Application Note AN M126

Analysis of composite films

Composite films are mainly used for the packaging of food where many requirements have to be met in order to preserve taste and freshness of the product. The packaging film needs an adequate mechanical stability and has to prevent water vapor entering or leaving the packaging. Furthermore, the foil should effectively block gases like for instance aerial oxygen or any potentially used protective atmosphere that prevents the product from oxidation. In practice, it is also of importance that the foil material is as inexpensive as possible and that the foil thickness is low in order to save costs and resources. Composite films allow to adapt the properties of a film to the needs of a particular application and to design tailor-made materials. For example, a PET layer results in a good transparency and impact resistance of the composite film, PE acts as an effective barrier against water vapor and EVOH (ethylene-vinyl alcohol) is impermeable for gases.

The analysis of composite films is often very complicated since these films are generally very thin and sometimes consist of three or more layers. For the analysis of such complex multi layered films, a microscopic examination is often essential. With a conventional optical microscope, it is indeed possible to differentiate between various layers but it is not possible to identify the respective materials. In contrast, the FTIR (Fourier Transform Infrared) microscopy allows identifying different materials in composite films and to determine their distributions. Furthermore, also filler particles or defects in the polymer matrix can be localized and identified.

Keywords	Instruments and Software
Defect analysis	LUMOS II FTIR microscope
Microtome cut	HYPERION 3000 FTIR imaging microscope
ATR-technique	OPUS spectroscopy software
Composite films	SliceIR sample holder
Layer thickness deter-mination	
Material identification	
Polarization microscopy	

With the FTIR microscope LUMOS II (Figure 1) fully automated grid-measurements of the cross section of composite films can be performed by sequentially measuring spectra point by point. The FTIR microscope HYPERION 3000 additionally allows measuring thousands of spectra simultaneously via an integrated focal-plane-array (FPA) detector, so that large sample areas can be analyzed with the highest lateral resolution.

Figure 1: LUMOS II FTIR microscope.

By classical means, the analysis of a composite film is performed in transmission. This approach yields good results but the sample preparation is very time consuming and requires expensive equipment. Prior to a transmission measurement, microtome cuts with a thickness of less than 10 µm have to be prepared. On the other hand, a measurement with the attenuated total reflection technique can be done without an extensive sample preparation. Here, only the production of a smooth intersection of the foil cross-section is needed, which is possible by means of a sample holder and a sharp blade.

Instrumentation

The FTIR microscope LUMOS II is an all in one system with an integrated spectrometer, a high degree of automation and a dedicated user interface. Its 8x objective provides the measurement modes ATR, transmission, reflection and high quality visual inspection capabilities. With optional polarizers, it is possible to enhance the visual contrast and thus making differences in the material more apparent. The innovative motorized ATR germanium-crystal in combination with a motorized sample stage allows fully automated measurements.
The sample holder "MicroVice SliceIR" permits the fixation of samples at different angles by using clamps with cutting angles of 90°, 30° and 15°. By using a cutting angle of 30° or 15° the intersection is enlarged by a factor of two or four, respectively thus facilitating the analysis of very thin samples.

For very demanding samples that require the highest possible resolution and measurement speed, the HYPERION 3000 FTIR microscope is the equipment of choice. It has an FPA detector, which allows measuring thousands of spectra simultaneously. Compared to the LUMOS II, the HYPERION microscope is much more configurable, there are for example different objectives and detectors available.

Analysis of a composite film by using ATR

Our first example shows the analysis of a multi layered composite film. The sample was fixed between two slices of PVC using the 30° "Slice IR" clamps and then cut with a microtome knife. This type of sample preparation is very simple and fast and increases the intersection due to the tilted setup of the clamps.

The analysis of the sample was performed with the LUMOS II FTIR microscope in ATR. Altogether 50 measurement points were measured automatically with an aperture size of 8x30 µm. The measured spectra were then evaluated by means of a so-called cluster analysis. Thereby the spectra are grouped according to their spectral similarity and the measurement points are given colors according to their group membership. Figure 2 shows the visual image in combination with the color-coded measurement points. Since the measurement points of the surrounding PVC-foil are white, altogether four layers belong to the composite film.

