

Raman Characterization of Polymers in Industrial Applications

For many years Raman spectroscopy has been applied to characterisation of polymers. However, the applications have tended to be research-oriented, rather than designed for routine analysis. With the revolutionary developments in Raman instrumentation, it is now possible to acquire spectra quite rapidly on equipment that is much more affordable and easier to use than in the past. The following will summarise how Raman spectroscopy has been used successfully for the study of polymers, and will indicate which effects can be monitored on a routine basis for industrial analytical purposes.

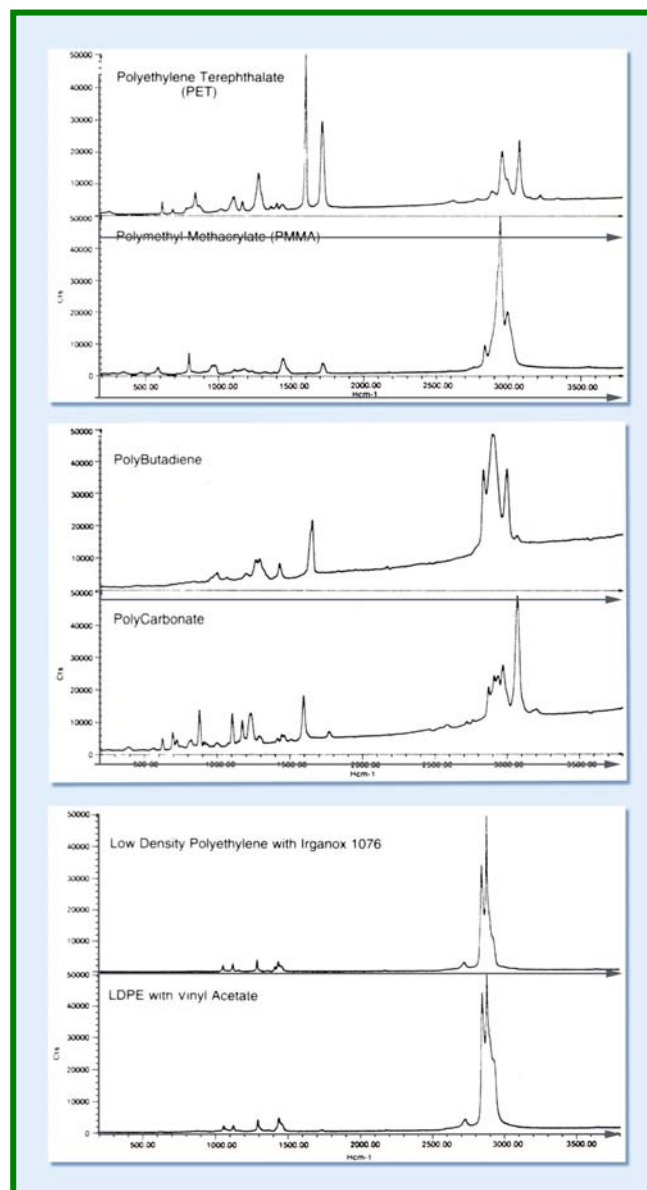
Chemical Fingerprint

Raman spectra can be used for identification purposes by cataloguing a collection of fingerprint spectra. These spectra can be used for

- ❖ confirming incoming product (QC)
- ❖ identification of contaminants appearing during manufacture of "something"
- ❖ monitoring production of product

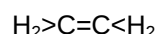
Examination of the attached fingerprint spectra in Figure 1 demonstrates how easy it can be to identify an unknown polymer from its Raman spectrum. For instance, polymers with a carbonyl group have a band between 1650 and 1750 cm^{-1} . And the spectrum of teflon, a material which has no hydrogen, has no bands in the CH stretching region between 2800 and 3200 cm^{-1} .

Figure 1



Polymerisation

When a monomer is polymerised to form a polymer there is almost always the loss of a double bond. For instance, the chemical form of ethylene is

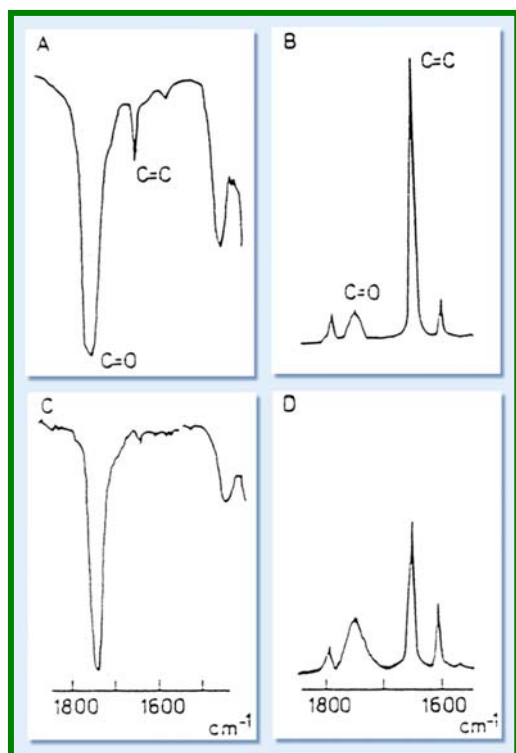


whereas the chemical form of polyethylene is



The carbon double bond frequency is about 1650 cm^{-1} and usually does not mix with other bands. Thus if one wishes to follow the polymerisation process, this can be done by following the disappearance of the band of the carbon double bond.

