Application Note AN M112

Failure analysis of packaging materials

Introduction

Packaging materials are often composed of various layers that fulfill different functions. The actual packaging foil has a barrier function and is, depending on its intended purpose, already made from different layers. As foil material mainly polymers are used but also other materials like for instance aluminum. Added are other layers like an adhesive sealing or printing. Defects in such complex multi layered systems like inclusions can result in product malfunctions. Since many of the different materials cannot be distinguished visually and the defects are often microscopically small the selective analysis of these defects is often difficult.

FT-IR microscopy is an attractive method for failure analysis. It allows to measure an IR spectrum from structures in the micrometer range at high lateral resolution. The IR spectra provide information about the chemical identity of the defects and allow to distinguish between different layers. With FT-IR microscopy a chemical image of the sample can be recorded showing its compsition and distribution of the defect.

Instrumentation

The LUMOS II FT-IR microscope (figure 1) is an all in one solution with an integrated spectrometer, a high degree of motorization and a dedicated user-interface. Its 8x objective

Keywords	Instrumentation and Software
FT-IR microscopy	LUMOS II FT-IR Microscope
Packaging films	OPUS 7.5
Multilayer films	OPUS/SEARCH
Failure analysis	ATR-COMPLETE spectral library
Coatings	
Polymers	
Mixture analysis	
Principal Component Analysis (PCA)	

Fig. 1: LUMOS II stand-alone FT-IR microscope.

provides the measurement modes ATR, transmission and reflection with high quality visual inspection capabilities. The innovative motorized **A**ttenuated **T**otal **R**eflectance (ATR) crystal allows performing the complete measurement procedure fully automated including background and sample measurements. Due to the high refractive index of the ATR crystal material (Germanium) even very dark materials can be analyzed. A high working distance and the unobstructed access to the sample stage facilitate an easy positioning of the sample. The large field of view of 1.5 x 1.2 mm and the high depth of focus make sample inspection very comfortable. In combination with a motorized stage, fully automated mapping measurement can be performed. The dedicated OPUS Video-software is guiding the user through the whole measurement procedure and always provides the most suitable functions for the current measurement step.

Also all data evaluation is performed using the OPUS spectroscopic software. For identification of sample components spectrum search and mixture analysis are applied using the functionality of the OPUS/SEARCH package. Chemical images of the spectral data are generated from univariate and multivariate analysis results.

Example: Failure analysis of a packaging foil

A transparent packaging foil with a defective area was analyzed in this example. Several measurement positions were set on the defect but also on the intact foil. The measurements were performed fully automated using the ATR-mode with an acquisition time of 20 seconds/spectrum and at spectral resolution of 4 cm^{-1}. The polymer used as foil material could be identified as a polyvinylidene chloride – acrylate copolymer by spectrum search with the comprehensive ATR-COMPLETE library (figure 2).
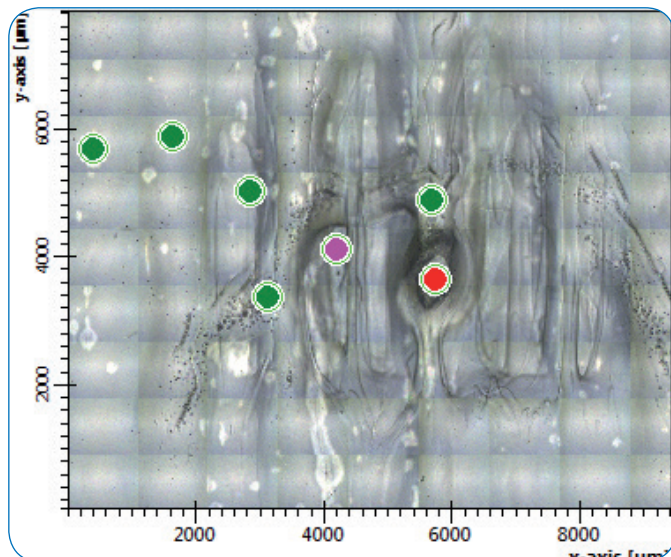

