



Polymer Identification Using Mid Infrared Spectroscopy

Introduction

Synthetic polymers are very widely used today, with diverse applications in various industries such as food, automotive, and packaging. The quality of plastic products depends on the quality of the polymers or polymer blends used during manufacturing,

so identity verification and quality testing of those materials during every stage of manufacturing is necessary to ensure that only high-quality material is used.

Infrared (IR) spectroscopy is ideally suited to qualitative analysis of polymer starting materials and finished products as well as to quantification of components in polymer mixtures and to analysis of in-process samples. IR spectroscopy is reliable, fast and cost-effective. This application note describes several approaches to the measurement and analysis of IR spectra of typical polymer samples, and applies the techniques to the identification of some industrial polymer samples. The compact and rugged Spectrum Two™ FT-IR spectrometer supports a range of reflectance and transmission sampling accessories that are suitable for polymer analysis, and is now available with a Polymer Resource Pack that provides information and advice to help generate good quality spectra and extract meaningful information as simply as possible.

Mid Infrared Spectroscopy

The IR spectrum derives from absorption of light exciting molecular vibrations. The positions of absorption bands in the spectrum give information about the presence or absence of specific functional groups in a molecule and as a whole the spectrum constitutes a “fingerprint” that can be used to determine the identity of the sample. A difference between two spectra indicates that the two samples are made up of different components.

Figure 1 shows the IR spectra of several common polymers: polyethylene (PE), polypropylene (PP), polystyrene (PS), and polytetrafluoroethylene (PTFE), measured using the PerkinElmer Spectrum Two FT-IR with UATR sampling accessory, as shown in Figure 2. The clear differences between the spectra allow a ready discrimination between the materials by visual inspection. Additional interpretation of the spectra can yield information about the structure: for example, looking at the C–H stretch region around 2950 cm^{-1} , differences can be seen between PE and PP due to the differing ratios of CH_2 and CH_3 groups. PS has bands above 3000 cm^{-1} , indicating the presence of aromatic groups. PTFE has no C–H groups at all, so the very weak bands present must be due to impurities or surface contamination.

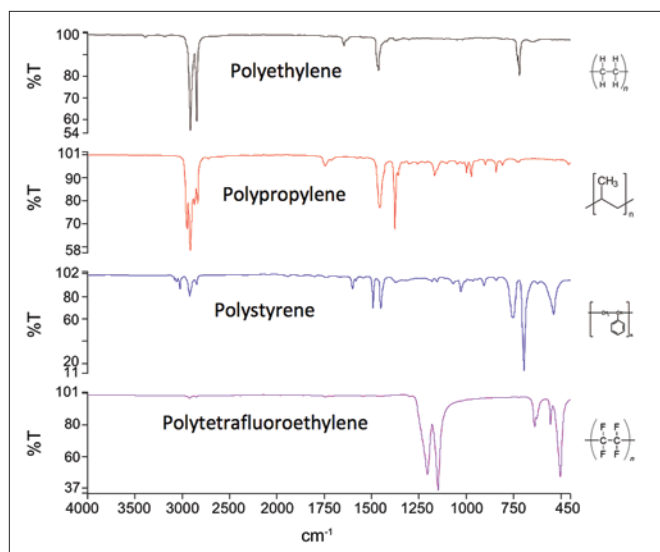


Figure 1. Mid-IR spectra of common polymers.

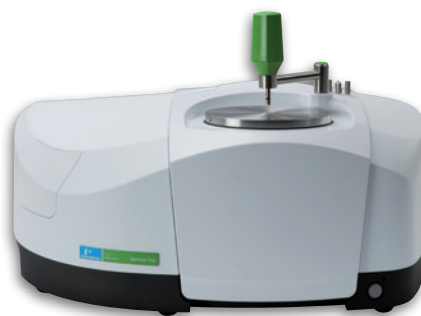


Figure 2. Spectrum Two FT-IR with UATR.

Sampling methods

Selection of the appropriate sampling method and sample preparation is critical to achieving good results. Which method is appropriate depends on the type, form, and amount of sample to be analyzed. Polymer samples can take a number of forms, as shown in Table 1. Transmission measurements require a short pathlength, and this can be obtained by pressing the sample into a thin film or, for soluble samples, obtaining a film through solvent casting. However, the most popular method today for measuring polymer spectra is attenuated total reflectance (ATR), in which the sample is pressed against a diamond, zinc selenide or germanium crystal and the absorption of the evanescent wave is measured. This technique requires little to no sample preparation and very reliably produces high quality spectra.

Diffuse reflectance (DRIFT) has been widely used in the past for polymers, and remains a useful technique where the sample is physically too large to measure with ATR and a sample can be taken by abrasion.

Table 1. Sampling techniques for FT-IR spectroscopy of polymers.