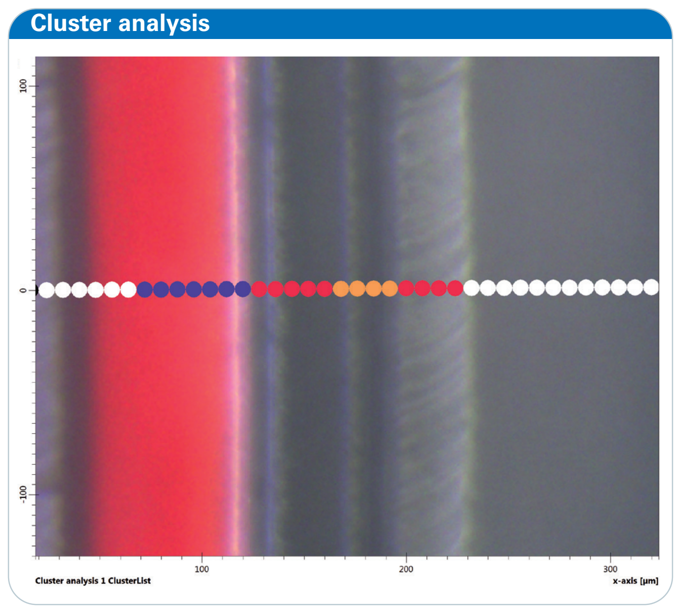

Figure 2: Cluster analysis of the composite film. Example spectra are shown in figure 4.

The identification of the foil materials was done via the OPUS spectrum search function. In all cases the agreement of the searched spectra with the library spectra was excellent. Figure 3 shows as an example the search result for polyester. The composite film consists of a sequence of polyester (blue), polyethylene (red), polyamide (PA6, orange) and again polyethylene. Representative examples of the measured spectra are shown in the respective colors of the layers in figure 4.

Result of the library-search

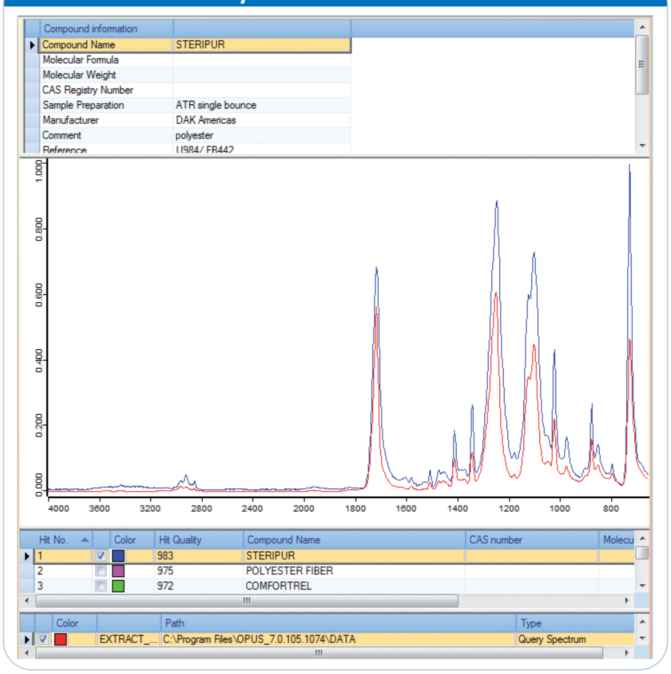

Figure 3: Library search result of a sample spectrum (red). The spectrum of the best hit is shown in blue, clearly identifying the sample as polyester.

Spectra of the composite film

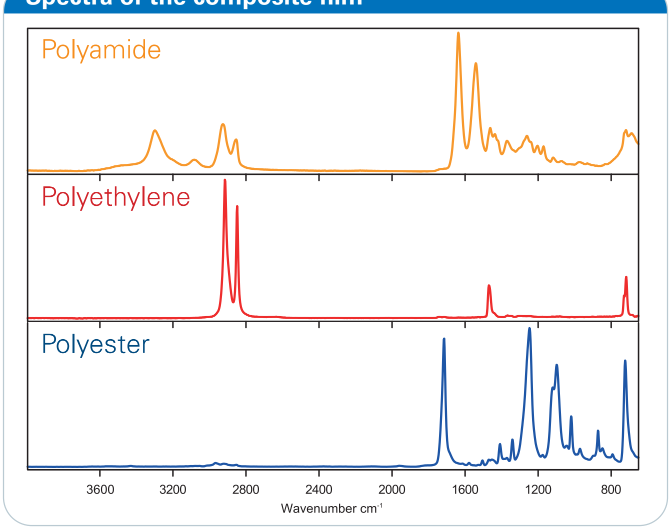

Figure 4: Representative spectra of the composite film in the respective colors of figure 2.

Layer thickness determination of a thin section

To determine the thickness of individual layers accurately, the ATR method is less suitable, since the sample is being altered by the cutting procedure and the sample holder. In addition, the pressure of the ATR crystal can deform the sample.

The optimal sampling approach for this purpose is the preparation of a thin section that can be viewed in transmission and allows to draw precise conclusions about the thickness of the single layers. The sample is first embedded in epoxy resin, sectioned with a microtome and then analyzed. Figure 5 shows the microscopic image of a thin section from which the widths of the single layers were determined by using the distance measurement function integrated in the OPUS software. From left to right, the measured layer thicknesses are 22, 33, 14 and 59 µm.