Fig.2 a: Visual microscopic image of foil with defects. Measurement positions are indicated as circles.
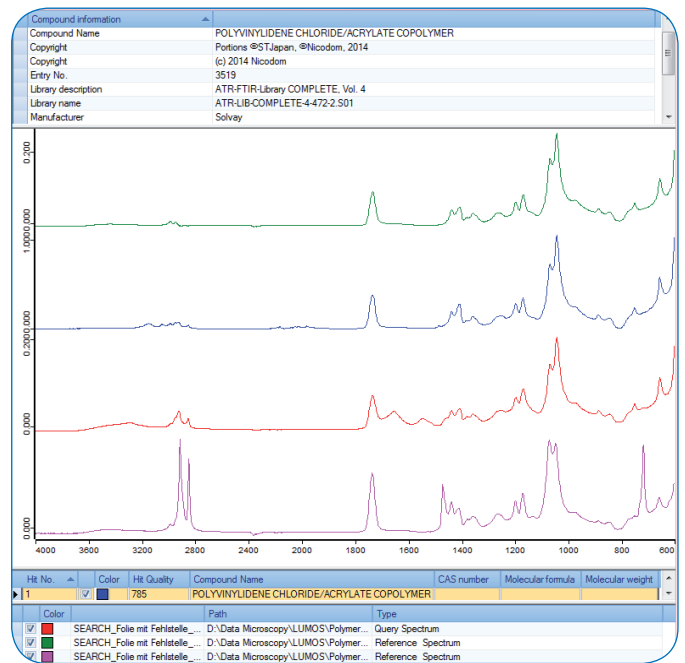

Fig.2 b: Identification of the foil spectrum (green) by spectrum search as polyvinylidene chloride – acrylate copolymer (blue spectrum). The spectra measured on the defects (red and pink) clearly show additional bands.

The spectra measured on the defective area show the spectral signature of the basic foil material but also additional bands. The library search functionality in OPUS provides powerful tools to determine the components that contribute to such mixed spectra:

- If the result of a spectrum search explains some but not all of the bands of the query spectrum an automatic subtraction of the library spectrum and the search of the residual spectrum can be performed with a single mouse click. In case of the spectrum measured in the center of the black spot on the foil (red) this function provides the clear result that the additional component is a polyamide resin (figure 3 a).
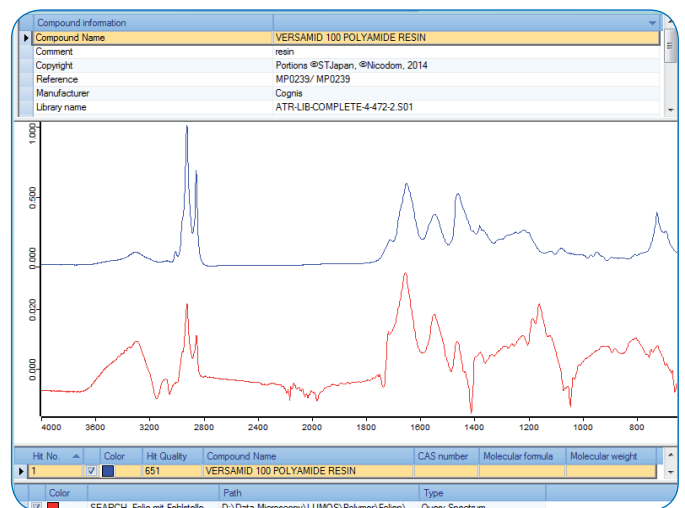

Fig.3 a: Identification of the additional component in the spectrum of the defect (red) by search of the difference spectrum between the query spectrum and the library spectrum of the basic foil material.