Sample Form	Suitable Techniques
Thin films (<25 μm)	Transmission
Fine powders (<2 μm)	Transmission (KBr), ATR, DRIFT
Large items	DRIFT (abrasive sampling)
Irregular shapes, pellets	ATR, DRIFT (abrasive sampling)
Polymers soluble in volatile solvents	Transmission (cast film)
Flat, reflective surfaces	Specular reflectance, ATR, DRIFT (abrasive sampling)
Single fibers	Diamond ATR or IR microscope

The PerkinElmer Polymer Resource Pack provides step by step instructions in order to obtain a good quality sample spectrum for a variety of sample types using both ATR and transmission. The Polymer ATR library included with the Pack can be used to determine sample identity.

Several of these sampling techniques are illustrated below, using polystyrene as an example material.

ATR

The sample was directly placed on the UATR top plate mounted in the sample beam of the spectrometer. The measurements were completed within 30 seconds and ATR spectrum was obtained as shown in Figure 3.

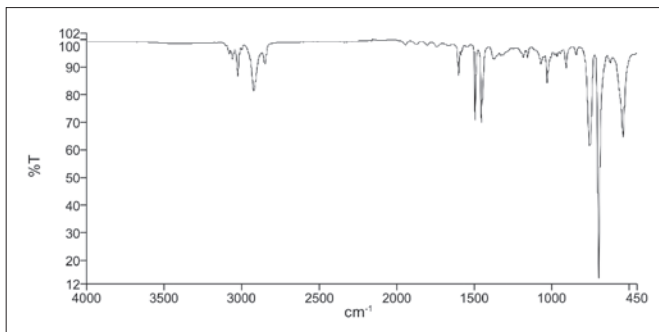


Figure 3. ATR spectrum of plastic sample.

While the short pathlength afforded by ATR makes it easy to measure good quality spectra, it is important to remember that, because of this factor, ATR is effectively a surface technique. If the surface of the sample is not representative of the bulk – for example, due to migration of plasticizer to the surface – some sample preparation is necessary. Additionally, if the sample is very hard but not flat, it may be difficult to get sufficient contact with the crystal. Accordingly the following general approach can be used:

1. If the sample is soft, cut a bulk sample with a sharp knife or scalpel to prepare a flat piece of polymer with a fresh surface and press this against the ATR crystal.
2. For hard and round-shaped samples like granulates that are more difficult to cut, use a pair of clean flat-nose pliers to flatten the sample.
3. In all other cases, use the sample as it is.

ATR spectra exhibit some differences from transmission spectra, the most obvious of which is that, since the effective pathlength varies inversely with wavelength, the bands at high wavenumber are relatively weaker than in transmission. This can affect library searching, so it is recommended either to use an ATR library or to apply an ATR correction (such as that built into Spectrum software) to the spectrum prior to searching.

Film casting

The sample was found to dissolve in xylene, so a thin film of the sample was prepared by the following procedure:

1. Dissolve 2 g of the sample in 10 mL xylene.
2. Place an IR crystal (such as KBr) window on top of a paper towel on a hot plate set at 40 °C.
3. Deposit 2–3 drops of the sample solution on the crystal window.
4. Allow the solvent to evaporate, leaving behind the thin film of the sample.

The thin film so obtained was placed in the IR beam and the IR spectrum obtained (Figure 4).

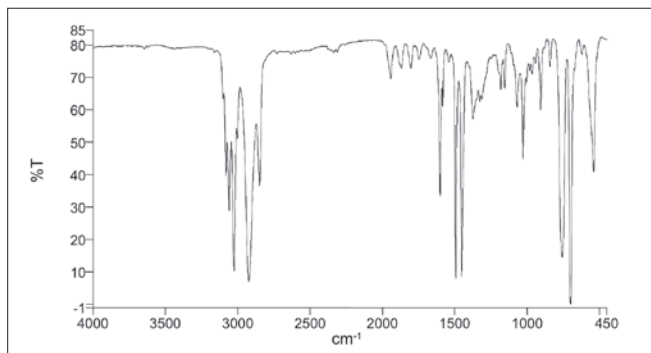


Figure 4. Transmission spectrum of plastic sample prepared as thin cast film.

The film casting technique is simple and cost effective and can produce a good quality spectrum. However, it is only applicable to soluble polymers and is rather time-consuming.

DRIFT

DRIFT measurements of the same sample were carried out using DRIFT accessory and an abrasive stick. The background was acquired with a clean abrasive stick in place. The stick was then rubbed against the sample and placed in the DRIFT accessory. Figure 5 shows the resulting spectrum.