Layer thickness measurement

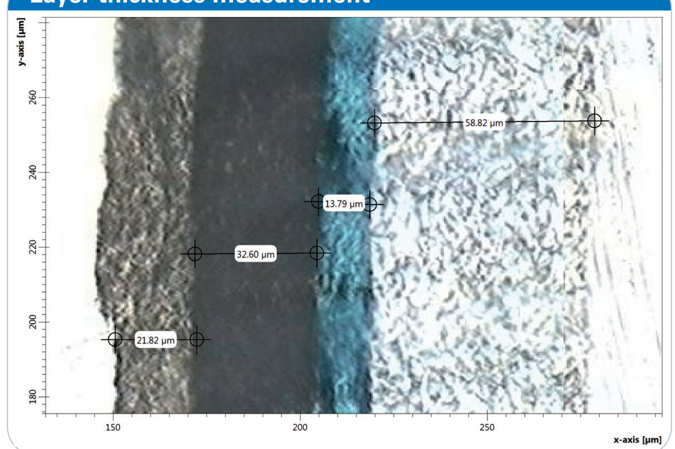

Figure 5: Layer thickness determination in transmission.

Cluster analysis

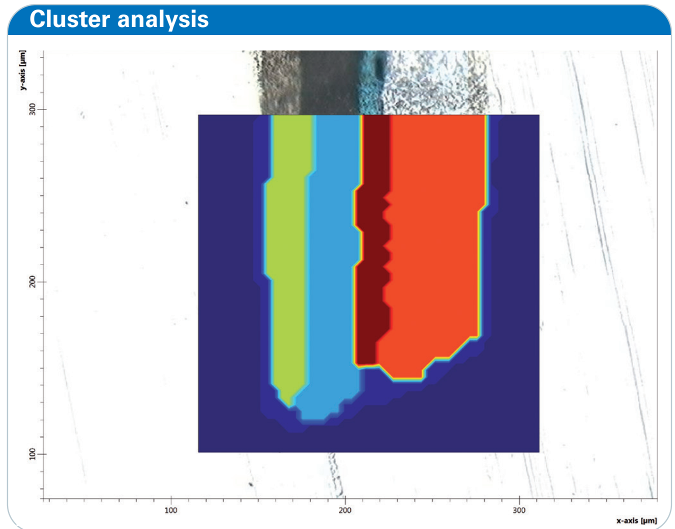

Figure 6: Cluster analysis of the transmission sample.

After the visual picture was recorded, a chemical image was generated by the fully automated mapping function. By using a motorized stage, 50x50 measurement points were measured in transmission with the knife-edge apertures set to 10x10 µm. The evaluation of the spectral data was carried out again by performing a cluster analysis. The result of this analysis is shown in figure 6. Spectra of the respective layers could be identified by a library search; from left to right the following polymers were identified: Polyurethane (green), polyester (light blue) as well as two different acrylic resins (dark red and red).

Imaging of a five-layer foil

In the following example, the analysis of a section of a five-layer polymeric film is shown. The film was embedded in epoxy resin and a smooth cross-section was cut. The embedded film cross section was measured in ATR with a HYPERION 3000 FTIR microscope equipped with a focal plane array (FPA) detector. A FPA detector is an imaging detector with up to 128x128 detector elements with each element generating a single spectrum. By this, it is possible to measure thousands of spectra simultaneously. A FPA detector can quickly measure large sample areas. The HYPERION microscope allows measuring at the diffraction limit and can thus resolve the smallest structures.

Here a measurement of 2x2 tiles was automatically performed on an area of 64x64 µm with a lateral resolution of 0.5 µm. Figure 7 shows the visual image superimposed by the chemical image. The latter one is shown as a so-called WTA-image ("winner takes it all") which assigns the color of the dominant component to each individual image pixel. In both chemical and visual image, the thinnest layer of the sample, with a thickness of merely six microns, can be identified easily. The total thickness of the foil is 42 µm; the single layers could be identified subsequently by a library search. Thereby the following materials were identified: Embedding resin (light blue), polyurethane (green), acrylic resin (blue) and polyethylene terephthalate (red). Spectra of the respective materials are shown in figure 8.