- The OPUS mixture analysis finds the best combination of library spectra to match the bands of the sample spectrum. For the second spectrum measured on the defect (pink) the mixture analysis determines the presence of a polyethylene additionally to the basic foil material (figure 3 b).

		Color	Content [%]	Compound Name	CAS number	Molecular formula	Molecular weight
1	☑		50.7	POLYVINYLIDENE CHLORIDE/ACRYLATE COPOLYMER			
2	☑		49.3	POLYETHYLENE, HOSTALEN GM 7040	9002-88-4	(C2H4)n	

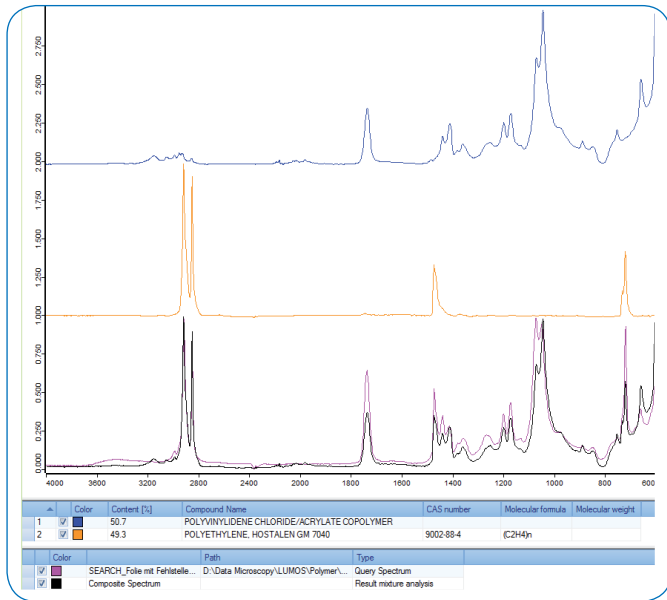|	Color	Path	Type
☑		SEARCH_Folie mit Fehlstelle...	D:\Data Microscopy\LUMOS\Polymer\...	Query Spectrum
☑		Composite Spectrum		Result mixture analysis

Fig.3 b: Result of the mixture analysis of the second spectrum measured on the defect (pink). Apart from the basic foil material (blue spectrum, polyvinylidene chloride – acrylate copolymer) polyethylene is detected (orange spectrum). The combined spectrum (black) of the two determined components is overlaid with the sample spectrum.

Example: Analysis of the homogeneity of a coating

The second example shows the analysis of a clear and colorless plastic foil which is coated with a layer of melamine resin. The goal was to determine whether the resin layer is covering the whole surface and whether there were defects in the layer. An area of 1.5 x 2.0 mm in size was analyzed via an automated grid measurement in ATR-mode. 1200 spectra were measured with a spatial resolution of 32 x 32 μm, a measurement time of 3.5 seconds per spectrum and a spectral resolution of 4 cm^{-1}.

To detect any deviations in the spectral matrix a cluster analysis was applied: all spectra within the measurement area were grouped into two classes according to their spectral similarity. The algorithm used for classification was Euclidian distance.

The chemical image resulting from the cluster analysis is shown in figure 4. It is obvious that the dark spots in the visual image also show a spectral deviation as they are assigned to another class (colored in red) than the matrix (colored in black).

The comparison of spectra from the „red class" against those of the „black class" reveals a lower spectral intensity of bands which belong to the melamine coating (figure 4 below). Additionally the library search clearly identifies a higher contribution of polypropylene-co-ethylene which is likely to originate from the substrate beneath the melamine coating.

