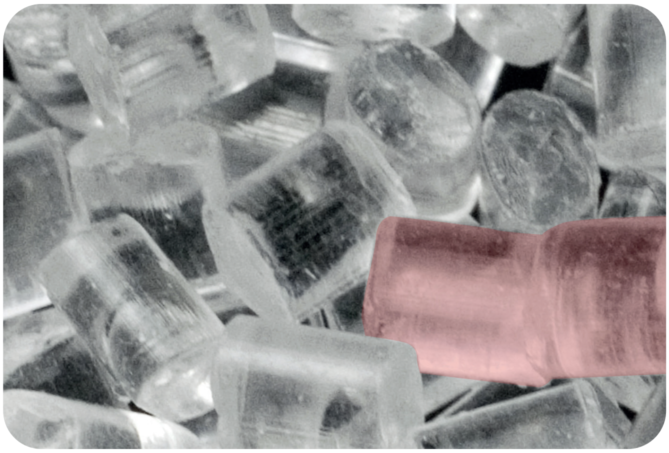

Application Note AN M123

Identification of Inorganic Filler Materials in Polymers by Combined FIR-MIR ATR Studies

Introduction

Today there is a high demand for modern polymeric materials which can be adapted to specific tasks. There is a wide variety from homopolymers to copolymers, consisting of different types of monomers, and up to polymer blends. All of them are mostly blended with further additives and filler materials to improve the properties of the pure material or to reduce material costs. By adding inorganic filler materials many attributes can be enhanced, e. g. the mechanical and optical properties, the processability or the fire retardancy. For the complete characterization of these composite materials the mid and far infrared regions of the spectrum are of interest.

Both regions of the infrared light make complemental information about the investigated substances accessible. The mid-infrared is a valuable resource of information about the composition and structure of organic compounds (4000 to 400 cm^{-1}) which is needed for the identification of the polymeric host material. In contrast the far infrared or THz spectral region reveals important information about vibrations of groups containing heavier atoms or about lattice vibrations (below to 400 cm^{-1}) in the crystal structure of solids. This makes the latter region especially useful for the characterization of inorganic ionic compounds which are used as polymer filler materials.

Keywords	Instrumentation and Software
Polymers	INVENIO R and VERTEX 70v
Fillers	A225/Q ATR accessory
Inorganics	Wide-range beamsplitter
Bruker FM FIR-MIR option	Wide-range DLaTGS detector
Bruker FM ATR Library	

By the introduction of adequate components for the combined FIR-MIR spectroscopy, consisting of a wide range mid to far IR beamsplitter and detector, an investigation of both spectral regions in a single step is possible. This setup is bundled within the Bruker FM (Far and Mid IR) technology for INVENIO R and VERTEX 70v spectrometers.[1] Alternatively an automated beam splitter changer for the VERTEX 80v offers the more ingenious possibility to investigate samples in 4 different spectroscopic regions without the break of the vacuum.[2] The use of a vacuum optical bench is always recommended for investigation in the far infrared region in order to avoid the strong interference from the water vapor absorption.

Currently the most frequently used measurement technique for polymer investigations is the ATR (Attenuated Total internal Reflection) measurement which offers a fast and easy to use approach. Hereby the sample is pressed against the ATR crystal without further sample preparation and the IR radiation penetrates only few microns into the sample (depending on the crystal material). The use of a diamond ATR crystal of the Platinum ATR accessory (8000-10 cm^{-1}) again makes the investigation down to the FIR region possible.

For better comparison of the data obtained in ATR measurements with transmittance data it is wise to use the integrated advanced ATR correction in the OPUS program package. In this context recent investigations of different carbonate minerals show the versatility and the benefits of this function.[3] One has to keep in mind that for small fractions of filler materials, which are included in the polymeric matrix, the band positions differ from ATR measurements of the neat powder filler materials and compare better with transmittance data. This is the case because in the composite system, which was measured in the ATR mode, the inorganic filler is diluted in the polymer matrix. The accordance to transmittance data seems reasonable given the fact that for FIR transmission measurements the substance is commonly prepared elaborately and time consuming by dilution in a polyethylene matrix and by pressing a pellet. The identification of different components of a composite system is conventionally done by comparison with spectral library data. Despite different infrared regions of the prominent features of the polymeric matrix and the fillers, they are usually only compared with spectral data in the mid-infrared region. If, for example, an inorganic material is thereby not well identifiable, a look in a second FIR database is required. With the introduction of a FIR-MIR ATR library the additional work can be avoided and all information is accessible at once.[4]

Table 1: Identification of the filler materials

Ammonium polyphosphate (15 % in SB)			
powder ATR cm^{-1}	polymer matrix ATR cm^{-1}	powder ATR cm^{-1}	polymer matrix ATR cm^{-1}
62	70	882	880
124	133	1009	1011
159	161	1058	1053
339	339	1244	1250
440	440	1422	1424
479	478	2891	
546	545	3013	
797	798	3169	

Identification of ammonium polyphosphate, as powder sample and in the polymer matrix.