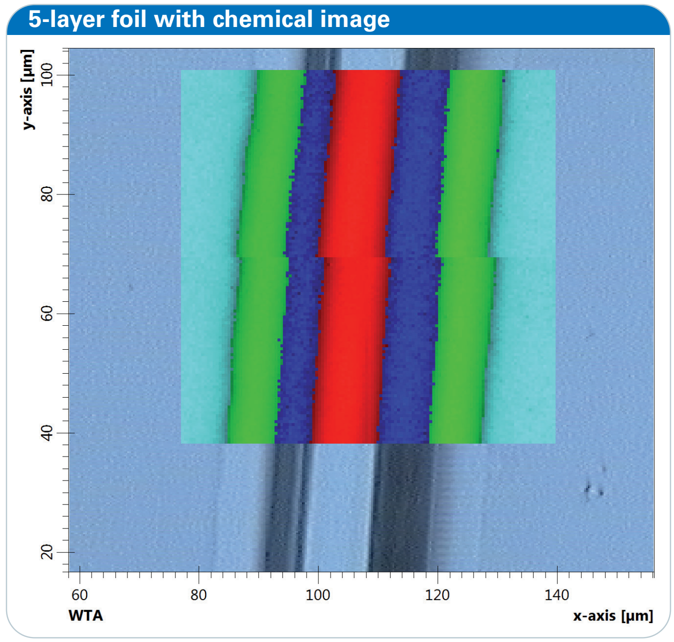

Figure 7: Visual image of the 5 layer foil with chemical image.

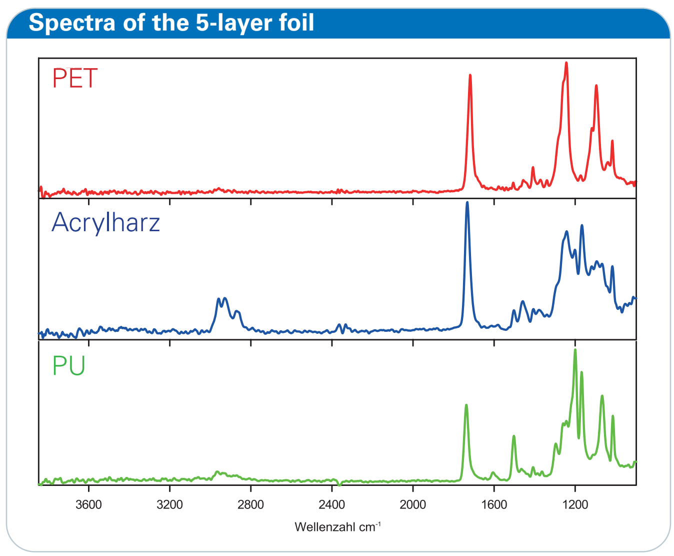

Figure 8: Spectra of the 5 layer foil in the respective colors of fig. 7.

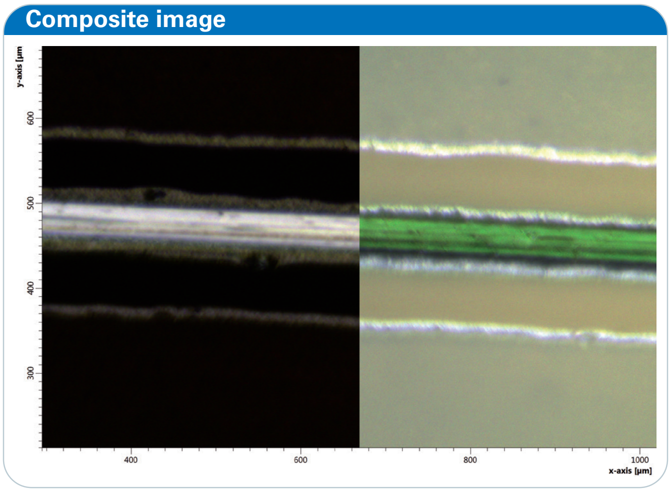

Figure 9: Visual composite image. Left without and right with polarizers.

Using polarizers to enhance the contrast

The LUMOS II microscope offers just as the microscopes of the HYPERION series optional polarization filters that facilitate the visual imaging of low contrast multi-layer samples. Figure 9 is showing the visual image of a sample; on the left side without and on the right side with the aid of polarizers. The contrast is increased and the different materials can be more easily discerned.

Summary

FTIR microscopy is a very effective method for the analysis of composite films. Using FTIR microscopy allows identifying both material and thickness of the individual layers in a foil.

The LUMOS II is compact and easy to use IR-microscope with a high sensitivity. With the HYPERION 3000, the smallest structures can be analyzed with the highest possible lateral resolution. Both systems are equipped with high- performance ATR-objectives that facilitate the fast analysis of foils without the need for an extensive sample preparation.

Bruker Scientific LLC

Billerica, MA · USA
Phone +1 (978) 439-9899
info.bopt.us@bruker.com

Bruker Optics GmbH & Co. KG

Ettlingen · Germany
Phone +49 (7243) 504-2000
info.bopt.de@bruker.com

Bruker Shanghai Ltd.

Shanghai · China
Tel.: +86 21 51720-890
info.bopt.cn@bruker.com

www.bruker.com/optics