



Application Note AN M113

IR-spectroscopic polymer analysis

Introduction

The classic analysis for polymer identification uses various methods as for example determining the solubility behaviour as well as the density and the softening or melting range. Also the analysis of pyrolysis products and combustion behaviour, which is partially associated with an olfactory test, are still-used procedures. In addition, also complex wet-chemical methods are used in which the polymer must be first solubilized before the analysis, e.g. by using sodium. All in all the expenditure of time and chemicals is often very high for these methods, so that a rapid quality control is sometimes not possible. Moreover many of the plastics used today are complex multi-component systems composed of different polymers, fillers, plasticizers, flame retardants and stabilizers. Therefore in the analysis of such plastics it is of great interest to identify and quantify the individual components.

The Fourier Transform Infrared (FTIR) spectroscopy is a very fast and accurate method for the analysis and quality control of polymers. High quality IR spectra can be measured within a few seconds and normally there is no need for an extensive sample preparation. In only a minute, the FTIR spectroscopy allows to make a statement about the quality of the product or to determine whether a product is within the specification. With the help of the FTIR microscopy also microscopic

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FTIR spectroscopy	ALPHA II FTIR spectrometer
FTIR microscopy	LUMOS II FTIR microscope
Polymer analysis	OPUS 7 spectroscopic software
Identification	
Quantification	
Polyamides	
Fillers	
Failure analysis	
ATR spectroscopy	

samples such as particles, inclusions and fibers can be analysed very efficiently. The spatially-resolved examination of polymers is very helpful especially in the analysis of product defects, because these are often caused by punctual inhomogeneity, inclusions or contaminations. Furthermore individual layers of complex composite materials, such as multi-layer films, can be analysed and visualized with FTIR microscopy.



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

Identification of polymers with the FTIR spectrometer ALPHA II

The ALPHA II (see fig. 1) is a very compact spectrometer which is used in combination with a diamond ATR unit and is able to measure even very hard plastics. The ATR technique is based on the Attenuated Total Reflection and is a very comfortable and fast measuring method as there is virtually no sample preparation required. For recording the IR spectrum the sample must only be brought into contact with the ATR crystal.

Example: Differentiation of polymers

Most of polymers can be spectrally very easily distinguished because they are, from a chemical point of view, very different. As an example, figure 2 shows the spectra of polyethylene terephthalate (PET), polystyrene (PS) and polypropylene (PP). Clear differences in the spectra can be seen here at first sight.

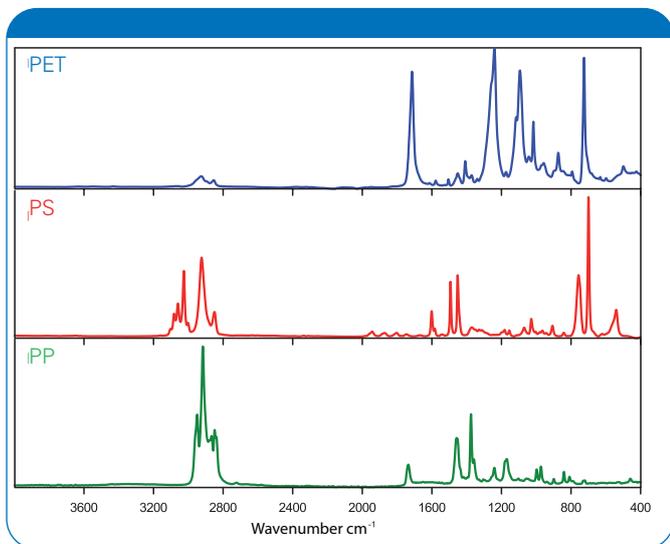


Figure 2: IR spectra of polyethylene terephthalate (top), polystyrene (middle) and polypropylene (bottom).

This looks somewhat different for the group of polyamides: despite different physical properties the polyamides 6, 6.6, 6.10 and 6.12 are chemically very similar. The only difference between the polyamides 6.6, 6.10 and 6.12 is the carbon chain length of the dicarboxylic acids which are used as monomers. Since the basic structure of the polyamides is the same one would not expect significant differences in the IR spectra. Indeed, at first glance, the spectra of the measured polymers look very similar and it seems difficult to say which spectrum belongs to which polymer (see figure 3). A closer examination shows that there are differences in the region between 1800-400 cm⁻¹ (see figure 4). These small differences are sufficient to discern the single polymers from each other. With the help of the „spectra comparison“ function in OPUS, all of the four polyamides can be identified successfully and no false positive result occurs.

