Application Note AN M129

FTIR Analysis of Glues for Quality Control and Development

FTIR Analysis of glues

Adhesives have become indispensable in today's world and are used for various applications. In the automotive industry front consoles, windshields, seating elements, and car body parts are glued with special automotive adhesives which have led to significant weight savings. In medicine cyanoacrylate, which is well-known from its use as superglue, is used for rapid bonding of wounds. By now, adhesives with tailored properties in terms of curing time and strength are available for the most diverse applications. Modern adhesives are often complex mixtures that contain various solvents, resins, fillers, and additives. In order to ensure consistent product quality, it is necessary to check both the raw materials and the finished product and to test both chemical and physical properties.

FTIR spectroscopy is a valuable analytical technique for a variety of questions in quality control, production and the development of adhesives. The method is very suitable for both the testing of identity and quality of the incoming raw materials and the examination and quantification of the finished product. In the product development IR-spectroscopy allows to analyze the composition of a competitive product and to monitor the curing process of an adhesive. The IR microscopy is a powerful method for failure analysis, because even the smallest product defects can be analyzed and visualized in the micrometer range.

Keywords	Instrumentation and Software
Adhesives	LUMOS II FTIR microscope
Quality control	ALPHA II FTIR spectrometer
Failure analysis	OPUS spectroscopic software
Reaction monitoring	
Reverse engineering	

With the ALPHA II FTIR spectrometer, Bruker offers the right instrument for incoming goods inspection, quality control, and product development. The spectrum of a substance can be measured in seconds without any sample preparation, reagents, or consumables.
By using the FTIR microscope LUMOS II also microscopic samples such as defects, particles and inclusions can be analyzed and usually no sample preparation is required. The spatially resolved investigation of adhesives is particularly helpful when analyzing product defects, since often punctual inhomogeneities, inclusions, or impurities are the cause.

Incoming goods inspection the FTIR spectrometer ALPHA II

The ALPHA II (see figure 1) is a very compact spectrometer which can be adjusted via interchangeable measurement modules to various requirements. The most frequently used measurement technique is the so-called attenuated total reflection (ATR). Since no sample preparation is needed, the ATR technique is a very comfortable and fast measuring method. In order to measure an IR spectrum, the sample only needs to be brought into contact with the ATR crystal. For the identity check of a raw material, the spectrum is automatically compared against on or more reference spectra by the quick compare function of the OPUS spectroscopy software.

Figure 1: LUMOS II FTIR microscope and ALPHA II FTIR spectrometer (detail).

Our example shows the quality control of an amine curing agent of a two-component epoxy resin with the aid of the OPUS quick compare function. The incoming raw material (blue spectrum) is compared against a previously measured spectrum of a reference sample (red spectrum, see figure 2). A correlation value of more than 99% indicates that the sample spectrum is in very good agreement with the reference spectrum. As the correlation of the reference and sample spectrum is above the predefined threshold value of 98% the sample is rated with an „OK“.
In addition to the shown comparison against one single reference spectrum, it is also possible to compare against an average spectrum of many reference spectra in order to model product tolerances. As a third option, one can also compare against a set of different substances.

Measurement of the curing time of an adhesive with the ALPHA II spectrometer

This example illustrates the reaction monitoring of an adhesive with the ALPHA II spectrometer. By using the reaction monitoring function of OPUS, it is possible to monitor the whole curing process with a time resolution

Fast spectral comparison

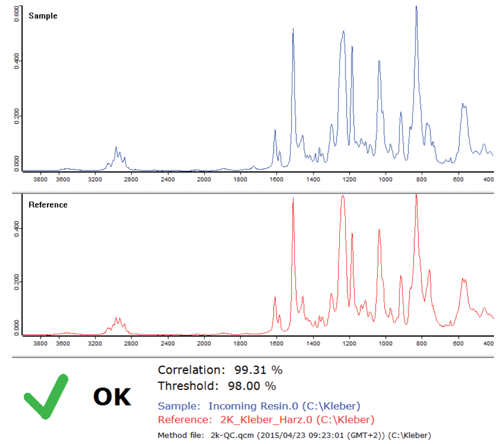

Figure 2: Incoming goods control: The result of the spectra comparison of an amine hardener (blue) against an according reference spectrum (red) verifies the correct identity of the material.

down to one second. In the following, we show the curing of a plastic adhesive. The adhesive consists mainly of butyl acetate, acetone, and poly methyl methacrylate (PMMA). For the measurement, a small drop of the adhesive was placed on the diamond crystal of the ATR unit. Then a spectrum was automatically measured every 30 seconds. Figure 3 shows the temporal evolution of the components butyl acetate and PMMA.
The evaluation was performed via the integration of spectral bands that are specific for PMMA (1144 cm^{-1}) and butyl acetate (1040 cm^{-1}). The concentration of PMMA (blue curve) rises as expected due to the evaporation of the solvent while the concentration of butyl acetate (red) shows an increase prior to the continuous decrease. This increase can be explained by the fast evaporation of the acetone in the first minutes. Thereby the concentration of the slowly evaporating butyl acetate increases initially. Finally, after the complete evaporation of the acetone, the butyl acetate concentration also decreases. The 3D-plot in figure 3 (left) shows the temporal evolution of the butyl acetate-band around 1040 cm^{-1}.