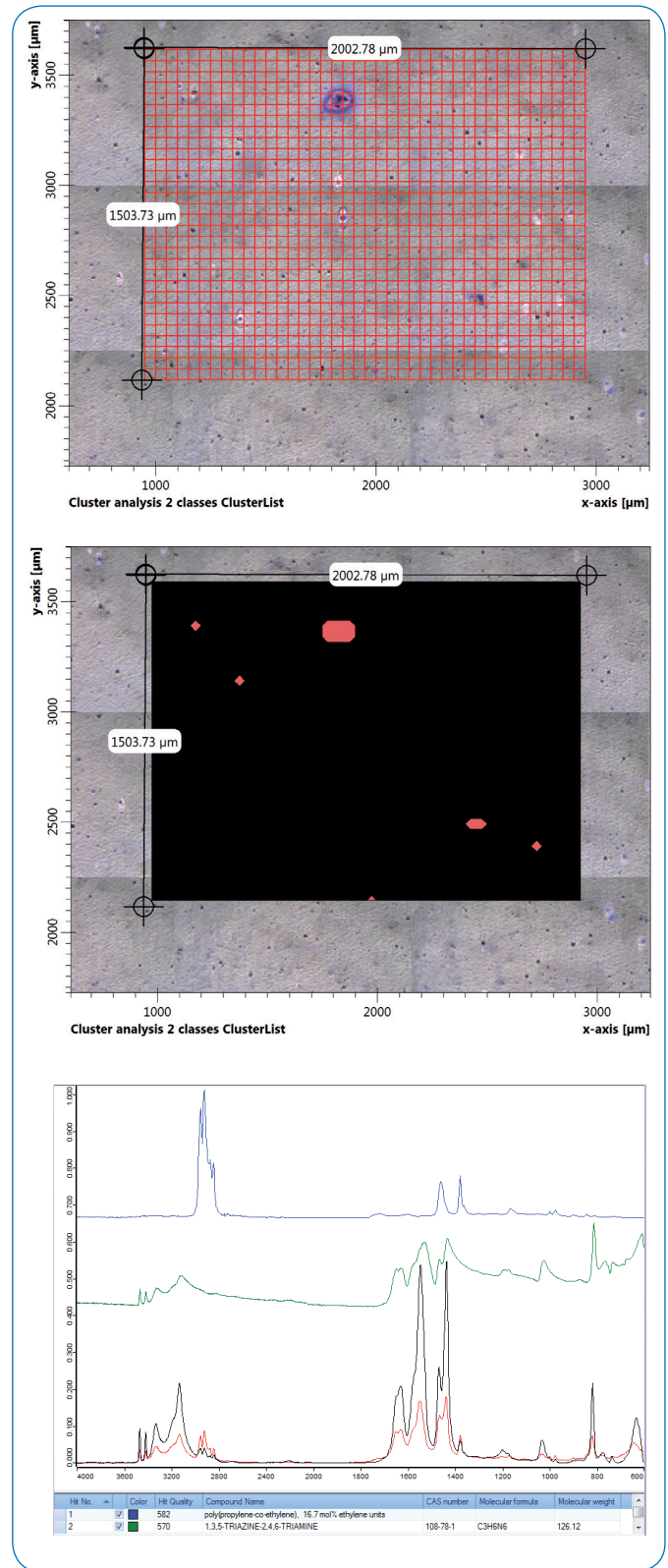| Hit No.		Color	Hit Quality	Compound Name	CAS number	Molecular formula	Molecular weight
1	☑		582	poly(propylene-co-ethylene), 16.7 mol% ethylene units			
2	☑		570	1,3,5-TRIAZINE-2,4,6-TRIAMINE	108-78-1	C3H6N6	126.12

Fig. 4: Top: Visual microscopic image of a melamine coated plastic foil. The red rectangles indicate the measurement grid that was set for the IR-spectroscopic analysis. Middle: Chemical image resulting from the cluster analysis of the spectra measured on the foil. Bottom: Spectra from the two classes with according colors (red/black) compared against hits from library search. The red spectrum shows a much lower melamine content (green) than the black one but higher contribution of polypropylene-co-ethylene (blue).