Figure 2 shows spectra of a monomer starting material and a partially reacted batch of polymer. Not only can one easily follow the degree of polymerization in the Raman spectrum, it is also possible to see how much more sensitive is the Raman spectrum over IR to the presence of the unpolymerized $\text{C}=\text{C}$ band. (This figure was reproduced from O'Donnell and O'Sullivan, A Kinetic Study of Crosslinking Vinyl Polymerisation by Laser Raman Spectroscopy. Polymer Bull 5, 103-110, 1981.)



Orientation and Crystallization

When extruded, polymers tend to "orient". That means that the molecular axis aligns along the extrusion direction. By orienting the sample in the instrument coordinate system and analysing the polarisation of the Raman light, one is able to deduce information on the orientation of the polymer in the part. This can have implications on the mechanical and other physical properties of the polymer.

Like inorganic materials and molecular crystals, polymers can exist in a crystalline form. The degree of crystallinity which is usually not greater than 50% is determined by the thermal and stress history of the sample. One can monitor the crystalline form of polymers by following some details in the spectra: in polyethylene terephthalate, for example, the $\text{C}=\text{O}$ band

tends to sharpen significantly in the crystalline form. The effects of both orientation and crystallinity in the Raman spectra of polyethylene terephthalate fibres have been documented in Adar and Noether, Raman Microprobe Spectra of Spin-Oriented and Drawn Filaments of polyethylene terephthalate Polymer 1985 26 1935-1943.

Raman vs. IR Spectroscopy

While FTIR has been used more extensively than Raman for routine analysis of polymers, there are some things that IR spectroscopy cannot analyze. The Raman bands of double and triple bonds tend to be much stronger than those of the IR. In some cases these bonds may be totally inactive in the IR.

Other vibrational features are likewise more amenable to study by Raman than IR. Some examples are $-\text{S}-\text{S}-$, $-\text{C}-\text{S}-$, and elemental carbons. Note that the ability to detect sulphur species can be important when studying vulcanisation. Aqueous solutions are difficult for IR analysis because the solvent tends to be so opaque. The Raman spectrum of water is very weak so it provides an ideal solvent when monitoring chemistry in solution. Thus if one is interested in emulsion polymerisation. This can be more readily monitored by Raman than IR.

Figure 2. Spectra of CR-39 monomer: A - infrared and B -Raman. and of partly polymerized monomer (ca. 80% consumption of $\text{C}=\text{C}$ bonds): C - infrared and D - Raman.

Figure 3 shows spectra of a polyacrylic acid recorded at different degrees of neutralisation. Differences in the spectra reflecting chemical differences are easy to identify. The water solvent is also easily identified at about 1640 cm^{-1} , and can be used as an internal intensity standard, making calibrations of concentration possible. (These spectra are reproduced from Koda. et.al, Raman Spectroscopic Studies on the Interaction Between Counterion and Polyion, Boiphysical Chem., 15, 65-72, 1982).

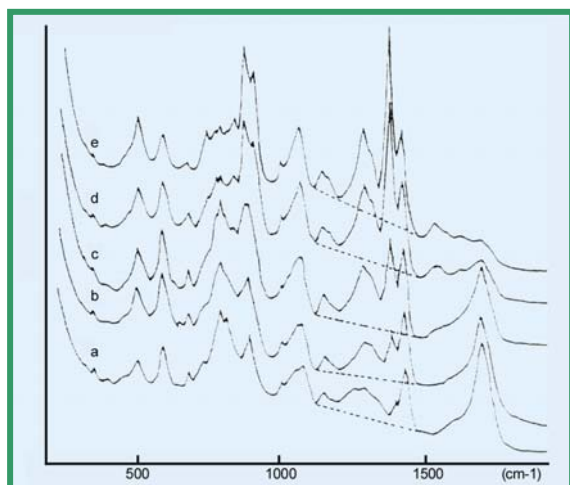


Figure 3: Raman spectra of poly(acrylic acid) at different degrees of neutralisation. Degree of neutralisation, α : (a) 0, (b) 0.2, (c) 0.4, (d) 0.8, (e) 1.0. 25% aqueous solution. The dashed lines indicate the backgrounds.

However, a large proportion of these materials can now be studied by dispersive Raman with a red laser (HeNe at 633 nm, Kr at 647 and 752 nm, and diode lasers at 780-830 nm). In addition, there are a significant number of materials that can be studied by dispersive Raman that cannot be studied by FTR.

Dispersive vs. FT Raman Spectroscopy

Historically Raman has been studied with dispersive spectrometers, as was IR absorption spectroscopy in the early years. More than 25 years ago it was shown that IR spectra could be generated by a Michelson interferometer by performing a "Fourier Transform" on the interferometric data. For various instrumental reasons interferometric collection of spectral data has been done almost exclusively in the mid IR (the region of the spectrum where vibrational frequencies occur). About 6 to 8 years ago it was demonstrated that Raman spectra could be recorded with an

interferometer working in the Near IR (NIR) by exciting the spectra with a YAG laser.

FTRaman (FTR) has been very useful for studying many fluorescing materials that were nearly impossible to study with visible lasers. These include:

- ❖ inorganics, esp. oxides (because they fluoresce!)
- ❖ carbons and other black materials (too much heating and black body radiation)
- ❖ aqueous solutions (the YAG laser is coincident with the 2nd overtone of water).
- ❖ catalysts
- ❖ carbons
- ❖ emulsion polymerisation

Thus one could not use FTR to study but dispersive Raman could provide very useful spectra.

SUMMARY:

Recent developments in Raman instrumentation have made the technique easier to use, more compact, and more affordable. Consequently, all of the demonstrated potential of the spectroscopy for industrial uses can now be exploited, including its use in combination with statistical methods for concentration calibrations.