The Benefits of Raman Spectroscopy for the Identification and Characterization of Polymers

Introduction

The benefits of Raman spectroscopy are well recognized for the molecular identification of unknown samples and, as a result, the technique is being used routinely in applications areas such as pharmaceutical manufacturing, medical diagnostics, forensic analysis, and the food and agricultural industries. More recently, the technique has gained widespread acceptance in the characterization of plastics and various polymers, not only for qualitative identification, but also for more demanding applications requiring quantitative analysis. Previously, these materials needed to be dissolved and analyzed using either wet chemical techniques, chromatographic separation or burn tests that were destructive to the sample. Today, Raman analysis is the preferred method because it requires no material preparation, avoids errors that are common to extractive chemical methods and examines additives directly within polymers.

With the growing regulatory complexities in the plastics industry, it is crucial for manufacturers to know the exact composition of their polymer matrices, not only to ensure compliance but also to better understand performance metrics to meet customer specifications. Raman spectroscopy provides a simple, non-destructive and rapid tool for the analysis of polymers and additives. By combining a high resolution Raman spectrometer with intelligent chemometric software, users can now process their data with multivariate regression algorithms (MRA) or principal component analysis (PCA) to correlate all available spectral information to the chemical properties of interest. By using this approach, unique and subtle differences in the matrices can be used for rapid analysis, based on a wide variety of performance metrics, which would not have been possible using traditional univariate techniques.

Before we present some typical polymer characterization applications being carried out by Raman spectroscopy, let's first give a brief overview of the fundamental principles of the technique.

Raman Spectroscopy

Similar to infrared (IR) absorption techniques, Raman spectroscopy measures vibrational, rotational, and other low frequency modes of a molecule. While IR spectroscopy is based on focusing a broad range of IR wavelengths of light onto the sample and measuring which ones are absorbed, a Raman spectrum is obtained by directing a single wavelength of light and collecting the resulting "scattered" light. The frequencies of the scattered light depend on the bond strength of the molecules, the mass of the bound atoms and other factors such as intermolecular interactions. The pattern of vibrational and rotational frequencies from a molecule is highly characteristic of a given molecular species or the structural arrangement of those molecules.

A typical laboratory Raman analyzer consists of five major components: a source of strong monochromatic light to excite the sample such as a laser, the collection/focusing device, the spectrograph, the detector and the post-processing software. The technique relies on molecules in the sample scattering the incident laser light, and the scattered light is then collected and analyzed using a Raman spectrometer to produce a spectrum. Raman spectra are generally well resolved and rich in features enabling unambiguous identification of molecular compounds. However, spontaneous Raman scattering, (also known as inelastically scattered light) is typically very weak. Unless the spectrometer is designed correctly, it can be difficult to separate this weak light from the other, more intense elastically (Rayleigh) scattered laser light. Figure 1 shows the basic principles of a Raman analyzer, together with Raman spectra of five similar molecules (top to bottom) – Acetone, Ethanol, Dimethyl Sulfoxide, Ethyl Acetate, and Toluene. These Raman spectra are clearly differentiable, even to the untrained eye.

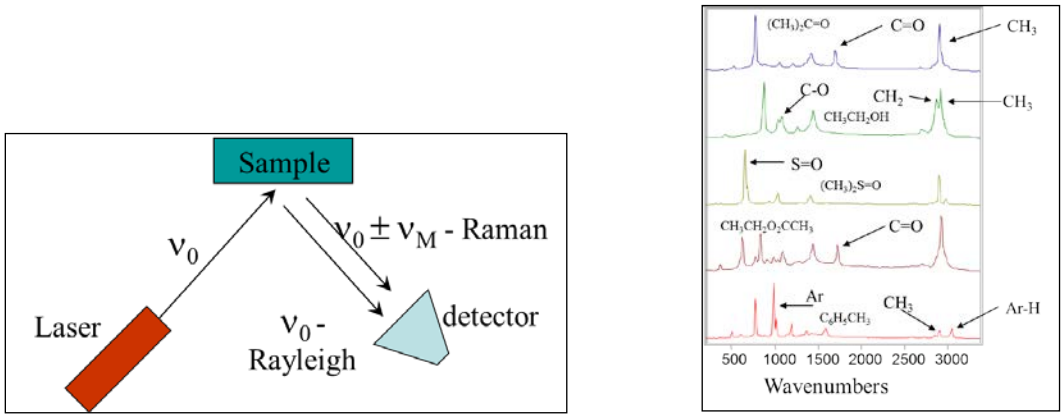

***Figure 1**: Principles of Raman spectroscopy, showing spectra of five similar molecules (top to bottom) – Acetone, Ethanol, Dimethyl Sulfoxide, Ethyl Acetate, and Toluene*