Spectra of a Styrene Butadiene copolymer

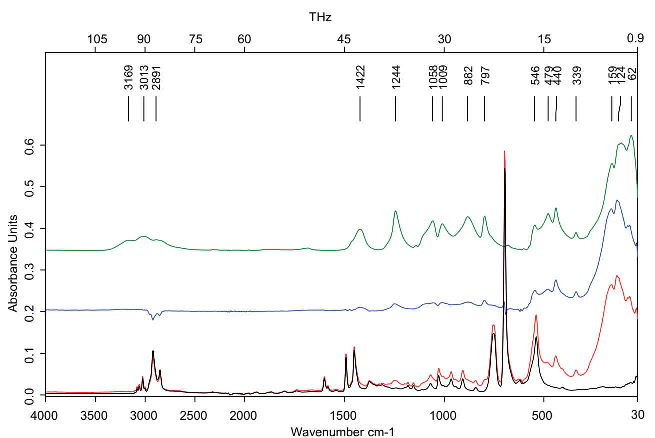

Figure 1: IR spectra of a Styrene Butadiene copolymer (SB) containing fifteen percent of ammonium polyphosphate as filler. Top: IR spectrum of a powder ammonium polyphosphate sample. Middle: Difference spectrum obtained by subtracting the IR spectrum of the neat polymer from the IR spectrum of the filled polymer. Bottom: IR spectrum of the neat polymer (black) and of the filled polymer (red). The y scale of the inserted curves in all graphs is arbitrary for better display purposes.

Instrumentation and advanced ATR correction

The polymeric molded pieces and powder samples were measured using a VERTEX 70v vacuum spectrometer with the standard mid IR source, a wide range FIR-MIR beamsplitter and a wide range room temperature DLaTGS detector (Bruker FM functionality). The measurement parameters were 4 cm^{-1} resolution and one minute scan time. For improved spectroscopic data in the far infrared region the source was changed to a water cooled Hg arc lamp for a second set of measurements using: 4 cm^{-1} resolution and 6 minutes scan time. All measurements were performed with a Bruker Platinum single crystal diamond ATR unit. For good reproducibility a pump time of 10 minutes before the start of each measurement was used to obtain a stable vacuum condition. The displayed data show spectra merged of a mid-infrared spectrum using the internal standard source (4000-50 cm^{-1}) and of a far infrared section of a spectrum using the HG arc lamp (680-30 cm^{-1}). For the correction of the ATR absorbance data of the inorganic powdered samples the correction function implemented in the OPUS FTIR software was used with the following parameters: Refractive index of the ATR crystal (2.4), angle of incidence (45 degrees), number of reflections (1.0), the sample refractive index was set to an averaged value of 1.6 for all inorganic filler materials. [5]

Spectra of a polystyrene homopolymer

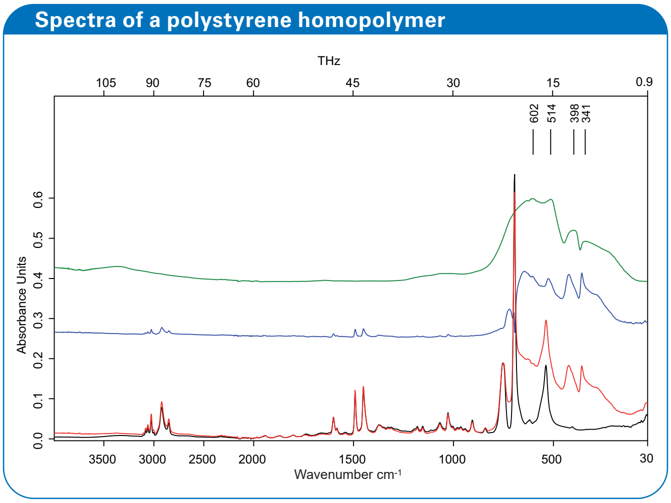

Figure 2: IR spectra of a polystyrene homopolymer (PS) containing ten percent of titanium dioxide (rutile) as filler. Top: ATR corrected spectrum of a powder titanium dioxide sample. Middle: Difference spectrum obtained by subtracting the IR spectrum of the neat polymer from the IR spectrum of the filled polymer. Bottom: IR spectrum of the neat polymer (black) and of the filled polymer (red).

