APPLICATION NOTE

Infrared Spectroscopy

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Polymer Identification Using the PerkinElmer Mid-Infrared Polymer Analysis System

Introduction

Synthetic polymers are 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. Identity verification and quality testing of those materials during every stage of manufacturing is necessary to ensure that only high-quality material is used.

Fourier Transform Infrared (FT-IR) spectroscopy is ideally suited to qualitative analysis of polymer starting materials and finished products, quantification of components in complex polymer mixtures, and analysis of in-process samples. IR spectroscopy is reliable, fast and cost-effective. Furthermore, in conjunction with the data analysis packages included in the polymer analysis bundle, this analysis bundle gives the user the ability to gain valuable insights into a particular material.

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Mid-Infrared Spectroscopy

Infrared spectra are the result of molecular vibrations which occur due to absorption of light in the infrared region. The positions of absorption bands in an IR spectrum provide information about the presence or absence of specific functional groups in a molecule. A spectrum as a whole constitutes a "fingerprint" which may be used to determine the identity of a sample. A difference between two spectra indicates the samples are made up of different components.

Figure 1 shows IR spectra of several common polymers; polyethylene, nylon 6/12, polystyrene and poly(tetrafluoroethylene). These spectra were measured using the PerkinElmer Polymer ID Analyzer with the universal attenuated total reflectance sampling accessory (UATR, Figure 2). The clear differences between the spectra allow for discrimination between materials by visual inspection. Additional interpretation can yield information about the structure. For example, Nylon 6/12 has a sharp band around 1700 cm^{-1}, indicating the presence of a carbonyl (C=O) group. However, various algorithms may be employed for more specific types of analysis, including quantitative estimation of components.

Data Analysis

Once spectral data has been collected, PerkinElmer's Spectrum 10™ software is capable of carrying out a wide range of spectral analyses. The available options in the Polymer ID analyzer include:

- **Search** – for identification of samples comprising a single polymer where the identity of the sample is unknown.
- **MultiSearch™** - for estimation of polymer mixtures where the components' spectra are available.
- **Compare** – for verifying the materials quality by comparing its spectrum against those of samples of known quality or composition.
- **Quant™** - for determining the composition of mixtures using a pre-developed calibration to calculate the component concentrations from the spectra.
- **Verify** – similar to compare, but more effective when it is necessary to take into account within-batch and/or between-batch variability when confirming the materials spectrum against those of known identity/quality.

Search

The Search function provides a simple and robust method for fast identification of samples using spectral libraries. Here the spectrum is compared with a library of database samples of known identity and a 'hit-list' is generated showing the degree of similarity between the sample spectrum and those in the spectral library. Search is best suited to situations where the sample is a single unknown component. Search can utilise small to large commercial libraries or user-developed libraries. The PerkinElmer FT-IR polymers introductory library supplied with this polymer supplement contains ATR and transmission spectra of:

- **Polymers** – Both commercial polymers and polymers with well-defined structure and extensive sample information.
- **Coatings** – including various types of binders, resins, enamels and primers.
- **Paints** – materials used in historical and modern paintings.
- **Petrochemicals** – A large range of aliphatic, aromatic and naphthenic chemicals and their important derivatives.

This library can be easily utilised in Spectrum 10 software to provide a robust analytical solution for simple polymer identification. Furthermore, using ATR as the sampling method, samples with unusual shapes are easy to analyze.