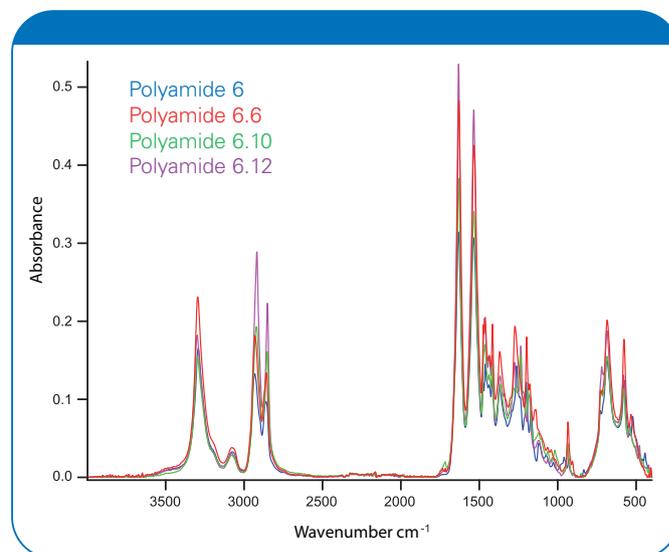


Figure 3: Spectra of polyamides measured with an ALPHA II-P spectrometer.

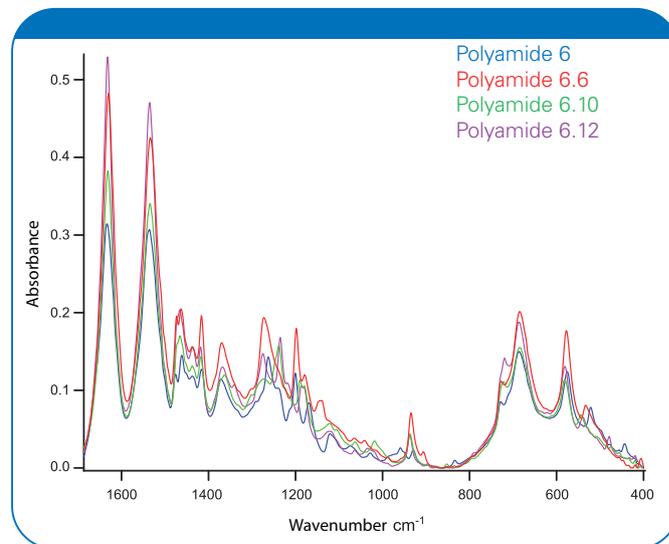


Figure 4: Magnification of the spectra from figure 3.

Example: Identification of a filler

Talcum is used as a filler in many polymers and can be both identified and quantified IR-spectroscopically. Talcum is from a chemical point of view the powdered form of the silicate mineral talc with the sum formula $Mg_3Si_4O_{10}(OH)_2$. It is mixed with polymers in order to optimize their properties like for instance elasticity, impact resistance or color fastness. The result of the measurement of four different polypropylene (PP) samples with different talcum contents can be seen in figure 5. The upper spectrum is pure PP; the spectra below have increasing talcum content up to 40%. The most prominent features are broad bands around 1000cm^{-1} and 670cm^{-1} that result from the Si-O stretching modes. Furthermore a broad band around 400cm^{-1} can be attributed to the Si-O bending modes. It is obvious that the amount of talcum directly relates to the intensity of the named bands, a fact that can be used for a quantitative analysis.

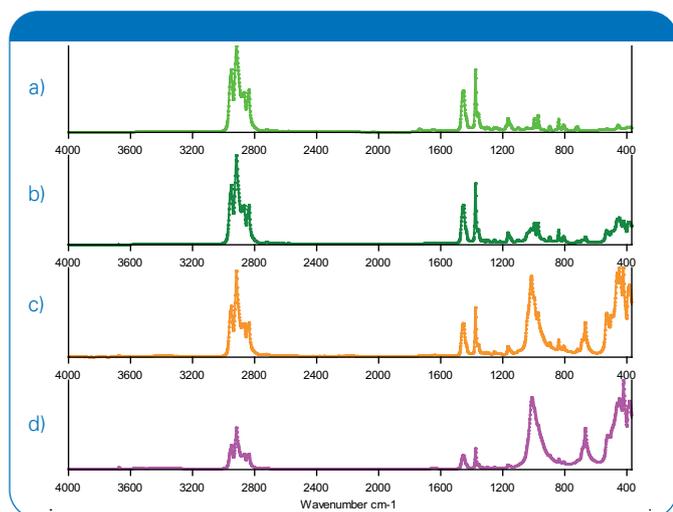


Figure 5: Spectra of polypropylene with varying talcum content: 0% (a), 10% (b), 20% (c) and 40% (d). All spectra were measured with an ALPHA II-P.