Reaction monitoring

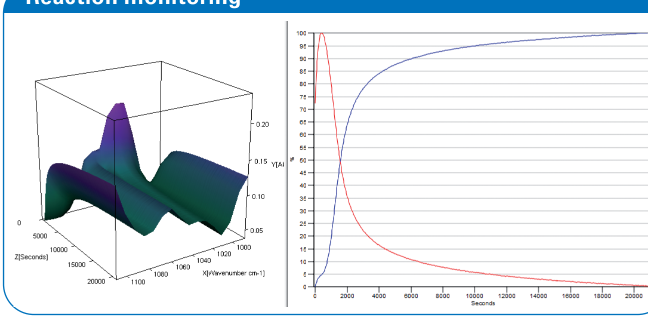

Figure 3: Screenshot of a reaction monitoring of the curing of a plastic glue. Left: 3D plot of the spectra vs. time. Right: Concentration change of butyl acetate (red) and PMMA (blue) calculated from the spectral change during the curing process.

Reverse engineering of an adhesive

The analysis of competitive products can stimulate the development of own products and can help to identify patent infringement. For the identification of unknown materials, the spectrum search in reference libraries is used. The OPUS spectroscopy software also contains a mixture analysis function for the identification of single components in complex mixtures. Our example shows the analysis of a multi-purpose glue with an unknown composition. A drop of the glue was placed on the diamond crystal of the ATR unit, measured and finally evaluated with the mixture algorithm. Figure 4 shows the result of the mixture analysis:

Mixture analysis

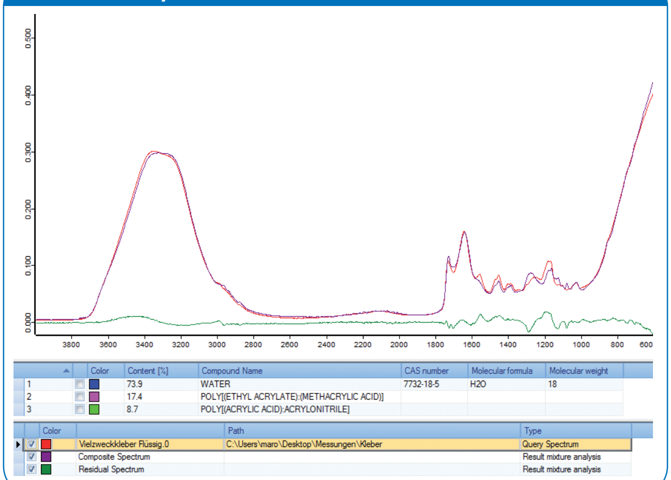

Figure 4: Result of a mixture analysis of an unknown adhesive. The composite spectrum (blue) calculated from the identified components shows a good match with the sample spectrum (red). The difference spectrum between composite and sample is shown in green.

The composite spectrum (shown in blue), which is calculated from the identified single component spectra, is in a very good agreement with the measured query spectrum. The difference spectrum (green) from the query- and composite-spectrum thus shows only small deviations. In short, the adhesive is water based with acrylate polymers.

Failure analysis with the FTIR microscope LUMOS II

The FTIR microscope LUMOS II (figure 1) is a powerful tool for the analysis of product defects. It allows to measure an IR-spectrum anywhere on the sample with high lateral resolution and thereby to identify the chemical composition of a defect. Due to the outstanding performance when measuring in ATR, the LUMOS II is able to analyze most samples without preparation. By virtue of its complete automation and intuitive user guidance, it is very easy to operate the LUMOS II.

Our sample is a piece of hardened adhesive on a piece of PET-foil, which shows microscopically small white needle like crystals.
For the analysis, the sample was fixed in a sample holder and a smooth sample cross section was generated using a scalpel. Since the defect was only barely visible with unpolarized light, the motorized polarizers of the LUMOS II were used for contrast enhancement. In the following, a sample area of 375x250 µm was analyzed by an automated grid measurement where 15x10 points were measured with an aperture size set to 25x25 µm.
The obtained spectra can be converted into so-called chemical images by mathematical methods (integration, cluster analysis, factorization), which allow conclusions about the local chemical composition of the sample. Figure 5 shows representative spectra of the pure adhesive in blue and crystalline defect in red.

The enlarged view shows the spectral differences and also the band at 1680 cm^{-1} which has been integrated to visualize the chemical image in figure 6.