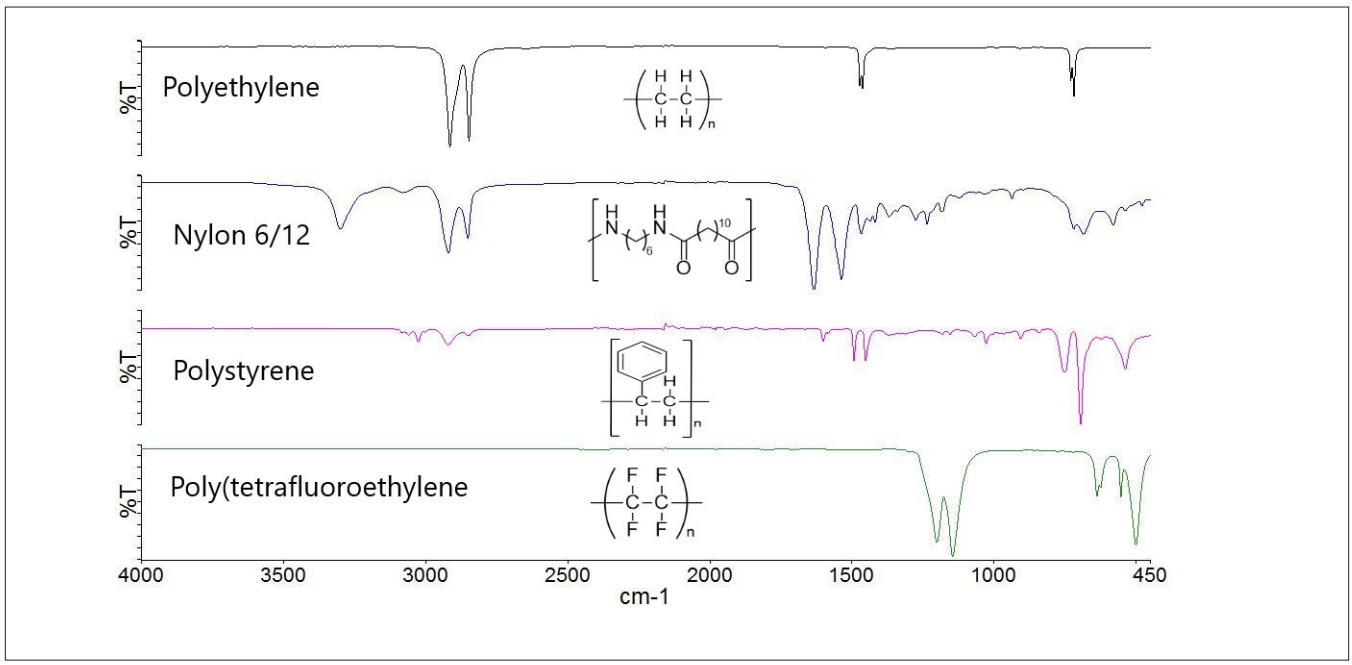

Figure 1. Mid-IR spectra of common polymers.

Figure 2. PerkinElmer Polymer ID Analyzer FT-IR spectrometer with UATR sampling accessory.

The ST-Japan library contains over 10,000 spectra of common copolymers and terpolymers in the database. This allows the user to qualitatively identify most simple copolymers and terpolymers as well as homopolymers. For example, the result obtained by search for an acrylonitrile/butadiene/styrene resin against the ST-Japan library is shown in Figure 3.

The results from the search will give a description of the best hit from the library, as well as other properties which may include physical parameters depending on how well characterized the polymer of interest is.

MultiSearch

The MultiSearch algorithm provides an alternative approach where the sample to be identified comprises a mixture of components and the spectra of pure components are available in the library. Since the algorithm works by forming a best least-squares fit between the sample spectrum and linear combinations of contributions from the library, it works best when the library entries are single, distinct polymers or additives. It is not recommended with large commercial libraries where the entries could comprise multiple types of the same polymer (e.g. from different manufacturers). It often works best where the components in the unknown spectrum are present as single distinct library entries. It can provide a semi-quantitative estimate of the relative concentrations of components in a mixture.

Compare

The Compare algorithm will find the correlation between the sample spectrum and a specified reference spectrum. This is the most popular algorithm for simple confirmation of spectra of samples. It requires a library containing spectra of samples of known identity or quality and simply analyzes sample spectra to indicate the closing match from the library.

In this example, a spectrum of high-density polyethylene is compared to a reference spectrum. Figure 4 shows the result given in Spectrum 10 for this material.

