



APPLICATION NOTE

Infrared, IR Microscopy

Author:

Ian Robertson

PerkinElmer, Inc.

Seer Green, UK

Characterizing Polymer Laminates Using IR Microscopy

Introduction

Multilayer polymer films, or laminates, are used in a wide variety of industries. A major use of these materials is for packaging of foods and consumer products. The composition of multilayer films can often

be quite complex as they may have to satisfy a variety of requirements to preserve the contents. A package must collate and contain the product, requiring strength and the ability to seal the packaging. It must be machineable at a reasonable cost. In the case of food products, it must be able to preserve the contents and protect it from external influences that would affect the product quality or safety, ultimately leading to increased shelf-life. Each of the layers in the laminate will perform a different barrier function, protecting the product from different external factors, such as moisture, light, oxygen, microbial materials and other chemicals or flavors.

Generally, traditional polymer materials, such as polyethylene terephthalate (PET), polyethylene (PE), polystyrene (PS), and polypropylene (PP), have been used for packaging materials. These packaging materials account for a significant proportion of materials ending up at landfill sites or recycling plants. Some of these materials biodegrade slowly or do not biodegrade at all and are environmentally unfriendly. Consequently, there is increasing focus on the use of biodegradable or compostable polymers that can be used as packaging materials. Bio-based materials are partly or entirely made of renewable raw materials, such as cellulose, starch or polylactic acid (PLA). These bio-based plastics can be biodegradable, but are not always. Compostable plastics can be completely biodegraded by microorganisms leaving only water, carbon dioxide, and biomass. These materials are more environmentally friendly and are expected to be used increasingly in the future.

Infrared microscopy has long been the most important technique for characterizing multilayer polymer films. Infrared spectroscopy has the ability to identify materials and the addition of an infrared microscope allows for small samples (down to <10 microns) to be analyzed, including the determination of the identities of the different layers of laminates. This Application Note describes the use of infrared microscopy applied to “traditional” multilayer polymer films as well as the newer compostable materials.

Infrared Microscopy of Multilayer Polymers

Infrared microscopy of polymer films can be performed using transmission or Attenuated Total Reflectance (ATR) techniques. Infrared transmission measurements require the sample to be optically thin, generally not thicker than 20 to 30 microns. This requires the sample to be prepared as a thin film by the use of a microtome. The sample can then be placed on an infrared-transmitting window material, such as potassium bromide (KBr), for measurement of transmission spectra. ATR measurements can be performed on optically thick materials as ATR is a surface technique. The sample needs to be physically supported, either in an embedding resin or in a sample clamp specially designed for use in infrared microscopes. ATR measurements have the additional benefit of generating spectra at a significantly better spatial resolution than transmission measurements.¹

Transmission of Laminate

A polymer laminate sample was cut to a thickness of 25 microns using a microtome and taped flat onto a 7 mm diameter KBr window. This sample was then placed in a standard microscope sample holder on the microscope stage of the PerkinElmer Spotlight™ 200i. A visible image of the sample is shown as Figure 1. The laminate is approximately 350 micrometers across (top to bottom).

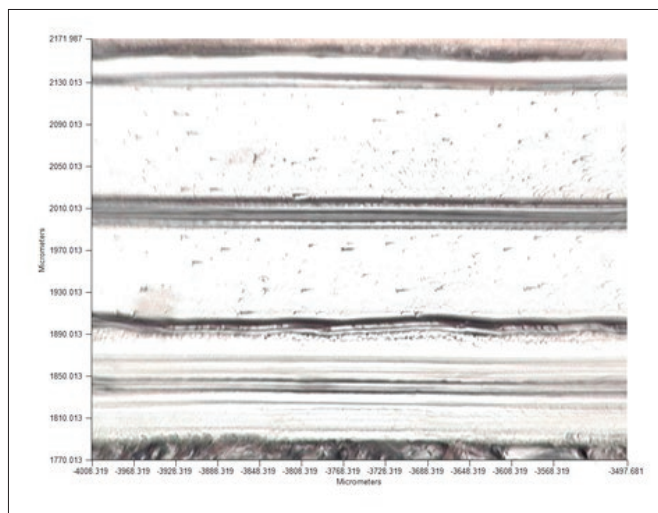


Figure 1: Visible image of polymer laminate measured in transmission.

