Application Note AN M136

Quality Control and Failure Analysis of Rubber Samples

Keywords	Instrumentation and Software
Rubber	ALPHA II FT-IR spectrometer
Failure Analysis	LUMOS II FT-IR microscope
O-Rings	OPUS spectroscopic software
Polymers	

Rubber materials can be classified into natural and synthetic variants whereupon the majority of the traded materials are of synthetic origin. Often these products are complex mixtures that contain a multitude of different components. In order to guarantee a constant product quality, it is crucial to check the quality of in- and outgoing goods on a regular base.

The infrared (IR) spectroscopy is an efficient analysis method to check the chemical identity of incoming goods as well as intermediate- and end-products. Alongside quality control, the IR-spectroscopy is a helpful tool for reverse engineering of competitive products and also allows quantifying single components such as fillers. The ideal tool for routine IR-measurements is the compact FT-IR spectrometer ALPHA II (figure 1, right). It can be equipped with a very broad range of sampling modules like for instance ATR, transmission of diffuse reflection (DRIFT) units and can be used for a multitude of different applications.

When analyzing product failure, it is often not easy to determine the source of errors since in many cases microscopically small defects are present that are not accessible by a macroscopic measurement approach. For such small

Figure 1: LUMOS II FT-IR microscope and ALPHA II FT-IR spectrometer

and inhomogeneous polymer samples, the FT-IR microscope LUMOS II (see figure 1, left) is the system of choice, since it allows to visualize and measure the smallest inclusions and blooming. For the identification of the unknown sample components, the measured spectrum is searched in dedicated and extensive libraries.

Principle of the FT-IR spectroscopy

The FT-IR (Fourier-Transform Infrared) spectroscopy is an analysis technique that is established for many decades. It uses the fact that each chemical substance has its own spectral signature, just like a fingerprint. Figure 2 shows the spectra of a monomer, a polymer and a filler. Therefore, the FT-IR spectroscopy is applied for the analysis of organic and inorganic substances and can be used for both pure substances and mixtures. It uses invisible infrared light that is being absorbed differently at different wavenumbers, depending on the sample characteristics. The position and intensity of the measured absorption bands can be used for both identification and quantification of samples and mixtures.

Smaller samples can be analyzed with the aid of the FT-IR microscopy that allows to measure samples down to the micrometer scale, such as fibers and particles. Since it is possible to measure precisely defined sample areas, thin layers, or inclusions can be identified selectively. Via fully automated raster measurements so called chemical images of the sample can be generated, that show the distribution of individual chemical compounds.

Instrumentation

Today most routine measurements are mainly performed with the ATR (Attenuated Total Reflection) technique, as this is much more comfortable to use than the conventional transmission mode. Hereby the IR radiation penetrates slightly (a few microns) into the sample surface. The IR detector of the FT-IR spectrometer can then measure the absorbance resulting from the sample. Typically, only a small amount of sample and no sample preparation are required. Another benefit are the very low running costs since no consumables are needed.

The ALPHA II FT-IR spectrometer from Bruker is a compact instrument for incoming goods inspection and quality control that can also be used for many applications in the product development. For the measurement, the sample just has to be brought into contact with the ATR-crystal. Solid samples need to be pressed against the crystal via a pressure mechanism, liquid samples can be measured directly (see figure 3). The most common crystal material is diamond since it is extremely hard and chemically inert. Especially for dark samples with high soot content, however, germanium is often the better choice due to its significantly higher refractive index.

With the aid of the FT-IR microscope LUMOS II it is also possible to analyze microscopically small samples like defects, particles und inclusions without any sample preparation.

