

Application Note AN # 104

IR-Spectroscopic analysis of polymer fillers and compatibilizers

Many of today's plastics are multi component systems with multiple constituents like different polymers, fillers, plasticizers and compatibilizers. By systematic selection and blending of these constituents in appropriate mixture ratios tailor made substances with optimized material properties can be made. An important topic for quality control and analytical purposes is the identification and quantification of the individual components present in such plastics.

Fourier transform infrared (FT-IR) spectroscopy is one of the fastest and most accurate methods for the analysis and quality control of polymers. High quality IR spectra can be recorded in a few seconds; usually there is no need for sample preparation or costs for expensive consumables. Within only a minute FT-IR spectroscopy allows to verify that a given product is within its specification or to quantify one or more of its constituents.

Measurement approach

Nowadays, quality control and routine analysis using IR spectroscopy is mainly performed applying the ATR (Attenuated Total Reflection) technique. As there is virtually no sample preparation required ATR is much more comfortable to use than the conventional transmission mode. For the analysis the sample has to be pressed on the ATR-crystal,



Figure 1: ALPHA-P high pressure with diamond ATR.

which is the measurement interface. From the ATR-crystal, 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. The ATR-technique can be applied for almost all types of samples (e.g. solids, liquids, powders, pastes, pellets, slurries, fibres etc.). The analysis takes less than a minute, including sampling, measurement and data evaluation. By using ATR, it is even possible to differentiate between the top layers of a polymer laminate, which cannot be achieved in transmission mode.

Instrumentation

The very compact ALPHA FT-IR spectrometer with the high pressure Platinum diamond ATR-module is a robust and affordable system that is very easy to operate. Diamond is a very hard-wearing, chemically inert and therefore ideal material for the analysis of a wide range of samples. In the platinum ATR-module the diamond is brazed into tungsten carbide. This extremely robust design allows the application of very high pressure so that even the hardest plastics can be measured. For the measurement of highly absorbing dark samples (e.g. black polymers) and thin layers an ATR-material with a high refractive index is required to limit the penetration depth of the IR-light into the sample. Therefore the Platinum ATR module can be equipped with a germanium ($n_{\text{Ge}}=4.0$) crystal plate. To provide the user an unobstructed access to the sampling area, the pressure applicator can be rotated by 360°. The software is very intuitive and a software wizard guides the user through the analysis procedure.

Results

Our first example deals with the identification of talcum that is used as a filler in polymers. Talcum is from a chemical point of view the powdered form of the silicate mineral talc

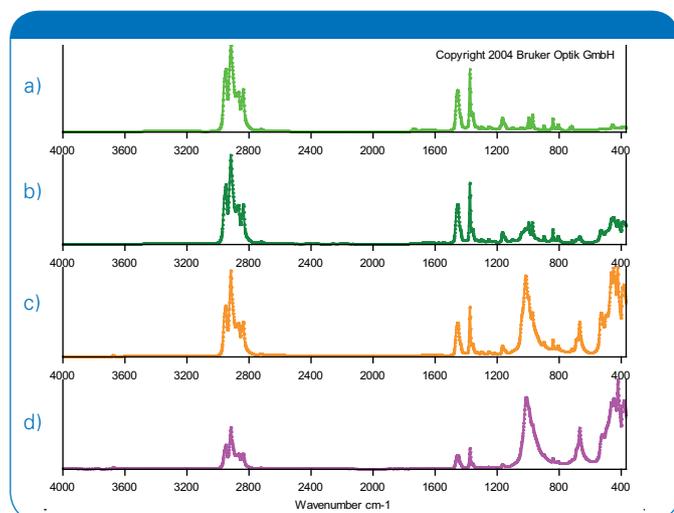


Figure 2: Spectra of polypropylene with varying talcum content: 0 % (a), 10 % (b), 20 % (c) and 40 % (d).

with the sum formula $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$. It is mixed with polymers in order to optimize their properties like for instance elasticity, impact resistance or color fastness. Talcum can be easily identified by using FT-IR spectroscopy. The result of the measurement of four different polypropylene (PP) samples with different talcum contents can be seen in figure 2.

The upper spectrum is pure PP; the spectra below have increasing talcum content up to 40 %. The most prominent features are broad bands around 1000 cm^{-1} and 670 cm^{-1} that result from the Si-O stretching modes. Furthermore a broad band around 400 cm^{-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.

In our second example we want to show the quantification of the styrene content in a thermoplastic elastomer sample. As reference sample with known styrene contents we use the triblock copolymer "styrene-ethylene-butylene-styrene" (SEBS) as shown in figure 3. SEBS is a very versatile compatibilizer that stabilizes polymer blends and is also used as a stand-alone polymer. Since the contents of the individual monomeric units are variable (indicated in figure 3 by the variables u, p and q) there are many possible repeating units with different styrene contents. Our reference sample has a content of 14.5 % styrene. Additionally we use a similar polymer with a styrene content of 4.9 % and the polyethylene/polypropylene copolymer "Tafmer" as a sample that contains no styrene at all.