If detailed information is required about all of the layers in the laminate then it is possible to setup a linescan, collecting spectra at very small intervals across the laminate. Such an experiment was set up to collect spectra at 3 micrometer steps across the laminate, using an aperture size of 5 micrometers with a total of 140 spectra collected. The linescan data is shown as Figure 2.

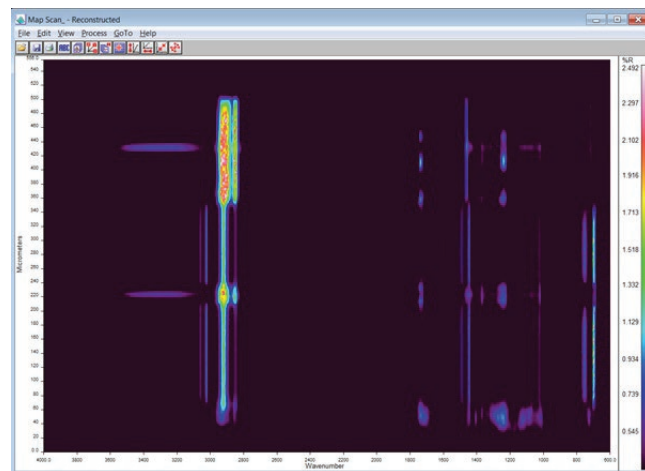


Figure 2: Linescan data for polymer laminate transmission measurements.

The results indicated that several different polymer types were present in the sample as shown in Figure 3. These were identified using Search libraries as; PET, modified PS, PE, ethylene-vinyl acetate (EVA), and ethylene-vinyl alcohol (EVOH).

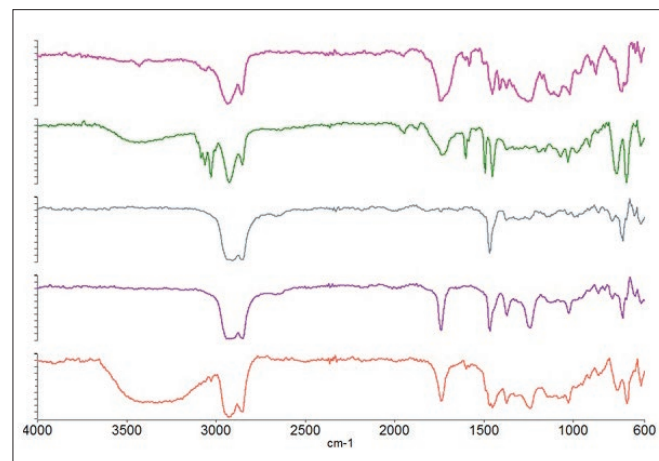


Figure 3: Spectra of the polymers present in the different laminate layers.

Profiles can be generated to show the distribution of the different polymer types throughout the laminate giving significant structural information. The profiles for polystyrene (1600 cm^{-1}), polyethylene (1450 cm^{-1}), ethylene-vinyl acetate copolymer (1746 cm^{-1}), and ethylene-vinyl alcohol copolymer (3334 cm^{-1}) are shown as Figure 4.

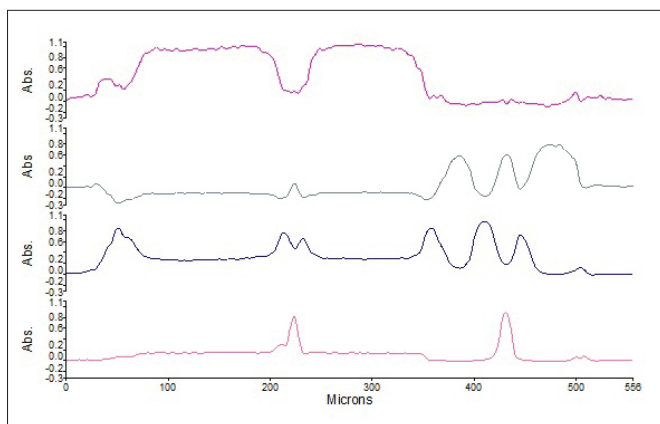


Figure 4: Distribution profiles for polymer types in laminate. From top to bottom: polystyrene, polyethylene, ethylene-vinyl acetate co-polymer and ethylene-vinyl alcohol co-polymer.