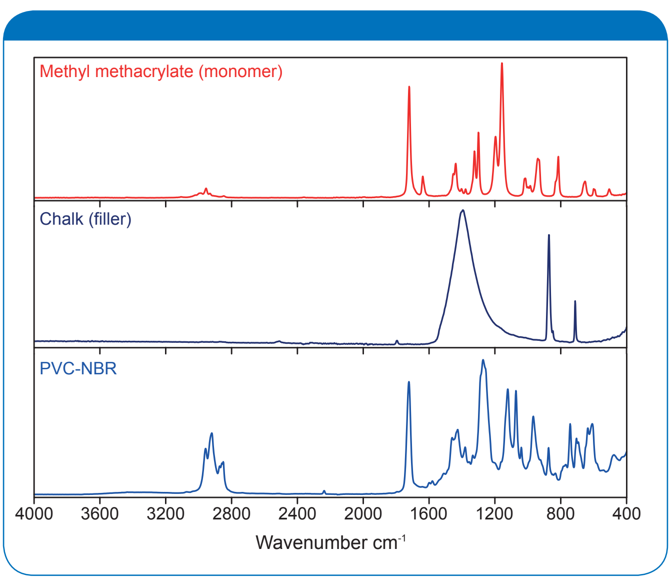

Figure 2: IR-Spectra of a monomer, a filler and the polymer PVC-NBR

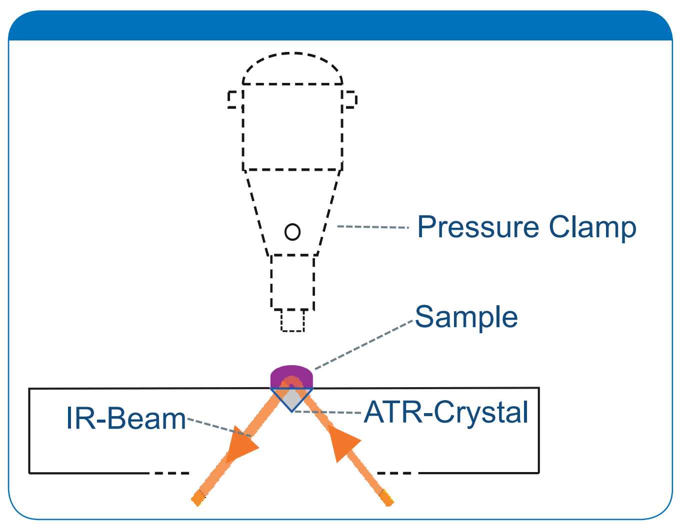

Figure 3: Schematic picture of the ATR measurement technique. The infrared light is guided through the ATR-crystal.

Application example: Analysis of an O-Ring

The use of wrong O-rings poses a high risk of severe accidents and expensive damages as it might result in failure of machines and even complete industrial production facilities. O-rings are made from a very broad range of different compositions, which can differ dramatically in terms of chemical and physical properties.

The following example shows the measurement of a 7 mm O-ring made from an unknown material. The spectrum was measured with germanium-ATR unit and thereafter identified with an automated comparison against a digital library with ca. 280 spectra. Figure 4 shows the result of the library search with the sample spectrum shown in red and the library spectrum of the first hit shown in blue. The baseline drift of both spectra results from the very high black carbon content of the sample. With a very good hit-quality of 924 (max. 1000), the sample is being identified as a Nitrile Butadiene Rubber (NBR).

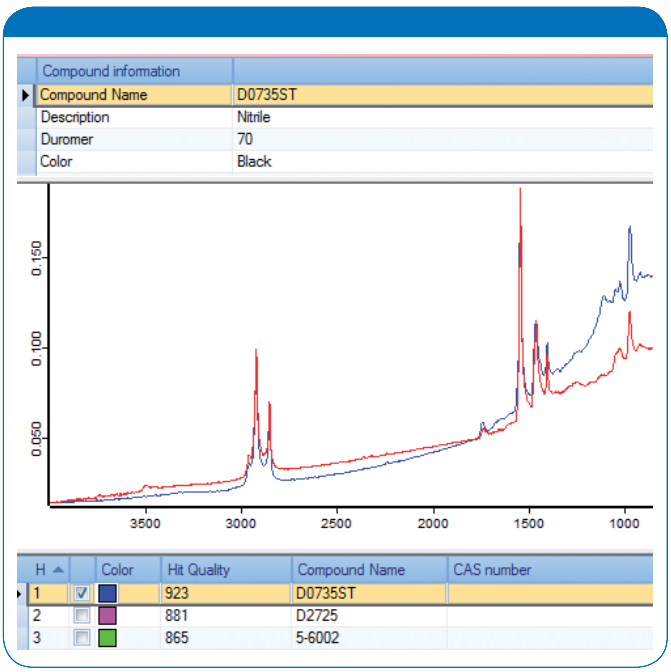

Figure 4: Result of the spectra search with sample- (red) and library-spectrum (blue).

Application example: Failure analysis of a rubber sample

The black rubber sample examined here has microscopically small impurities in the form of white spots. Furthermore, there are vaguely discernable inhomogeneities with much weaker contrast in the visible image. For the determination of the composition, the sample was analyzed by using IR-microscopy.

The measurement was performed with the Bruker FT-IR microscope LUMOS II with the sample fixed in a miniature sample holder. An area of 1000 x 1250 µm (20 x 25 measurement points) was measured fully automated. This approach allows assigning an individual spectrum to each 50 x 50 µm sized image area.
These spectra can be transferred by mathematical methods (integration, cluster analysis, factorization) into so called chemical images which allow drawing conclusions about the local chemical composition. The chemical image in figure 5 was generated with the cluster analysis function of OPUS that groups spectra according to their similarity.
It clearly shows the contaminations on the sample that can also be seen in the visual image. Additionally, also such contaminations are visible that are invisible in the visual image due to a lack of contrast.