Example: Examination of a cold sealing area

The packaging foil that was examined in this example has an acrylic coating and an overlying cold seal strip. The aim of the study was to determine if upon opening of the pakkaging, the acrylic layer is damaged and to what extent the cold seal is peeled off. An area of 1.5 x 2.0 mm in size was analyzed with a spatial resolution of 32 x 32 µm and similar measurement parameters like in the previous example.

The evaluation was performed by applying a principal component analysis (PCA). By automated analysis of all spectra inside the 3D data the PCA helps to detect the different spectral characteristics inside the sample. Thereby the used sample materials and also little aberrations like defects are tracked, even if they are not detectable in the visual image.

During PCA the spectra are transformed into a matrix of factor spectra and the associated factor weights called „scores". The scores are coefficients that show the share of a factor spectrum on a certain measured spectrum. Inside a spectral dataset typically only a few factors are sufficient to represent the spectral variance which originates from different sample components. The large majority of factors mainly contains noise.

In this example the first two factors of the PCA represent the expected sample materials: The acrylic layer and the cold seal. The distribution of these two components is visualized in the chemical images 5.1 and 5.2 that result from the according score plots. Though, the score plot of factor 3 reveals a third component which is present only in a very limited region of the sample (figure 5.3).
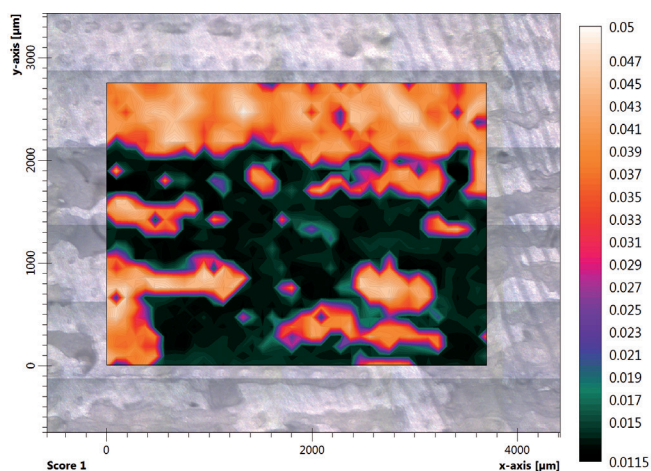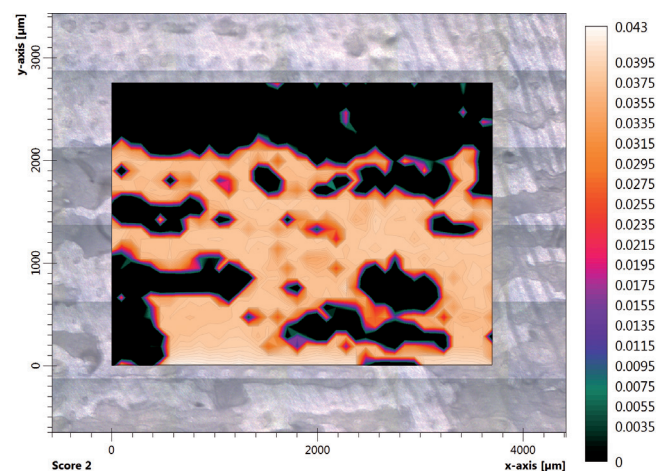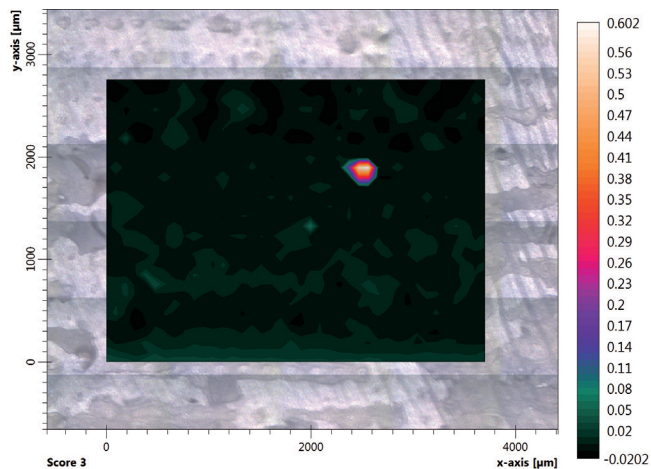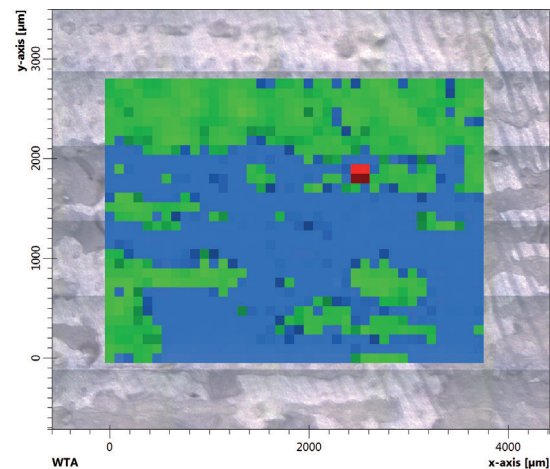