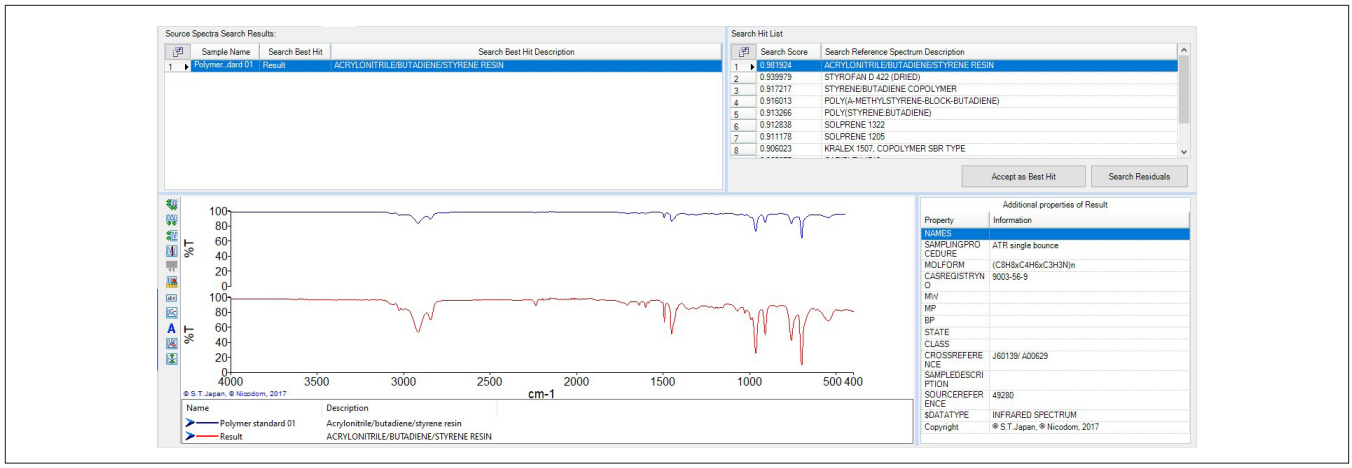

Figure 3. Search result from an acrylonitrile/butadiene/styrene resin.

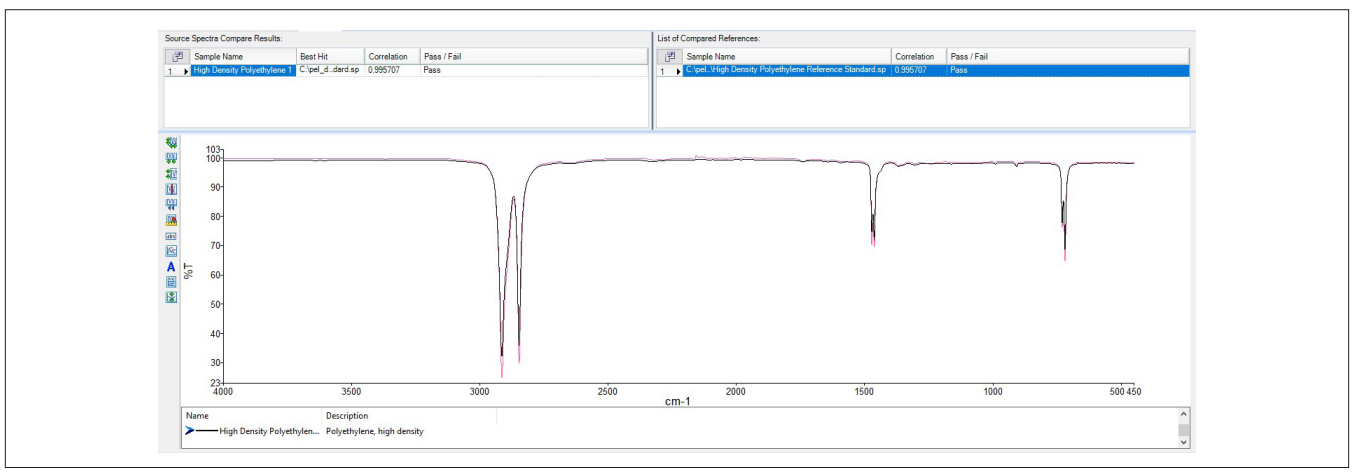

Figure 4. Compare result from high density polyethylene sample.