If the only requirement for the analysis is to detect and identify the layers in the laminate, then the Analyze Image function within the Spectrum 10 software can be used. This function will analyze the visible image of the sample, detect the layers present, and maximize the measurement area for each layer, all completed automatically. In the case of a multilayer sample, it will collect a single spectrum for each layer, giving the maximum signal-to-noise and significantly reduce the analysis time compared to mapping or measuring a linescan on the same sample. Figure 5 shows an example of a five-layer laminate.

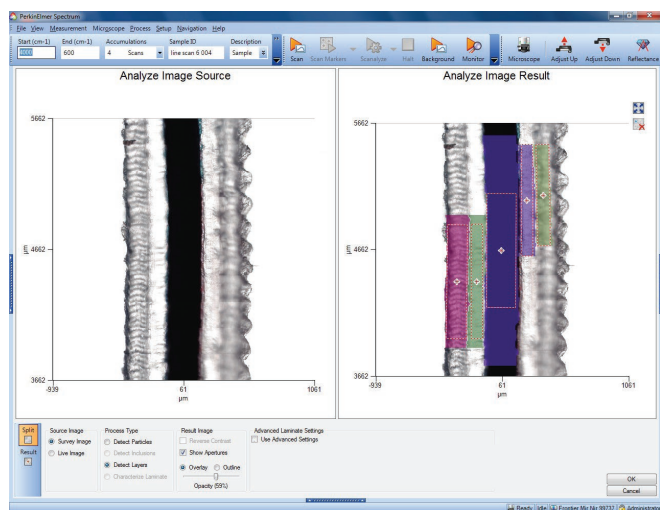


Figure 5: Automatic detection of layers in a laminate shows five layers.

After detection of the laminate layers, spectra were automatically recorded at the marker positions, shown in Figure 6. An automatic library search identified each of the layers as polyethylene terephthalate (layers 1 and 5), ethylene-vinyl acetate copolymer (layers 2 and 4), and silica-loaded polyethylene (layer 3).

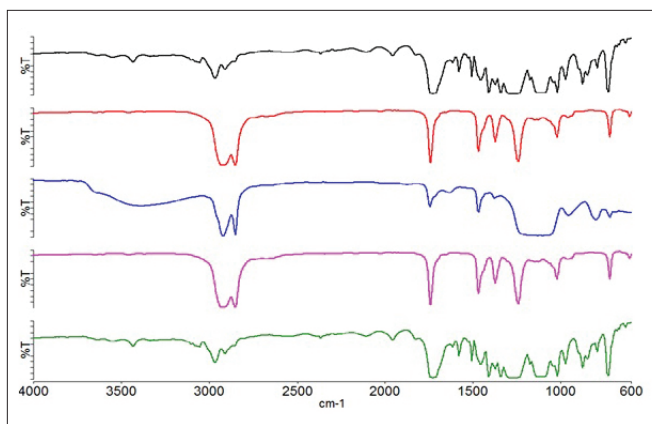


Figure 6: Spectra of layers 1 are shown (top) to 5 (bottom) in polymer laminate.

ATR Measurements of Polymer Laminates

ATR provides a fast and easy way of measuring an infrared spectrum of a material. ATR on an infrared microscope is capable of measuring spectra of very small materials down to just a few micrometers in size. A macro ATR crystal/accessory for the microscope has been utilized to collect data on food packaging laminates. This ATR accessory can generate spectra at a significantly better spatial resolution than transmission measurements¹. For the ATR measurements the samples were embedded in a resin and polished to give a flat, clean surface for the ATR measurement. Embedding the sample generates a stronger multilayer surface than simply clamping the sample and prevents deformation or compression of the sample under ATR pressure.

A sample of a multilayer food package manufactured using "traditional" polymers was prepared for ATR measurement in the Spotlight 200i. The visible image of this sample was measured and is shown as Figure 7. The width of the laminate is seen to be approximately 200 micrometers and consists of several polymer layers.