Ideal Characteristics of a Raman Spectrometer

The design of the Raman spectrometer is very important, especially when the requirement is to detect weak signals in the presence of very high background noise. For that reason, the optical components must be of the highest quality to ensure the optimum performance. This is very important when the technique is being used for the analysis of different kinds of polymer materials, which might contain very low levels of additives. Samples like this can be quite similar, which makes it very difficult to tell them apart. For that reason, a well-designed Raman spectrometer being used for this type of work should have the following characteristics:

- The quality of the generated Raman peaks are directly impacted by the sharpness and stability of the delivered light source, so it is essential to use a high quality laser that produces a clean, narrow bandwidth of the wavelength of interest

- The laser unit should have high quality filters to clean up any side bands to ensure a narrow excitation wavelength is delivered to the sample, even when the peak power is increased
- To allow easy transition between different liquid and solid samples, the system should be equipped with a fiber optic measuring probe which provides a high rejection rate of Rayleigh scatter
- The spectrometer should be specifically designed for a wide array of Raman applications, so it should be configurable to cover a wide spectral range for more general, routine type analysis or offer very high spectral resolution for research grade applications
- The detector should incorporate CCD (charge-coupled device) detector technology with thermoelectric cooling (TEC) in order to reduce dark current noise to increase the dynamic range and lower the detection capability
- The software should have the capability to carry out multivariate statistical analysis to interrogate the data with the objective of identifying relationships between spectral information and the chemical properties of interest
- Ideally, for use in a manufacturing environment, the instrument should be highly portable so it can be used in various locations around the plant

Let's now take a look at some typical problems encountered in the polymer industry and how they have been solved using Raman spectroscopy. The two case studies highlighted used the PolymerIQ™ system which combines the i-Raman™ high resolution, portable Raman spectrometer (B&W Tek, Inc.), with expert chemometric software (Gnosys Global Ltd), to identify and measure the polymers of interest. The primary specifications of the instrument used in this study are given in Table 1.

Component	**Specification**
Laser excitation wavelength	785 nm
Laser power	<300mW
Laser line width	<0.3 nm
Spectrometer wavelength range	175-3200 cm^{-1}
Spectrometer resolution	4.5 cm^{-1} @ 912 nm
CCD detector type	TE cooled linear array
Size and number of pixels on detector	14x200 µm, 2048
Detector TEC temperature	10 °C
Software platform	PolymerIQ with Gnosys expert chemometrics - multivariate statistical analysis software

Table 1: *Specifications of the PolymerIQ system used in this study*

The Measurement on Flame Retardants in Plastics

Brominated flame retardants (BFRs) are the largest group of additives used in the plastics industry. However, most are extremely toxic and even though they are still being used in small quantities, they are slowly being phased out in many parts of the world. The traditional way of measuring these compounds has been by chromatographic separation coupled with mass spectrometry. However, this approach is very time consuming and requires a lengthy sample preparation procedure of chemical pre-treatment. In addition, the sample has to be destroyed in order to analyze it. For that reason, high resolution Raman spectroscopy is becoming the technique of choice for this analysis because it is non-destructive, requires no sample preparation and only takes a few minutes to carry out a full characterization of the material.

These capabilities are very attractive to the plastics industry, particularly for masterbatchers and compounders who are responsible for blending all the individual additives into the materials to create exactly the right properties and coloring for the desired application. Therefore, the need for a rapid and cost-efficient measurement is vital in order to ensure product performance, minimize waste, and reduce delays.

