Analysis of Polymers by ATR/FT-IR Spectroscopy

Polymer materials have become widely utilized for many different applications ranging from food packaging and consumer products to use in medical devices and in aerospace technologies. The composition of polymer materials may be readily determined by measuring their infrared spectra using a Fourier transform infrared (FT-IR) spectrometer and then comparing the results with a commercially available or specifically prepared spectral database.[1] This application note describes the benefits of using attenuated total reflectance (ATR) in combination with FT-IR for the analysis of polymeric materials.

Experimental

A PIKE MIRacle™ ATR accessory equipped with a single reflection Zinc Selenide (ZnSe) or diamond ATR crystal was used for all of the analysis shown in this work.[2] The MIRacle accessory was fitted with a High-Pressure Clamp, providing intimate contact between the sample and the ATR crystal. The MIRacle ATR (shown in Figure 1) has a unique optical design offering high throughput of the IR beam and thereby provides the ability to collect high quality spectral data within a minute or less.[3] The MIRacle ATR accessory utilizes a pre-aligned, pinned-in-place crystal plate design enabling easy exchange of the ATR crystal for sampling optimization.

The FT-IR spectrometer was equipped with a KBr beamsplitter and a DLaTGS detector. The instrument was sealed and desiccated to minimize purge effects. Polymer samples were placed over the ATR crystal and maximum pressure was applied using the slip-clutch mechanism of the clamp. All spectra were collected at 4 cm^{-1} spectral resolution using 1 minute sample and background collection times. Resulting spectra were searched using the PIKE Technologies ATR Spectral Database.[4]

Figure 1. PIKE MIRacle ATR accessory with High-Pressure Clamp.

Benefits of ATR vs. Transmission for FT-IR Analysis of Polymers

Polymer samples presented for analysis are often too thick for measurement by transmission sampling techniques since the ideal IR beam pathlength for sample identification is typically less than 20 microns. However, the relatively thin depth of penetration of the evanescent wave (typically 0.5 to 2.0 microns) in ATR generally eliminates the need to do sample preparation. This benefit is shown in Figure 2 for the FT-IR analysis of a 150 micron thick polymer film.

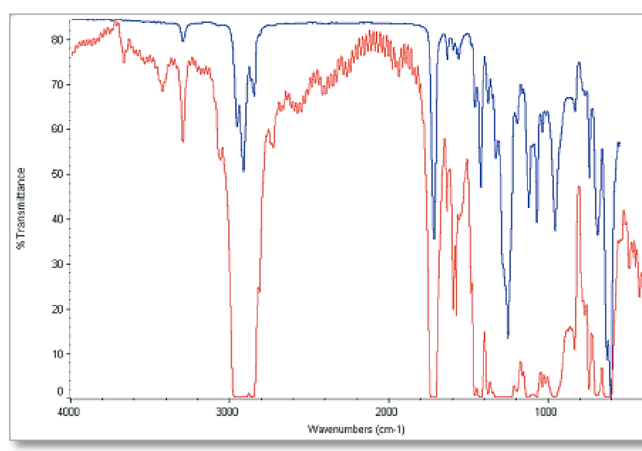

Figure 2. FT-IR spectra of thick polymer film by ATR (upper blue) and Transmission (lower red).

In Figure 2, the transmission spectrum of the thick polymer film shows numerous totally absorbing IR bands preventing a high quality comparison with the spectral database. However, the thick polymer film measured using the MIRacle ATR shows an excellent result and is identified as a polyvinyl chloride based polymer.

Choice of ATR Crystal for Polymer Analysis

The two most popular ATR crystal materials used for polymer analysis are ZnSe and diamond. Both of these crystals have a refractive index of 2.4 and with a typical polymer refractive index of 1.5 at a 45° angle of incidence and at 1000 cm^{-1} the ATR depth of penetration is about 2 microns. The most likely differentiation for use of ZnSe or diamond is the form and hardness of the polymer sample. The Knoop hardness (kg/mm^2) of diamond is 5700 whereas that of ZnSe is 120.[5] In practical terms this means that for softer or for flat polymer samples we can routinely use ZnSe as an ATR crystal material.

In Figure 3, results for the ATR analysis of inner and outer layers of a polymer electronic storage bag using the MIRacle ATR fitted with a ZnSe crystal.