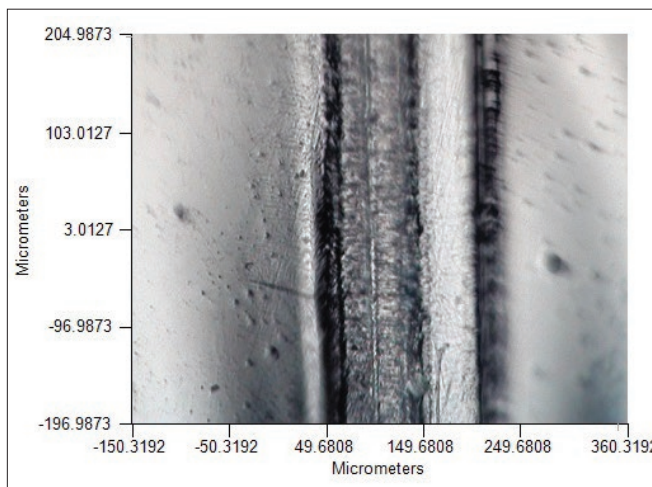


Figure 7: Visible image for multilayer food packaging material.

The macro ATR crystal for the IR microscope was placed in contact across the entire width of the sample. Spectra were collected across the laminate with an effective aperture size of 5 x 5 micrometers at a step size of 5 micrometers. The linescan data collected is shown as Figure 8.

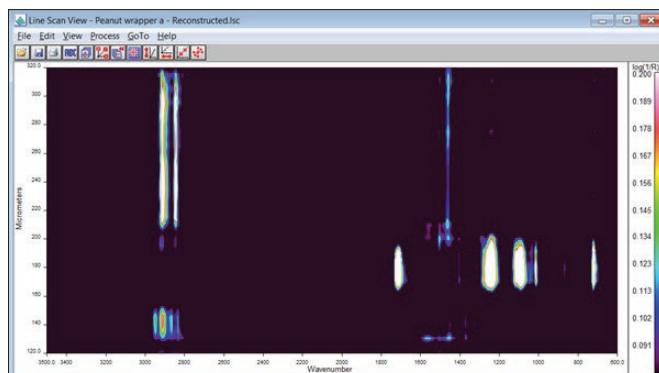


Figure 8: Linescan data for food packaging material.

Several different polymer types seem to be present in the sample. The spectra obtained from the major layers are shown in Figure 9. A search against polymer databases identifies the layers as polypropylene, polyethylene terephthalate, polyethylene, and modified polyethylene.

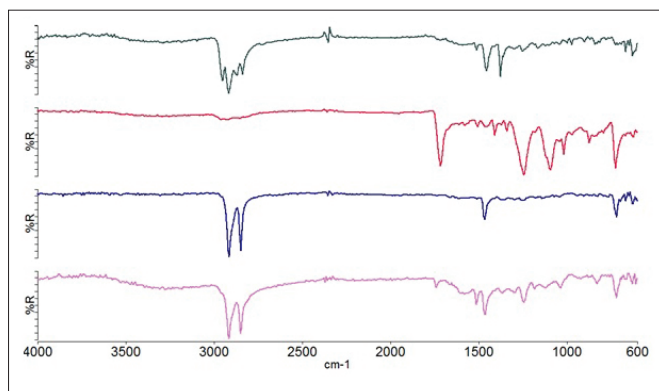


Figure 9: Spectra of major layers are identified as PP, PET, PE and modified PE.

In addition, several other minor layers were detected and their infrared spectra shown as Figure 10. A region of the data (around 160 micrometers in the display) gave no spectral details at all, as it was a thin foil layer.

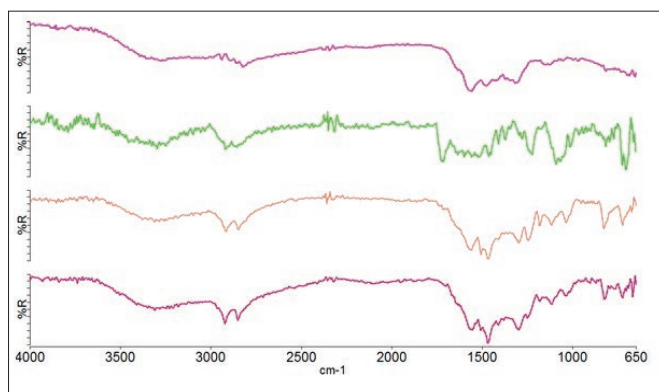


Figure 10: Spectra of minor layers in multilayer food packaging material.

A new generation of biodegradable polymer materials has been developed as a replacement for the “traditional” polymer packaging material. A compostable food packaging material has been analyzed on the Spotlight 200i. The sample was prepared for IR-ATR microscopy in the same way as the “traditional” packaging material that was shown previously.