Spectra comparison

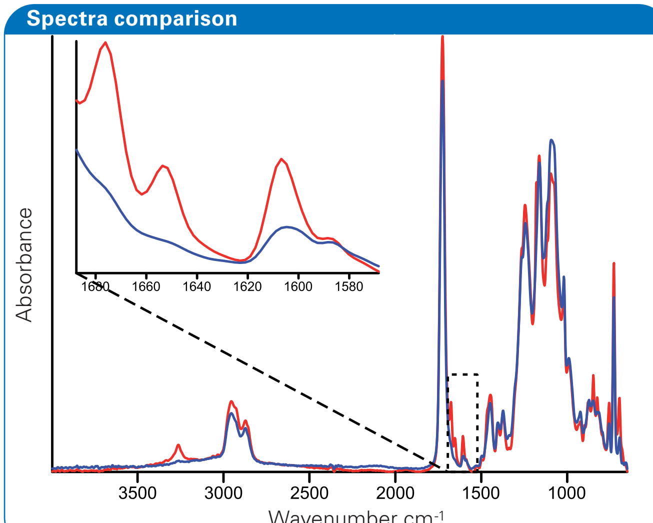

Figure 5: Spectra of the hardened adhesive (blue) and the crystals (red) show distinct differences.

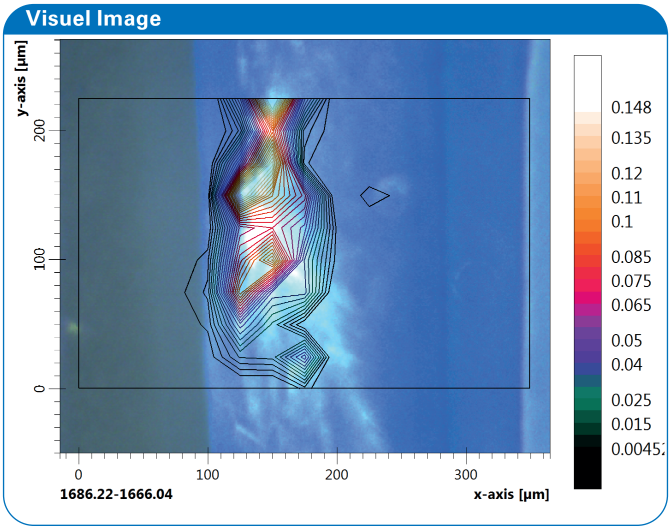

Figure 6: Superimposed chemical image on top of the visual microscopic image of an adhesive layer. The chemical image was generated by integration of a spectral band around 1680 cm^{-1} which is characteristic for crystals that were formed inside the layer.

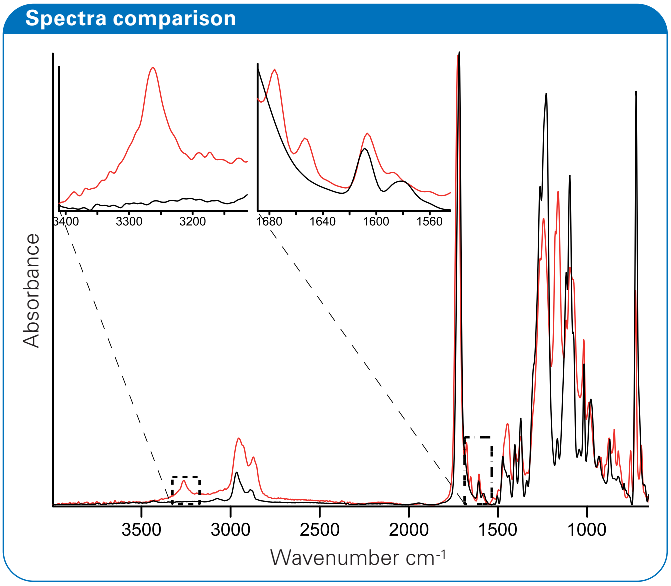

Figure 7: Spectrum of the crystals in the defect (red) in comparison with a reference sample (black). The specific spectral characteristics of the crystals are different from those of the reference spectrum.

Based on the additional band at 3267 cm^{-1} it can be concluded, that the contamination is probably a nitrogen-containing compound (e.g. an amide).

The spectrum of the crystalline substance was compared with the spectrum of a reference substance which was suspected to be the cause of the defect (figure 7). As the specific spectral characteristics of the crystals are completely different from those of the reference spectrum it is clear that the suspected substance can be ruled out as a reason for the observed product failure.

Summary

The FTIR spectrometer ALPHA II offers a variety of possible applications in the analysis of adhesives. In addition to incoming goods inspection and quality control of the product, FTIR spectroscopy also allows monitoring the reaction of adhesives and the analysis of competitive products. With the FTIR microscope LUMOS II it is possible to analyze defects and inclusions in adhesive surfaces with an achievable resolution in the range of only a few micrometers.

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