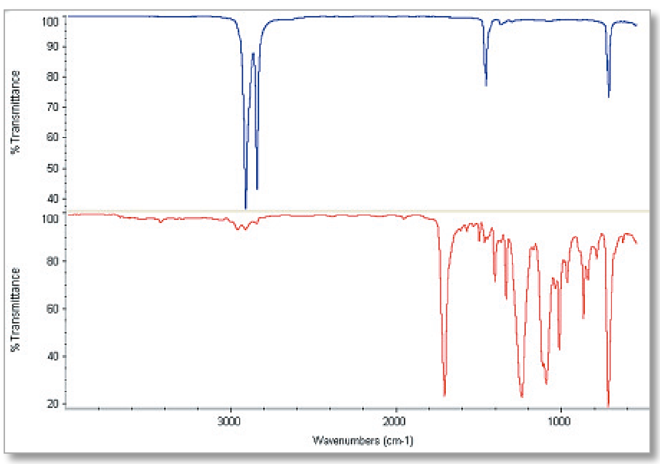

Figure 3. ATR/FT-IR spectra of inner (upper blue) and outer (lower red) sides of an electronics storage bag.

The upper blue spectrum is identified as polyethylene and the lower red spectrum is identified as a polyethylene terephthalate. For relatively hard polymer samples where the material is irregular such that application of pressure may cause deformation of the ZnSe crystal surface, the use of diamond as an ATR crystal material is recommended. The hardness of diamond is such that it will not scratch and it will not deform with application of high pressure onto the polymer sample.

Examples of the ATR analysis of rigid and irregular shaped polymer materials are shown in Figure 4. The upper blue spectrum is generated from a single polymer pellet about 3 mm in diameter and is identified as Nylon 6/6. The lower red spectrum is collected from a screwdriver handle placed directly upon the diamond crystal of the MIRacle ATR and is identified as a cellulose acetate.

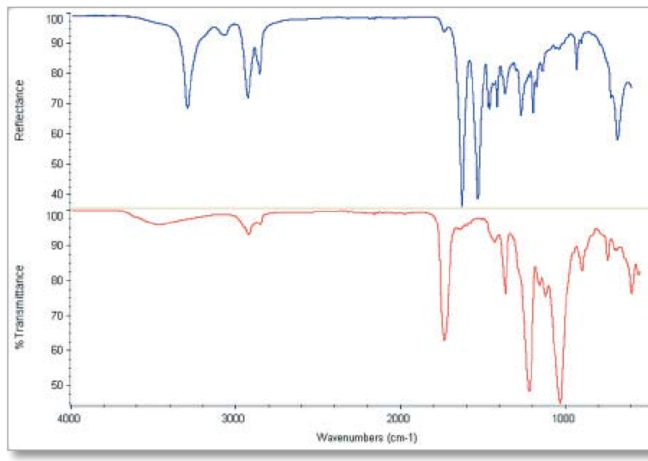

Figure 4. ATR/FT-IR analysis of a hard polymer pellet (upper, blue) and a screw driver handle (lower, red).

Summary

The MIRacle ATR accessory with an FT-IR spectrometer is a powerful sampling tool for the analysis of polymers. ATR eliminates sample preparation generally required for FT-IR analysis by transmission sampling techniques and thereby greatly speeds the measurement. Analysis and identification of unknown polymer samples can be routinely done within 1 minute using the MIRacle ATR. A ZnSe crystal works very well for the routine analysis of relatively soft polymer materials and also is compatible with flat polymer samples. The diamond crystal is compatible with all polymer samples including irregular shaped, rigid polymers because it cannot be scratched or deformed by application of high pressure onto the polymer sample.

References

[1] B. H. Stuart, Polymer Analysis (John Wiley & Sons, UK, 2002).

[2] MIRacle ATR, Product Data Sheet, PIKE Technologies, 2013.

[3] United States Patents 5,965,889 and 6,128,075, Philip R. Brierley, PIKE Technologies, 1999, 2000.

[4] ATR Spectral Databases, Product Data Sheet, PIKE Technologies, 2013.

[5] Transmission Sampling Techniques – Theory and Applications, Application Note, PIKE Technologies, 2013.