The PolymerIQ system is able to detect the difference between similar types of BFR additives, even for very similar compounds such as polybromo diphenyl ethers (PBDE). This is exemplified in Figure 2 which shows a spectral overlay of three different BFR's: penta-, octa- and deca-bromodiphenyl ether. The spectral display on the left shows all three brominated compounds together for comparison purposes, indicating the characteristic Raman shifts for the brominated aromatic molecules of each compound; while the three spectra on the right show them separately.

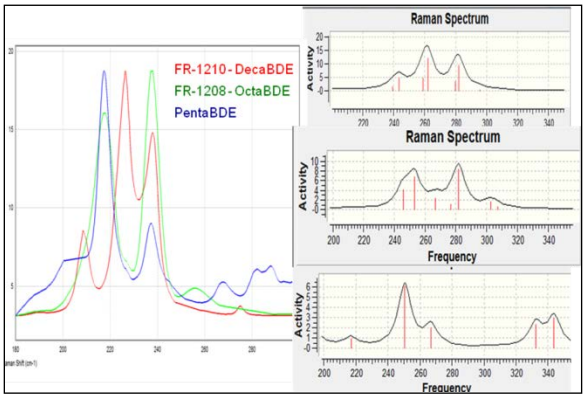

Figure 2: *Raman spectral data for three brominated flame retardants, displayed together on the left and separately on the right - deca- (top), octa- (middle) and penta-bromodiphenylether (bottom). They clearly show the distinct differences between the intensity and frequency of the brominated aromatic molecules of each compound*

A range of acrylonitrile butadiene styrene (ABS) polymer materials were tested for their BDE content. The resulting spectra are shown in Figure 3. It can be seen that the three ABS compounds with varying amounts of BDE present (0%, 2%, 10% bromine) show subtle but distinct differences in their Raman

spectral shifts, particularly below 500 cm^{-1} where the brominated aromatic molecules are most intense. Two commercial ABS polymer materials (S-8010, AO-112) are also shown for comparison purposes. These spectra can be further compared and confirmed by a library of PBDE Raman spectra, and/or their concentrations in the polymer materials can be quantified using the PolymerIQ software if desired.

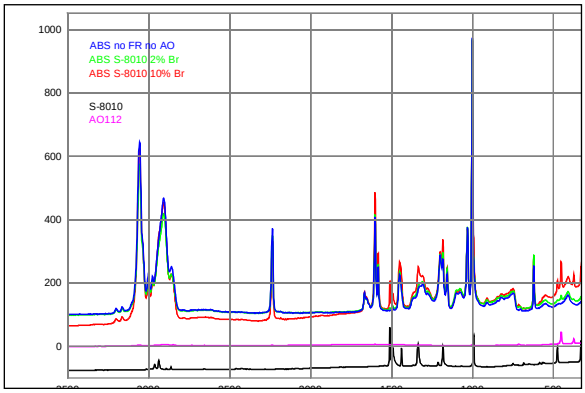

Figure 3: *Raman spectral data for a range of acrylonitrile-butadiene styrene (ABS) polymer materials, all with varying amounts of BDE present (0%, 2%, 10% Bromine), together with two commercial ABS polymer materials (S-8010, AO-112). Note: the brominated aromatic bands of interest are mostly seen below 500 cm^{-1}*

Measurement of Polymers used as Pharmaceutical Excipients

Polyethylene oxides (PEO) are a group of high molecular weight polymers used in the manufacturing of hydrogels and hydrophilic compounds found in adhesives, water-soluble films, thickeners, absorbents, household products and also used as excipients in pharmaceutical products. The recognized properties of PEO and its regulatory acceptance have helped extend the polymer's application to various drug delivery systems, particularly for the intravenous injection of drug compounds. For that reason, the growing use of this group of polymers in the pharmaceutical industry demands stringent control above and beyond the normal requirements of the polymer industry.

In this study, the PolymerIQ system was used to investigate varying batches of PEO which had given both 'good' and 'bad' performance with regard to its drug delivery properties. The Raman spectra appeared identical to the human eye, as seen in Figure 4, which shows multiple overlaid samples. However, when principal component analysis (PCA) was applied to the Raman data, the software detected minute differences from the high quality spectra. Figure 5 shows a plot from the principal component analysis. It can be seen that the bad, lower viscosity samples (blue) are easily distinguished from the good, higher viscosity samples (red).