Fig. 5.1

Fig. 5.2

Fig. 5.3

Fig. 5.4

Fig. 5.1 - 5.4: Chemical images of the cold seal area of a packaging foil on top of the visual image. Distribution of the cold seal (5.1), the acrylic layer (5.2) and of the defect (5.3). The image number 5.4 shows the information of the individual chemical images combined in one single WTA-image (green = acrylic layer, blue = cold seal and red = defect).

With the aid of a so called „Winner Takes it All" (WTA) algorithm one plot can combine the information of different chemical images in one image. The WTA-algorithm assigns to each individual pixel the color of the dominating component thus allowing to visualize more than one component in one image. The image on the lower right (figure 5.4) shows the cold seal in green, the acrylic layer in blue and the defect in red. The according spectra of the three components are shown in figure 6.
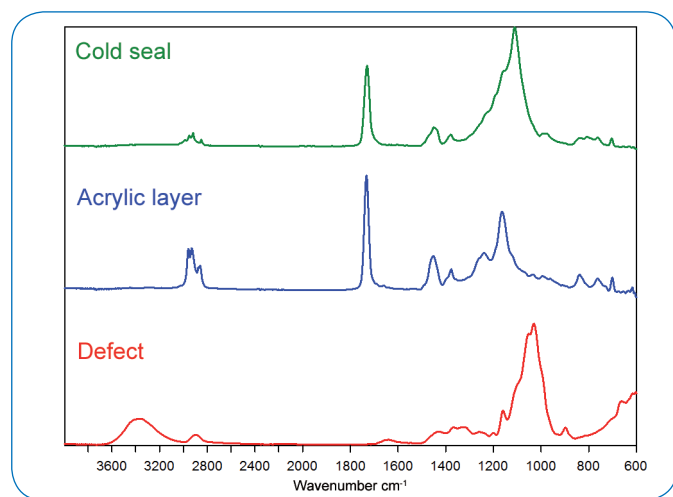

Fig. 6: Typical spectra of the different components found in the cold seal area

Identification of the components was performed by library search. As expected the coating spectrum was identified as an acrylic dispersion in dried form (trade name "Neocryl"). Also, the cold seal consists of a acrylic based polymer but additionally includes silicate as filler. The spectra measured on the defect are typical for viscose.

Summary

The LUMOS II FT-IR microscope allows to detect and to analyze smallest defects in packaging materials. Beside visual analysis and punctual IR-measurements also fully automated mapping measurements can be performed. Evaluation by functions like integration of bands, principal component analysis or 3D-cluster analysis results in chemical images. These chemical images can be graphically analyzed and presented in a variety of ways. With these tools product defects can be identified and their causes be tracked.