Application Note AN M98

Differentiation of Polyamides via FTIR Spectroscopy

Introduction

Polyamides are thermoplastic polymers consisting of monomers joined by an amide bond. The polyamide group includes many different polymers with different chemical and physical properties. One differentiates for example between aliphatic, semi-aromatic and aromatic polyamides depending on the chemical nature of the monomers. Further classification can be done via the number of repeating units (homopolyamides, copolyamides) and the melting behaviour depending on the crystallinity. Some nomenclature basics will be discussed after the next paragraph.

In everyday live there are many prominent examples of polyamides such as Nylon, Perlon or Aramid (Kevlar). Since polyamides are produced in large quantities recycling is also a major issue. Generally as thermoplastics polyamides can be recycled mechanically via thermal shaping but it is also possible to recycle them chemically e.g. via acid or base-catalysed hydrolytic depolymerisation. In order to get an acceptable recycling product a reliable method to differentiate between different polyamides is needed since the product quality depends on the purity of the recycling material. In this application note we will evaluate the use of Fourier transform infrared spectroscopy in combination

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

with a simple spectra comparison method to differentiate between the polyamides 6, 6.6, 6.10 and 6.12.

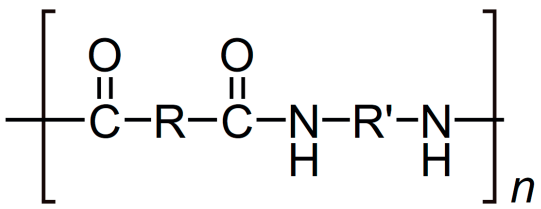
Fourier transform infrared (FTIR) spectroscopy is one of the fastest and most accurate methods for the differentiation and quality control of polymers. It provides information about the identity of incoming raw materials, possible contaminations, quality of the products and can even identify unknown polymeric samples. 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 FTIR spectroscopy allows to identify an incoming raw material or to verify that a given product is within its specification.

Instrumentation

Nowadays, incoming goods inspection and quality control using IR spectroscopy is mainly performed applying 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 FTIR spectrometer can then measure the absorbance resulting from the sample. All types of samples (e.g. solids, liquids, powders, pastes, pellets, slurries, fibres etc.) are just put on the accessory before the data acquisition is performed. 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, something that cannot be done when measuring the sample in transmission mode.

The very compact ALPHA II FTIR spectrometer with the high pressure Platinum diamond ATR-module is a robust and affordable system that is very easy to operate. To provide the user an unobstructed access to the sampling area, the pressure applicator can be rotated by 360°. Diamond is a very hard-wearing, chemically inert and therefore ideal material for the analysis of a wide range of samples. For the measurement of highly absorbing dark samples (e.g. black polymers) and thin layers, the Platinum ATR module can be equipped with a germanium (Ge) crystal plate. The software is very intuitive and a software wizard is guiding the user through the analysis procedure.



Example: Polyamide 6.10
Monomers:
Hexamethylenediamine (R'= $(CH_2)_6$)
Sebacic acid (R = $(CH_2)_8$ with a total of 10 carbon atoms)

Figure 2: Basic structure of polyamides made by polycondensation of dicarboxylic acids with diamines.

Results

Despite different physical properties the polyamides 6, 6.6, 6.10 and 6.12 are chemically relatively similar. Polyamide 6 is synthesised out of ε-caprolactam via a ring opening polymerisation and is therefore slightly different to the other named polyamides that are synthesised by a polycondensation of diamines with dicarboxylic acids. The only difference between the polyamides 6.6, 6.10 and 6.12 is the carbon chain length of the dicarboxylic acids used as monomers. Figure 2 shows the basic structure of these