Quant

PerkinElmer Spectrum Quant allows for quantitative methods to be produced from a selection of common algorithms; Beer's law, partial-least squares regression (PLS1) and principal component regression (PCR). Once produced using calibration standards of known concentration, Quant methods may be implemented in Spectrum 10 and Spectrum Touch™ to quantify materials in unknown samples.

In this example, IR spectra of ethylene pellets containing varying quantities of vinyl acetate were used to produce a calibration curve (Figure 5). This quantitative model can subsequently be implemented in either Spectrum 10 or Spectrum Touch. The results obtained from analysis of an unknown sample are shown in Figure 6.

If a different algorithm is used, i.e. PLS1 or PCR, information relevant to these methods will be displayed in both Spectrum 10 and Spectrum Touch. The Spectrum Touch macro setup allows the user to choose what information is displayed on the results screen.

Verify

Spectrum 10 and Spectrum Touch also house the ability to implement SIMCA (soft independent modelling of class analogies) models produced in AssureID™. These models are created using a chemometric algorithm and will account for variation seen within a class. In this example, the model is created using different samples of high-density polyethylene which may exhibit small spectral variations. Figure 7 shows the result when an unknown material is identified as something other than high-density polyethylene. In this case, the material was oxidized polyethylene. The results include a pass/fail result, as well as a variety of more detailed chemometric information.

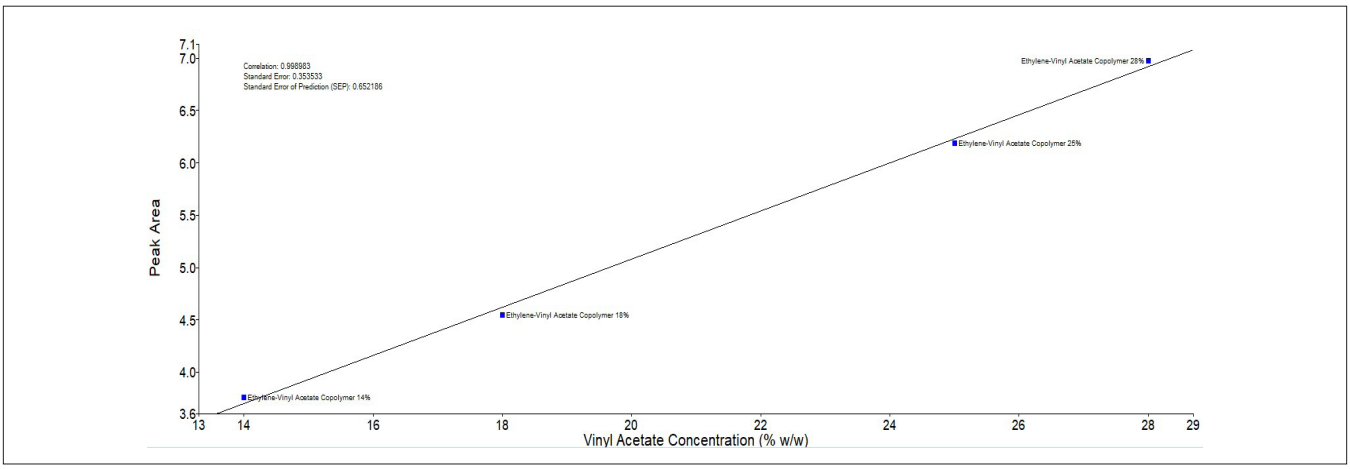

Figure 5. Vinyl acetate in polyethylene calibration curve.