Spectra of an Acrylonitrile Butadiene Styrene copolymer

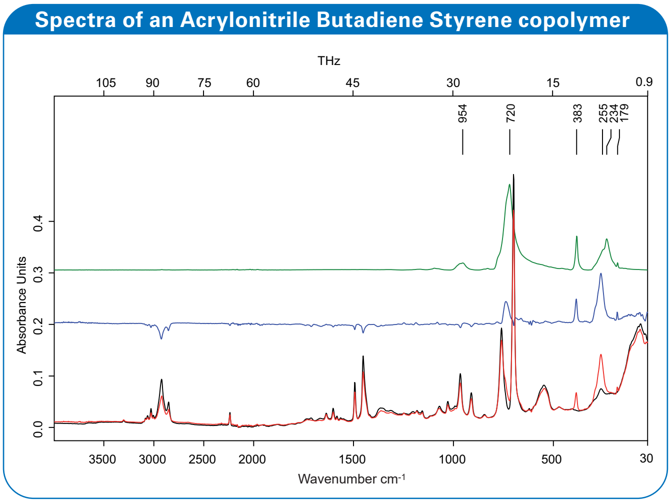

Figure 3: IR spectra of an Acrylonitrile Butadiene Styrene copolymer (ABS) containing three percent of antimony trioxide and five percent of hexabromocyclodecane (HBCD) as filler. Top: ATR corrected spectrum of a powder antimony trioxide sample. Middle: Difference spectrum obtained by subtracting the IR spectrum of the neat polymer from the IR spectrum of the filled polymer. Bottom: IR spectrum of the neat polymer (black) and of the filled polymer (red).

Table 2: Identification of the filler materials

Titanium dioxide (10 % in PS)		
powder ATR corrected cm^{-1}	polymer matrix ATR cm^{-1}	transmission cm^{-1} [6]
341	358	359
398	424	419
514	523	558
		589
604	644	653

Infrared band positions of TiO_2 as powder sample and in the polymer matrix. Transmittance data are listed for comparison [6].

Table 3: Identification of the filler materials

Antimony trioxide (3 % in ABS)		
powder ATR corrected cm^{-1}	polymer matrix ATR cm^{-1}	transmission cm^{-1} [6]
179	181	
234	263	
255	277	272
383	386	390
720	736	744
954	948	976

Infrared band positions of Sb_2O_3 as powder sample and in the polymer matrix. Transmittance data are listed for comparison [6].

Results and discussion

The applicability of this combined investigation method will be discussed with three examples consisting of different polymer matrices and inorganic filler combinations and ratios. Firstly a Styrene Butadiene copolymer (SB) filled with fifteen percent of weight of ammonium polyphosphate was compared to the pure polymeric matrix. The spectra of the complete FIR-MIR range is depicted in Figure 1 and ammonium polyphosphate can easily be identified by comparison of a reference powder sample with the difference spectra. The band positions of the polyphosphate filler material match very well the values of the ATR powder measurement. All significant band positions are listed in Table 1-3. The second example is a polystyrene polymeric host with ten percent titanium dioxide (rutile) as filler. Unlike the previous filler material titanium dioxide does not show significant absorptions in the mid-infrared spectral region and therefore the investigation of the far infrared spectral region is mandatory. In this case the difference spectrum is in fairly good agreement with the ATR corrected spectrum of the powder titanium dioxide (rutile) sample. The spectra are displayed in Figure 2. The deviance of the peak positions of both spectra is caused by the high refractive index of titanium dioxide (>2 depending on the polymorph) which actually exceeds for rutile the value of the diamond ATR crystal (n = 2.4) in the FIR region. A better accordance of the powder sample can be achieved by changing the parameters of the advanced ATR correction from the standard values. Nevertheless the identification with library data works with the standard settings. The band positions are listed in Table 2 in comparison to transmittance data from the literature.[6]

In the third and last sample described in detail an Acrylonitrile Butadiene Styrene copolymer (ABS) containing two different fillers (three percent antimony trioxide (inorganic) and five percent hexabromocyclododecane (HBCD, organic)) was investigated. The organic compound HBCD can't be well identified in the infrared spectra in this low concentration because its vibrational bands in the difference spectra are too weak. On the contrary the absorbance of antimony trioxide is apparent and the peak positions fit the values of the ATR corrected spectrum of the antimony trioxide powder sample very well. So the identification of the inorganic filler succeeds. All the examples shown herein are part of the novel Bruker FM ATR library. [4]

Conclusion

Combined investigations in the far and mid infrared region in a single step can offer great value for analysis. Herein it was shown that the identification of inorganic filler materials in polymer samples can be improved in two ways. On the one hand it is only necessary to measure one spectrum per sample to get access to the whole information in the far and mid infrared region. On the other hand the identification can be simplified by comparison of the spectral data with just one combined FIR-MIR library. The required instrumentation can be found in the FM functionality of the INVENIO R and VERTEX 70v spectrometers which combines a wide range beam-splitter and detector.

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