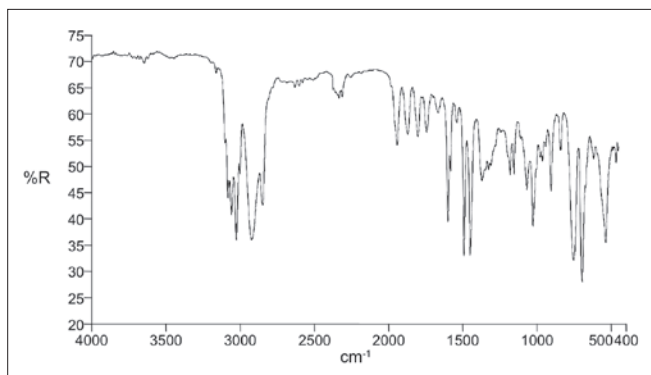


Figure 5. DRIFT spectrum of plastic sample.

DRIFT measurements with abrasive sticks provide a convenient sampling option for large samples, but it is sensitive to the amount of sample used so a greater degree of skill is required than for ATR sampling.

Identification of Industrial Samples

Three samples were provided by an automotive parts manufacturer: one plastic headlight cover and two black interior trim pieces (Figure 6). The aim of the infrared analysis is to identify these materials.



Figure 6. Automotive plastic samples. Left: headlight glass, right: interior trim parts.

Spectra were obtained with the UATR accessory as described above. The headlight cover was found to have a coating, so this was removed prior to analysis. The spectrum was compared against the PerkinElmer ATR polymers library (included with the Polymers QA/QC FT-IR Reference Pack) using the Search function in Spectrum 10 (Figure 7). The results indicate that the sample is polycarbonate.



Figure 7. Search results for the headlight cover, showing a good match against the Polycarbonate reference.

Spectra of the black trim materials were also measured with the UATR accessory. Often, black materials require an even shorter pathlength than diamond ATR provides, and benefit from a germanium crystal. In this case, however, satisfactory spectra were obtained with diamond (Figure 8).

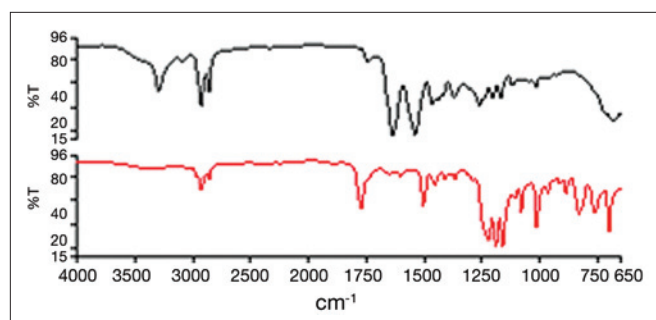


Figure 8. Mid IR spectra of auto-components. Top: sample 1, bottom: sample 2.

Using the Search function of Spectrum software and the ATR Polymers library, the materials were identified as nylon (sample 1) and polycarbonate (sample 2).

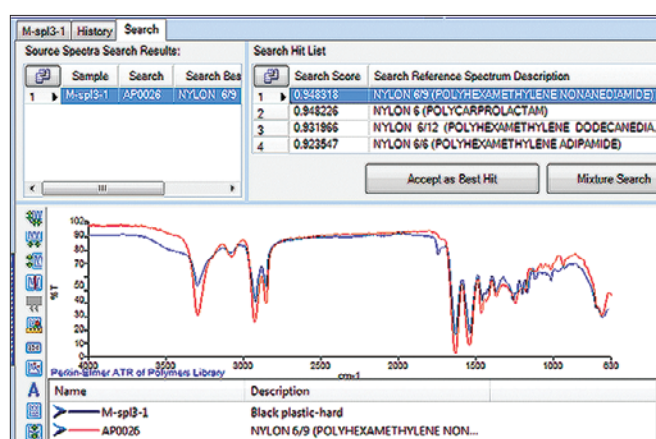


Figure 9. Sample 1 identified as Nylon base material.



Figure 10. Sample 2 identified as Polycarbonate base material.

Conclusions

FT-IR spectroscopy is a powerful tool for polymer analysis, and a range of sampling methods are available with varying degrees of sample compatibility and time requirements.

The Spectrum Two FT-IR spectrometer with the UATR sampling accessory and the Polymers QA/QC FT-IR Resource Pack is the ideal system for routine analysis and identification of polymer samples. With ATR sampling, good-quality spectra were obtained from industrial samples in seconds, and the materials were identified by searching against the library supplied with the system.

Ordering Information

FT-IR Polymer Resource Pack:	L1608013
PerkinElmer Spectrum Two Polymer QA/QC Analysis System:	L160000V
Rectangular semi-demountable Potassium Bromide cell windows	L1271192
Metal-coated Abrasive Sticks	L1275105
Diamond Abrasive Sticks	L1275102
Silicon Carbide Abrasive disks	L1272348
Diamond Abrasive disks	L1272349

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