer, very similar to the first, but displayed a clear hydroxyl peak indicating an additional component in this layer that is consistent with co-polymerized vinyl alcohol. The third layer was a polyamide (polyamide 11). The spectra from the final layer were consistent with a co-polymer of ethylene, butyl acrylate and maleic anhydride. The borders between the layers are not distinct. It is not clear if this is a result of the sample preparation (deformation) or spatial resolution limitations.

FIGURE 5. FT-IR Mapping of a blue polymer composite film

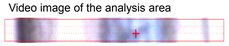
Blue polymer film sample

Micro-compression cell and diamond windows

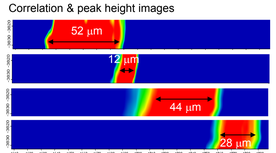
Sample cross-section on a diamond window

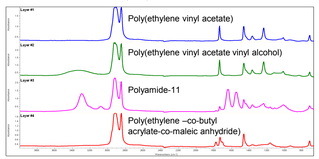


Video image of the analysis area



Correlation & peak height images





Raman imaging results on the same sample are shown in Figure 6. The sample was prepared using the polymer slicing tool shown. This tool allows for a flat, even cross-section of the film and also serves as the sample holder during the analysis. A visual image of the side view of the film is shown in the figure. The area imaged was 88 x 20 µm and the image pixel size was 0.5 µm. The image is made up of 7262 spectra. Lower laser power (0.5 mW) was used because the lazurite pigment is very susceptible to laser damage. The exposure time was 0.1 s and 100 scans were averaged. Figure 6 shows five distinct layers. The chemical images are the result of either correlation or multivariate curve resolution (MCR) profiles. The MCR profile did not identify some of the layers as different components because the spectral differences were very minor. Layer #1 looks like polyethylene but has a very small peak at 1738 cm^{-1} (Figure 7), consistent with co-polymerized vinyl acetate. Layer #2 appears very much like polyamide but does not show the amide peaks; it does not show any hydroxyl peaks but seems to be consistent with poly(vinyl alcohol). Based on FT-IR spectra, this is likely what it is. Layer #3 looks very much like polyethylene but there is a small peak consistent with traces of lazurite. The lazurite is predominately found in layer #4. It appears to be mixed with a polyamide (Figure 8). The lazurite was unexpected and not observed in the FT-IR analysis but is consistent with the blue color of the polymer film. The majority of the lazurite appears to be homogenously dispersed throughout layer 4. However, there were some larger (< 3 µm) lazurite particles observed (Figure 8). The final layer appears to be polyethylene from the Raman spectra and there is no evidence for the butyl acrylate or the maleic anhydride observed in the FT-IR spectra. While Raman imaging provides greater resolution, better definition of the layers, and no layer deformation due to sample preparation, and gives evidence to the nature of the blue pigment, it does not do as well with identifying the polar functional groups of some of the co-polymerized components. These might be inferred from the Raman spectra but are confirmed by the FT-IR spectra.

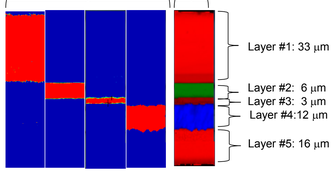
FIGURE 6. Raman imaging of a blue polymer composite film

Blue polymer film sample

Polymer slicing tool for DXR Raman microscopes

Video image of the analysis area

Correlation images | MCR image



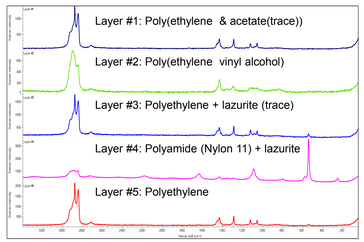


FIGURE 7. Acetate Carbonyl peak (1738 cm^{-1}) in polymer layer #1

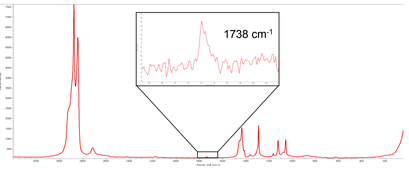
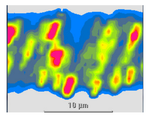
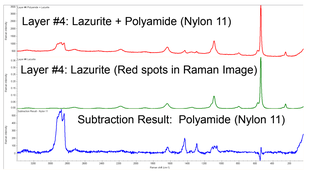


FIGURE 8. Particles of Lazurite in layer #4



Raman Image showing the larger lazurite particles in layer 4 (red)



Conclusion

Whether the goal is quality assurance, failure analysis, or even reverse engineering of layered polymer composites, Raman and FT-IR micro-spectroscopy are both valuable analytical tools for these types of applications. Imaging and mapping generates visual images depicting the distribution of the polymer components or variations in molecular structure.

Advantages & Challenges of FT-IR Microscopy

1) Sensitive to polar functional groups found in many different types of polymers
2) Very useful for identifying different polymer types
3) Transmission analysis is a high throughput techniques but requires extensive sample preparation with the potential for sample deformations
4) ATR requires much less sample preparation and has the potential for higher spatial resolution but requires contact with the sample and possible sample deformation.

Advantages & Challenges of Raman Microscopy

1) Superior spatial resolution
2) Access to low wavenumber spectral range – great for identification of pigments
3) Requires very little sample preparation
4) Raman spectroscopy is very sensitive to molecular structure and highlights polymer backbones as opposed to polar functional groups.
5) Some polymer components and additives can show fluorescence that obscures Raman spectroscopy
6) In some cases highly focused laser sources may require lower power to avoid potential damage to the samples.

A concerted approach utilizing both of these techniques provides for superior analysis of layered polymer composites because they support each other by addressing the shortcomings of the other technique and providing complementary information.

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