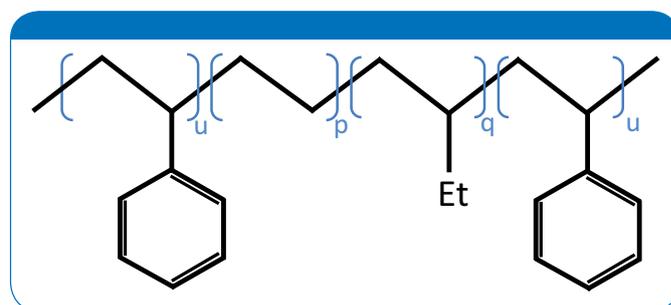


Figure 3: Structural formula of the triblock copolymer styrene-ethylene-butylene-styrene (SEBS)

With these spectra it is an easy task to set up a calibration method by using the built-in functions of the Bruker OPUS spectroscopy software. First a band that correlates with the styrene content and that is unobstructed by matrix effects has to be identified. A closer look at the fingerprint region of the reference spectra shown in figure 4 reveals two possible areas where integration can be performed: First the C=C stretching vibration band from aromatic systems around 1492 cm^{-1} and secondly the more pronounced band at 699 cm^{-1} that results from the ring out-of-plane deformation vibrations of the phenyl group.

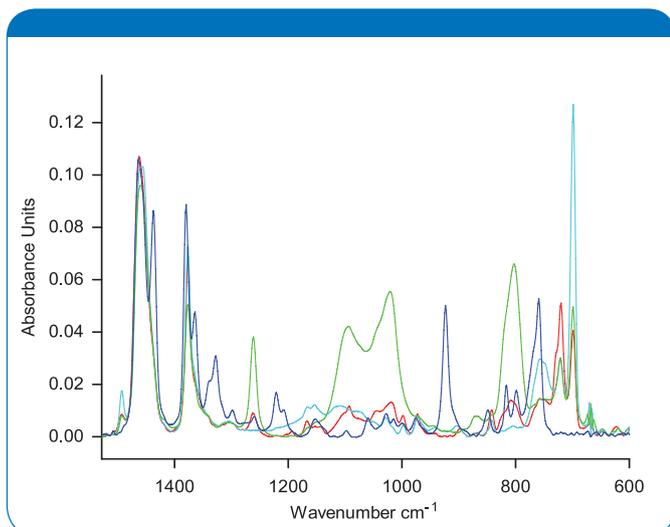


Figure 4: Fingerprint region of the reference spectra: SEBS with 14.5 % (light blue), 4.9 % (light green) and 0 % styrene (blue). The sample spectrum with an unknown styrene content is shown in red

Figure 5 shows the magnified area around the peak at 699 cm⁻¹, it is obvious that there is a direct correlation between the height/area of the peak and the styrene content: The SEBS spectrum with 14.5 % displays the highest peak whereas the peak is almost absent in the spectrum of Tafmer.

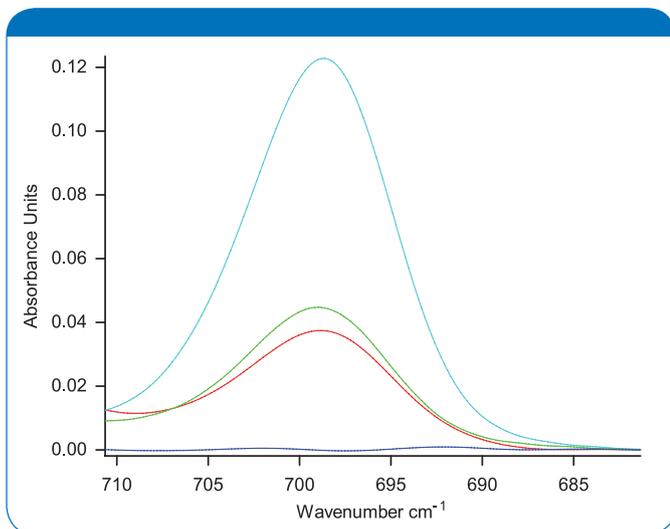


Figure 5: Integration region with calibration spectra and the unknown spectrum (red).

Using the Quant 1 function in OPUS a calibration based on the intensity of the styrene band at 699 cm⁻¹ can be set-up in a few steps. First the reference spectra are added to the method and the respective reference values of the styrene

content entered. Then the spectral range and method (height or area) are defined. Finally the software calculates the calibration formula. Figure 6 shows that a plot of the true styrene contents versus the values calculated from the calibration formula results in a straight line with a coefficient of determination very close to the ideal value of one. Using the three-point calibration model the styrene concentration of the unknown test sample is being determined to 3.6 ± 0.1 %.

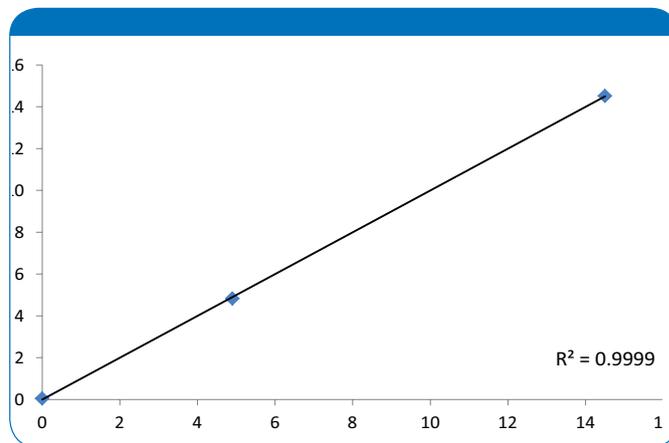


Figure 6: True vs. fit plot with coefficient of determination R².

Summary

The combination of Bruker Optics compact and robust FT-IR spectrometer ALPHA with a high pressure diamond ATR unit is an ideal tool to analyze polymers, fillers and polymer-additives. The system allows quantifying single components in complex mixtures. The setup of new methods even for chemically similar polymers is quick and straightforward. A very intuitive work-flow allows even spectroscopically inexperienced users to perform the analysis. Altogether the ALPHA is perfectly suited for the identification of fillers, the quantification of mixture components and the quality control of polymers.