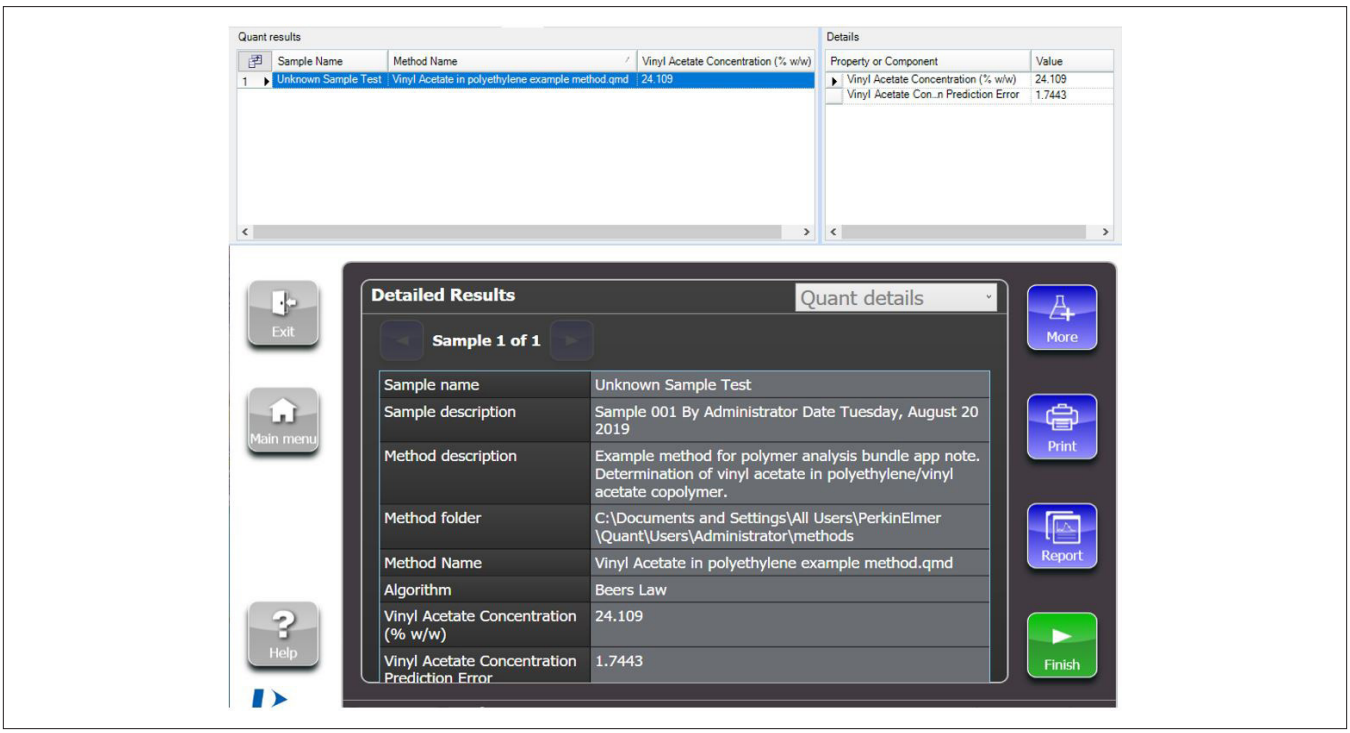

Figure 6. Quant results shown in Spectrum 10 (top) and Spectrum Touch (bottom).

Figure 7. Verify result from a suspect polyethylene sample.

Summary

The PerkinElmer Polymer ID Analyzer provides a simple, comprehensive solution for routine investigation and identification of polymers. The different data analysis tools give the user a wide range of options for polymer analysis in both a qualitative and quantitative capacity. The UATR accessory provides flexibility with sample size and shape, providing the capability to measure large and oddly shaped samples.

Spectrum Touch allows for implementation of workflow-oriented methods which may be implemented by analysts with minimal training.

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