Analysis of product defects with the FTIR microscope LUMOS II

The LUMOS II is a very compact FTIR microscope that needs no additional external IR spectrometer. Thanks to the high degree of automation and user-friendly software, it is very easy to use. With the fully motorized germanium ATR crystal, it is possible to measure small samples which are only a few micrometers in size. In addition, the LUMOS II enables the recording of high-quality visual images, transmission and reflectance measurements as well as fully automated mappings even in ATR.

Example: Analysis of a product defect

In our example we want to analyze black streaks on a polycarbonate sample shown in figure 6. The question is if the streaks are on the surface or embedded in the PC-matrix and what their chemical nature is. For the analysis altogether six measuring points were set on the

sample and then automatically measured (measuring time approx. 2 min.). The location of the measurement points is highlighted in figure 6 with colored dots. A selection of result spectra is shown in figure 7. The upper spectrum is from the polycarbonate matrix and the middle one from the contamination that is marked with a purple dot. Since the spectra of the black spots still contain strong bands of the polycarbonate matrix, a difference spectrum was created by subtracting the polycarbonate spectrum from the spectrum measured on the black spot. The lower spectrum in figure 7 shows the result. A library search reveals that the contaminations originate from a black ink marker (marker ink black 6558). With this information it is now feasible to track down the source of the black streaks and to prevent further contaminations.

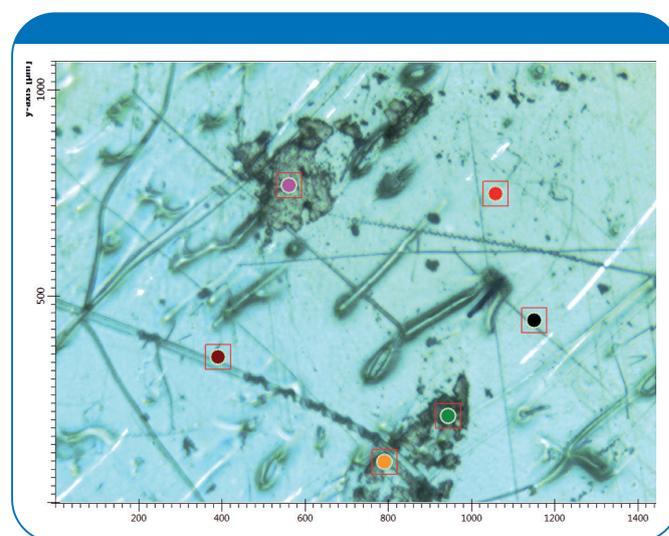


Figure 6: Visual image with the LUMOS II microscope of the polycarbonate sample with contaminations and measurement positions.

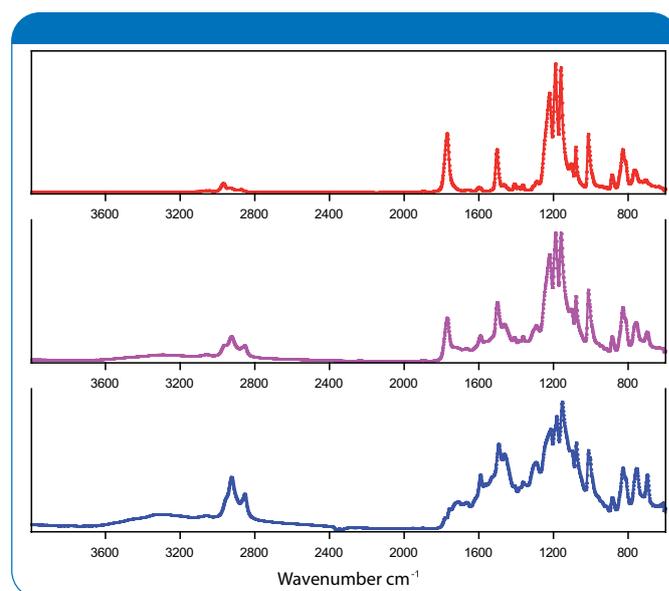


Figure 7: ATR spectra of the clean polycarbonate matrix (top) and the black spot (middle). The lower spectrum is the difference spectrum.

Chemical imaging of heterogeneous plastic materials with the FTIR microscope LUMOS II

Measurements with a local resolution in the micrometer range allow to characterize the composition of plastic materials. Mapping measurements on the sample reveal the distribution of individual components, e.g. the basic polymer, fillers and plasticizers. Such information is valuable during product development to determine the impact of variations in the processing conditions on the material homogeneity. Furthermore the composition of competitive products can be analyzed.