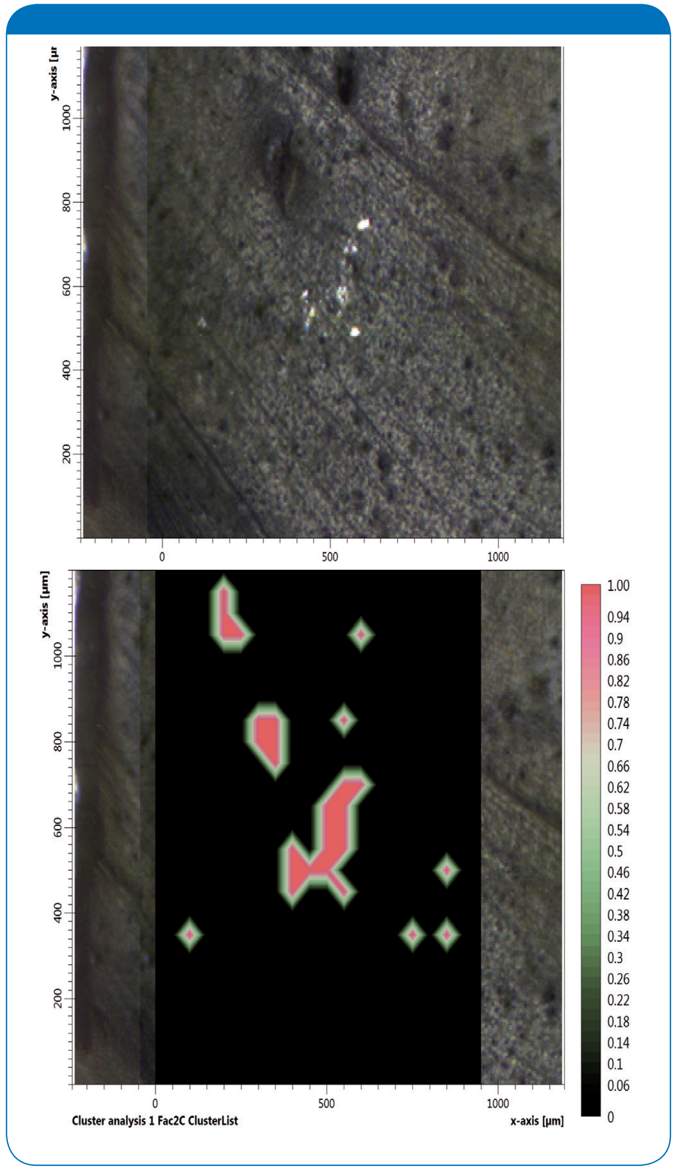

Figure 5: Visual (top) and chemical-image(bottom) of the defect on a rubber sample.

Figure 6 shows three example spectra, two spectra from the contaminated area and one spectrum of the rubber. The upper spectrum was measured in the area of the white contamination and was clearly identified via a library search as PTFE. The spectrum that was taken from the darker area is clearly a polyamide spectrum (see fig. 6 middle).

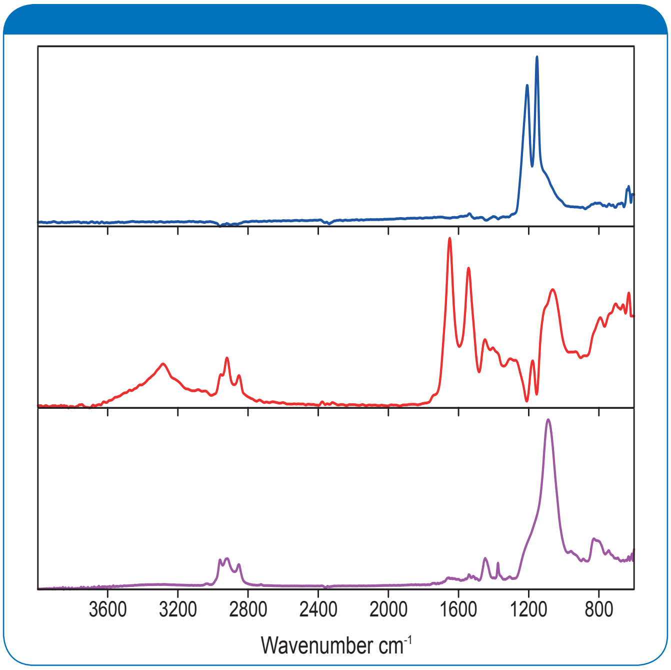

Figure 6: Subtraction-spectra of the contaminations. Top: PTFE, center: polyamide, bottom: rubber.

Summary

FT-IR spectroscopy offers a multitude of possible applications when it comes to the analysis of polymers like natural- or synthetic-rubber. Besides incoming goods inspection and product quality control, it also allows the analysis of competitive products. With the aid of extensive spectral libraries and powerful functions for the spectra search and mixture analysis, all kinds of different materials can be quikkly identified.

With FT-IR microscopy, it is possible to detect and analyze the smallest defects and inclusions. Furthermore, automated grid measurements allow creating chemical images that show the distribution of different sample components and contaminations.

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