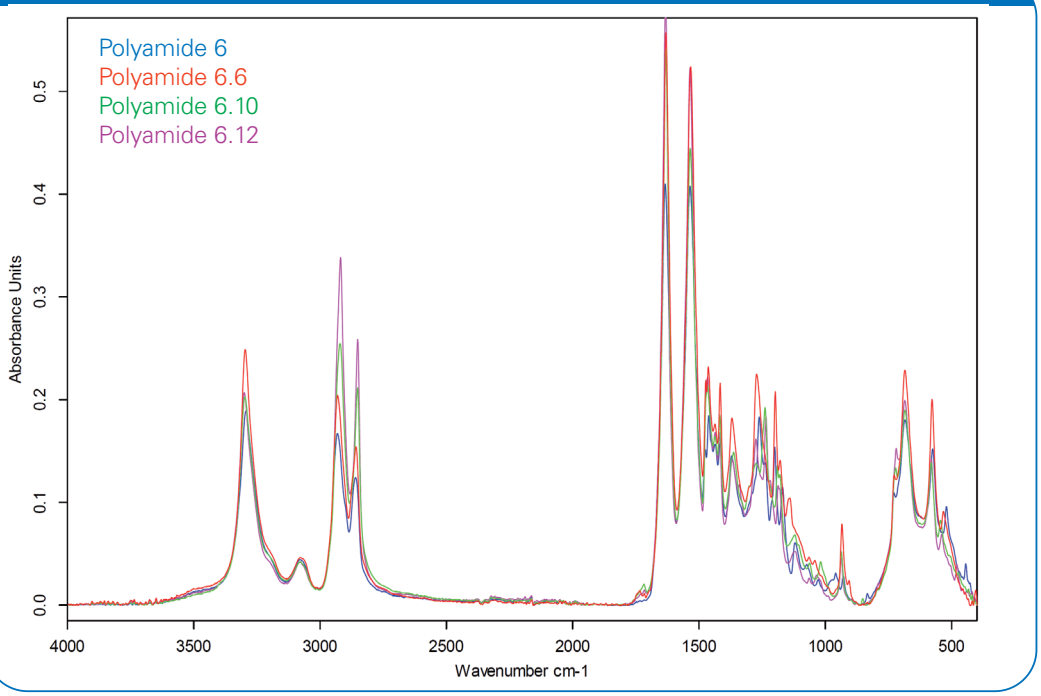


Figure 3: FTIR spectra of polyamides measured with a diamond ATR

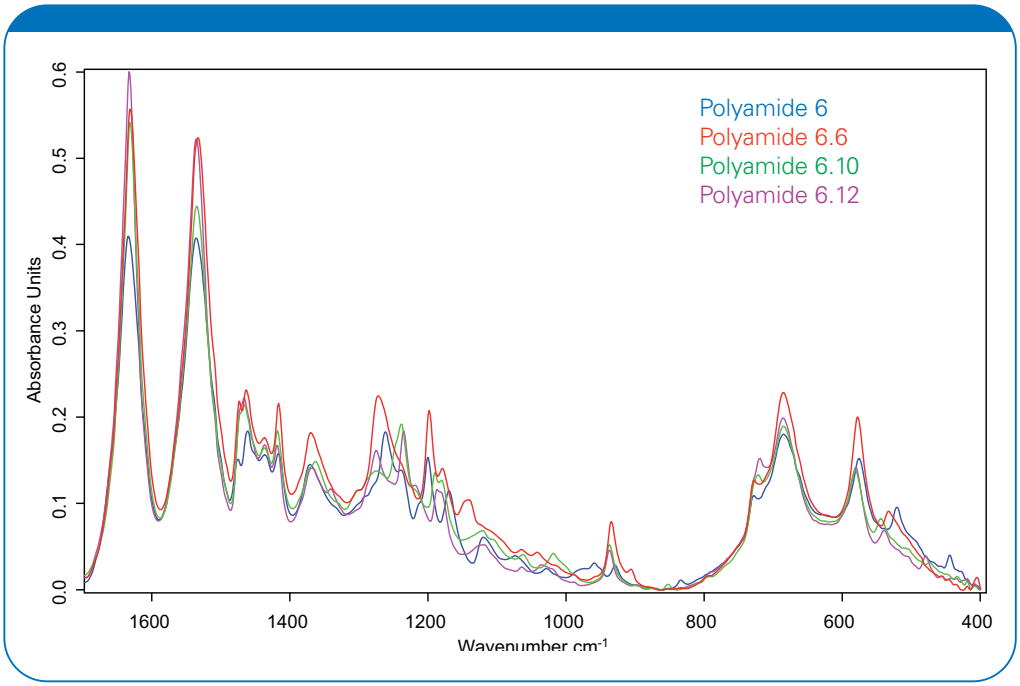


Figure 4: Magnification of the spectra from figure 3.

polyamides whereas R is the aliphatic chain of the dicarboxylic acid and R' the one of the diamine. The name of the polymer is based on the number of carbon atoms in the diamine, a point and thereafter the number of carbon atoms in the dicarboxylic acid. In contrast, polyamide 6 has only one number since it is based on one single monomer with six carbon atoms.

Since the basic structure of the polyamides is the same one would not expect significant differences in the IRspectra. 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. The comparison can be done via a quick spectrum comparison method where the correlation of the measured spectrum with a set of reference spectra is calculated. A successful identification will be displayed by a simple "OK" with the similarity given as a percentage value, when the sample is not within the specification "NOT OK" will appear in combination with a red cross. Threshold values and other method settings can be set individually for each substance enabling the user to adapt or create comparison methods. In our example all of the four polyamides can be identified successfully and no false positive result occurs.

Summary

The combination of Bruker Optics compact and robust FTIR spectrometer ALPHA II with a high pressure diamond ATR unit is an ideal tool to identify polymers. The system allows discriminating different polyamides using a quick spectrum comparison method. The setup of new methods even for chemically similar polymers is quick and straightforward. Hence, this function is the ideal tool for incoming goods inspection and product quality assurance in the field of polymer production and polymer recycling.

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