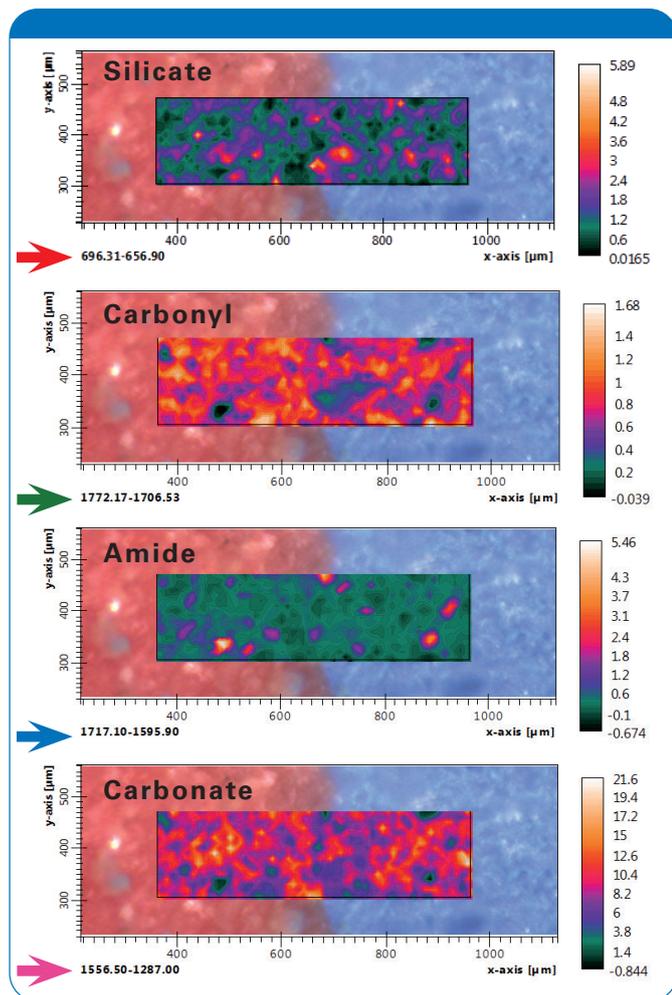


Figure 8a: Microscopic analysis of a rubber eraser. Chemical images on top of the visual sample image show the distribution of individual organic and inorganic components. The concentration is indicated by color coding (white/orange=high; black=low).

Example: Characterization of the composition of a rubber eraser

Rubber erasers are made from several components such as a natural or synthetic rubber as basic material, vegetable oil as softener and pumice, a natural mineral which makes the eraser more abrasive. In this example the distribution of some components in a rubber eraser was analyzed with LUMOS II. By applying a sequential mapping an area of 600x180µm was measured with a spatial resolution of 10x10µm. Figure 8a shows chemical images resulting from the acquired spectral data. For generation of the chemical images spectral bands which are specific for a certain component of interest were integrated (figure 8b). The images show the heterogeneity of the material's composition. Also the size of particles or clusters of individual components inside the material can be determined.

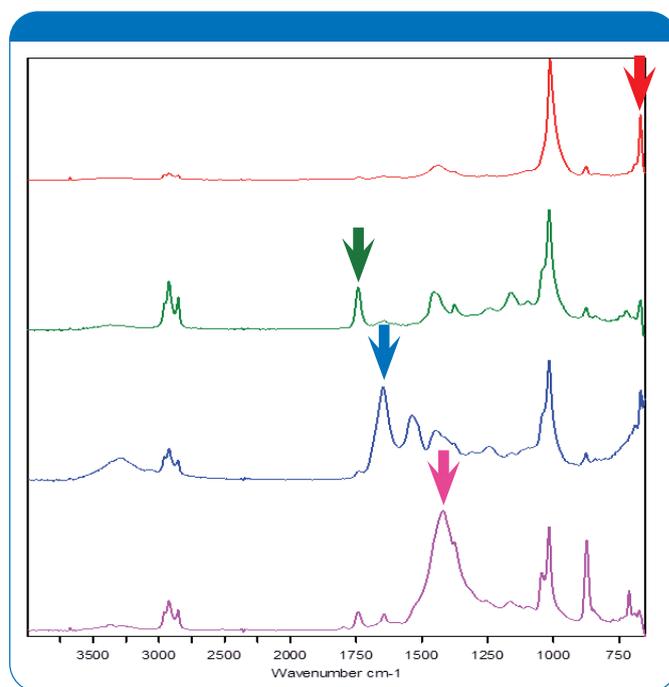


Figure 8b: Selected spectra from the rubber measurement. The indicated bands were used for generating the shown chemical images.

● 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

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