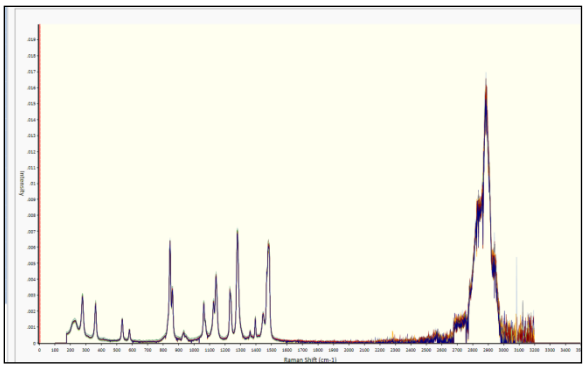

Figure 4: *Raman spectra of four similar PEO samples*

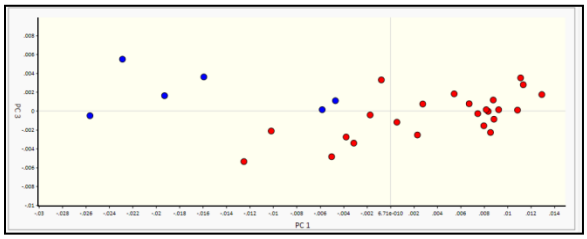

Figure 5: *PCA analysis of Raman spectral information showing the bad, lower viscosity samples (blue) that are easily differentiable in PC space from good, higher viscosity samples (red)*

For this study, correlations were also made with samples displaying deterioration from storage aging. This can be seen in Figure 6, which shows a PCA plot of samples aged at room temperature (blue) compared to samples aged at 40°C (red). It can be clearly seen that each set of samples is easily differentiable in PC space. This type of automated analysis in a rapid non-destructive method is unique to PolymerIQ and opens up further applications for *in-situ* measurements to monitor drug release, such as tracking the hydration of the PEO, since Raman is relatively insensitive to the signal from the water molecule.

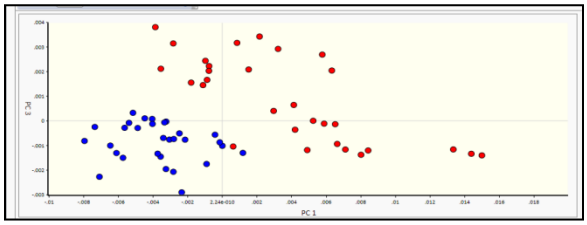

Figure 6*: Raman PCA analysis showing samples aged at room temperature (blue) are easily differentiable in PC space from samples aged at 40°C (red)*

Conclusion

The study clearly shows that Raman spectroscopy, combined with intelligent chemometric software, is ideally suited to the demands of the plastics industry, by providing a simple, non-destructive and rapid tool for the analysis of different polymers and additives. In particular, it has demonstrated how a well-designed solution such as the PolymerIQ system is a very cost-effective and efficient way of identifying and measuring brominated flame retardant additives used in the manufacturing of certain plastics materials, as well as characterizing the properties of excipients that are utilized as drug delivery compounds in the pharmaceutical industry.

Further Reading

- PolymerIQ specification and data sheet: http://www.bwtek.com/product/polymerIQ/index.html
- Quantitative Raman Analysis of Polymers and Additives Webcast: https://event.on24.com/eventRegistration/EventLobbyServlet?target=registration.jsp&eventid=398969&sessionid=1&key=2FA8EFCACBBB80BA51C5AB3216CB9B28&sourcepage=register
- i-Raman specification and data sheet: http://www.bwtek.com/product/raman/iraman.html
- Principles of Raman Spectroscopy: http://www.bwtek.com/technical/raman.html
- Advantages of TE cooled miniature fiber optic spectrometers for Raman and Fluorescence spectroscopy: http://www.photonicsonline.com/article.mvc/TE-Cooled-Miniature-Fiber-Optic-Spectrometers-0002