The visible image of the embedded sample appears as Figure 11. The laminate is seen to be approximately 80 micrometers wide, consisting of a small number of visible layers.

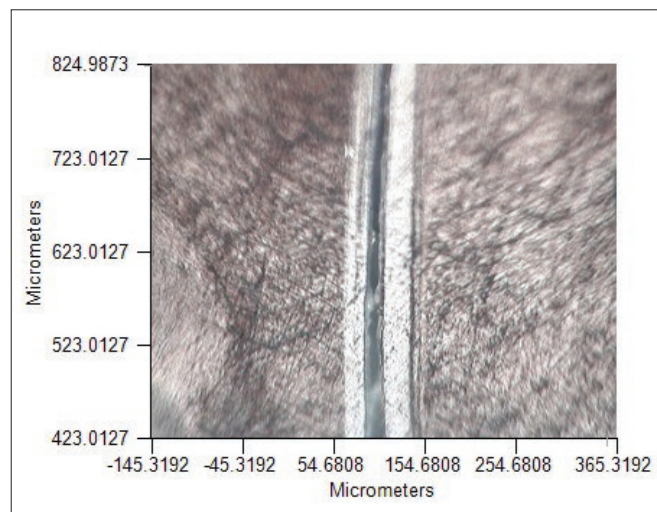


Figure 11: Visible image of a compostable food packaging laminate.

The infrared data collected on the sample is shown as Figure 12. The sample consists of three major layers each of approximately 25 micrometers width.

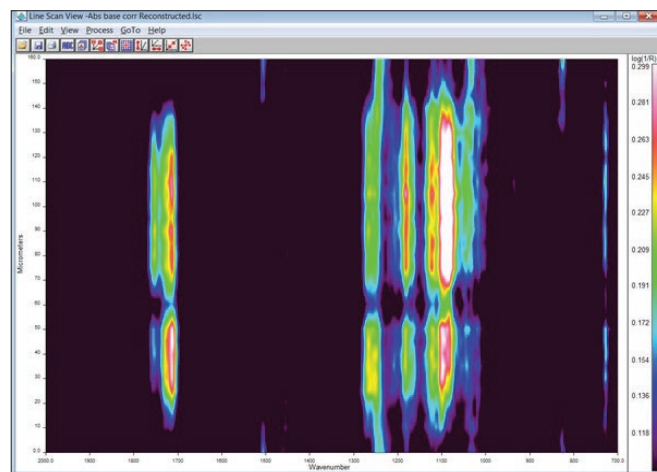


Figure 12: Linescan data for compostable laminate sample.

The spectra are shown as Figure 13. The spectra of the layers all look similar, however, they exhibit spectral differences in the C=O region between 1700-1760 cm^{-1} . The materials are known to be polylactic acid (PLA)-based copolymers. The region at approximately 60 micrometers in the display does not exhibit spectral features, as there is a thin layer of foil present in the sample.

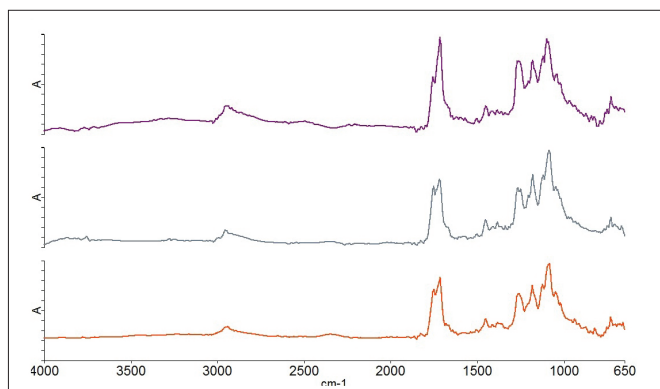


Figure 13: Shown here are spectra of the three different layers in the compostable polymer laminate.

Summary

Packaging materials, especially food packaging, are complex materials in order to satisfy the numerous requirements for the product contained within. Multilayer laminates are a means of fulfilling these requirements. However, disposal of food packaging materials is a significant environmental problem. Biodegradable packaging materials are a possible solution.

IR microscopy has been shown to be an excellent technique for the characterisation of these “traditional” and newer multilayer materials. Transmission or ATR measurements can easily be deployed depending on the sample preparation that is available.

Reference

1. PerkinElmer Technical Note 007641A_03, Spatial Resolution in ATR Imaging